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A THERMOGRAVIMETRIC PYROLYSIS STUDY OF THE INTERACTION OF DI(1,2,3-BENZOTRIAZOLATIUM) HEXACYANO-OSMATE(IV) WITH CERTAIN ORGANIC AMINES

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Summary—A thermogravimetric pyrolysis study of the interaction products of certain organic amines and tetramethylammonium chloride with di(1,2,3-benzotriazolatium)hexacyano-osmate(IV) is reported.

THIS paper results from a thermogravimetric study of certain amine derivatives obtained in the interactions of di(1,2,3-benzotriazolatium)hexacyano-osmate(IV) with several organic amines and with tetramethylammonium chloride previously reported.[1] In a prior paper, the thermogravimetric pyrolysis of the interaction products of dihydrogen-di(1,2,3-benzotriazolatium)hexacyanoferrate(II) with certain organic amines had been reported.[2] Thermogravimetric analysis of the amine derivatives gave support to the proposed formulae of the products formed in the interaction of tetramethylammonium chloride and certain organic amines with di(1,2,3-benzotriazolatium)hexacyano-osmate(IV).

EXPERIMENTAL

Apparatus

The thermobalance used in this study was assembled as described by Wendlandt.[3] Temperature measurements of the combustion chamber were obtained by using an iron-constantan thermocouple with an ice bath as a reference junction. A pontentiometer was employed to measure the voltage of the thermocouple. A synchronous motor driven powerstat was used to vary the voltage.

Procedures

The compounds were prepared according to the procedure of Wilson and Merchant[1] and dried for 8 hr in a vacuum desiccator using magnesium perchlorate as the desiccant. They were decomposed by placing 17–27 mg of each of the dried compounds in a platinum boat and suspending the boat in the combustion chamber. The output of the motor driven powerstat connected directly to the heating elements of the combustion chamber was set initially at 20 V and the input voltage of this powerstat was adjusted to 120 V by means of a second powerstat. The temperature of the combustion chamber was increased at an average of 3°/min. Readings on the balance and on the potentiometer were taken at short intervals until compounds had completely decomposed.

RESULTS

Pyrolysis curves of the compounds with the respective formulae:

$[(CH_3)_4N](C_6H_4N_2NH_2)Os(CN)_6$, $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Os(CN)_6$,
$[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Os(CN)_6$, $(m\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6$,
$(p\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6$, $(CH_3NH_3)_2(CH_3NH_2)_2Os(CN)_6$,
$[CH(CHCH)_2NH]_2Os(CN)_6$ and $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Os(CN)_6$

are presented graphically in Figs. 1–3 and the analysis of the curves is given in Table I.

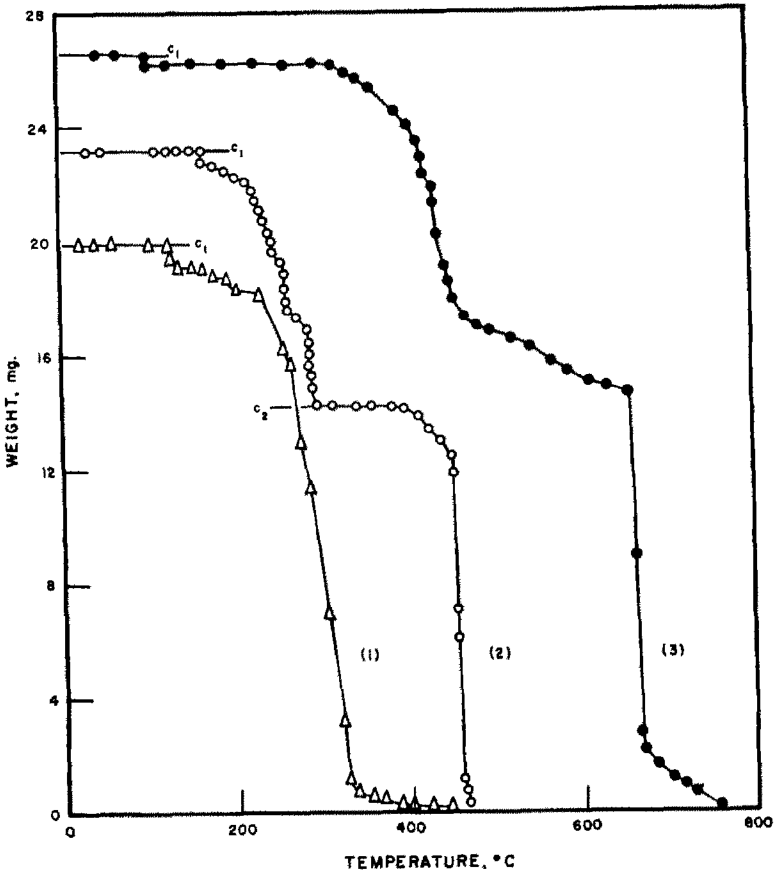

FIG. 1.—Thermogravimetric analysis of Compounds 1–3:
(1) $[(CH_3)_4N](C_6H_4N_2NH_2)Os(CN)_6$: —△—;
(2) $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Os(CN)_6$: —○—;
(3) $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Os(CN)_6$: —●—.

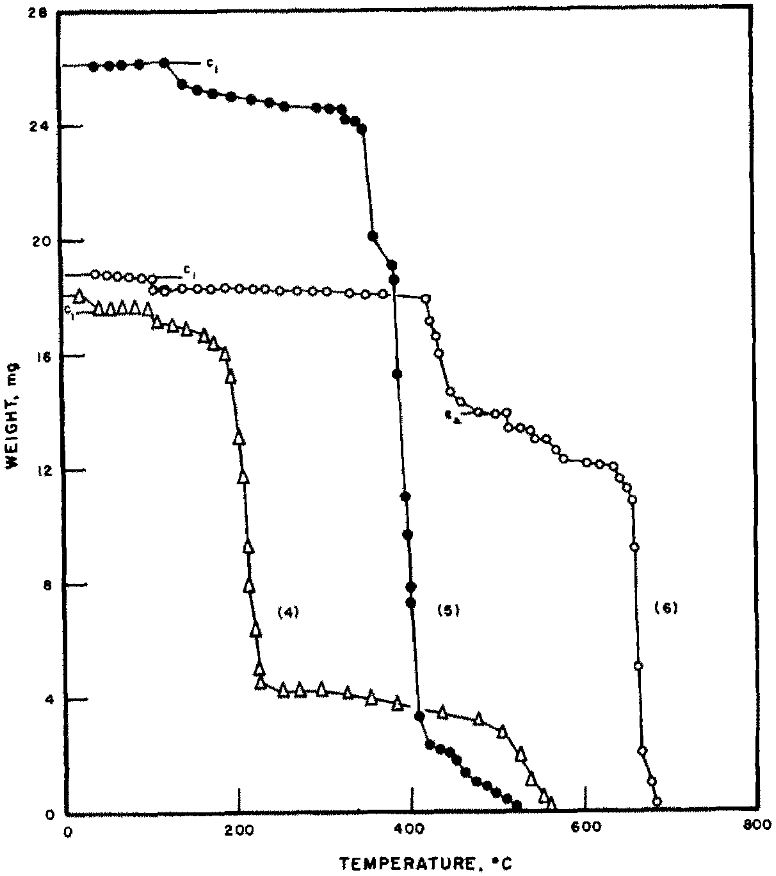

FIG. 2.—Thermogravimetric analysis of Compounds 4–6:
(4) $(m\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6$: —△—;
(5) $(p\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6$: —●—;
(6) $(CH_3NH_3)_2(CH_3NH_2)_2Os(CN)_6$: —○—.

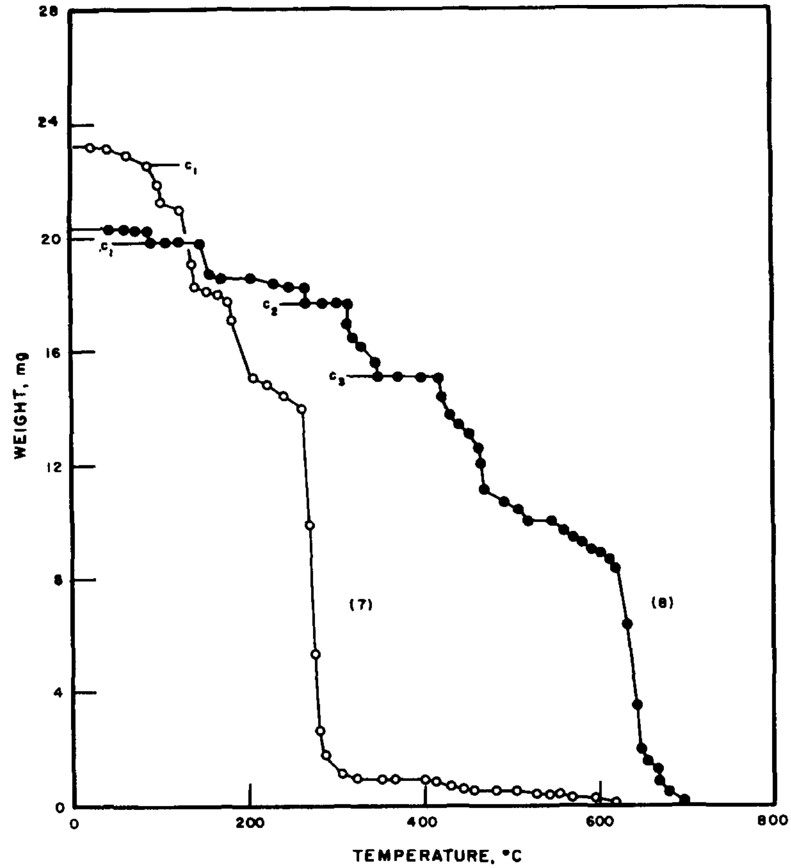

FIG. 3.—Thermogravimetric analysis of compounds 7–8:—
(7) $[CH(CHCH)_2NH]_2Os(CN)_6$: —○—;
(8) $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Os(CN)_6$: —●—.

TABLE I

	C_1			C_2			C_3		
Compounds	Initial weight, *mg*	Weight corrected for moisture, *mg*	Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*
				Calc.	Meas.		Calc.	Meas.	
1. $[(CH_3)_4N](C_6H_4N_2NH_2)$-$Os(CN)_6$	19.8	19.7	<120						
2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2$-$Os(CN)_6$	23.4	23.4	<160	14.1	13.2	290–405			
3. $[(CH_3)_2NH_2]_2[(CH_3)_2$-$NH]_2Os(CN)_6$	26.3	26.1	<110						
4. (*m*-$C_6H_4NH_3NH_2)_2$-$Os(CN)_6$	18.0	17.5	< 42						
5. (*p*-$C_6H_4NH_3NH_2)_2$-$Os(CN)_6$	26.0	26.0	<120						
6. $(CH_3NH_3)_2(CH_3NH_2)_2$-$Os(CN)_6$	18.8	18.5	<110	14.4	14.2	480–524			
7. $[CH(CHCH)_2NH]_2$-$Os(CN)_6$	22.8	22.3	< 84						
8. $[(C_2H_5)_2NH_2]_2$-$[(C_2H_5)_2NH]_2Os(CN)_6$	20.3	19.9	< 88	17.7	17.6	250–320	15.3	15.2	340–420

The weights at plateaus C_2 and C_3 were calculated for the compounds on the basis of the following reactions:

Compound 1

$$C_1\text{: } [(CH_3)_4N](C_6H_4N_2NH_2)Os(CN)_6 + 2O_2 \xrightarrow{(120-452)^\circ} (CH_3)_4NCN\uparrow + HCN\uparrow + C_6H_4N_2NH\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Compound 2

$$C_1\text{: } (C_6H_5NH_3)_2(C_6H_5NH_2)_2Os(CN)_6 \xrightarrow{(160-290)^\circ} H(C_6H_5NH_3)Os(Cn)_6 + 3C_6H_5NH_2\uparrow$$

$$C_2\text{: } H(C_6H_5NH_3)Os(CN)_6 + 2O_2 \xrightarrow{(405-478)^\circ} 2HCN\uparrow + 2(CN)_2\uparrow + C_6H_5NH_2\uparrow + OsO_4\uparrow$$

Compound 3

$$C_1\text{: } [(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Os(CN)_6 + 2O_2 \xrightarrow{(110-757)^\circ} 4(CH_3)_2NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Compound 4

$$C_1\text{: } (m\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6 + 2O_2 \xrightarrow{(42-560)^\circ} 2(m\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Compound 5

$$C_1 \ (p\text{-}C_6H_4NH_3NH_2)_2Os(CN)_6 + 2O_2 \xrightarrow{(120-530)^\circ} 2(p\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Compound 6

$$C_1\text{: } (CH_3NH_3)_2(CH_3NH_2)_2Os(CN)_6 \xrightarrow{(110-480)^\circ} H(CH_3NH_3)Os(CN)_6 + 3CH_3NH_2\uparrow$$

$$C_2\text{: } H(CH_3NH_3)Os(CN)_6 + 2O_2 \xrightarrow{(524-670)^\circ} CH_3NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Compound 7

$$C_1\text{: } [CH(CHCH)_2NH]_2Os(CN)_6 + 2O_2 \xrightarrow{(84-630)^\circ} 2[CH(CHCH)_2N]\uparrow + OsO_4\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow$$

Compound 8

$$C_1\text{: } [(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Os(CN)_6 \xrightarrow{(88-250)^\circ} [(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]Os(CN)_6 + (C_2H_5)_2NH\uparrow$$

$$C_2\text{: } [(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]Os(CN)_6 \xrightarrow{(320-340)^\circ} [(C_2H_5)_2NH_2]_2Os(CN)_6 + (C_2H_5)_2NH\uparrow$$

$$C_3\text{: } [(C_2H_5)_2NH_2]_2Os(CN)_6 + 2O_2 \xrightarrow{(420-692)^\circ} 2(C_2H_5)_2NH\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + OsO_4\uparrow$$

Isolation of pyrolytic products

The thermogravimetric data presented above suggested that certain stable decomposition products were liberated over carefully selected temperature ranges. In the thermogravimetric pyrolysis of the eight amine derivative compounds which were carried out in the open atmosphere, solid pyrolytic products could not be obtained because the intermediate residues at any plateau, on cooling apparently absorbed moisture which brought about complete decomposition of the residues. As further indication of the intermediate product residues and verification of the volatile organic products given off, 1-g samples of the respective amine derivatives were decomposed in a special decomposition apparatus previously described by Wilson and James.[4] Each of the compounds was heated separately in the decomposition apparatus until the compounds had completely decomposed. The temperature of the coolant (carbon dioxide) was sufficient to condense $C_6H_4NHN_2$ from the tetramethylammonium chloride derivative, and to condense $p\text{-}C_6H_4NH_2NH_2$ and $m\text{-}C_6H_4NH_2NH_2$ from their respective amine derivatives. The hydrochloride of aniline was obtained by dissolving the vapours resulting from the decomposition of the aniline derivative in water and bubbling dry hydrogen chloride into the solution. The vapours resulting from the decomposition of the pyridine, dimethylamine, diethylamine and methylamine derivatives were separately dissolved in carbon tetrachloride. Infrared data for the above mentioned intermediate and pure samples are presented in Table II. To verify

TABLE II.—Infrared Maxima

$C_6H_4NHN_2$			p-$C_6H_4NH_2NH_2$			m-$C_6H_4NH_2NH_2$			$C_6H_5NH_2HCl$		
Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated
			1660	S	S	1340	S	S	1400	S	S
1460	M	M	1540	S	S	1220	S	S	1340	M	M
1410	M	M	1420	M	S	1180	S	S	1300	M	M
1310	M	M	1260	S	S	1060	S	S	1280	M	M
1280	M	M	1120	M	M	995	M	M	1200	S	S
1200	S	S	1060	M	M	950	M	M	1180	M	M
1140	M	M							1130	S	S
1080	M	M							1100	S	S
1010	S	S							1060	M	M
980	S	S							1000	M	M
780	S	S							900	M	M
									750	S	S
									685	S	S

Pyridine			Diethylamine			Dimethylamine			Methylamine		
Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated	Wave number, *cm*$^{-1}$	Pure	Isolated
3500	S	S	4500	M	M	3500	S	S	3500	S	S
1990	M	M	3500	S	S	3000	S	S	3000	S	S
1600	S	S	2900	S	S	1600	M	M	2300	M	M
1280	M	M	1050	M	S	1460	M	M	1510	S	M
1220	S	M	790	M	M	1250	M	M	1250	M	M
1180	M	M				1020	M	M	1000	M	M
1140	S	S									
1070	S	S									
1030	S	S									
1000	S	M									

S = strong intensity; M = medium intensity.

the presence of hydrogen cyanide and/or cyanogen, 1-g samples of the respective amine derivatives were decomposed and the vapours were dissolved in aqueous solutions of silver nitrate. In each case a white precipitate of silver cyanide formed. The presence of osmium in the eight compounds previously studied was verified in each case by collecting the osmium tetroxide vapours, resulting from pyrolysis, in aqueous potassium thiocyanate solutions which contained acetic acid. These solutions each gave a yellowish-orange colour which is characteristic of the osmium thiocyanate complex.[5]

DISCUSSION

In this study the thermobalance was employed to follow the pyrolysis reactions taking place in certain complex products obtained in the interaction of several organic amines and tetramethylammonium chloride with di-(1,2,3-benzotriazolatium)hexacyano-osmate(IV). Decomposition of the amine derivatives gave hydrogen cyanide and/or cyanogen, osmium tetroxide, the respective amines and in one case 1,2,3-benzotriazole and tetramethylammonium cyanide.

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Zusammenfassung—Es wird über die thermogravimetrische Pyrolyse der Reaktionsprodukte einiger organischer Amine und Tetramethylammoniumchlorid mit Di-(1,2,3-benztriazolatium)hexacyanoosmat(IV) berichtet.

Résumé—On décrit, dans cette étude, la pyrolyse thermogravimétrique des produits d'interaction de certaines amines organiques et du chlorure de tétraméthylammonium avec l'hexacyanoosmate(IV) de di(1,2,3-benzotriazolatium).

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DETERMINATION OF COMBINED CARBON IN ALUMINIUM NITRIDE

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Summary—A conductimetric method for determination of combined carbon in aluminium nitride, based on the catalytic oxidation of methane formed by acid hydrolysis of carbide, is described. A series of combined carbon determinations in prepared standards at various levels in the range of 30–240 μg has been performed. The precision of the determination increases progressively through this range, the coefficient of variation being 13·6% and 2·0% at the 30- and 240-μg levels respectively. The over-all spread for the whole range has been evaluated at ± 4 μg.

INTRODUCTION

AN estimate of the combined carbon content of pure aluminium nitride, used for the production of ^{14}C through the nuclear reaction ^{14}N(n, p)^{14}C, is essential in order to ascertain the specific activity of the ^{14}C obtained. Because the matrix material here, on combustion, would give large amounts of oxides of nitrogen the usual methods[1–5] for the determination of carbon need modification. Carbide-carbon has been determined in beryllium metal by decomposition with acid, subsequent oxidation of the hydrocarbons produced to carbon dioxide, and measurement of the amount of carbon dioxide gravimetrically[1] or gasometrically.[4]

The present method describes the determination of combined carbon in aluminium nitride samples. The sample is decomposed with 60% sulphuric acid, whereby nitrogen is fixed as ammonium sulphate, and the carbide is hydrolysed to form methane, which, when swept over copper oxide at 900°, is converted to carbon dioxide. In the present case a conductimetric method was employed for the determination of carbon dioxide, by measuring the change in conductivity of a baryta solution before and after absorption of the carbon dioxide in it.

EXPERIMENTAL

Apparatus

The apparatus essentially consists of three parts: (1) the oxygen purification section, (2) the acid hydrolysis and oxidation section, and (3) the measuring section. A schematic diagram is given in Fig. 1. Because tank oxygen contains large amounts of hydrocarbon impurities, it was purified by passing over heated copper oxide at 900°, then over soda lime and dehydrated silica gel. A manometer controls the rate of flow of oxygen gas. The acid treatment part consists of a flask fitted with a dropping funnel with an inlet for oxygen and an outlet for the mixture of gases. A soda lime tube, which immediately follows, removes traces of sulphuric acid carried over by the gas mixture, which then passes through a quartz tube packed with copper oxide catalyst and heated to 900°. A silver vanadate trap removes traces of oxides of sulphur. A conductivity measurements were carried out in the manner described in an earlier communication.[3]

Reagents

Calcium carbonate standard: Pure calcium carbonate was mixed thoroughly with previously ignited 20- to 60-mesh quartz powder in an agate mortar to give a standard of 100 mg = 151 μg of carbon.

Aluminium carbide: Aluminium carbide[6] was prepared by heating pure aluminium metal powder at 800° in an atmosphere of carbon dioxide. This was cooled, ground in an agate mortar and allowed to pass through a 60-mesh sieve. The amount of combined carbon in this prepared carbide sample was determined by the procedure described later. For preparing standards in lower ranges of carbon, appropriate weights of this sample were diluted with finely powdered aluminium nitride and preserved in a desiccator. It has been assumed that all carbon from the carbide is converted to volatile hydrocarbon.

Barium hydroxide solution: An approx. 0·1% (w/v) solution of barium hydroxide was prepared from analytical grade $Ba(OH)_2.2\,H_2O$, as described under reference 3.

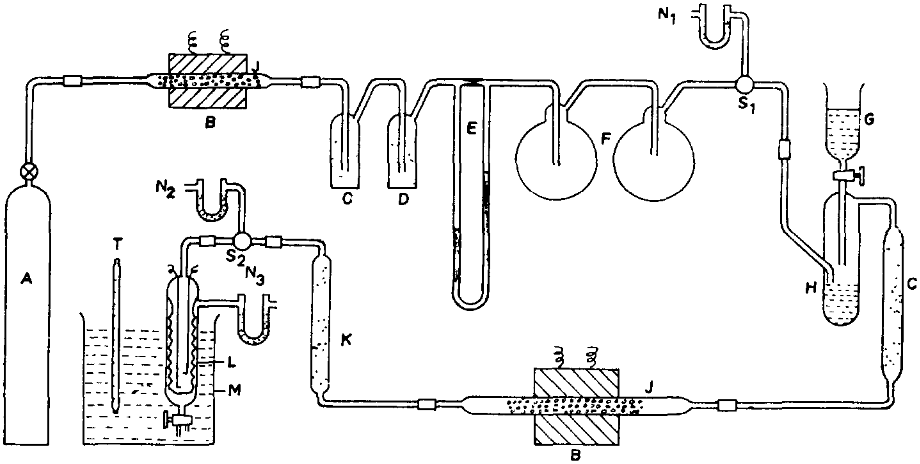

FIG. 1.—Determination of combined carbon in aluminium nitride:

A	Oxygen cylinder	F	Two 2-litre flasks	L	Absorption tube
B	Furnace	G	Acid funnel	M	Thermostat
C	Soda lime tube	H	Reaction tube	N	Soda lime guard tubes
D	Silica gel tube	J	Copper oxide tube	S	Stopcocks
E	Manometer	K	Silver vanadate tube	T	Beckmann thermometer

Standardisation of apparatus

Standardisation of the apparatus was done with calcium carbonate standards. For this purpose the copper oxide catalyst tube was replaced by a quartz combustion tube. A change in conductivity of 150 μmho corresponded to 300 μg of carbon.

Procedure

An appropriate weight of aluminium nitride was added to the reaction flask. The flask was fitted with an acid dropping funnel containing 60% sulphuric acid, and the flow of purified oxygen started at the rate of 25 ml/min. The inner and outer chambers of the absorption cell were rinsed and then filled up to the mark with baryta solution. After the solution had attained the temperature of the thermostat, its initial resistance was measured. The apparatus was completely flushed out with oxygen. Twenty-five ml of 60% sulphuric acid were added to the reaction flask and heated slowly nearly to boiling. Oxygen was passed for 30 min to sweep the gases through the heated copper oxide tube and absorption cell. The final resistance of the solution was measured. The repetition of the above experiment without the sample gave the blank value of the experiment, which was 26 μg, averaged over a number of such blank determinations. With a view to studying the time required for the complete absorption of carbon dioxide, oxygen was passed for 20, 30, 40 and 60 min. It was found that 30 min was sufficient to sweep all carbon dioxide from the apparatus through the absorption cell; hence this flow time at the rate of 25 ml/min was used for all subsequent experiments.

RESULTS AND DISCUSSION

The sample of aluminium carbide prepared was analysed for its combined carbon content and gave a value of 29·1 μg/mg. This was used in appropriate dilutions with a sample of aluminium nitride (C < 10 ppm) to give standards in the lower ranges, of 2 μg/mg and 4 μg/mg respectively. Appropriate weights of these diluted standards were taken and analysed for their combined carbon contents at the levels of 30, 50, 80, 160 and 240 μg. The results have been evaluated statistically and are tabulated in Table I along with the standard deviation at each of these levels. The over-all spread, calculated by the least-square method for the whole range, was found to be ±4 μg. It is obvious from Fig. 2 that the experimental values are in good agreement with the standard values obtained by calcium carbonate-quartz standards.

TABLE I.—STATISTICAL ANALYSIS OF RESULTS ON STANDARDS

No.	Amount of combined carbon taken, *μg*	Change in conductivity, *μmho*	Mean value, *μmho*	Standard deviation	Coefficient of variation
1	30	12·1, 12·5, 11·1, 16·2, 13·0, 14·3	13·2	1·8	13·6
2	50	26·6, 24·5, 22·0, 22·7, 25·8, 22·3	24·0	1·9	7·9
3	80	38·0, 42·9, 40·0, 34·3, 35·8, 40·5, 39·6, 36·9	38·5	2·8	7·3
4	160	76·9, 81·1, 77·8, 78·9, 81·0, 80·0, 84·3	80·0	2·5	3·1
5	240	116·1, 123·1, 120·8, 121·0, 120·0, 118·2	120·0	2·4	2·0

One aluminium nitride sample was analysed several times by taking about 1 g as sample weight. This yielded a mean value of 55.5 ppm of combined carbon (Table II). To approximately 1 g of this sample standard additions were made from

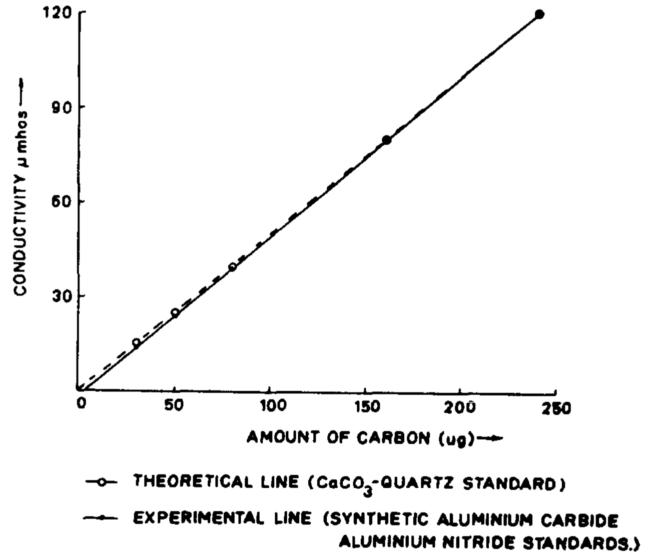

FIG. 2.—Comparison of standard and experimental values.

TABLE II.—ANALYSIS OF AN ALUMINIUM NITRIDE SAMPLE
(sample weight ≈ 1 g)

Combined carbon obtained, *ppm*	Mean, *ppm*	Standard deviation	Coefficient of variation
56·0, 49·3, 58·7, 52·2, 60·7, 55·8	55·5	3·7	6·7

TABLE III.—ANALYSIS OF ALUMINIUM NITRIDE[a] WITH ADDED COMBINED CARBON
(sample weight ≈ 1 g)

No.	Carbon, μg				
	In aluminium nitride	In additive	Total	Found	Deviation
1	55·8	31·6	87·4	96·3	+8·9
2	54·0	46·1	100·1	105·2	+5·1
3	55·1	97·8	152·9	147·8	−5·1
4	55·3	145·0	200·3	192·5	−7·8
5	55·1	197·9	253·0	253·0	0
6	55·1	249·8	304·9	311·2	+6·3

[a] Combined carbon content, 55·5 ppm (Table II).

30 to 250 μg of combined carbon to yield 85–300 ppm of combined carbon in the aluminium nitride, and these were analysed. The results are tabulated in Table III and show good agreement between the expected and experimental values.

Zusammenfassung—Eine konduktometrische Methode zur Bestimmung von gebundenem Kohlenstoff in Aluminiumnitrid wird beschrieben, die auf der katalytischen Oxydation des durch saure Hydrolyse von Carbid gebildeten Methans beruht. Eine Reihe von Bestimmungen gebundenen Kohlenstoffs wurde an Standardmischungen ausgeführt, die verschiedene Mengen, von 30–240 μg, enthielten. Die Genauigkeit der Bestimmung steigt in diesem Bereich steigt an, der Variationskoeffizient beträgt 13,6% bzw. 2,0% bei 30 μg bzw. 240 μg. Die Streuung im gesamten Bereich ist ±4 μg.

Résumé—On décrit une méthode conductimétrique d'évaluation du carbone combiné dans le nitrure d'aluminium, basée sur l'oxydation catalytique du méthane formé par hydrolyse acide du carbure. On a effectué une série de dosages du carbone combiné dans des étalons préparés, à diverses teneurs comprises entre 30 et 240 μg. La précision du dosage croît progressivement dans ce domaine, le coefficient de variation étant 13,6% et 2,0% à 30 et 240 μg respectivement. La dispersion globale dans l'ensemble de ce domaine a été évaluée à ±4 μg.

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SOLID-STATE REACTIONS IN ANALYTICAL CHEMISTRY

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Summary—An account is presented of the nature of analytical reactions between solids; the history of their origin and the rules established for them are summarised. Examples are given of the detection of certain elements. The technique for carrying out the reactions is described and the possibilities are indicated of using solid-state analytical reactions not only for qualitative analysis but also for quantitative analysis.

IN the years after World War II a new section of analytical chemistry began to be developed in the U.S.S.R., namely, solid-state analytical reactions. This section may be considered essentially as a branch of microchemical analysis, because the amounts of both the substance taken for investigation and the reagents used are within the limits usually associated with microchemistry. These reactions may also be considered as a special section of solid-state chemistry and surface chemistry.

The first analytical reactions between solids were suggested by Flavitskii, a professor at Kazan University, at the end of the last century.[1] After his death, however, the subject was not pursued until about 1947 when, almost simultaneously, several people in the U.S.S.R. began to concern themselves with solid-state analytical reactions. The first publication on the subject in the new era was made by Isakov.[2] This section of analytical chemistry was not revived by chance but because of the planned development of science under the conditions of a socialist state and the requirements of industry, chiefly geological services.

There are now many published papers and books[3] on solid-state reactions. An examination of this literature leads to the conclusion that the surfaces of solids, especially minerals, are not particularly stable and the ions present in a crystal lattice are not localised. The electrical conductivity of surface layers shows that the transport of ions is not only characteristic of solutions but that it is inherent in the nature of a solid. On such a basis it is possible to explain the chemical activity of the surface of a solid and its ability to take part in chemical reactions. Of course, the crystal structure of the reacting substances is of great importance, because both the nature of the reaction and its rate depend on the position in the crystal lattice occupied by the ion which is to react with the reagent being used. If the ion in which one is interested occurs at the periphery, loose packing and voids and, consequently, increased chemical activity are possible. These concepts may also be taken as a basis for solid-state analytical reactions. So far no attention has been paid in analytical chemistry to this aspect of the subject.

Solid-state analytical reactions acquired special importance in the investigation of minerals where it frequently becomes necessary to establish the presence of one element or another, only qualitatively at first, although under field conditions the qualitative testing of minerals is of particular importance.

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It is now considered as firmly established that all reactions which take place in solutions are also observed in the reactions between the solids, particularly on trituration where there is close contact between the reacting substances. Furthermore, it is established that many reactions between solids take place not only after crushing and triturating them but also on simply contacting the reacting substances, particularly a mineral and a solid reagent. Such reactions are called *contact reactions*. When using these reactions the presence of the element of interest to the investigator is sometimes revealed by such a simple procedure. For example, on contacting sodium metavanadate crystals with crystalline potassium bisulphate or any solid organic acid, a reddish-orange colour which is characteristic of vanadium pentoxide appears at the contact boundary. Also, if crystals of potassium or ammonium thiocyanate are brought into contact with potassium bisulphate a reddish coloration immediately appears at the contact boundary and a pungent odour (mainly sulphur dioxide) is detected.

Certain conditions must be observed when carrying out solid-state analytical reactions. The degree of grinding is important in reactions between crushed materials, the rate of reaction increasing with an increase in the extent of grinding.

Gas and vapour phases as well as water, particularly water of crystallisation, affect the course of solid-state analytical reactions very greatly and, of course, it is impossible to avoid the effects of these factors under the usual conditions of carrying out the reactions. Water vapour is always present in the atmosphere and it has either a positive or negative effect on the course of the reaction, either accelerating or retarding it or even making it impossible.

When carrying out solid-state analytical reactions one is sometimes obliged to resort to moistening the reactions at the instant they react, for which it is sufficient simply to breathe on the mass or add a small drop of distilled or demineralised water.

Heat is sometimes necessary to induce individual reactions but rarely up to a comparatively high temperature.

As in the reactions of substances in solution, the presence of a proton (or hydronium) or the hydroxyl ion is of importance when carrying out solid-state analytical reactions. This is achieved by adding to the reaction mass solid organic acids or such acid salts as sodium or potassium bisulphate, or even solid potassium or sodium hydroxide, depending on the reaction. Instead of aqueous ammonia, ammonium carbonate is used. However, this factor, *viz.*, the creation of an acid or alkaline medium, is less important when carrying out analytical reactions between solids than for reactions in solution. This is particularly notable when carrying out analytical reactions in which organic reagents take part, *e.g.*, using Arsenazo I for aluminium. Any aluminium salt may be triturated with Arsenazo I and the reaction takes place readily. As is well-known, however, it is necessary to establish a definite pH when carrying out this reaction in solution.

As yet only those reactions which lead to the formation of coloured reaction products are suitable for solid-state analytical reactions, but it may soon be possible to use reactions which lead to the formation of white products. In particular, this may be achieved by applying luminescence methods of analysis using pocket "luminescopes".

A great advantage of solid-state analytical reactions is that it is possible to take very small quantities of both the material to be tested and the reagents for an investigation. Even 1 mg is a large quantity. The reactions may be carried out using a simple binocular magnifier, should this be necessary, or under a low-power microscope, manipulations on the stage being made with quartz or glass needles.

The reactions being considered are essentially fractional, because when studying minerals one usually has to carry out the reaction for the required ion in the presence of many other ions. In this respect certain rules are of considerable importance.

Solid-state analytical reactions usually proceed in the direction involving the formation of a compound with the highest stability constant, K; this is normally expressed as pK, the logarithm of either the solubility product or the stability constant of complex ions.

If several ions capable of reacting with some reagent are present in a mixture, then the first to react will be that ion which forms a compound having the highest pK with the particular reagent.

The following characteristics of solid-state analytical reactions have also been noted:

1. If several ions can react with a particular reagent, then the ions having the highest valency react first.
2. If ions having the same valency are present, all of which react with a particular reagent, then those having the higher atomic number or atomic weight react first.
3. The ability of minerals to react depends chiefly on their chemical structure, while the kinetic behaviour (the rate of reaction) depends on their physical structure.
4. Crystal grains do not have the same chemical reactivity.

The sensitivity of solid-state analytical reactions is sufficiently high and in very many cases is almost as good as the sensitivity of crystal deposition reactions observed under the microscope, the sensitivity of the latter usually being expressed in micrograms. Geologists are more interested in the percentage content of an element in a mineral or ore. For example, the presence of 0·001 % of boron in a sample may be detected by the reaction with Beryllon 2.[4] If *ca.* 1 mg of sample is taken for testing, the sensitivity of this reaction for boron will be of the order of 10^{-2} μg.

When studying minerals and ores one sometimes has to take into account the interference of certain ions which may be present in the test sample and to take measures to remove this detrimental effect. This may be achieved:

1. By masking the interfering ions in stable complex compounds using appropriate reagents;
2. By changing the valency of the interfering ions, *i.e.*, using redox reactions;
3. By converting the interfering ions into readily volatile or sublimable compounds and removing them from the sphere of the reaction;
4. By converting the interfering ions into compounds having a high pK.

This matter has been dealt with in detail by Voskresenskii.[4]

When selecting a method for removing the interference of some ion or other, the individual characteristic of the ion to be detected must be taken into account. For example, by using complex formation (masking), the ion being detected may also combine to form a stable complex. Only those ligands may be used which give compounds having a high pK with the interfering ion and compounds with a low pK with the ion being determined.

There are a large number of substances, chiefly organic, which are suitable as ligands.[4] It should be noted, however, that the stability of complexes of ions having a variable valency depends on the latter. The ions having the highest valency usually have a pK considerably greater than those ions having the lower valency. For example, pK = 14·5 for the Trilon complex of iron(II) while for iron(III) it is 25·1. There is a still more striking difference in the values of pK for the salicylate complexes of iron: 6·55 for iron(II) and 33·6 for iron(III).

The procedure involving redox reactions can be used for a few ions, chiefly for the removal of the effects of copper and iron. This procedure is, however, rarely used.

The procedure involving the conversion of interfering ions into volatile compounds is of great interest, not only as a means of removing interfering ions but also as a means of concentrating the ion to be determined. Many halides have a comparatively low boiling point or sublimation temperature, *e.g.*, $SiCl_4$ boils at 68°, $SnCl_4$ at 114°, $TiCl_4$ at 136°, $SbCl_5$ at 140°, $FeCl_3$ at 185°, *etc.* This property may be used to separate them from accompanying ions. For ions of the same element there is a variation of boiling point with valency. For ions having a variable valency the boiling point of the chloride of a compound incorporating the higher valency is always considerably lower than that of the chloride of a compound incorporating the lower valency. An exception is mercury, for which a reverse relationship is observed.

On reacting with organic substances, metal ions very often form complexes having a comparatively low boiling point. For example, beryllium may be separated from a mixture as its oxyacetate, tin and nickel as their dimethylglyoxime complexes,[5] and polonium as its diphenylcarbazone,[6] *etc.*

When carrying out a reaction without crushing the minerals but directly on their surface, one frequently succeeds in detecting the required ion of an element without taking any measures to remove the effects of interfering ions.

In cases where a contact reaction or a reaction on the surface of a mineral does not take place, the mineral should be decomposed. The best way of doing this is to heat the crushed mineral with a five- or six-fold quantity of ammonium sulphate or with a mixture of three ammonium salts, the sulphate, chloride and nitrate, taken in a definite ratio. The mass obtained after decomposing the mineral should have a white or grey colour. In rare cases the decomposition procedure has to be repeated to obtain a white or grey mass.

The technique for carrying out solid-state analytical reactions is very simple. They may be carried out in a suitable porcelain crucible, still better in a quartz crucible, or on a piece of filter paper or simply on the surface of the mineral. The quantities of materials have already been mentioned. Reagents, particularly organic reagents having a colour of their own, are best used in the form of a mixture with carefully purified and finely-ground quartz sand or with pure silica gel. Depending on the reagent, such mixtures should be prepared with a reagent content not exceeding 1%.

A glass rod, not exceeding 3 mm in diameter and some 50–60 mm in length, is used to triturate the reactants when placed in a crucible, on paper or on a mineral surface.

Solid potassium or sodium bisulphate may be used in almost all cases where the presence of a proton or hydronium is required.

If the reaction requires heat, gas or alcohol burners or solid fuels (urotropine, dry alcohol, paraffin wax) are used. In summer, sunlight may be used for local heating with the help of a lens.

When carrying out reactions directly on the surface of a mineral, the selected position is first cleaned with a knife, which activates the surface, or the reaction is carried out at the position of a fresh break. Reactions at a surface proceed somewhat more slowly than in a crucible containing the crushed mineral but, nevertheless, they take place sufficiently quickly. For example, if one takes millerite, place a little ammonium carbonate and a small crystal of dimethylglyoxime on its surface and triturate it on as small an area as possible, using a glass rod: the characteristic, stable ruby-red colour of nickel dimethylglyoximate develops very rapidly.

On placing a small crystal of 1,10-phenanthroline on the surface of siderite and triturating, the red coloration characteristic of the reaction with iron(II) rapidly appears. All minerals containing this ion behave in this way.

The use of pure metal salts is very convenient for demonstrating solid-state qualitative analytical reactions. Let us now examine a few such reactions for certain ions.

Beryllium may be detected by reactions with quinalizarin or Beryllon 2. A little solid sodium hydroxide is first added to a beryllium salt followed by trituration, then the reagent is added, again followed by trituration. A characteristic blue coloration appears with either reagent.

After adding a little solid sodium hydroxide and a little Magneson I or II to a magnesium salt, the characteristic colorations appear on trituration.

Any boron compound is mixed with potassium bisulphate and a very small amount of Beryllon 2 is added. On mixing and heating gently just to a molten mass, the melt acquires a beautiful blue colour.

Any molybdenum compound is mixed with excess ammonium sulphate and heated until the evolution of sulphur trioxide ceases. On cooling, the mass should have the blue colour of molybdenum blue.

On mixing a tin salt and potassium iodide, a golden-yellow colour rapidly appears.

Any bismuth compound is triturated with a certain excess of potassium iodide to form an iodide complex and hydroxylamine hydrochloride then added. On further trituration the mass acquires a characteristic orange-red or pinkish-red colour. If hydrazine sulphate is used instead of hydroxylamine hydrochloride, the colour obtained on trituration will be more pink. For antimony compounds a yellowish-brown colour is obtained under these conditions.

Many other qualitative reactions could be quoted for various ions. At present rather more than 200 solid-state reactions for more than 50 elements are known.

It is a characteristic of solid-state analytical reactions that completely insoluble substances are quite capable of entering into reaction.

Solid-state analytical reactions may be used not only for the detection of elements. The determination of elements in minerals is possible by using solid-phase colorimetry. It is possible to carry out solid–phase colorimetry both visually and instrumentally. Visual determination by comparison of the colour obtained with the colours of a previously constructed colour scale gives sufficiently satisfactory results. The content of lead, as well as of iron and nickel,[7] has been determined in this way, but under conditions where the content of these elements did not exceed 1 %.

Besides the study of minerals, solid-state analytical reactions may also be used for the qualitative testing of alloys, mineral fertilisers, *etc.*

To aid mineralogists and geologists in the U.S.S.R., Voskresenskii chemical kits for use in the field, designed for a fixed group of elements (10–12) are issued. Their contents may be varied as desired.

Finally, attention is drawn to the studies carried out by Feigl in recent years. He has shown the existence of new or hitherto little considered possibilities by using solid-state reactions in qualitative organic analysis. These include hydrolytic and ammonolytic cleavages and displacement, condensation and redox reactions that occur when organic compounds are melted or sintered with suitable reagents. Many sensitive and strikingly simple tests have resulted from this work.[8]

Zusammenfassung—Die Natur analytischer Reaktionen zwischen Festkörpern, ihre Entstehungsgeschichte und die dafür aufgestellten Regeln werden zusammenfassend behandelt. Beispiele für den Nachweis verschiedener Elemente werden angegeben. Es wird beschrieben, wie die Reaktionen auszuführen sind, und die Möglichkeiten zur Anwendung analytischer Festkörperreaktionen nicht nur in der qualitativen, sondern auch in der quantitativen Analyse aufgezeigt.

Résumé—On présente un compte-rendu sur la nature des réactions analytiques entre solides; on résume l'histoire de leur origine et les règles établies à leur sujet. On donne des exemples de détection de certains éléments. On décrit les techniques des réactions et indique les possibilités d'emploi des réactions analytiques à l'état solide non seulement en analyse qualitative, mais aussi en analyse quantitative.

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THE COULOMETRIC TITRATION OF WEAK ACIDS IN NON-AQUEOUS MEDIA

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Summary—Weak acids have been successfully titrated by coulometric generation of a base in a non-aqueous solvent. A platinum cathode and a silver anode, both placed in a solution of benzene-methanol or tertiary butyl alcohol-methanol, were employed with a supporting electrolyte of sodium perchlorate and tetrabutyl ammonium iodide. The procedure permits the titration of many weak acids with an accuracy of 2% or better. A method of preparing CO_2-free quaternary ammonium bases is outlined.

INTRODUCTION

RECENTLY, several workers have reported results for the non-aqueous titration of acids. Johansson[1] reports a procedure for the determination of acids in isopropanol by generating isopropoxide coulometrically; both a cell arrangement in which the anode and cathode are separated, and one in which they are in the same vessel, are described. Streuli *et al.*[2] report the titration of acids by generating hydroxide coulometrically in a water-acetone medium. In this laboratory, satisfactory coulometric titrations have been performed in a single vessel containing silver, platinum and glass electrodes, a quaternary ammonium halide, and either a benzene-methanol or a tertiary butyl alcohol-methanol solvent. In effect, tertiary butylammonium methoxide is prepared by this procedure. Methanol is reduced at the cathode to form methoxide, and silver is oxidised at the anode in the presence of tertiary butylammonium halide, thus precipitating the insoluble silver halide. This method has the advantage that satisfactory titrations may be performed in a single cell, using solvents which possess favourable dissolution abilities and which give well-defined curves.

EXPERIMENTAL

Apparatus

A constant-current supply, modelled after that reported by Ehlers and Sease[3] was used throughout. The titration cell consisted of a 400-ml wide-mouthed glass jar 8 cm in diameter and 8 cm high. This carried a 100-cm (24 gauge) silver-wire anode wound in a coil around the side of the jar, and a 1-cm platinum wire cathode. The indicator system consisted of a glass electrode and the silver anode, which was used as a reference electrode. The end-point was detected potentiometrically by a Leeds and Northrup 7401 pH meter. The current was determined by measuring the IR drop across a precision resistor (0.2%), using a Leeds and Northrup Potentiometer. Magnetic stirring was used.

Procedure

Approximately 50 ml of the solvent containing $0.2F$ $NaClO_4$ and $0.02F$ tertiary butylammonium iodide were pipetted into the titration vessel. Often the sodium perchlorate contained acidic impurities, and a blank correction was necessary. If a blank correction was necessary, the solvent containing the sodium perchlorate and the tertiary butylammonium iodide was pre-titrated until the potentiometric end-point of the acid was reached. The acid sample was added, and base was generated until the potentiometric end-point of the acid was observed. Visual indicators, such as Bromthymol Blue, gave results identical with those obtained potentiometrically. The amount of acid was calculated from Faraday's laws.

RESULTS AND DISCUSSION

In order to evaluate the method, the non-aqueous base was generated in various solvent systems, as indicated in Table I. The generated base was titrated with perchloric acid in a 9:1 methanol-benzene solution (v/v). As a further check on the efficiency of the generation, benzoic acid was placed in the cell containing 50% benzene-50% methanol electrolyte solution and titrated to a potentiometric end-point directly with generated base. Although the results in a benzene-methanol solvent were satisfactory, the acidic nature of the alcohol suggested the need to find other solvent systems. For this reason, investigations were extended to tertiary butyl alcohol in the presence of various amounts of methanol. In solutions 0.2*F* in $NaClO_4$, and at high concentrations of tertiary butyl alcohol, the current throughout the titration was very erratic. This may result from the low dielectric constant of the solvent. The presence of high concentrations of tertiary butyl alcohol is advantageous, however, because the sharpness of the end-points is increased. At 60% (v/v) of tertiary butyl alcohol the current was quite stable and the results accurate within 2%.

TABLE I.—THE EFFICIENCY OF GENERATION OF QUATERNARY AMMONIUM BASES IN VARIOUS SOLVENTS

Solvent	Number of trials	Accuracy
Methanol	6	99.4 ± 2.1%
Benzene–methanol (75:25)	10	99.4 ± 1.3%
Tertiary butyl alcohol–methanol (90:10)	14	97.2 ± 1.5%
Tertiary butyl alcohol–methanol (60:40)	7	100.3 ± 1.9%

Initial studies indicated that when a large cathode was employed, a precipitate of silver appeared on the cathode. This phenomenon was also observed by Johansson.[1] When small platinum electrodes were employed, the deposit on the cathode was very small. The size of the cathode and the amount of sodium perchlorate required were interdependent to some extent. Small cathodes required large quantities of sodium perchlorate; perchlorate concentrations greater than 0.15*F* were required with a 1-cm cathode, using 0.05*F* tertiary butylammonium iodide. Attempts to titrate acids or to prepare a tertiary butylammonium methoxide titrant using larger quantities of the iodide and completely omitting the sodium perchlorate were unsuccessful. The current was very erratic using only the tertiary butylammonium iodide as the electrolyte, and titrations were possible only to 4% precision when the perchlorate was not present. The tertiary butylammonium methoxide, when prepared in a nitrogen atmosphere, was found to be carbonate free. Titration of this base with non-aqueous perchloric acid gave only one end-point inflection. For this reason the base should be useful in the titrimetric as well as in the coulometric titration of very weak acids with high precision.

Although high currents up to 30 mA were employed, it is apparent that lower currents may also be used. The end-point detection methods appear to be the main limitation to lower concentrations. Visual indicators, such as Bromthymol Blue, gave results identical with those for potentiometric detection procedures. It may be possible to extend the method to lower acid concentrations by using a photometric end-point procedure.

Titrations of acids such as adipic, tartaric, succinic and salicylic, and of dinitrophenol were successful to 4% or better using a benzene-methanol solvent system. The titration of phenol was unsuccessful. Results indicate that the 60% tertiary butyl alcohol-40% methanol solvent system may be used to titrate mixtures of acids. In most cases, where the aqueous dissociation constants of the acids differed by a factor of 10^3, two sharp end-point breaks were obtained.

Zusammenfassung—Durch coulometrische Bildung einer Base in einem nichtwäßrigen Lösungsmittel wurden schwache Säuren mit Erfolg titriert. Es wurden eine Platinkathode und eine Silberanode in einer Lösung von Benzol-Methanol oder Tertiär-Butanol-Methanol verwendet, als Trägerelektrolyt Natriumperchlorat und Tetrabutylammoniumjodid. Das Verfahren erlaubt die Titration vieler schwacher Säuren mit einer Genauigkeit von mindestens 2%. Eine Methode zur Herstellung CO_2-freier quartärer Ammoniumbasen wird skizziert.

Résumé—On a dosé avec succès des acides faibles par génération coulométrique d'une base en solvant non aqueux. On a utilisé une cathode en platine et une anode en argent, toutes deux placées dans une solution benzène-méthanol ou *tert*-butanol-méthanol, avec un électrolyte support de perchlorate de sodium et d'iodure de tétrabutylammonium. La méthode permet le dosage de nombreux acides faibles avec une précision égale ou supérieure à 2%. On décrit de façon sommaire une méthode de préparation de bases ammoniums quaternaires exemptes de CO_2.

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ERIOCHROMBLAU S.E. ALS REDOXINDIKATOR

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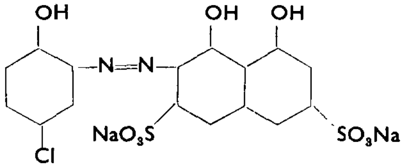
Zusammenfassung—Eriochromblau S.E. ist als Redoxindikator zu in saurer Lösung erfolgenden Titrationen mit Cer(IV)sulfatmasslösung und Kaliumbromatmasslösung und zu in alkalischer Lösung erfolgenden Titrationen mit Natriumhypobromitmasslösung dienlich. Der Farbumschlag ist sowohl in 0,1 und 0,01 n Mass scharf, der Indikatorfehler ist vernachlässigbar. Das Redoxnormalpotential des Indikators beträgt +0,87 V/n H_2. Bei der Oxydation des Farbstoffes durch Cer(IV)-Ionen bildet sich wahrscheinlich reversibler Weise ein Azoxyprodukt.

DER Farbstoff Eriochromblau S.E. (1-Oxy-4-chloro-2,2-diazobenzol-1,8-oxy-naphthalin-3,6-disulfonsaures Natrium),

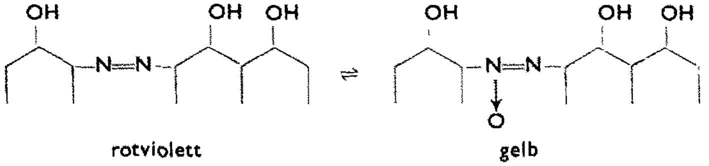


wurde in der chemischen Analyse als Reagens zuerst zur photometrischen Bestimmung des Calciumgehalts von Serum angewandt.[1] Bei der titrimetrischen Bestimmung des Calciumgehalts von Blutserum und Milch mit ÄDTA-Masslösung fand die Verbindung auch als Indikator Gebrauch.[2] Ausser Calcium kann man sie auch bei der komplexometrischen Titration von anderen zweiwertigen Metallionen zu Indikation heranziehen, da sie mit diesen im pH-Gebiet 10–12 rosa oder violette Komplexverbindungen bildet.[3,4] Der Indikator selbst hat bei pH < 7 eine rötlich-violette, in der Umgebung von pH 10 eine blauviolette Farbe. Wir fanden, dass Eriochromblau S.E. auch als Redoxindikator wirkt. Im folgenden wollen wir über die diesbezüglichen Versuche berichten. Der Farbumschlag tritt auch in 0,01 n Mass sehr scharf ein, der Indikatorfehler ist vernachlässigbar.

Bestimmung des Umschlagspotentials des Indikators

Eriochromblau S.E. ist in stark schwefelsaurer oder salzsaurer Lösung rotviolett, bei pH Wert >10 blauviolett, auf Einwirkung von starken Oxydiermitteln in saurer Lösung gelb, in alkalischer Lösung farblos. Um den Umschlagspotentialwert zu bestimmen, wurden 5 ml 0,1 bzw. 0.01 m Eisen(II)sulfatlösung in Gegenwart von 0,1 ml 0,2% iger Eriochromblau S.E.-Lösung mit Cer(IV)-sulfatmasslösung von entsprechender Konzentration titriert. Die Lösungen enthielten 5, 10 und 20% Schwefelsäure, das Endvolumen betrug in jedem Fall 50 ml. Als Elektroden dienten eine glatte Platinindikatorelektrode und eine Bezugselektrode aus gesättigtem Kalomel. Die Messungen wurden mit Hilfe eines Polymetron 42 B Gerät unternommen. Die Farbänderungen während der potentiometrischen Titration wurden ebenfalls registriert. Für Umschlagspotentialwert galt derjenige Potentialwert, bei welchem die Farbe von rötlich-violett ins gelb änderte. Die Farbänderung trat in der steilen, sprunghaften Strecke der Titrationskurve auf. Der Wert des Umschlagpotentials betrug unabhängig von der Säurekonzentration +0,87 V/n H_2. In Abb. 1. sieht man beispielshalber die in 5%iger Schwefelsaurelösung erhaltene potentiometrische Titrationskurve.

Unserer Anschauung nach bildet sich bei der Oxydation reversibler Weise ein Azoxy-Produkt:



Zur endgültigen Klärung der Frage sind infrarot spektrophotometrische Untersuchungen im Gang.

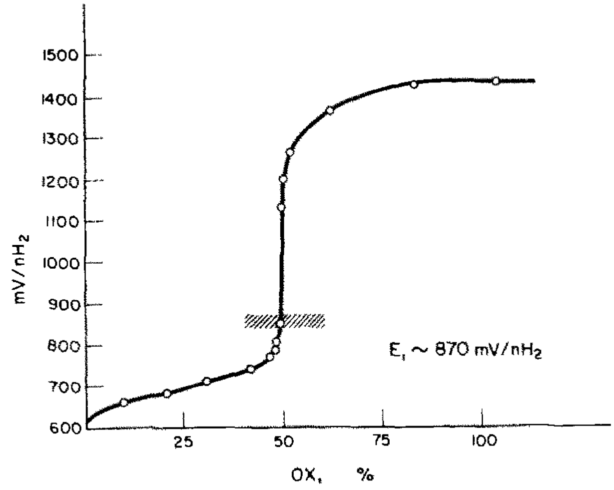


ABB. 1.—Cerimetrische Eisentitration in Gegenwart von Eriochromblau S.E.

Zur Untersuchung der Farbänderung wurden die Absorptionskurven des Indikators in 5%iger Schwefelsäure, in 0,01 n Natriumhydroxydlösung, weiterhin die Absorptionskurve des oxydierten Produkts in 5%iger Schwefelsäurelösung aufgenommen. Zur Oxydation diente 0,01 n Cer(IV)sulfatmasslösung. Die Kurven sind in Abb. 2. dargestellt. Das Absorptionsmaximum der sich in saurer Lösung ausbildenden rötlichvioletten Form liegt bei 535 mμ, das der blauvioletten alkalischen Form bei 550 mμ. Die Absorptionskurven wurden an einem Hilger-Watts Gerät mit Wolfram Glühbirne in einer 1 cm Quarzküvette mit 0,14 Spaltbreite gegen destilliertes Wasser aufgenommen. Die Absorptionskurve des oxydierten Produkts wurde gegen die indikatorfreie Versuchlösung gemessen. Der Farbumschlag ist der Abb. 2. gemäss scharf und kontrastvoll.

Praktische Anwendungen des Indikators

Da der Umschlagspotentialwert des Eriochromblau S.E. sehr hoch liegt, war es zu erwarten, dass es zur Endpunktsindikation von Bestimmungen mit stark oxydierenden Masslösungen dienlich sein wird.

Bei den Versuchen wurden folgende Masslösungen und Reagenzien benützt:

0.1 und 0.01 m schwefelsaure Eisen(II)sulfatmasslösung, 0,1 und 0,1 n schwefelsaure Cer(IV)-sulfatmasslösung, 0,1 und 0,01 n Kaliumbromatlösung, 0,1 und 0,01 n Arsentrioxydlösung, 0,1 n Natriumhypobromitlösung, weiterhin 0,1 n Ascorbinsäurelösung. Die 0,1 n Kaliumbromatlösung und die 0,1 n Arsentrioxydlösung wurden durch Einwaage bereitet. Der Wirkungswert der 0,1 n Cer(IV)sulfatmasslösung wurde gegen p.a. Eisen(II)ammoniumsulfat neben Ferroin als Indikator eingestellt. Die 0,1 m schwefelsaure Eisen(II)sulfatlösung wurde aus Mohrschem Salz bereitet. Die 0,1 n Natriumhypobromitlösung wurde nach Erdey und Buzás[5] hergestellt, 500 ml frisch bereitetes gesättigtes Bromwasser wurden mit 500 ml n Natriumhydroxydlösung vermischt, der Wirkungswert wurde mit 0,1 n Arsentrioxydlösung bestimmt, dann die Lösung mit 0,5 n Natriumhydroxydlösung dermassen verdünnt, dass der Hypobromitgehalt eben 0,1 n sei und der Wirkungswert mit 0,1 n Arsentrioxydlösung definitiv eingestellt.

0,5 m Natriumhydroxydlösung, 50%ige Schwefelsäure, cc und 10%ige Salzsäure, 0,2%ige wässrige Eriochromblau S.E.-Lösung, 0,2%ige alkoholische *p*-Äthoxychrisoidinlösung, 0,4%ige wässrige Methylorangelösung, 0,025 m Ferroinlösung und 0,01%ige wässrige Luminollösung.

Cerimetrische Eisenbestimmung: Eisen(II)lösungen von verschiedenen Konzentrationen werden mit 4 ml 50%iger Schwefelsäure und 2–3 Tropfen 0,2%iger wässriger Eriochromblau S.E. Indikatorlösung versetzt und das Volumen mit Wasser auf 50 ml verdünnt. Man titriert die rötlichviolette Lösung unter beständigem Schütteln mit Cer(IV)sulfatmasslösung bis zur gelben Farbe. In einer bis Endpunkt titrierten Lösung rückwandelt das gelbe "oxydierte" Produkt auf Einwirkung von Eisen(II)Ionen in die rotviolette "reduzierte" Form, die Farbstärke ist jedoch geringer. Das bedeutet, dass der Indikator während der Titration eine gewisse Zerstörung erleidet. Wird die Indikatorfarbe während der Titration schwächer, so sind gegen den Endpunkt noch 1–2 Tropfen Indikatorlösung zuzusetzen. Die Indikatorkorrektion beträgt bei Anwendung von 1 Tropfen 0,2%iger wässriger Indikatorlösung 0,3 ml 0,01 n Cer(IV)sulfatmasslösung. Ein grösserer Überschuss der Masslösung zerstört den Indikator. Die mit Eriochromblau S.E. erhaltenen Titrationsergebnissen wurden mit den Resultaten der Titration mit Ferroin-Indikator verglichen und in Tab. I. dargestellt. Die standard Deviation betrug bei der Titration von ~55 mg Eisen ±0,04 mg bzw. ±0,07%.

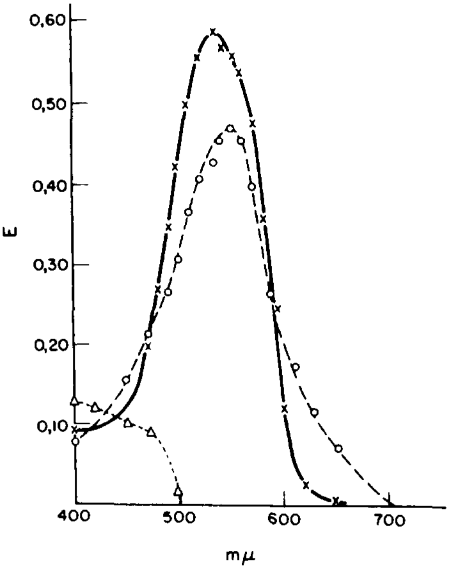


Abb. 2.—Absorptionskurven von Eriochromblau S.E.
—×— H_2SO_4: rotviolett, λ_{max} 535 mμ;
—○— NaOH: blau-violett, λ_{max} 550 mμ;
—△— Ox.: gelb.

Bromatometrische Arsenbestimmung: Die Arsen(III)Ionen enthaltende Lösung wurde mit 20 ml cc. Salzsäure und 2–3 Tropfen 0,2%iger Eriochromblau S.E. Indikatorlösung versetzt und soviel Wasser zugegeben, dass das Endvolumen etwa 100 ml beträgt. Vor der Titration wurde die Lösung auf 50–60° erwärmt, dann solange mit Kaliumbromatmasslösung versetzt, bis die rotviolette Farbe des Indikators nach Gelb umschlug. Die Ergebnisse wurden mit den Resultaten der Arsenbestimmung nach Győry unter Anwendung von Methylorange als Indikator verglichen (Tab. I.). Das im Äquivalenzpunkt freiwerdende Brom zerstört den Indikator, weshalb die Indikatorfunktion irreversibel ist. Die standard Deviation betrug bei der Titration von ~37 mg Arsen(III) ±0,04 mg bzw. ±0,10%.

Arsenbestimmung mit Natriumhypobromit-Masslösung: Zur Endpunktsindikation dieser Reaktion sind Carminsäure, Brasilin und Santalin bisher empfohlen worden.[6-8] Diese funktionieren aber nur in Gegenwart verschiedener Katalysatoren oder bei höherer Temperatur. Erdey und Buzás[5] empfahlen zu dieser Endpunktsindikation Luminol, das den Endpunkt durch einige Sekunden lang dauerndes Leuchten bekannt gibt. Eriochromblau S.E. bewährt sich sehr gut als Indikator bei dieser Bestimmung. Alkalische Lösungen (5 ml 1 n NaOH/100 ml) von verschiedenem Arsengehalt werden solange mit 0,1 n Natriumhypobromit-Masslösung titriert, bis der Indikator farblos wird. Die Variation der Laugekonzentration zwischen pH 10–13 ist ohne Einfluss auf die Resultate. Die Ergebnisse der Titrationen sind in Tab. I. dargestellt. Die standard Deviation betrug beim Bestimmen von 37 mg Arsen ± 0,9 mg bzw. ±0,23%.

TABELLE I.—RESULTATE DER TITRATIONEN

Cerimetrische Eisenbestimmung								
Ferroin. Fe, *mg*	110,36	82,85	55,34	27,64	13,62*	10,92*	6,00*	3,02*
Eriochromblau S.E. Fe, *mg*	110,37	82,95	55,32	27,66	13,50*	10,82*	5,94*	2,99*
Abweichung, *mg*	+0,01	+0,1	−0,02	+0,02	−0,12	−0,10	−0,06	−0,03
Bromatometrische Arsbenbestimmung								
Methylorange. As, *mg*	92,50	74,04	37,67	18,50	9,22*	7,38*	3,69*	1,84*
Eriochromblau S.E. As, *mg*	92,50	74,00	37,68	18,49	9,23*	7,41*	3,72*	1,87*
Abweichung, *mg*	—	−0,4	+0,01	−0,01	+0,01	+0,03	+0,03	+0,03
Arsenbestimmung mit Hypobromit Masslösung								
Luminol. As, *mg*	75,01	56,17	37,64	18,72				
Eriochromblau S.E. As, *mg*	74,98	56,23	37,68	18,88				
Abweichung, *mg*	−0,03	+0,06	+0,04	+0,16				
Bromatometrische Ascorbinsäurebestimmung								
p-Äthoxychrisoidin. A.S., *mg*	97,36							
Eriochromblau S.E. A.S., *mg*	97,48							
Abweichung, *mg*	+0,12							

Die Resultate gewonnen mit Eriochromblau S.E. sind Mittelwerte von sechs Titrationen.
* Die Titrationen wurden in 0,01 n Mass ausgeführt.

Bromatometrische Ascorbinsäurebestimmung: Zur bromatometrischen Ascorbinsäurebestimmung entwarfen Schulek und Kovács[9] eine Methode. 10–200 mg Ascorbinsäure sind in 10 ml Wasser zu lösen, mit 0,5 g Kaliumbromid zu versetzen und mit 5–10 ml 10%iger Salzsäure anzusauern. Sie titrierten in Gegenwart von 1 Tropfen *p*-Äthoxychrisoidin mit 0,1 n Kaliumbromatmasslösung bis Farbumschlag. Wie in Tab. I. zu sehen ist, erhält man auch mit Eriochromblau S.E. genaue Resultate. Die standard Deviation beträgt bei der Titration von 100 mg Ascorbinsäure ±0,12 mg bzw. 0,12%.

Summary—Eriochrome Blue S.E. can be used as a redox indicator for titrations with cerium(IV) sulphate and potassium bromate standard solutions in acidic medium, and for titrations with sodium hypobromite standard solution in alkaline medium. The colour change is sharp both in 0·1 and 0·01*N* titrations, and the indicator error is negligible. The standard redox potential of the indicator is +0·87 V (against H_2). When oxidised with cerium(IV) ions, presumably an azoxy-product is formed reversibly.

Résumé—On peut utiliser le bleu Eriochrome S.E. comme indicateur redox pour des dosages au moyen de solutions titrées de sulfate de cérium(IV) et de bromate de potassium en milieu acide, et pour des dosages au moyen d'une solution titrée d'hypobromite de sodium en milieu alcalin. Pour des dosages aux concentrations 0,1 et 0,01 N, le changement de couleur est net, et l'erreur d'indicateur est négligeable. Le potentiel redox normal de l'indicateur est +0,87 V (par rapport à H_2). Par oxydation au moyen d'ions cérium(IV), il se forme probablement, de façon réversible, un composé azoxy.

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2,3,5-TRIPHENYL-2*H*-TETRAZOLIUM CHLORIDE AS A REAGENT FOR THE DETERMINATION OF SUGAR MIXTURES BY A DIFFERENTIAL REACTION-RATE TECHNIQUE

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Summary—The rates of reaction of 2,3,5-triphenyl-2*H*-tetrazolium chloride with the more common hexoses (glucose, fructose, mannose, sorbose and galactose) and pentoses (xylose and ribose) have been studied. Under certain conditions, over a limited range of reaction, the extent of the reaction is directly proportional to the time of reaction (a "pseudo zero-order" reaction). Also, the rates of reaction of the sugars are quite different in most cases. Thus, the behaviour of this reagent is quite satisfactory for the determination of binary mixtures of most of the sugars tested, by a simple differential rate technique developed for "zero-order" competitive reactions. The rates of reaction of 2,3,5-triphenyl-2*H*-tetrazolium chloride with ascorbic acid, creatinine and glutathione, often found in blood serum, which interfere with most blood serum sugar analysis methods, have also been examined to determine if they would interfere with the determination. Glutathione and creatinine do not react with the reagent and do not interfere with the analysis of sugar mixtures. Ascorbic acid, however, reacts rapidly, and as little as 1–2% leads to error in the sugar-mixture determination.

INTRODUCTION

IN general, the analysis of sugar mixtures is carried out in two steps: the mixture is first separated by paper or column chromatography, and this is followed by a quantitative evaluation of the spots or fractions.[1] Gas chromatographic techniques have also been employed, following methylation of the sugars.[2–4] Methods for the *in situ* determination of sugar mixtures based on techniques employing differential reaction rates have also been reported.[5–7] None of these differential reaction-rate methods are entirely satisfactory for rapid routine analysis, because of either laborious procedure or slow time-consuming reactions. The method of Siggia *et al.*,[5] based on the differential rates of dialysis of the sugars, although reported to be very accurate, and capable of determining three-component mixtures, is somewhat time-consuming, requiring 15–50 titrations during the course of an individual mixture determination. The two chemical reaction-rate methods, based on the differential rates of reaction of

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* Participant in the University of Michigan Undergraduate Honors Research Programme.

the sugars with anthrone,[6] or with ammonium molybdate,[7] are somewhat less laborious, requiring only two simple spectrophotometric measurements for each mixture analysis. However, both reagents have distinct disadvantages: in the anthrone[6] method two measurements are made at two different temperatures, 25° and 100°; and the ammonium molybdate method employs a very slow reaction (2 hr reaction time at 100°).

The compound 2,3,5-triphenyl-2*H*-tetrazolium chloride (THTCl) reacts readily under mild conditions with reducing compounds, such as sugars,[8] to form a red water-insoluble formazan;[9,10] the quantity of this is directly proportional to the concentration of the sugars.[11] This red precipitate is readily dissolved on adding acid-pyridine to the solution, and this reagent also serves to stop the reaction. Therefore the amount of formazan formed at any time during the course of the reaction is readily measured spectrophotometrically.[11] Mattson and Jensen[11] also observed that fructose had a "seven-fold greater reducing power" (a faster rate of reaction) than glucose. It therefore appeared that THTCl might be a very suitable reagent for the analysis of sugar mixtures by a differential reaction-rate technique. This paper reports the results of the investigation of the reaction of this compound with sugar mixtures and its applicability as a reagent for their analysis.

EXPERIMENTAL

General procedure

The reaction solution is prepared by dissolving the sugar mixture in water to give a solution which is approximately 1–5 m/molar in total sugar, a concentration range of sugar which gives convenient absorbance values on reaction (generally between 0.2 and 0.8). Two 10-ml samples of the sugar solution are then introduced into 50-ml volumetric flasks, placed in a thermostatted water bath at 25° ± 0.05 and allowed to come to thermal equilibrium; 5.0 ml of 1.00*M* NaOH are then added to each flask, and the solution is mixed and allowed to stand for about 6 min to ensure thermal equilibrium. The reaction is started by the addition of 1.0 ml of a freshly prepared 0.015*M* solution of THTCl. One of the sample solutions is allowed to react for 20 min and the other for 50 min. The reactions of the two samples are stopped at the appropriate times by the addition of 15 ml of a pyridine-conc. hydrochloric acid solution (20:3, v/v). The addition of this reagent also dissolves the red formazan product of the reaction. The extent of the reaction at these two times is determined by measuring the absorbance of the resultant solutions at 490 mμ. A Beckman model DU spectrophotometer was employed in this study and the blank was a solution containing all the species, except the sugar, in the concentrations initially added to the sample solution.

The rates of reaction of the pure individual sugars were determined in the same manner. The extent of the reactions for the individual sugars were, however, measured over a large range of time intervals.

Calculation of the composition of the mixtures

In the reaction conditions described, the rates of formation, for all the sugars A studied, of the red formazan product, R, in the reaction:

$$A + \text{THTCl} \rightarrow R \tag{1}$$

were directly proportional, over a limited part of the initial portion of reaction, to the time of the reaction, as shown in Fig. 1. The amount of R formed at any given time, t, during the course of the reaction, was directly proportional to the initial concentration of the sugar present (see Fig. 2). Thus, a very simple proportional relationship describes the concentration of the formazan product, as a function of time and initial concentration of sugar:

$$[R]_t = k_A t[S_A]_0 \tag{2}$$

where $[R]_t$ is the concentration of the product at any time, t, k_A is the proportionality constant which can be considered to be a "*pseudo zero-order*" rate constant for the reaction of the sugar, A, and $[S_A]_0$ is the initial concentration of the sugar, A. Because the absorbance of the formazan is the measured parameter, and because the formazan obeys Beer's Law, the measured absorbance, P_t, at any time,

t, is also directly proportional to t and $[S_A]_0$; and at a fixed value of t it is directly proportional to $[S_A]_0$ only:

$$P_t = \varepsilon b k_A t [S_A]_0 = K_{A,t}[S_A]_0 \tag{3}$$

where ε and b are the molar absorptivity of R and the path length of light in the spectrophotometer cell, respectively; and $K_{A,t}$ is the proportionality constant relating P_t to $[S_A]_0$ at any fixed value of t.

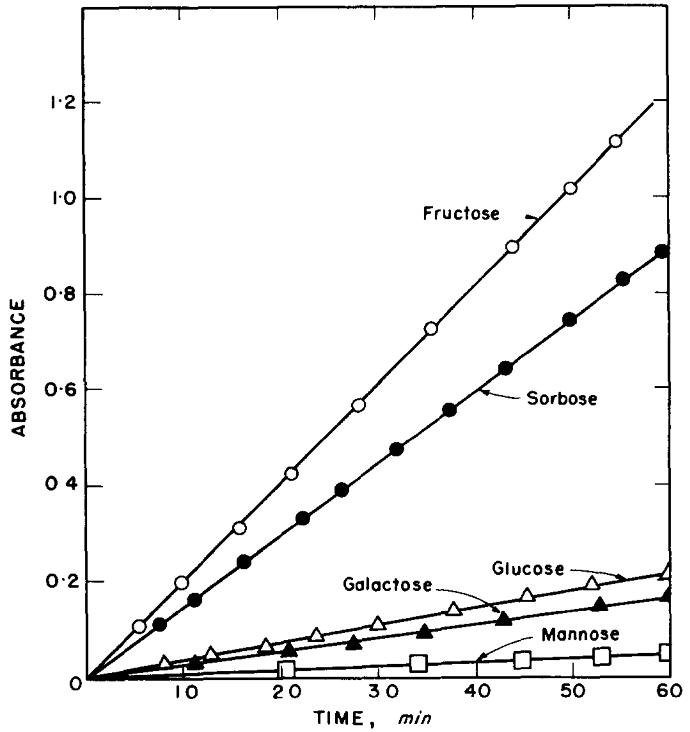

FIG. 1.—Reaction rate curves of five hexoses.
Concentration of hexose = $1 \times 10^{-3}M$;
concentration of THTCl = $0.94 \times 10^{-3}M$;
temperature = 25° ± 0.05°.

If two sugars, A and B, react simultaneously and competitively with THTCl to form the formazan products, but with different rate constants, K_A and K_B respectively:

$$A + \text{THTCl} \xrightarrow{k_A} R \tag{4}$$

and

$$B + \text{THTCl} \xrightarrow{k_B} R \tag{5}$$

The total concentration of formazan, measured as an absorbance value, P, at two different times, t, and t^1, during the course of the reaction is given by:

$$P_t = K_{A,t}[S_A]_0 + K_{B,t}[S_B]_0 \tag{6}$$

and

$$P_t^1 = K_{A,t^1}[S_A]_0 + K_{B,t^1}[S_B]_0 \tag{7}$$

Where $K_{A,t}$ is defined by equation (3), K_{A,t^1} is equal to $\varepsilon b k_A t^1$, and $K_{B,t}$ and K_{B,t^1} are proportionality constants of the same form, except that they contain k_B [the "pseudo zero-order rate constant" of the reaction of B; equation (5)] rather than k_A. The values of these four K constants in equations (6) and (7) are easily determined experimentally by measuring the values of P obtained for the reactions of known initial concentrations of pure A and B at the two time intervals, t and t^1 [see equation (3)]. The values of ε, b, k_A and k_B do not have to be known separately.

With the values of the K constants predetermined, the analysis of a two-component sugar mixture is then accomplished by simply measuring the absorbance, P, at the two times t and t^1. These values can then be used with equations (6) and (7), which can be solved simultaneously to give $[S_A]_0$ and $[S_B]_0$. This type of calculation using proportional equations is the same as that employed for the analysis of mixtures undergoing first-order reactions[12] and enzyme catalysed reactions.[18] Only the form of the proportional equations is different in each case.

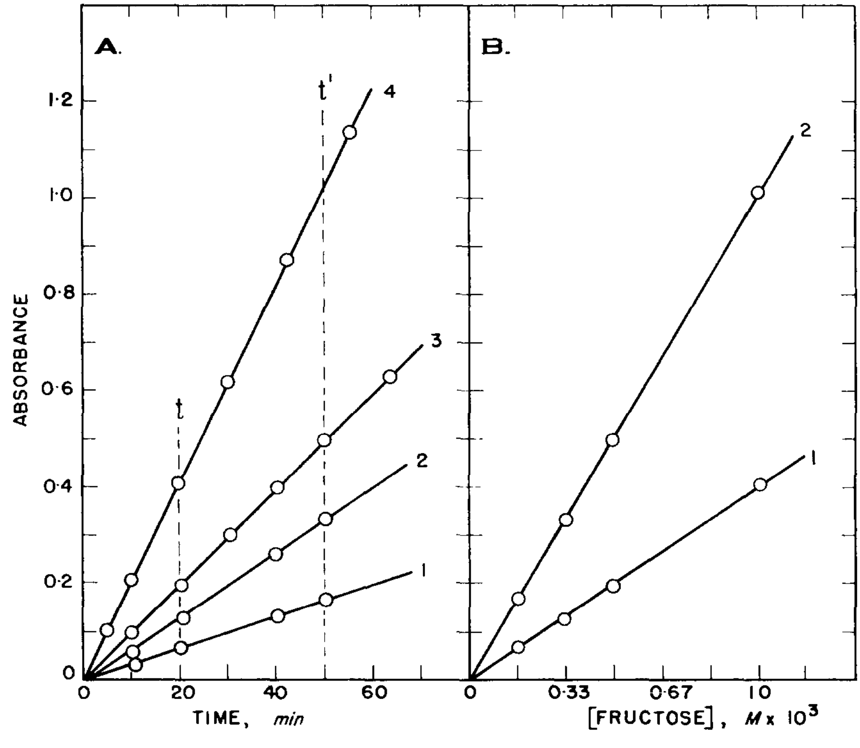

Fig. 2.—Effect of concentration of fructose on the rate of reaction. Concentration of THTCl = 0.94 × $10^{-3}M$; temperature = 25° ± 0.05°.

A: Curve 1. Concentration of fructose = 0.17 × $10^{-3}M$.
Curve 2. Concentration of fructose = 0.33 × $10^{-3}M$.
Curve 3. Concentration of fructose = 0.50 × $10^{-3}M$.
Curve 4. Concentration of fructose = 1.00 × $10^{-3}M$.
B: Curve 1. Extent of reaction at time, t = 20 min.
Curve 2. Extent of reaction at time, t' = 50 min.

RESULTS AND DISCUSSION

In order to determine the optimum conditions for the analysis of sugar mixtures using the THTCl reagent, the rates of reaction of the different hexoses were investigated over a range of sugar and reagent concentrations. The most reproducible rate values were obtained when the ratio of the total concentration of sugars to THTCl was approximately 1 : 15 to 1 : 1, *i.e.*, second order conditions. Under these conditions the reaction at 25° is quite slow. It can be seen in Fig. 3, that the reaction with the fastest reacting sugar, fructose, requires over 6 hr to go to completion. This slow rate of reaction under these conditions makes this reagent unsuitable for the usual graphical second order differential rate methods,[14–15] which require the reaction of the mixture to approach completion. Also, the rate results obtained for times greater than about 3 hr were not very reproducible. This may possibly be either because the over-all reaction is quite complex (the linear behaviour of the initial rate also suggests this) or because the formazan product is somewhat unstable (as discussed below). However, because the rate values during the initial portion of the reaction (up to 2 hr) were quite reproducible, and the extent of the reaction was conveniently linear with respect to time during this period, the determination of sugar mixtures can easily be made as explained above. The one disadvantage in using merely the initial reaction rate values is that only a small per cent, 10–20 %, of the reaction has taken place. Thus.

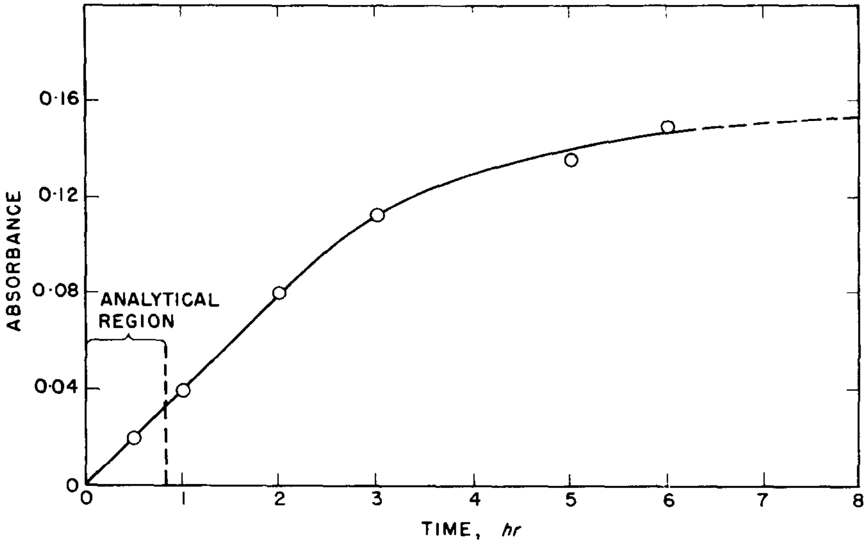

FIG. 3.—The rate curve for the reaction of 0.5 × $10^{-4}M$ fructose and 0.94 × $10^{-3}M$ THTCl at 25° ± 0.05°.

the absolute sensitivity of method is about 10 % of what could be realised by using a method which allows the reaction to go to completion. However, it is felt that the time saved, the simplicity of the calculations, and the increase in precision obtained by using this initial portion of the reaction, more than compensate for the loss of sensitivity.

At present, the explanation of the "pseudo zero-order" behaviour (linearity of the extent of reaction with time) during the initial 20 % of the reaction is not known. The mechanism of the reaction must be considerably more complex than might be expected.

The value of the different proportionality constants, K, at $t = 20$ min and $t' = 50$ min.* for the seven sugars studied are given in Table I. Also listed in Table I are the relative rates of reaction of these sugars using glucose as the basis of comparison. It was found experimentally that for mixtures whose ratio of rates (rate of faster reacting component: rate of slower reacting component in equal concentrations) was 2:1 or less, unsatisfactory results were obtained. Thus it appears that the

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* These times were arbitrarily chosen in this study; 20 min for t was convenient because sufficient colour was usually developed at this time to give an accurate and precise absorbance measurement; and 50 min for t' ensured that the optical density was not too great to obtain a reading.

TABLE I.—THE RELATIVE RATE CONSTANTS FOR THE REACTION OF SUGARS WITH 2,3,5-TRIPHENYL-2*H*-TETRAZOLIUM CHLORIDE
Concentration of sugar = $1.0 \times 10^{-3}M$;
concentration of THTCl = $0.95 \times 10^{-3}M$;
concentrations of NaOH = $0.31M$. Temperature = 25° + 0.05°

Compound	Proportionality constants		Relative rate constant
	K_t(20 min)	K_t(50 min)	
Fructose	0.68	1.70	5.3
Sorbose	0.52	1.28	4.0
Glucose	0.13	0.32	1
Galactose	0.090	0.23	0.72
Mannose	0.029	0.070	0.22
Xylose	0.12	0.30	0.94
Ribose	0.091	0.23	0.73
Creatinine	—	—	No reaction
Glutathione	—	—	No reaction
Ascorbic acid	—	—	131

experimental errors in measuring the various parameters, P_t, P_t', t, t', and the values of K in this method are sufficiently large to introduce significant errors in the determination when the ratio of rate constants is small. A similar restriction on low ratios of rate constants was also observed for the first-order "method of proportional equations."[16,17] THTCl is not suitable for the differential rate of determination of fructose-sorbose, glucose-galactose, glucose-xylose, glucose-ribose or xylose-ribose mixtures. It is, however, quite suitable for analytical determinations of all the other binary combinations of the sugars. A few specimen results are given in Table II.

TABLE II.—THE ANALYSIS OF SOME SUGAR MIXTURES

	Mixture	[A], $M \times 10^3$		[B], $M \times 10^3$	
		Present	Found	Present	Found
1.		0.33	0.33	3.0	2.6
		0.55	0.44	2.8	3.2
	A. Fructose	1.3	1.3	2.0	2.3
	B. Glucose	1.65	1.7	1.65	1.8
		2.2	2.3	1.1	1.2
		2.5	2.3	0.83	1.1
2.	A. Fructose	1.65	1.7	1.65	1.6
	B. Galactose	2.2	2.2	1.1	0.83
3.	A. Fructose	1.65	1.7	1.65	1.6
	B. Ribose	1.0	1.0	2.3	2.3
4.	A. Glucose B. Mannose	1.0	0.8	2.3	2.1
5.	A. Sorbose	0.83	0.8	2.5	2.8
	B. Glucose	1.65	1.7	1.65	1.8
		2.5	2.7	0.83	0.7

A relative error of ~3·4% was obtained for approximately 50 binary sugar mixtures analysed.

The compounds ascorbic acid, creatinine and glutathione occur in blood serum in varying amounts, and interfere with all the analytical methods of sugar determinations in blood serum utilising their reducing ability.[7,18,19] The analysis of mixtures of sugar in blood serum is of interest,[20] and a differential rate technique has been successfully employed for the analysis of fructose-glucose mixtures in blood serum (but is subject to error when the above compounds are present in concentrations greater than 4%).[7] It was therefore decided to measure the rates of reaction of these species to see if they would also interfere with the method presented here. It was found that creatinine and glutathione did not react to any detectable extent after 1 hr and do not, therefore, interfere with the determination of the sugar mixtures. Ascorbic acid, however, reacted with the THTCl very rapidly, as shown in Table I, and as little as 2% of ascorbic acid in a sugar mixture would result in appreciable error in a determination.

The red formazan product of the reaction is reasonably stable, but does undergo some decomposition with time. When dissolved on the addition of the acid-pyridine solution (which stops the reaction), the absorbance of the resulting solutions decreased by about 4% in a 4-hr period.

Acknowledgment—Acknowledgment is made to the Petroleum Research Fund (PRF), administered by the American Chemical Society, and of a grant from the Horace H. Rackman School of Graduate Studies of the University of Michigan for partial support of this research. Two of the authors (L. M. B. and D. P.) are indebted to the National Science Foundation for Undergraduate Summer Research Fellowships.

Zusammenfassung—Die Reaktionsgeschwindigkeiten von 2,3,5-Triphenyl-2*H*-tetrazoliumchlorid mit den häufigeren Hexosen Glucose, Fructose, Mannose, Sorbose, Galactose und den Pentosen Xylose und Ribose wurden gemessen. Unter bestimmten Bedingungen wurde in einem gewissen Bereich des Umsatzes gefunden, daß der Umsatz der Reaktionszeit direkt proportional war (Reaktion "pseudonullter" Ordnung). Außerdem waren die Reaktionsgeschwindigkeiten dieser Zucker meistens stark verschieden. Demnach erwies sich dieses Reagens als sehr zufriedenstellend, um binäre Mischungen der meisten geprüften Zucker mit der in dieser Arbeit entwickelten Methode des Geschwindigkeitsunterschiedes bei Konkurrenzreaktionen "nullter" Ordnung zu analysieren. Mehrere Bestimmungsbeispiele werden angegeben. Die Reaktionsgeschwindigkeiten von 2,3,5-Triphenyl-2*H*-tetrazoliumchlorid mit Ascorbinsäure, Kreatinin und Glutathion, Verbindungen, die häufig im Blutserum vorkommen und die meisten Zuckeranalysen im Blutserum stören, wurden ebenso gemessen, um festzustellen, ob sie auch hier stören würden. Glutathion und Kreatinin reagieren nicht und stören bei den Zuckeranalysen nicht. Ascorbinsäure dagegen reagiert schnell und führt schon in einer Menge von 1–2% zu falschen Zuckerwerten.

Résumé—On a étudié les vitesses de réaction du chlorure de 2,3,5-triphényl-2*H*-tétrazolium avec les hexoses et pentoses les plus courants: glucose, fructose, mannose, sorbose et galactose, xylose et ribose. On a trouvé que, dans certaines conditions limitées le rendement atteint par la réaction est directement proportionnel à la durée de celle-ci (réaction d'ordre "pseudo-zéro"). Les vitesses de réaction de ces sucres sont également très différentes dans la plupart des cas. Ainsi, le comportement de ce réactif est tout à fait satisfaisant pour le dosage de mélanges binaires de la plupart des sucres essayés, par la technique simple de vitesse différentielle développée dans ce mémoire pour des réactions concurrentes d'ordre zéro. Quelques dosages sont donnés à titre d'exemples. On a aussi étudié les vitesses de réaction du chlorure de 2,3,5 triphényl-2*H*-tétrazolium avec les composés suivants: acide ascorbique, créatinine et glutathion, que l'on trouve souvent dans le sérum sanguin et qui interfèrent dans la plupart des méthodes d'analyse du sucre du sérum sanguin; ceci afin de voir si ces composés interfèrent dans le dosage effectué selon la méthode décrite dans ce mémoire. On a trouvé que le glutathion et la créatinine ne réagissent pas le avec réactif et n'interfèrent pas dans l'analyse de mélanges de sucres. L'acide ascorbique, cependant, réagit rapidement, et une quantité de 1–2% seulement conduit à une erreur dans le dosage du mélange de sucres.

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COPRECIPITATION KINETICS—I

COPRECIPITATION OF LEAD WITH BARIUM SULPHATE

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Summary—An equation has been derived describing the logarithmic distribution coefficient in coprecipitation as a function of the rate of precipitation, the number of growing crystals, and two rate constants, the ratio of which is the distribution coefficient at zero rate of precipitation. In the system lead sulphate-barium sulphate, the derived equation adequately describes the precipitation rate-dependence of the distribution coefficient. The distribution coefficient at zero precipitation rate is 0·010, which agrees satisfactorily with the value predicted from the solubility product constants.

INTRODUCTION

If solid barium sulphate is placed in a solution containing lead ion, some of the barium in the solid will be replaced by lead to form a solid solution. The distribution reaction can be written:

$$Pb^{2+}(aq) + BaSO_4\ (crystal) \rightleftharpoons Ba^{2+}(aq) + PbSO_4\ (crystal) \qquad (1)$$

The corresponding equilibrium expression is:

$$K_{eq} = \frac{a_{Ba^{2+}(aq)}\, a_{PbSO_4(crystal)}}{a_{Pb^{2+}(aq)}\, a_{BaSO_4(crystal)}} = \frac{K_{sp(BaSO_4)}}{K_{sp(PbSO_4)}}.$$

This equation may be rearranged to give the homogeneous distribution law of Henderson and Kracek:[1]

$$\left(\frac{Pb^{2+}}{Ba^{2+}}\right)_{crystal} = D\left(\frac{Pb^{2+}}{Ba^{2+}}\right)_{aq} \qquad (2)$$

in which D is called the homogeneous distribution coefficient:

$$D = \frac{K_{sp(BaSO_4)}}{K_{sp(PbSO_4)}}\left(\frac{\gamma Pb}{\gamma Ba}\right)_{aq}\left(\frac{\gamma Ba}{\gamma Pb}\right)_{crystal} \qquad (3)$$

and γ = activity coefficient.

Hermann[2] has written a similar equation in which the non-ideality of the solid solution is expressed as a free energy term rather than as a ratio of activity coefficients in the crystal.

Equations (2) and (3) predict both the extent and the form of the distribution of

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lead and barium between the solid and the solution. In a system in which precipitation is taking place, both predictions are wrong. The distribution of ions between the solid and the solution during precipitation does not correspond to the form of equation (2), and the observed values for D are not simply related to the solubility product constants.

According to the homogeneous distribution law, the entire crystal is involved in the distribution reaction. The distribution reaction is, however, a surface reaction; the interior of the crystal can react with the solution only through diffusion in the solid, or through re-solution and re-precipitation. If these processes are slow, it may be assumed that only the surface of the crystals takes part in the distribution reaction and that the distribution within the crystal is fixed. In a precipitating system, the term (Pb^{2+}/Ba^{2+}) at the crystal surface may be replaced by $(dPb^{2+}/dt)/(dBa^{2+}/dt) = d(Pb^{2+})/d(Ba^{2+})$, and equation (2) becomes

$$\frac{d(Pb^{2+})}{d(Ba^{2+})} = \lambda \frac{(Pb^{2+})}{(Ba^{2+})} \tag{4}$$

where D and λ have the same thermodynamic significance, but describe a different form of distribution.

In its integrated form, with the assumptions given above, equation (4) is the logarithmic distribution law of Doerner and Hoskins:[3]

$$\log \frac{(Pb^{2+})_i}{(Pb^{2+})_f} = \lambda \log \frac{(Ba^{2+})_i}{(Ba^{2+})_f}, \tag{5}$$

where the subscripts *i* and *f* refer to the initial and final solution concentrations. The form of the logarithmic distribution law is followed by a number of systems, particularly when the technique of precipitation from homogeneous solution is employed.[2,4] The observed values of the logarithmic distribution coefficient, λ, are not, however, simply related to the solubility product constants. Equations (4) and (5) may therefore be accepted as statements of experimental facts which have not been rationalised in terms of theory.

Several investigators[2,5] have observed that λ is a function of precipitation rate, and that λ approaches 1 (the precipitation becomes less selective) as the rate of precipitation increases. The present paper describes the derivation and testing of an equation relating λ to thermodynamic and kinetic parameters.

KINETICS OF COPRECIPITATION

Crystal growth is generally considered to proceed by incorporation of ions or molecules at kinks in the growth steps on the crystal surface.[6] A kink site is represented by the dotted volume of Fig. 1. Kinks are the most active sites for both deposition and solution of ions, because (*a*) they provide the maximum number of nearest neighbour interactions for deposition of an ion, (*b*) they provide the minimum number of nearest neighbour interactions for removal of an ion, and (*c*) they are regenerating, because deposition or removal of an ion does not destroy the active site, but merely moves it.

We will assume that coprecipitation of lead ion in a system in which barium sulphate is precipitating involves the following steps:

A: Lead and barium diffuse from the bulk solution to the active sites. Because of the similarity of the ions, their diffusion coefficients are essentially equal, and so they reach the active sites in proportion to their concentration in solution.

B: Every ion which approaches an active site is incorporated into the crystal. Therefore, precipitation is initially unselective.

C: Once incorporated at an active site, the reactions [equation (1)] leading to distribution equilibrium begin.

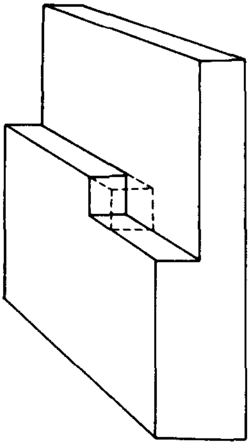

FIG. 1.—Representation of the surface of a crystal, showing an active site.

This scheme rationalises the observed relationship between λ and precipitation rate. As the rate of precipitation increases, ions are incorporated into active sites more rapidly, and the time each ion is in an active site decreases; therefore, there is less chance for equilibration, and the precipitation remains less selective.

In the derivation below, the charges have been omitted for simplicity.

$$\text{Let } I = \text{total precipitation rate} = d[Ba]/dt + d[Pb]/dt \tag{6}$$

According to the proposed steps A and B, the rate of deposition of lead at the active sites is $I\left(\frac{[Pb]}{[Pb]+[Ba]}\right)$, and the rate of deposition of barium is $I\left(\frac{[Ba]}{[Pb]+[Ba]}\right)$. The equilibration reaction of step C is

$$Pb(aq) + BaSO_4(crystal) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ba(aq) + PbSO_4(crystal),$$

for which R_f, the rate of the forward reaction, is

$$R_f = k_1M\left(\frac{d[Ba]/dt}{I}\right)\left(\frac{[Pb]}{[Pb]+[Ba]}\right).$$

In this equation, k_1 is a rate constant, M is the number of active sites, $\left(\frac{d[Ba]/dt}{I}\right)$ is the fraction of sites occupied by barium, and $\left(\frac{[Pb]}{[Pb]+[Ba]}\right)$ is the fraction of ions available at the site which are lead. Analogously, R_r, the rate of the reverse reaction, is

$$R_r = k_2M\left(\frac{d[Pb]/dt}{I}\right)\left(\frac{[Ba]}{[Pb]+[Ba]}\right).$$

The equilibrium constant for the distribution reaction in terms of the rate constants for the forward and reverse reactions is $K_{eq} = k_1/k_2$.

The rate equation for the precipitation of lead by steps A, B and C, is

$$d[Pb]/dt = \frac{I[Pb]}{[Pb] + [Ba]} - R_f + R_r,$$

or

$$\frac{d[Pb]}{dt} = \frac{I[Pb]}{[Pb] + [Ba]} - \frac{k_1 M}{I}(d[Ba]/dt)\left(\frac{[Pb]}{[Pb] + [Ba]}\right) + \frac{k_2 M}{I}(d[Pb]/dt)\left(\frac{[Ba]}{[Pb] + [Ba]}\right).$$

Analogously, the rate equation for the precipitation of barium is

$$\frac{d[Ba]}{dt} = \frac{I[Ba]}{[Pb] + [Ba]} + \frac{k_1 M}{I}(d[Ba]/dt)\left(\frac{[Pb]}{[Pb] + [Ba]}\right) - \frac{k_2 M}{I}(d[Pb]/dt)\left(\frac{[Ba]}{[Pb] + [Ba]}\right).$$

Rearranging, and substituting from equation (6) we obtain

$$\frac{d[Pb]}{dt}\left([Ba] + [Pb] - \frac{k_1 M}{I}[Pb] - \frac{k_2 M}{I}[Ba]\right) = [Pb](I - k_1 M),$$

and

$$\frac{d[Ba]}{dt}\left([Ba] + [Pb] - \frac{k_1 M}{I}[Pb] - \frac{k_2 M}{I}[Ba]\right) = [Ba](I - k_1 M),$$

from which

$$\frac{d[Pb]}{d[Ba]} = \frac{[Pb]}{[Ba]}\left(\frac{I - k_1 M}{I - k_2 M}\right).$$

This equation is of the same form as equation (4), so that the proposed mechanism correctly predicts the form of the distribution in a precipitating system. Further, by comparing this equation with equation (4), we obtain

$$\lambda = \left(\frac{I/M - k_1}{I/M - k_2}\right), \qquad (7)$$

which describes the observed value of λ in terms of the rate of precipitation per active site, and two rate constants the ratio of which is the equilibrium constant for the distribution reaction.

The lead sulphate-barium sulphate system was employed to test equation (7).

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used without further purification.

Determination of I, the rate of precipitation

Sulphate ion was generated electrolytically, by oxidation of thiocyanate at constant current.[7] All solutions were seeded with solid barium sulphate, and in such systems the rate of precipitation is identical to the rate of generation of sulphate.[7] In all experiments the current was such as to make $I = -4.17 \times 10^{-7}$ mole. litre^{-1}. sec^{-1}.

Determination of M, the number of active sites

Turnbull[8] has shown that after nucleation has occurred, the effective growth area (the number of active sites) of barium sulphate remains constant despite expansion of the total surface area. The number of active sites was therefore assumed to be proportional to N, the total number of crystals, with the proportionality constant incorporated into the rate constants k_1 and k_2. Conventional microscopic blood cell counting techniques were used to determine N.

A seed suspension was freshly prepared for each run by mixing equal volumes of 0.125*F* $Ba(ClO_4)_2$ and Na_2SO_4. Different volumes of the suspension (3–75 ml) were taken, so that N varied from run to run, but the size and shape of the seed crystals was constant. The number of seed crystals did not change from the beginning to the end of a run, indicating that the seed crystals did not fracture or aggregate.

Determination of λ, the logarithmic distribution coefficient

The values required are the initial and final concentrations of lead and barium. The initial concentrations were determined by potentiometric EDTA titrations using the mercury indicator electrode. Lead was titrated in an acidic solution, the pH was raised, and barium was titrated in the same solution.

Because the concentration of barium in the final solution was too small to be determined by the above method, the final concentrations of lead and barium were determined by X-ray fluorescence, using a Norelco apparatus equipped with a lithium fluoride crystal and a scintillation detector. Aliquots of the final solution were precipitated with excess Na_2SO_4 and deposited on a membrane filter. The filter was supported in the X-ray beam, and the barium K_α and lead L_α lines were counted. By the use of appropriate standards and background corrections, the ratio $[Pb^{2+}]/[Ba^{2+}]$ in the final solution was obtained. The ratio $[Pb^{2+}]/[Ba^{2+}]$ in the final precipitate was determined in the same way. From these two concentration ratios and the initial concentrations, the final solution concentrations of lead and barium were calculated.

Procedure. Two hundred ml of a stock solution of barium and lead perchlorates were mixed with the appropriate volume of seed suspension, the pH was adjusted to 1.0 with perchloric acid, and the solution was diluted to 250 ml. Two hundred ml of this seeded solution were placed in a beaker thermostatted at 25.0 ± 0.1°, and electrolysed for approximately 3·5 hr, with vigorous stirring. A portion of the original seeded solution was filtered and titrated for lead and barium, and aliquots of the final solution and precipitate were taken immediately for X-ray fluorescence analysis. An additional sample of the final solution was taken for microscopic counting, to determine N.

RESULTS AND DISCUSSION

The logarithmic distribution coefficient, λ, was measured in a series of experiments in which the initial ratio $[Pb^{2+}]/[Ba^{2+}]$ and the rate of precipitation per particle were varied. Results of these experiments are presented in Table I. The precipitation rate per particle was varied over a 25-fold range, and the corresponding values of λ varied over a 18-fold range.

TABLE I.—LOGARITHMIC DISTRIBUTION COEFFICIENTS FOR COPRECIPITATION OF LEAD WITH BARIUM SULPHATE[a]

N × 10^{-3} litre^{-1}	10.8	8.01	4.72	3.50	2.56	1.69	1.20	0.88	0.65	0.65	0.41
[Ba] × 10^3 initial	4.76	4.84	4.96	10.24	5.02	4.98	9.31	5.03	9.28	8.91	9.60
[Pb] × 10^3 initial	4.31	4.63	4.77	2.80	4.92	4.85	2.80	4.95	1.52	2.71	2.74
λ	0.018	0.031	0.058	0.071	0.085	0.102	0.158	0.188	0.224	0.264	0.331

[a] Rate of precipitation, $d[Pb^{2+}]/dt + d[Ba^{2+}]/dt = -4.17 \times 10^{-7}$ mole. litre^{-1}. sec^{-1} in all experiments.

Equation (7) may be rearranged to give

$$I/N(\lambda - 1) = k_2\lambda - k_1,$$

and the results of Table I, plotted as $I/N(\lambda - 1)$ against λ, should yield a straight line of slope k_2 and intercept $-k_1$. Fig. 2 is such a plot. The experimental results appear to be adequately represented by the least squares straight line, supporting the validity of equation (7). The initial ratio $[Pb^{2+}]/[Ba^{2+}]$ does not appear to influence λ, within the accuracy of the experiments. The slope and intercept of the least squares line lead to the values $k_1 = 2{\cdot}0 \times 10^{-11}$ mole.sec^{-1}. particle^{-1} and $k_2 = 2{\cdot}1 \times 10^{-9}$ mole. sec^{-1}. particle^{-1}.

The ratio k_1/k_2 is the equilibrium constant for the distribution reaction of equation (1), and should therefore also be equal to D in equation (3). Because of the similarity of size and charge, it is reasonable to assume that the activity coefficients of lead and barium ion in the solution are approximately equal. Because only a small amount of lead is incorporated into the barium sulphate crystals, and because lead and barium are similar in charge and size, it may also be assumed that the lead forms an essentially ideal solid solution in the barium sulphate crystals. With these assumptions, the equilibrium constant for the distribution reaction should be approximately equal to $K_{sp}(BaSO_4)/K_{sp}(PbSO_4)$.

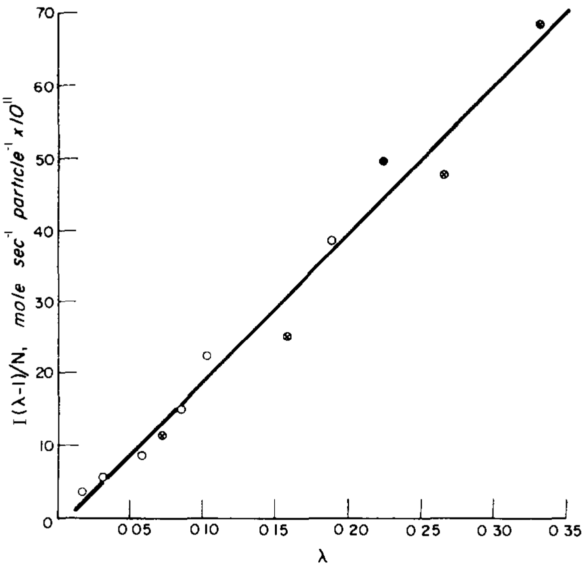

FIG. 2.—Variation of logarithmic distribution coefficient λ with rate of precipitation I and number of crystals N:

○ $[Pb^{2+}]/[Ba^{2+}]$, initially approximately 1.0.
⊗ $[Pb^{2+}]/[Ba^{2+}]$, initially approximately 0.30.
● $[Pb^{2+}]/[Ba^{2+}]$, initially approximately 0.15.

Thus if equation (7) is valid,

$$k_1/k_2 \simeq K_{sp(BaSO_4)}/K_{sp(PbSO_4)}.$$

The literature value[9] for the ratio of solubility product constants is 0·007 and the ratio k_1/k_2 is 0·010, so that the two values agree, within the accuracy of the experiments.

It appears, therefore, that the observed value of the logarithmic distribution coefficient depends upon both thermodynamic and kinetic factors, the form of the dependence being that of equation (7). In the lead-barium sulphate system, the value of the distribution coefficient at zero rate of precipitation is given by the ratio of solubility product constants. Other sulphate systems are now being studied, to determine if equation (7) is generally applicable, and if the distribution coefficient at zero precipitation rate may in general be predicted from values of the K_{sp}.

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Zusammenfassung—Eine Gleichung wurde abgeleitet, die den logarithmischen Verteilungskoeffizienten bei der Mitfällung als Funktion der Fällungsgeschwindigkeit, der Anzahl der wachsenden Kristalle und zweier Geschwindigkeitskonstanten darstellt, daren Verhältnis der Verteilungskoeffizient bei der Fällungsgeschwindigkeit Null ist. Im System Bleisulfat-Bariumsulfat beschreibt die Gleichung die Abhängigkeit des Verteilungskoeffizienten von der Fällungsgeschwindigkeit richtig. Der Verteilungskoeffizient bei Fällungsgeschwindigkeit Null ist 0,010. Das stimmt gut mit dem aus den Löslichkeitsprodukten vorausgesagten Wert überein.

Résumé—On a dérivé une équation qui représente le coefficient de partage logarithmique dans la coprécipitation comme une fonction de la vitesse de précipitation, du nombre de cristaux en développement, et de deux constantes de vitesse dont le rapport est le coefficient de partage à la vitesse de précipitation nulle. Dans le système sulfate de plomb-sulfate de baryum, l'équation dérivée décrit correctement la dépendance entre le coefficient de partage et la vitesse de précipitation. Le coefficient de partage à la vitesse de précipitation nulle est 0,010 ce qui est en accord satisfaisant avec la valeur prévue à partir des produits de solubilité.

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THE DIRECT DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS

A STUDY OF VARIOUS MODIFICATIONS

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Summary—The Schütze method for the direct determination of oxygen in organic compounds has been modified by a number of investigators. It has not always been clear whether a particular modification offers any advantage. Several of these modifications have, therefore, been examined in turn and compared. In the course of this work the gases obtained by pyrolysis have been analysed in a mass spectrometer. As a result of this examination it is recommended that the organic oxygen-containing compound be pyrolysed over platinised carbon heated at 900°, that both reduced copper and soda asbestos be used to remove interfering gases, and that the determination be completed gravimetrically after conversion of carbon monoxide to carbon dioxide with Schütze reagent at room temperature. Alternative methods of determining carbon dioxide are discussed.

THE method for the direct determination of oxygen in organic compounds, based on thermal decomposition in a stream of nitrogen and conversion of all the oxygen-containing material to carbon monoxide by reaction with heated carbon, was described by Schütze in 1939.[1,2] Since that time the method has been subjected to many modifications and it is not apparent from the available literature which particular combination of modifications is the most convenient and efficient.

The more important modifications are:

(i) The use[3] of platinised carbon at 900° instead of pure carbon at 1120°.

(ii) Methods for converting carbon monoxide to a suitable form for the final measurement.

Some of the reagents which are used are Schütze's reagent[2] (iodine pentoxide and sulphuric acid on silica gel) at room temperature, heated iodine pentoxide (measurement of the iodine[4] or of the carbon dioxide liberated[5]), heated copper oxide,[6] or heated mercury(II) oxide.[7]

(iii) The method of final measurement.

Iodine is always determined by the amplification method (see p. 49), but carbon dioxide is determined gravimetrically or titrimetrically.[8] In one method both iodine and carbon dioxide are removed together in the same absorption tube so that an improved gravimetric factor is obtained.[9]

A number of these modifications has been examined critically by the present authors and from the experience gained it is possible to make definite recommendations. The general method is not, however, universally applicable, because many uncertainties still remain, *e.g.*, the effect of phosphorus, fluorine and metals. Our studies of these problems will be described in a later communication.

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As often occurs with methods which undergo considerable modification whilst retaining the original principle, *e.g.*, the use of tricobalt tetroxide (Co_3O_4) in the determination of carbon and hydrogen[10] and the oxygen flask method,[11] the original work is sometimes lost sight of and is ascribed to later workers.

The basic procedure for the direct determination of oxygen seems to have been first used by Markert,[12] a student of Hempel at Dresden Institute of Technology in 1904. All that the present authors know of this method (for we have not seen the thesis) is that the substance was pyrolysed over carbon at "a high temperature" in a stream of nitrogen. The carbon monoxide was burnt to carbon dioxide which was determined gravimetrically.

Apart from Boswell[13] in 1914, who pyrolysed samples in hydrogen over carbon, combusted carbon monoxide to carbon dioxide and then weighed the latter and the water separately, no similar work appears to have been done until Schütze described his method in 1939. Schütze discovered the method independently; this is not surprising because the Hempel-Markert studies were not published in the literature.

Schütze, who also used the method for determining oxygen in zinc oxide, used a temperature of 1000°. He completed the method gravimetrically after oxidising carbon monoxide at room temperature using the preparation now called the Schütze reagent.

Sample weights of 20–50 mg were used in Schütze's method, and Zimmermann[14] adapted it to the micro scale (3–5 mg).

Unterzaucher[4] studied the method in detail and made several modifications, the most important being the raising of the temperature to 1120° to ensure complete reaction. Unterzaucher also replaced the Schütze reagent by heated iodine pentoxide so that an amplified iodimetric titration could be used. This particular modification became widely used, but in more recent times a return has been made to the Schütze reagent.

The most important later contribution was the discovery by Oita and Conway[3] that platinised carbon heated to 900° was as effective as pure carbon at 1120°. In a comprehensive review of methods for determination of oxygen, Elving and Ligett[15] described an incomplete investigation of metal-carbon packings, and this led Oita and Conway to make an intensive study of such materials. Oita and Conway also emphasised the need for using reduced copper in addition to soda asbestos to remove interfering gases.

Oliver[16] later simplified the Oita-Conway assembly and his modification is now generally used wherever platinised carbon is preferred.

It was not possible for us to compare every modification, for this would have been too time-consuming; hence, some selection had to be made. It was, however, a simple matter to choose between pure carbon at 1120° and platinised carbon at 900°. If both are equally efficient, then platinised carbon at 900° is to be preferred, because it has the double advantage of extending the lives of the silica tube and of the furnace.

Extended tests with platinised carbon showed that this packing was highly efficient; it was, therefore, used exclusively in all subsequent work.

The following methods of oxidising carbon monoxide and determining the reaction products were examined:

(1) Schütze reagent at room temperature; gravimetric determination of carbon dioxide.
(2) Anhydro-iodic acid at 118°; gravimetric determination of carbon dioxide.
(3) Schütze reagent at 118°; iodimetric method.
(4) Anhydro-iodic acid at 118°; iodimetric method.

The products of decomposition from organic compounds pyrolysed at 1120° over pure carbon have been analysed by Maylott and Lewis,[17] and by Dundy and Stehr,[5] but, so far as was known to us, similar information on the composition of the gases at the lower temperature was not available. Hence, the effluent gases were nalysed in a mass spectrometer.

Comparison of Reagents for Oxidising Carbon Monoxide and for Completing the Determination

In all the comparison tests the same procedure was used (see *Experimental*). To avoid complications, compounds containing carbon, hydrogen, oxygen and nitrogen only were examined. The effluent gases were passed through soda asbestos before the oxidation of carbon monoxide. Sample weights of 3–5 mg were taken.

In the examination of anhydro-iodic acid at 118° (gravimetric method), sodium thiosulphate crystals were packed after the anhydro-iodic acid to absorb the iodine liberated.

The Schütze reagent is not, of course, intended for use with the iodimetric titration; nevertheless, the comparison was made. It was necessary to heat to 118° to volatilise the iodine.

Discussion of results

Only a few determinations were done using the Schütze reagent and iodimetric titration. The blank values were not constant. The results (Table I) tended to be slightly higher than those obtained by other methods. The reagent deteriorated rapidly when heated, and survived for only 5–8 determinations.

There is probably no significant difference in the efficiency of the other three methods. The iodimetric method is slightly speedier than the gravimetric method, and would undoubtedly have advantages when trace amounts of oxygen were determined because of amplification. Nevertheless, the gravimetric method using the Schütze reagent was preferred for the following reasons:

(a) The product measured (carbon dioxide) contains the element sought.

(b) The reagent is used at room temperature and eliminates the need for a further heating device.

(c) Some samples of anhydro-iodic acid rapidly became inactive even though prepared under what appear to be exactly the same conditions as samples which are satisfactory. All the samples of Schütze reagent were efficient.

The gravimetric method was used for measuring carbon dioxide because it was the most convenient. Infrared methods appear to be insufficiently sensitive. Conductimetric methods are more promising but the equipment is expensive.* Titration methods based on absorption in barium hydroxide solution[18] are too inaccurate. The method of Blom and Edelhausen,[19] in which the carbon dioxide is absorbed in pyridine and titrated with sodium methoxide, appears promising and will be examined critically at a later date.

Other methods of oxidising carbon monoxide, *e.g.*, heated copper oxide or mercury(II) oxide, were not examined because they are less convenient to use then the Schütze reagent and are unlikely to offer any other advantages.

Composition of Gases Obtained by Pyrolysis over 50% Platinised Carbon at 900°

The mass spectrometer used was not equipped with a double focussing device and it was, therefore, impossible to differentiate between nitrogen and carbon

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* H. Westhöff, OHG, Bochum, Bundesrepublik Deutschland, now sell a complete assembly for the direct determination of oxygen, in which the final measurement of carbon dioxide is done by their recording instrument. Excellent results are reported.

Table I.—Determination of oxygen in organic compounds by various procedures

Compound (% of oxygen present)	Schütze reagent-gravimetric (ambient temp.)			Anhydro-iodic acid-gravimetric (118°)			Anhydro-iodic acid-iodimetric (118°)			Schütze reagent-iodimetric (118°)		
	Oxygen found,[a] %	Error	Range[b]	Oxygen found,[a] %	Error	Range[b]	Oxygen found,[a] %	Error	Range[b]	Oxygen found,[a] %	Error	Range[b]
Naphthalene (0)	0·11	+0·11	0·06–0·15	0·12	+0·12	0·11–0·14	0·18	+0·18	0·12–0·22	0·23	+0·23	0·19–0·30
Benzoic acid (26·20)	26·10	−0·10	0·14–0·29	26·12	−0·08	0·08–0·19	26·22	+0·02	0·09–0·21	26·38	+0·18	0·15–0·22
Sucrose (51·46)	51·49*	+0·03	0·01–0·23	51·50	+0·04	0·06–0·11	51·54*	+0·08	0·06–0·23	50·94	−0·52	0·04–1·67
m-Dinitrobenzoic acid (45·26)	45·49	+0·23	0·09–0·46	45·26	0·00	0·03–0·21	45·18	−0·08	0·06–0·24	—	—	—
8-Hydroxyquinoline (11·05)	10·92‡	−0·13	0·06–0·61	10·90	−0·15	0·16–0·31	11·13	+0·08	0·06–0·24	—	—	—
p-Nitroaniline (23·18)	23·20*	+0·02	0·06–0·14	23·23	+0·05	0·05–0·25	23·31	+0·13	0·09–0·33	—	—	—
Acetanilide (11·84)	11·79*	−0·05	0·03–0·25	11·80	−0·04	0·06–0·14	11·88	+0·04	0·02–0·15	11·90†	+0·06	0·04–0·11
Phenacetin (17·86)	18·05	+0·19	0·06–0·33	17·78	−0·08	0·01–0·21	17·77	+0·09	0·10–0·27	—	—	

[a] Percentage (absolute) of oxygen found is the average of 3 results except for * (4 results), † (2 results), ‡ (8 results).

[b] Range represents the minimum and maximum divergence from theoretical (percentage) result stated without regard to sign.

monoxide. Hence, at this stage of the work, only qualitative analysis was attempted. The results are given in Table II.

TABLE II

Type of compound[f]	Gases present[a]
C, H or C, H, O	CO, H_2, N_2 (from carrier gas), HCN[b]
C, H, N, O	CO, H_2, N_2, HCN
C, H, O, S	CO, H_2, N_2, H_2S, CS_2, COS, HCN[d,e]
C, H, O, Cl	CO, H_2, N_2, HCN, HCl
C, H, O, N, Br	CO, H_2, N_2, HCN[c]
C, H, O, N, I	CO, H_2, N_2, HCN[c]

[a] With some hydrocarbons, traces of methane were found (*cf.* Table IV).

[b] Presumably HCN is produced from the nitrogen gas used as carrier, because it was found even when compounds not containing nitrogen were pyrolysed.

[c] Bromine, iodine, and their acids were not detected. The exit end of the pyrolysis tube, however, developed a reddish-brown colour, so that the free halogens are probably adsorbed on the cool silica walls.

[d] When sulphur is present, H_2S, CS_2 and (if oxygen is present) COS are always formed. These products were still detectable when bromobenzoic acid was analysed 1 day later. Even after 3 days of continuous sweeping with nitrogen, CS_2 was still detectable. Therefore, if compounds not containing sulphur are analysed after sulphur-containing compounds, it is still essential to retain the absorbent for removing the sulphur-containing products of the pyrolysis.

[e] Sulphur appears mainly as H_2S, but if there is a deficiency of hydrogen, more CS_2 is formed.

[f] When compounds containing both sulphur and halogen are pyrolysed, sulphur-halogen compounds are not detected in the effluent gases.

When sulphonal was pyrolysed the effluent gases had the composition shown in Table III, calculated on a nitrogen/carbon monoxide-free basis.

TABLE III.—COMPOSITION OF THE EFFLUENT GASES FROM SULPHONAL

Gas	% by volume
H_2	91·5
H_2S	4·3
HCN	2·2
COS	1·8
CS_2	0·2
CH_4	trace

Removal of Interfering Gases

The effluent gases were also analysed after passage through soda asbestos. The results are summarised in Table IV.

TABLE IV.—COMPOSITION OF THE EFFLUENT GASES AFTER PASSAGE THROUGH SODA ASBESTOS

Compound	Gases unabsorbed	Gases absorbed
Anthracene	H_2	HCN
Sulphonal	H_2, CH_4, CS_2	HCN, COS
2,4-Thiazolidinedione	H_2, CH_4, CS_2	HCN, H_2S, COS
1-Chloro-2,4-dinitrobenzene	H_2, CS_2[a]	HCN, HCl

[a] CS_2 is from sulphur-containing compounds pyrolysed in previous experiments.

Soda asbestos absorbs hydrogen sulphide, hydrogen cyanide, carbonyl sulphide and hydrogen chloride. Absorption of carbonyl sulphide leads to loss of oxygen and it is best decomposed with heated copper as recommended by Oita and Conway before the gases pass on to the soda asbestos; sulphur is removed and carbon monoxide is produced. Copper also removes carbon disulphide, but hydrogen sulphide still appears in the effluent gases probably as a result of the reaction

$$Cu_2S + H_2 \rightarrow H_2S + 2Cu.$$

Because this is removed later by the soda asbestos, there is no interference.

It is thus essential to use both heated copper and soda asbestos to remove interfering gases.

Effect of hydrogen and carbon disulphide on reagents

Hydrogen (500 ml) was passed through Schütze reagent at room temperature and at 118° and through anhydro-iodic acid at 118°. The results are reported in Table V.

Table V.—Effect of hydrogen on Schütze reagent and anhydro-iodic acid

	Oxygen, *mg*	
	Iodimetric	Gravimetric
Schütze reagent		
Room temp.	—	0·03
118°	1·04	—
Anhydro-iodic acid		
118°	0·10	0·04

The effect of hydrogen is most pronounced with heated Schütze reagent. Large amounts of iodine are liberated and this must account for the large and variable blanks reported earlier (p. 45). Neither gravimetric method is affected, as would be expected. The blank is slightly higher with anhydro-iodic acid iodimetrically, but the amount would be insignificant in an actual determination. If 5 mg of a compound containing 5% of hydrogen were analysed, and if all the hydrogen were produced as gaseous hydrogen, the amount of iodine liberated would be equivalent to less than 4 μg of oxygen.

The effect of carbon disulphide on Schütze reagent was examined by volatilising a weighed amount in a stream of nitrogen through the apparatus (Table VI). Carbon disulphide reduced the Schütze reagent and must be removed.

Table VI.—Effect of carbon disulphide on Schütze reagent

CS_2, *mg*	CO_2, *mg*
40	4·6
20	2·4
20	2·8

The Iodimetric Determination

The liberated iodine is determined, after absorption in sodium hydroxide solution, by oxidising iodide to iodate with bromine-acetic acid, destroying the excess of bromine with formic acid, then determining the iodate iodimetrically. A six-fold amplification of the original iodine is thus obtained. This is a well-established procedure and was first used in micro-analysis for the determination of iodine[20] and of alkoxyl groups.[21,22]

It is generally assumed that free iodine does not react with formic acid, but it has been shown recently[23] that the reaction is dependent on pH and time. Even at pH 1.6 there is a significant reaction in 30 min.

Because this may provide a source of error in the iodimetric determination, some tests were done to find if formic acid reacted with iodine under the conditions of the determination. No evidence was found of any such reaction. This is ascribed to the fact that the excess of sodium hydroxide is neutralised before oxidation of iodide to iodate, and that only a slight excess of formic acid is ever present, so long as the bromine is destroyed carefully.

Fildes and Macdonald[24] preferred to use phosphoric acid for neutralisation so that the acetic acid-sodium acetate buffer need not be used. This reduced the electrolyte

TABLE VII.—BLANK VALUES REPORTED AS PERCENTAGE OF OXYGEN ON A 4-mg SAMPLE

Conditions	Oxygen, *mg*	Error, % (absolute) (4-mg sample; 20% of oxygen)
Gravimetric		
Schütze reagent (room temp.)	0·007–0·025	0·175–0·625
Anhydro-iodic acid (118°)	0·011–0·036	0·275–0·900
Iodimetric		
Schütze reagent (room temp.)	0·020–0·056	0·50–1·5
Anhydro-iodic acid (118°)	0·015–0·036	0·375–0·90

TABLE VIII.—BLANK VALUES REPORTED BY VARIOUS INVESTIGATORS

Author	Temp.*	Sample wt., *mg*	Blank value, *mg* of oxygen	Reagent
Unterzaucher[4]	H	3–30	0·0	HI_3O_8-iodimetric
Oita and Conway[3]	L	3–80	0·004–0·007	HI_3O_8-gravimetric
Campanile *et al.*[25]	H	5–50	0·020	I_2O_5-iodimetric
Maylott and Lewis[17]	H	3–30	>0·11	I_2O_5-iodimetric
Dundy and Stehr[5]	H	3–30	0·007–0·036	I_2O_5-gravimetric
Hinkel and Raymond[8]	H	15–30	0·02–0·026	I_2O_5-titrimetric
Zimmermann[14]	H	5	0·036	Schütze reagent -gravimetric
Aluise *et al.*[27]	H	5–10	0·073	I_2O_5-iodimetric
Dinerstein and Klipp[28]	H	15–25	0·1	I_2O_5-iodimetric
Berret and Poirier[29]	H	10–20	0·018	Schütze reagent -gravimetric
Gouverneur *et al.*[26]	H	30–60	0·34	I_2O_5-iodimetric
		100	0·07	I_2O_5-gravimetric
Belcher, Davies and West	L	3–5	0·007–0·025	Schütze reagent -gravimetric

* H = high temperature; L = low temperature.

concentration by about one-half. Better starch end-points are then obtained because electrolyte concentration affects the sensitivity. These observations were confirmed and the Fildes-Macdonald procedure was used exclusively to obtain the results reported in this paper.

Blank Values

Unterzaucher reported that zero blanks were obtained, but only one other investigator within our knowledge has had similar experiences. Our own blanks varied over a narrow range, but were consistent over a period of several days. They are similar to those obtained by many other investigators (see Table VIII). The Schütze reagent gave the best results and this is a further point in its favour.

The results obtained are reported in Table VII. Table VIII compares the blank values obtained by various investigators.

EXPERIMENTAL

Reagents

Nitrogen. "White Spot" (British Oxygen Company Limited), containing less than 10 ppm of oxygen.

Paraffin oil

Reduced copper in wire form. Prepared[4] from micro-analytical reagent grade wire-form copper(II) oxide which was treated with hot dilute acetic acid, filtered, washed thoroughly with distilled water, dried, then heated for several hours in air at approximately 800°. The product obtained is carefully reduced in a quartz tube heated at 250–300° by passing a slow stream of hydrogen over it.

Soda asbestos, micro-analytical reagent grade (14–22 mesh)

Anhydrone, micro-analytical reagent grade (14–22 mesh)

Platinum

Platinised carbon (50%). Obtainable from Johnson and Matthey Limited, or prepared according to the method of Oliver.[16]

Schütze reagent. Obtained from Badische Anilin und Soda Fabrik A.G., Ludwigshafen, Bundesrepublik Deutschland (U.K. Agents: Kodak Co., Kirby, Liverpool). The preparation of the reagent has been described.[2] There is no need to absorb the liberated iodine as in other gravimetric procedures, because it is retained by the reagent and shows up as a zone of liberated iodine which grows slowly in length during the life of the filling. The filling is usable until only a narrow band of the original yellow material remains.

Apparatus (*Fig.* 1)

Nitrogen purification system. The last traces of oxygen are removed from the nitrogen by the large surface area of the reduced wire-form copper heated at 550°.

Combustion tube filling. To clean the tube before use it was treated with 40% hydrofluoric acid. This was done by filling the tube with the acid and allowing it to stand vertically for about 1 hr followed by thorough washing with water. The tube filling (Fig. 2) consists of 8 cm of 50% platinised carbon in two portions, 3 and 5 cm long, respectively, separated by a 1-cm layer of platinum gauze. These layers were held in place by layers of quartz wool.

Oxidation tube filling. This tube contains materials (Fig. 3) separated by quartz wool plugs. Iodised cotton is made by soaking cotton wool in saturated potassium iodide solution and drying at 100°.

Operation of apparatus

When a newly assembled oxygen micro-determination apparatus is brought into operation, a flow of nitrogen is passed through the reverse flushing device (J), into the combustion tube (H) so that the nitrogen passes through the packed platinised carbon layer and out into the atmosphere at the ground-joint end (K). The long heater (M) is then switched on and its temperature raised to 900°. After sweeping out the apparatus for 1–2 days, the empty portion of the combustion tube is heated, starting from the platinised carbon end and going towards the ground-glass end, using the movable burner to remove any foreign substances that may have possibly come from the platinised carbon. The heating of the combustion tube is continued with nitrogen flowing in the forward direction until low and constant blank values are obtained.

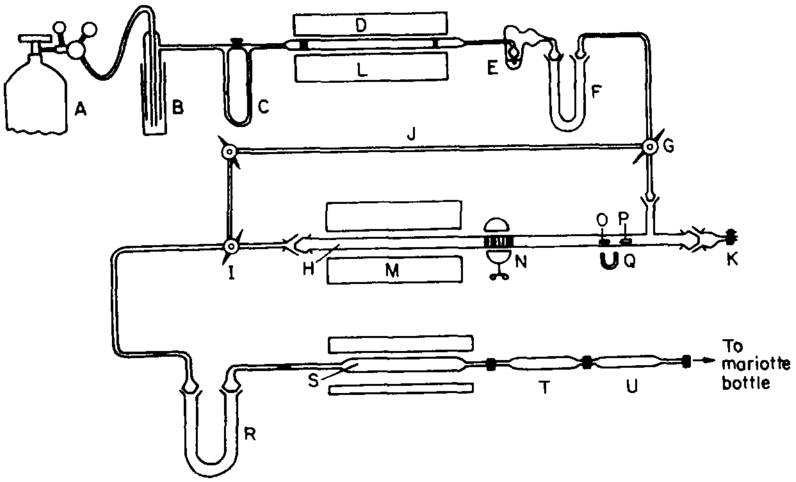

FIG. 1.—Apparatus for gravimetric determination of oxygen in organic compounds:

A—Nitrogen cylinder
B—Pressure regulator, containing mercury
C—Flowmeter
D—Quartz preheater tube (*ca.* 15 mm × 180 mm) containing pure copper
E—Bubble counter containing paraffin oil
F—Drying U-tube, containing soda asbestos and anhydrone
G, I—Three-way stopcocks
H—Quartz combustion tube
J—Reverse flushing tube
K—Stopcock for admitting samples
L—Preheater furnace, adjusted to approximately 550°
M—Long heater, adjusted to 900°
N—Movable burner
O—Platinum sample boat (Fig. 2)
P—Glass-covered iron rod (Fig. 2)
Q—Magnet (Fig. 2)
R—Scavenging U-tube containing soda asbestos and anhydrone
S—Oxidation tube
T—Micro-absorption tube
U—Guard tube

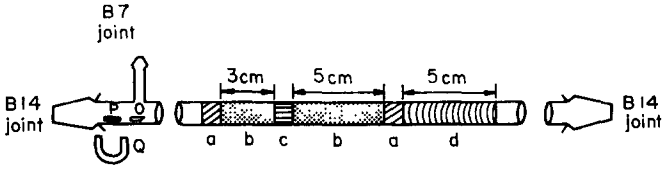

FIG. 2.—Combustion tube filling:
a—quartz wool,
b—50% platinised carbon,
c—platinum gauze,
d—copper gauze (only used in the mass spectrometric studies).

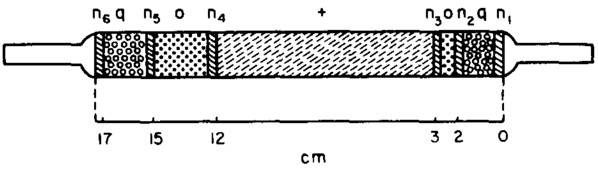

FIG. 3.—Oxidation tube filling:
n_1 - - n_6—quartz wool,
o—iodised cotton,
+—Schütze reagent,
q—Anhydrone.

Method of analysis

Adjust the main furnace (M) to a temperature of 900° and the nitrogen flow to 10 ml/min. Connect the carbon dioxide absorption tube (T) to the oxidation tube (S) and also to the guard tube (U) and Mariotte Bottle. Sweep out the apparatus for 10 min with the absorption tube attached. Meanwhile, weigh a sample (3–5 mg) in a platinum boat on a micro balance. Remove the absorption tube at the end of 10 min, wipe and weigh at the 15th min.

Set the three-way stopcocks (G) and (I) to allow the nitrogen to flow through the thick-walled capillary into the combustion tube (H) and then through the opened stopcock (K) on the closing tap. Remove the closing tap and introduce the sample boat 5 cm into the combustion tube with a glass-covered iron rod in position behind it. Replace the closing tap and sweep out the combustion tube for 5 min with an increased flow rate of 20 ml/min. Close stopcock (K), open the guard tap and change the gas flow to the forward direction at a rate of 10 ml/min.

By means of the magnet and glass-covered iron rod "push" the sample boat to within 5 cm of the furnace, and return the rod to the entrance of the tube. Start the pyrolysis with a low heat about 5 cm upstream from the sample. Move the heater towards the furnace at a slow rate of 2 cm/min. When the sample is completely volatilised, increase the temperature of the heater to its maximum and repeat the pyrolysis as follows: keep the heater around the sample for 5 min, then move it slowly towards the furnace at the rate of 2 cm/min. When the furnace is reached, keep the heater stationary for another 5 min; the pyrolysis is completed in 20 min.

Switch off the heater and sweep the combustion tube through for 30 min. In the meantime, weigh another sample. Remove the absorption tube, wipe and weigh on the 15th min.

Determine blank values by introducing an empty boat and repeating the above procedure.

Calculate the percentage of oxygen as follows:

$$\left(\text{factor } \frac{\text{O}}{\text{CO}_2} = 0{\cdot}3636\right)$$

$$\%\ \text{Oxygen} = \frac{36{\cdot}36(W_1 - W_2)}{W_3}$$

where W_1 = weight of CO_2 from sample,
W_2 = weight of CO_2 from blank,
and W_3 = weight of sample.

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Zusammenfassung—Die Methode nach Schütze zur direkten Sauerstoffbestimmung in organischen Verbindungen wurde von einigen Autoren modifiziert. Es war nicht immer klar, ob eine bestimmte Änderung überhaupt Vorteile bietet. Daher wurden mehrere von diesen Änderungen von neuem geprüft und verglichen. Im Lauf dieser Arbeit wurden die pyrolytisch erhaltenen Gase in einem Massenspektrometer analysiert. Auf Grund dieser Untersuchung wird empfohlen, daß die sauerstoffhaltige organische Verbindung über auf 900°C erhitzter platinierter Kohle pyrolysiert wird, daß sowohl reduziertes Kupfer als auch Natronasbest zur Entfernung störender Gase eingesetzt werden und daß die Bestimmung gravimetrisch zu Ende geführt wird, nachdem Kohlenmonoxyd mit Schütze-Reagens bei Zimmertemperatur zu Kohlendioxyd umgesetzt ist. Andere Methoden zur Bestimmung von Kohlendioxyd werden diskutiert.

Résumé—La méthode de Schütze de dosage direct de l'oxygène dans les composés organiques a été modifiée par un certain nombre de chercheurs. Les avantages offerts par une modification particulière n'ont pas toujours été montrés clairement. Plusieurs de ces modifications ont, par conséquent, été examinées successivement et comparées. Au cours de ce travail, les gaz obtenus lors de la pyrolyse ont été analysés au spectromètre de masse. En résultat à cette étude, on recommande de pyrolyser le composé organique contenant de l'oxygène sur du carbone platiné chauffé à 900°, d'utiliser à la fois le cuivre

réduit et l'aminante sodée pour éliminer les gaz interférents, et de terminer le dosage gravimétriquement, après conversion de l'oxyde de carbone en gaz carbonique au moyen du réactif de Schütze à température ambiante. D'autres méthodes de dosage du gaz carbonique sont discutées.

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EIN QUALITATIVER TRENNUNGSGANG FÜR URANSPALTPRODUKTE MITTLERER BIS LANGER HALBWERTSZEIT MIT HILFE DER RINGOFENMETHODE

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Zusammenfassung—Es wird ein qualitativer Trennungsgang in einem Tropfen für Uranspaltprodukte mittlerer bis langer Halbwertszeit (Isotope des Cs, J, Sr, Ba, Zr, Nb, Ru, Y und der Seltenen Erden) mit Hilfe der Ringofenmethode beschrieben. Der Probetropfen, welcher die Radionuklide und Submikrogrammengen der entsprecnenden inaktiven Träger enthält, wird auf ein Rundfilter aufgetragen. Durch eine Folge geeigneter Fällungs-, Umfällungs-, Demaskierungs- und Auswaschschritte werden nacheinander einzelne Isotope bzw. Isotopengruppen aus dem zentralen Tüpfelfleck selektiv herausgelöst und in verschiedenen Ringen konzentriert. Die Identifizierung der Nuklide bzw. Nuklidgruppen erfolgt durch Autoradiographie der einzelnen Ringe. (Expositionszeit 20 h bei einer Aktivität von 50–100 pC je Radioisotop). Die bei den einzelnen Trennungsschritten erzielten Ausbeuten werden in tabellarischer Form dargestellt. Die Interpretation der Autoradiogramme sowie die Anwendungsmöglichkeiten des Trennungsganges werden diskutiert.

Bei der Bewertung der Strahlenbelastung des Menschen durch natürlich und künstlich radioaktive Isotope schließt die bloße Gesamtaktivitätsmessung zur Ueberwachung von Luft-, Wasser-, Nahrungsmittel- und Bodenproben stets die Gefahr erheblicher Fehlbeurteilung mit ein.[1] Dies rührt daher, daß sich die einzelnen Radio-Isotope eines Nuklidgemisches, wie es etwa bei einer Kernwaffenexplosion entsteht, in ihrer Wirksamkeit auf den Organismus aus physikalischen (Art und Energie der Strahlung, Halbwertszeit) und physiologischen Gründen (Aufnahme in den Körper, Verweilzeit im Körper, Anreicherung in bestimmten Organen) erheblich voneinander unterscheiden; deshalb sind für sie jeweils verschiedene, oft um einige Zehnerpotenzen voneinander abweichende Konzentrationen im menschlichen Körper, in Atemluft oder Trinkwasser zulässig.[2,3] Aus diesem Grunde können eindeutige Aussagen über die Bedenklichkeit oder Unbedenklichkeit einer vorliegenden radioaktiven Probe erst dann gemacht werden, wenn durch chemische Trennverfahren und physikalische Meßmethoden festgestellt worden ist, welche Radionuklide vorliegen und welchen Anteil jedes Nuklid zur Gesamtaktivität der Probe beiträgt.

Radiochemische Methoden zur Isolierung und Bestimmung einzelner, zur Strahlenbelastung des Menschen beitragender Radionuklide sind in der Literatur für die verschiedenartigsten Materialien in größerer Zahl beschrieben.[1] Weiterhin gibt es eine Reihe von Vorschriften zur systematischen Auftrennung von Spaltproduktgemischen. Bei einigen[4–8a] dieser Verfahren wird im Makro- oder Halbmikromaßstab mit konventionellen Fällungs- und Filtrationsschritten, mit Ionenaustauschern und Extraktionsmethoden gearbeitet, bei anderen im Mikrobereich papierchromatographisch[9,10] oder papierelektrophoretisch[11] getrennt. Die praktische Anwendung solcher Trennvorschriften erfordert meist einen beträchtlichen Zeit- und Arbeitsaufwand, da vielfach die in geringer Konzentration vorliegenden Radionuklide aus einem gewaltigen Ueberschuß inaktiven Materials angereichert werden müssen, und da man im allgemeinen Wert auf größtmögliche radiochemische Reinheit der abgetrennten Nuklide legt. Ein mit geringen Probemengen durchführbarer Trennungsgang, der nur einen qualitativen Ueberblick über die in einer Probe anwesenden Radio-Isotope bzw. Isotopengruppen sowie eine grobe Abschätzung der entsprechenden Aktivitätsanteile ermöglichen soll, kann jedoch aus einer Folge einfacher und relativ schnell auszuführender Operationen aufgebaut sein. Ein solcher Gang, der die mit Submikrogrammengen Träger verdünnten Radio-Isotope des Cäsium, Jod, Strontium, Barium, Zirkon, Niob, Ruthenium, Yttrium und der Seltenen Erden berücksichtigt, wird in der vorliegenden Arbeit beschrieben. Die einzelnen Trennungsschritte werden mit Hilfe der Ringofenmethode[12] durchgeführt, die Nachweise der in sehr geringer Aktivität vorliegenden Radionuklide erfolgen autoradiographisch.[13,14]

Erläuterungen zum Trennschema

Der Trennungsgang ist so aufgebaut, daß aus einem zentralen Tüpfelfleck, der alle interessierenden Radionuklide zusammen mit Submikrogrammengen der entsprechenden Träger in gefällter bzw. löslicher Form enthält, einzelne Ionen oder Ionengruppen mit geeigneten Waschflüssigkeiten nacheinander selektiv herausgelöst und in Ringen von 22 mm Durchmesser konzentriert werden. Dabei finden übliche Fällungs- und Filtrationsschritte Anwendung, die den Gegebenheiten der Ringofenmethode angepaßt wurden. Trennungsschritt I erfolgt auf dem gleichen Rundfilter, auf dem sich der ursprüngliche Tüpfelfleck befindet. Anschließend wird ein Filterscheibchen von 17 mm Durchmesser mit diesem Tüpfelfleck (Durchmesser $\approx$12 mm) im Zentrum ausgeschnitten und bei allen folgenden Trennoperationen auf jeweils neue Rundfilter aufgepreßt. Es findet hier also stets eine Uebertragung von einem Filterscheibchen in ein darunterliegendes Rundfilter statt. Zwischen die einzelnen Trennstufen (I–VI) sind zur Entfernung störender Salze Auswaschschritte (I/II–V/VI) geschaltet.

Herstellung der Ausgangslösungen und Meßtechnik

Die Radio-Isotope ^{131}J, ^{137}Cs/^{137m}Ba, ^{90}Sr/^{90}Y, ^{95}Zr/^{95}Nb, ^{91}Y, ^{144}Ce/^{144}Pr, ^{140}Ba/^{140}La und ^{106}Ru/^{106}Rh standen in Form trägerfreier Lösungen oder als Lösungen mit zu vernachlässigenden Trägermengen für die Ausarbeitung des Trennungsganges zur Verfügung. Die Lösung eines Gemisches verschiedener Tellurisotope (^{125m}Te, ^{129m}Te, ^{121m}Te, ^{123m}Te, ^{127m}Te) mit 25 mg Te/ml als Träger diente nach Verdünnung auf das 20 fache für orientierende Versuche über das Verhalten von Tellur im Trennungsgang.

Eine etwa 2 n salzsaure, oxalsäurehaltige Trägerlösung, welche die isotopen Träger der eben genannten Radionuklide in Konzentrationen von je 0,2 mg/ml enthielt, wurde folgendermaßen bereitet:

12,08 mg Pr_6O_{11} wurden in einigen Tropfen 25%iger Salzsäure heiß gelöst. Nach Eindampfen bis zur Trockene (Verflüchtigung des gebildeten Chlors) wurde der Rückstand mit 11,5 ml 25%iger Salzsäure aufgenommen und zu einer wäßrigen Lösung (einige ml) von 12,66 mg CsCl; 24,15 mg

TRENNSCHEMA

Rundfilter: 2 Tr. $(NH_4)_2SO_4/Na_2SO_3$-Lsg. (1) + 1 Tr. Probelsg. + 1 Tr. $(NH_4)_2SO_4/Na_2SO_3$-Lsg. Ueber NH_3 räuchern; H_2S-Druckfällung. Filter über NH_3 räuchern, auf dem Ringofen mit äthanol., ammoniak. $(NH_4)_2SO_4$-Lsg. (2) waschen. Scheibchen von 17 mm Durchmesser ausschneiden.

Trennungs- bzw. Auswaschschritt	Ring ←	→ Filterscheibchen
I	**Cs, J** ↓ Baden in salpetersaurer $AgNO_3$-Lsg. (13)	**Sr, Ba, La, Ce, Pr, Y, Zr, Nb, Ru, Rh, (Te)** Auf neuem Rundfilter mit 50%-igem Aethanol waschen
Ia	**J**	↓
I/II	←	↓
		3–4 Tr. Ba^{2+}-Lsg. (4). Ueber NH_3 räuchern. Auf neuem Rundfilter mit NaCl-Lsg. (5) waschen.
II	**Sr**	**Ba, La, Ce, Pr, Y, Zr, Nb, Ru, Rh, (Te)** Auf neuem Rundfilter mit NH_3-Lsg. (6) waschen
II/III	**(Te)**	Auf neuem Rundfilter mit äthanol., essigsaurer NH_4F-Lsg. (7) waschen
III	**Zr, Nb**	**Ba, La, Ce, Pr, Y, Ru, Rh** Auf neuem Rundfilter mit äthanol. $(NH_4)_2SO_4$-Lsg. (8) waschen
III/IV	←	↓
		3–4 Tr. salpetersaure, $(NH_4)_2SO_4$-haltige H_3BO_3-Lsg. (9). H_2S-Druckfällung. Auf neuem Rundfilter zweimal mit äthanol., salzsaurer $(NH_4)_2SO_4$-Lsg. (10) waschen
IV	**Ce, Pr, Y, (La)**	**Ba, (La), Ru, Rh** Auf neuem Rundfilter mit NH_3-Lsg. (6) waschen
IV/V	←	↓
		Auf neuem Rundfilter mit ÄDTA/Na_2CO_3-Lsg. (11) waschen
V	**Ba, (La)**	**Ru, Rh** Auf neuem Rundfilter mit NH_3-Lsg. (6) waschen
V/VI	←	↓
		Zweimal 3–4 Tr. Perhydrol (12); über NH_3 räuchern. Auf neuem Rundfilter mit NH_3-Lsg. (6) waschen. Operation wiederholen
VI	**Ru, Rh**	↓

$Sr(NO_3)_2$; 17,80 mg $BaCl_2 \cdot 2H_2O$; 31,18 mg $La(NO_3)_3 \cdot 6H_2O$; 26,58 mg $CeCl_3 \cdot 7H_2O$; 34,18 mg $YCl_3 \cdot 6H_2O$; 20,55 mg $RuCl_3$ und 27,05 mg $RhCl_3 \cdot xH_2O$ (37% Rh) gegeben (Lösung A). 125 mg Oxalsäure wurden in ca. 10 ml Wasser gelöst und mit 1,5 ml einer äthanolischen $NbCl_5$-Lösung (6,6 mg Nb/ml) versetzt (Lösung B). Nach Zugabe von 35,35 mg $ZrOCl_2 \cdot 8H_2O$ und 34,12 mg $K_2TeO_3 \cdot 3H_2O$ zu Lösung A wurde diese mit Lösung B vereinigt, in einen 50 ml-Meßkolben filtriert und mit Wasser bis zur Marke verdünnt. Da Jodidionen in saurem Medium leicht zu flüchtigem Jod oxydiert werden, erfolgte die Zugabe von 13,10 mg KJ zur Trägerlösung erst ganz zum Schluß (nach dem Auffüllen). Aus dem gleichen Grunde mußten alle Versuche mit ^{131}J unmittelbar nach Ansetzen der Ausgangslösungen durchgeführt werden. Die Trägerlösung ist (von J^- abgesehen) etwa 14 Tage ohne wesentliche Veränderungen haltbar.

Die Ueberprüfung des Trennungsganges erfolgte mit Lösungen, die jeweils *ein* bestimmtes Radionuklid und *alle* inaktiven Trägerionen in Konzentrationen von je 0,1 mg/ml enthielten. Dazu wurden einige Zehntel ml Trägerlösung mit dem gleichen Volumen Radionuklidlösung + Wasser verdünnt, und zwar in solchem Verhältnis, daß 1 Tropfen der resultierenden Mischung, auf einem Filterpapier unter einem dünnwandigen Endfensterzählrohr (FHZ 15a, 1,17 mg/cm^2) gemessen (Abstand vom Zählrohr ca. 2 cm) eine Impulsrate von 100–300I/min · μl ergab. (Das sind bei etwa 6 μl Tropfengröße und 10 min Zähldauer Impulszahlen von 6000–18000). Die Messungen erfolgten mit Hilfe des Strahlungsmeßgerätes FH 49 der Firma Frieseke & Hoepfner GmbH., Erlangen-Bruck, und der dazugehörigen Universal-Bleikammer FH 447. Für jedes der erwähnten Radionuklide wurde bei jedem Trennungs- und Auswaschschritt unter Berücksichtigung eines entsprechenden Geometriefaktors die Aktivitätsverteilung zwischen zentralem Tüpfelfleck (Filterscheibchen) und Ringzone bestimmt. Aus diesen Einzelresultaten konnte dann nach Durchführung des Ganges ermittelt werden, wie sich das betreffende Radio-Isotop auf die Ringe I, Ia, I/II, II . . . V/VI und VI verteilt, und mit welchen Ausbeuten es von den anderen Nukliden abzutrennen ist. Die erhaltenen Ergebnisse sind (in Prozenten) in Tab. 1 aufgeführt.

Im Verlauf des Trennungsganges treten bei den Systemen ^{140}Ba/^{140}La und ^{90}Sr/^{90}Y partielle Mutter-Tochter-Trennungen auf. In diesen Fällen konnten daher die Ausbeutebestimmungen erst nach Wiedereinstellung des radioaktiven Gleichgewichtes, d.h. ca. 12 Tage ($\approx$7 Halbwertszeiten von ^{140}La) bzw. 19 Tage ($\approx$7 Halbwertszeiten von ^{90}Y) nach der Auftrennung erfolgen.

Die in Tab. 1 aufgeführten Prozentangaben sind Mittelwerte aus zwei, drei oder auch vier Versuchen und aus diesem Grunde statistisch relativ un sicher. Sie können von Fall zu Fall starken Schwankungen unterliegen und sagen nur soviel aus, daß z.B. ^{131}J und ^{137}Cs praktisch quantitativ in den Ring I wandern, daß ^{90}Sr etwa zur Hälfte in den Ring II gelangt, während ein beträchtlicher Teil dieses Isotops bei den Seltenen Erden (Ring IV) wiedergefunden wird, oder daß ^{91}Y und ^{144}Ce zu 80–90% in den Ring IV gewaschen werden. Diese Angaben gelten selbstverständlich nur für die Trägerkonzentrationen von je 0,1 mg/ml und die verwendeten Probetropfenvolumina von etwa 6 μl.

Geräte und Filtermaterial

Die Trennungen erfolgten auf einem Ringofen üblicher Bauart mit 22 mm-Bohrung.[12] Eine selbstfüllende Kapillarpipette mit einem Volumen von ca. 6 μl diente zum Auftragen von Probe- und Reagenstropfen, eine Kapillare mit etwa 40 μl Fassungsvermögen zum Waschen. Um bei den einzelnen Trennungs- und Auswaschschritten Substanzen aus dem Filterscheibchen möglichst gleichmäßig in das darunter liegende Rundfilter übertragen zu können, mußte das Scheibchen—besonders dessen Rand—in guten Kontakt mit dem Rundfilter gebracht werden. Dies geschah in der in Abb. 1 gezeigten Weise. Der auf das untere Ende des Führungsrohres für die Auswaschkapillare aufgeschobene, glockenförmige Ansatz, mit dem das Filterscheibchen leicht angedrückt wurde, besteht aus einem Gummistopfen und dem abgesprengten oberen Ende eines passenden Reagensglases.

Die verwendeten Rundfilter der Firma Macherey, Nagel u. Co., Düren (Nr. 2260; 5,5 cm Durchmesser) wurden vor Gebrauch in der von West, Llacer und Cimerman[15] beschriebenen Weise durch Waschen mit 10%iger Essigsäure noch besonders gereinigt und anschließend im Trockenschrank bei 100°C getrocknet.

Zu Beginn des Trennungsganges werden Ruthenium und Rhodium (auch Tellur) mit Schwefelwasserstoff im zentralen Tüpfelfleck gefällt. Versuche mit ^{106}Ru/^{106}Rh zeigten, daß eine quantitative Abscheidung der Platinmetalle in Form eines Sulfidniederschlages, der gegen die bei den folgenden Trennoperationen verwendeteten Waschflüssigkeiten einigermaßen resistent ist, nur durch eine 1½-stündige Druckfällung bei 100°C erreicht werden konnte. Die Druckfällungen erfolgten in einem 200 ml-Autoklaven aus Duranglas (Schott u. Gen., Mainz), der zur besseren Handhabung in einem Korkring stand (s. Abb. 2). Da der Innendurchmesser des zylindrischen Autoklaven 50 mm beträgt, konnte jeweils ein schmaler Rand des Runfilters, das im Zentrum den Tüpfelfleck trug, zusammen mit dem Dichtungsring zwischen den Planflanschen festgeklemmt werden.

TAB. I.—Prozentuale Verteilung der Radio-Isotope auf die einzelnen Trennungs- und Auswaschstufen. Die besonders markierten Zohlen deuten an, in welchen Ring die Hauptmenge des jeweiligen Nuklids im Verlauf der Trennoperationen gelangt.

Ring / Nuklid	Ia	I	I/II	II	II/III	III	III/IV	IV	IV/V	V	V/VI	VI	Rest
^{106}Ru/^{106}Rh		5,5	0,6	0,3	0,7	1,6	0,6	1,8	0,8	0,5	0,6	**78**	9
^{140}Ba/^{140}La		1	1,25	15,5	0,8	0,95	1,1	4,6	4,6	**67,5**	2		0,7
^{91}Y		1,9	0,4	1,9	0,35	0,5	0,4	**88**	1,7	4,5			0,35
^{144}Ce/^{144}Pr		0,7	0,35	0,7	0,15	0,05	0,25	**81**	1,3	14	0,9		0,6
^{95}Zr/^{95}Nb		0,25	0,6	1,1	0,8	**82,5**	7,25	5					2,5
^{90}Sr/^{90}Y	0,8	8	0,8	**50**	12	0,75	0,05	18	1,2	8			1,2
^{137}Cs/^{137m}Ba	1,25	**99,4**	0,1										0,5
^{131}J	**98,2**	**98,8**	0,35										0,85

Reagens- und Waschlösungen

(1) $(NH_4)_2SO_4/Na_2SO_3$-Lösung, die 1%ig in Bezug auf SO_4^{2-} und 0,5%ig in Bezug auf SO_3^{2-} ist.
(2) 50% äthanolische $(NH_4)_2SO_4$-Lösung, die 5% Ammoniak enthält und 0,05%ig in Bezug auf SO_4^{2-} ist.
(3) 50%iges Aethanol.
(4) $BaCl_2$-Lösung; 0,1%ig in Bezug auf Ba^{2+}.
(5) 0,5%ige NaCl-Lösung.
(6) 5%ige Ammoniaklösung.
(7) Mischung aus 47,5 ml einer 50% äthanolischen NH_4F-Lösung, die 0,5%ig in Bezug auf F^- ist, und 2,5 ml Eisessig,
(8) 50% äthanolische $(NH_4)_2SO_4$-Lösung, die 0,2%ig in Bezug auf SO_4^{2-} ist.
(9) Gemisch aus 1 Raumteil gesättigter Borsäurelösung und 1 Raumteil 2n Salpetersäure. Die Mischung enthält 1% SO_4^{2-} als $(NH_4)_2SO_4$.
(10) Mischung aus 49 ml einer 50% äthanolischen $(NH_4)_2SO_4$-Lösung, die 0,2%ig in Bezug auf SO_4^{2-} ist, und 1 ml 25% iger Salzsäure.
(11) Na_2CO_3-haltige ÄDTA-Lösung mit 0,5% Na_2CO_3 und 0,5% ÄDTA.
(12) 30%iges Wasserstoffperoxid (Perhydrol).
(13) 1n saltpetersaure 1%ige $AgNO_3$-Lösung.
(14) Konz. Ammoniaklösung (zum Räuchern).

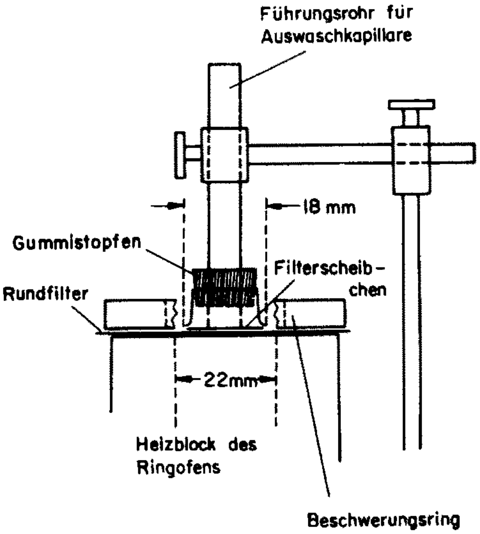

ABB. 1.—Auswaschen aus einem Filterscheibchen in ein darunterliegendes Rundfilter.

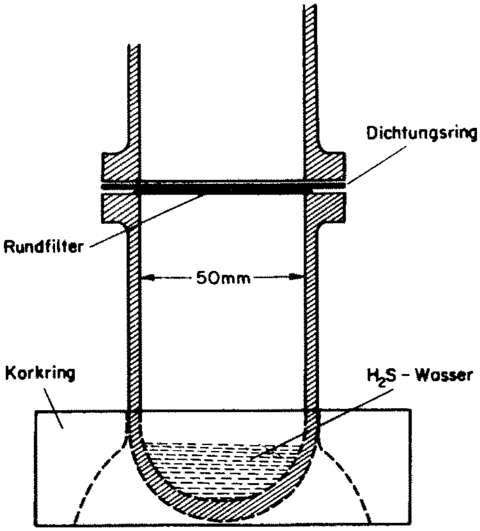

ABB. 2.—Druckfällung im Glasautoklaven.

Durchführung des Trennungsganges

Salzsaure Probelösung: ^{131}J; ^{137}Cs/^{137m}Ba; ^{90}Sr/^{90}Y; ^{95}Zr/^{95}Nb; ^{144}Ce/^{144}Pr; ^{91}Y; ^{140}Ba/^{140}La; ^{106}Ru/^{106}Rh; (Te-Isotope); je 0,1 mg/ml der entsprechenden Träger und 1,25 mg $(COOH)_2 \cdot 2H_2O$/ml.

Auf einen trockenen Tüpfelfleck aus 2 Tropfen $(NH_4)_2SO_4/Na_2SO_3$-Lösung (1), der sich in der Mitte eines Rundfilters befindet, trägt man 1 Tropfen Probelösung auf. Man räuchert über konz. Ammoniak, trocknet, tüpfelt mit 1 weiteren Tropfen $(NH_4)_2SO_4/Na_2SO_3$-Lösung nach, räuchert nochmals über konz. Ammoniak und trocknet wieder.

Inzwischen hat man in den unteren Teil des Glasautoklaven, in dem sich ca. 20 ml Wasser befinden, 5–10 min lang H_2S eingeleitet. Man legt das Rundfilter über die Öffnung des zylindrischen Gefäßes (s. Abb. 2), bringt darüber den zur Abdichtung erforderlichen Gummiring in die richtige Position und setzt schnell den oberen Teil des Autoklaven auf, nachdem auch aus diesem durch Einblasen von H_2S die Luft verdrängt worden ist. (Es können 2–3 Rundfilter gleichzeitig eingespannt werden). Mit Hilfe der Doppelschellenverbindung preßt man beide Hälften des Glasautoklaven zusammen und stellt diesen für 1½ Stunden in einen auf 100°C aufgeheizten Trockenschrank.

Nach Beendigung der Druckfällung liegen im zentralen Tüpfelfleck Sr und Ba als Sulfate, die

Seltenen Erden, Zr und Nb als Hydroxide bzw. Oxidhydrate, Ru und Rh als Sulfide (Te in elementarer Form), Cs und J jedoch als lösliche Salze vor.

Trennungsschritt I: Der noch heiße Autoklav (50–60°C) wird vorsichtig geöffnet. Man räuchert das Rundfilter kurz über konz. Ammoniak, zentriert es dann auf dem heissen Ringofen und wäscht die löslichen Anteile, darunter auch praktisch alles Cs und J, mit ca. 150 μl (4 Pipettenfüllungen) einer äthanolischen, ammoniakalischen $(NH_4)_2SO_4$-Lösung (2) aus dem zentralen Tüpfelfleck in die Ringzone. Der Waschflüssigkeit werden Aethanol und $(NH_4)_2SO_4$ zugesetzt, um die Löslichkeit der Erdalkalisulfate, besonders die des $SrSO_4$, zu verringern. Das $(NH_4)_2SO_4$ hat noch eine weitere Funktion: Cs kann nur dann nahezu vollständig aus dem Tüpfelfleck ausgewaschen werden, wenn die Waschflüssigkeit elektrolythaltig ist.

Trennungsschritt Ia: Aus dem Zentrum des getrockneten Rundfilters wird nun ein Scheibchen von 17 mm Durchmesser, mit dem Tüpfelfleck in der Mitte, ausgeschnitten. Nachdem man auf dem restlichen Filter (Ring I) die Summe der Aktivitäten von ^{137}Cs und ^{131}J bestimmt hat, badet man es 15–20 sec in einer salpetersauren $AgNO_3$-Lösung (13), spült es dann mit dest. Wasser und trocknet es. Ring Ia enthält jetzt nur noch die Jodaktivität.

Auswaschschritt I/II: Das Filterscheibchen, das noch alle Nuklide außer ^{137}Cs und ^{131}J enthält, wird auf dem Ringofen mit Hilfe der in Abb. 1 gezeigten Vorrichtung vorsichtig auf die Mitte eines neuen Rundfilters gepreßt. Man wäscht das im Scheibchen vorhandene $(NH_4)_2SO_4$ mit 200–250 μl (5–6 Pipettenfüllungen) 50%igen Aethanols in die Ringzone.

Trennungsschritt II: Alle Versuche zur Trennung von Sr und Ba, die in Submikrogrammengen auf Filterpapier als Sulfate vorliegen, verliefen wenig befriedigend, zumal noch besondere Rücksicht auf Seltene Erden, Zr und Nb genommen werden mußte. (ÄDTA kann hier z.B. nicht angewendet werden). Eine wenigstens für qualitative Zwecke ausreichende Trennung kann durch eine Verdrängungsreaktion erreicht werden: Da $BaSO_4$ erheblich schwerer löslich ist als $SrSO_4$, und da nur die radioaktiven Isotope von Interesse sind, kann man Sr^{2+} aus dem Sulfatniederschlag durch inaktive Ba^{2+}-Ionen verdrängen. Hierzu werden auf das nach dem Auswaschschritt I/II getrocknete Filterscheibchen 3–4 Tropfen einer $BaCl_2$-Lösung (4) aufgetragen, so daß es völlig von der Reagenslösung durchfeuchtet ist. Man trocknet das Scheibchen, räuchert es über konz. Ammoniak, drückt es gegen ein neues, speziell vorbehandeltes Rundfilter (s. unten) und wäscht mit ca. 150 μl (4 Pipettenfüllungen) 0,5%iger NaCl-Lösung. Etwa die Hälfte des Radiostrontiums gelangt hierbei in den Ring II, außerdem ein merklicher Teil des ^{140}Ba (vermutlich zum Teil durch Isotopenaustausch). Das bei diesem Trennungsschritt verwendete Rundfilter wird vor Gebrauch kapillar mit Wasser gewaschen,[15] getrocknet, über konz. Ammoniak geräuchert und nochmals einige Minuten in einen 100°C heißen Trockenschrank gelegt. Hierdurch wird die Essigsäure, die von der bereits geschilderten, anfänglichen Reinigungsoperation her noch im Filter vorhanden ist, entfernt bzw. neutralisiert. Mit dieser speziellen Vorbehandlung des Rundfilters wird vermieden, daß beim Waschen mit der NaCl-Lösung die Hydroxide bzw. Oxidhydrate der Seltenen Erden, des Zr und des Nb angegriffen werden.

Auswaschschritt II/III: Aus dem getrockneten Filterscheibchen wird auf einem neuen Rundfilter alles NaCl mit etwa 150 μl (4 Pipettenfüllungen) 5%iger Ammoniaklösung ausgewaschen. Wie autoradiographische Versuche zeigten, wandert hierbei die Hauptmenge des Te in die Ringzone.

Trennungsschritt III: Man preßt das trockene Filterscheibchen gegen ein neues Rundfilter und wäscht mit ca. 250 μl (6 Pipettenfüllungen) einer äthanolischen, essigsauren NH_4F-Lösung (7) etwa 80% des Zr/Nb-Paares in Form komplexer Fluoride in den Ring. Die Seltenen Erden werden hierbei in schwerlösliche Fluoride überführt.

Auswaschschritt III/IV: Auf einem neuen Rundfilter wird mit 150–250 μl (4–6 Pipettenfüllungen) äthanolischer $(NH_4)_2SO_4$-Lösung (8) alles NH_4F aus dem getrockneten Filterscheibchen ausgewaschen.

Trennungsschritt IV: Die Fluoride der Seltenen Erden werden durch Demaskierung mit Borsäure in stark salpetersaurem Medium in Lösung gebracht.[16] Dazu wird das trockene Filterscheibchen mit 3–4 Tropfen der sulfathaltigen Borsäure-Salpetersäure-Mischung (9) durchfeuchtet und 3–4 min in einen 100°C heißen Trockenschrank gelegt. Da die Sulfide der Platinmetalle durch die Salpetersäure-teilweise oxydiert werden, muß man anschließend nochmals eine 1½ stündige H_2S-Druckfällung bei 100°C in der eingangs beschriebenen Weise durchführen. Hierbei wird das Filterscheibchen auf ein Rundfilter gelegt und dieses zwischen die zwei Hälften des Druckgefäßes eingeklemmt.

Nach der Druckfällung preßt man das Filterscheibchen auf dem Ringofen gegen ein neues Rundfilter und wäscht mit etwa 250 μl (6 Pipettenfüllungen) einer äthanolischen, salzsauren $(NH_4)_2SO_4$ Lösung (10). Dieser Auswaschvorgang wird wiederholt, indem man das Filterscheibchen vorsichtig vom Rundfilter abhebt, kurz trocknet, wieder behutsam gegen das Rundfilter drückt (dieses darf sich dabei nicht verschieben) und nochmals mit 250 μl der gleichen Flüssigkeit wäscht. Erst durch die Wiederholung der Waschoperation wird erreicht, daß 80–90% des Ce und des Y in den Ring IV wandern. Die ^{140}La-Tochteraktivität des ^{140}Ba gelangt nur in mäßiger Ausbeute in diesen Ring, der neben den Seltenen Erden noch einen merklichen Anteil des Radiostrontiums enthält. Beim Trennungsschritt IV muß darauf geachtet werden, daß die in der Waschflüssigkeit enthaltene Salzsäure das Filterpapier in der heißen Ringzone nicht so stark angreift, daß es einreißt. Autoradiogramme des Ringes IV (s. Abb. 3) zeigen, daß dieser etwas unscharf ist und Ausbuchtungen, aufweist. Die Ursachen hierfür sind in den zwei aufeinanderfolgenden Auswasch-operationen und den im Ring konzentrierten, relativ großen Salzmengen zu suchen.

Die Freisetzung der Seltenen Erden aus ihren Fluoridniederschlägen kann auch mit Be^{2+}-Ionen erfolgen.

Auswaschschritt IV/V: Auf einem neuen Rundfilter wird aus dem getrockneten Filterscheibchen das $(NH_4)_2SO_4$ mit 150 μl (4 Pipettenfüllungen) 5 %iger Ammoniaklösung ausgewaschen.

Trennungsschritt V: Die Abtrennung der Hauptaktivität des Ba von den noch auf dem Filterscheibchen fixierten radioaktiven Platinmetallen wird mit ÄDTA in alkalischem Medium durchgeführt. Hierzu drückt man das getrocknete Scheibchen auf dem heißen Ringofen gegen ein neues Rundfilter und wäscht mit ca. 150 μl (4 Pipettenfüllungen) einer Na_2CO_3-haltigen ÄDTA-Lösung (11).

Auswaschschritt V/VI: Auf einem neuen Rundfilter werden restliches ÄDTA und Na_2CO_3 mit etwa 150 μl (4 Pipettenfüllungen) 5 %iger Ammoniaklösung aus dem getrockneten Filterscheibchen ausgewaschen.

Trennungsschritt VI: Das Filterscheibchen enthält jetzt nur noch das Mutter-Tochter-System $^{106}\mathrm{Ru}/^{106}\mathrm{Rh}$. Zum Zwecke der Autoradiographie müssen die Platinmetalle, die als Sulfide vorliegen, in einem Ring konzentriert werden. Dies geschieht nach Oxydation der Sulfide mit H_2O_2 in ammoniakalischem Medium. Man durchfeuchtet das getrocknete Filterscheibchen mit 3–4 Tropfen Perhydrol (12), räuchert 30 sec über konz. Ammoniak, trocknet im Trockenschrank und wiederholt die Operation. Anschließend preßt man das Scheibchen auf ein neues Rundfilter und wäscht mit ca. 150 μl (4 Pipettenfüllungen) 5 %iger Ammoniaklösung. Man läßt das Rundfilter auf dem Ringofen liegen, hebt das Filterscheibchen vorsichtig ab, trocknet es und wiederholt den ganzen Oxydationsvorgang mit Perhydrol und konz. Ammoniak. Danach wird das Scheibchen wieder gegen das Rundfilter gedrückt und nochmals mit etwa 150 μl 5 %iger Ammoniaklösung ausgewaschen. Etwa $\frac{3}{4}$ der Gesamt-Ru-Aktivität befinden sich im Ring.

Bei den geschilderten Operationen muß darauf Rücksicht genommen werden, daß das Filterscheibchen durch Perhydrol stark angegriffen wird.

Ring VI liefert ebenso wie Ring IV relativ diffuse Autoradiogramme (s. Abb. 3).

Autoradiographie

Der besondere Vorteil der Ringofenmethode bei der Anwendung auf radiochemische Probleme liegt darin, daß durch Kombination mit der Autoradiographie radioaktive Substanzen noch in sehr geringer Aktitivät (pC-nC-Bereich)[14,17] nachgewiesen werden können. Der erhöhte Zeitbedarf gegenüber instrumentellen Meßmethoden wird durch die einfache Arbeitstechnik und den äußerst geringen Materialaufwand wieder ausgeglichen.

Es lag nahe, das autoradiographische Nachweisverfahren auch auf den eben beschriebenen Trennungsgang anzuwenden. Der Gang wurde zu diesem Zweck mit Probelösungen durchgeführt, die wiederum *alle* inaktiven Ionen in Konzentrationen von je 0,1 mg/ml enthielten, jedoch wesentlich geringere Aktivitäten pro Volumeinheit (10–20 mal weniger) aufwiesen als die zur Ueberprüfung der einzelnen Trennschritte verwendeten Lösungen. Mit Ausnahme der $^{140}\mathrm{Ba}/^{140}\mathrm{La}$-lösung ($\approx 5$ I/min · μl) ergaben alle Proben unter einem FHZ 15a (s. unter "Meßtechnik") Impulsraten von je 10–15 I/min · μl pro Isotop. Auch die untersuchten Nuklidgemische enthielten jedes Radioisotop in dieser Aktivitätskonzentration. Mit jeder der hergestellten Probelösungen wurden alle Stufen des Trennungsganges durchgeführt, die Filter mit den Ringen Ia, I, I/II... V/VI, VI in dieser Reihenfolge nebeneinander auf Röntgenfilmstreifen (Adox-Doneo) gelegt und beschwert. (Die Röntgenfilme befanden sich dabei in Schutztaschen aus schwarzer Plastikfolie mit einem Flächengewicht von etwa 6,6 mg/cm²). Die Auswaschringe I/II, II/III u.s.w. haben für den Nachweis der einzelnen Radionuklide keine Bedeutung und wurden hier nur zu Kontrollzwecken mit aufgelegt. Nach 20 h Exposition in einer Tiefkühltruhe[14] (für $^{140}\mathrm{Ba}/^{140}\mathrm{La}$ betrug die Expositionszeit unmittelbar nach Beendigung des Trennungsganges 70 h und 12 Tage später 122 h) wurden die Filme entwickelt. Sie zeigten dann an einigen Stellen, welche ganz bestimmten Trennungs- bzw. Auswaschschritten entsprachenden, die von den jeweiligen Nukliden herrührenden schwarzen Ringe.

In Abb. 3 ist eine Auswahl der so erhaltenen Autoradiogramme in tabellarischer Form zusammengestellt. Das Nuklidgemisch MT26 enthielt $^{137}\mathrm{Cs}/^{137m}\mathrm{Ba}$, $^{90}\mathrm{Sr}/^{90}\mathrm{Y}$, $^{95}\mathrm{Zr}/^{95}\mathrm{Nb}$, $^{144}\mathrm{Ce}/^{144}\mathrm{Pr}$, $^{91}\mathrm{Y}$ und $^{106}\mathrm{Ru}/^{106}\mathrm{Rh}$, das Gemisch MT27 $^{137}\mathrm{Cs}/^{137m}\mathrm{Ba}$, $^{95}\mathrm{Zr}/^{95}\mathrm{Nb}$, $^{144}\mathrm{Ce}/^{144}\mathrm{Pr}$, $^{91}\mathrm{Y}$ und $^{106}\mathrm{Ru}/^{106}\mathrm{Rh}$.

Es wurden (mit einer Ausnahme beim Jod-Cäsium-Gemisch) nur diejenigen

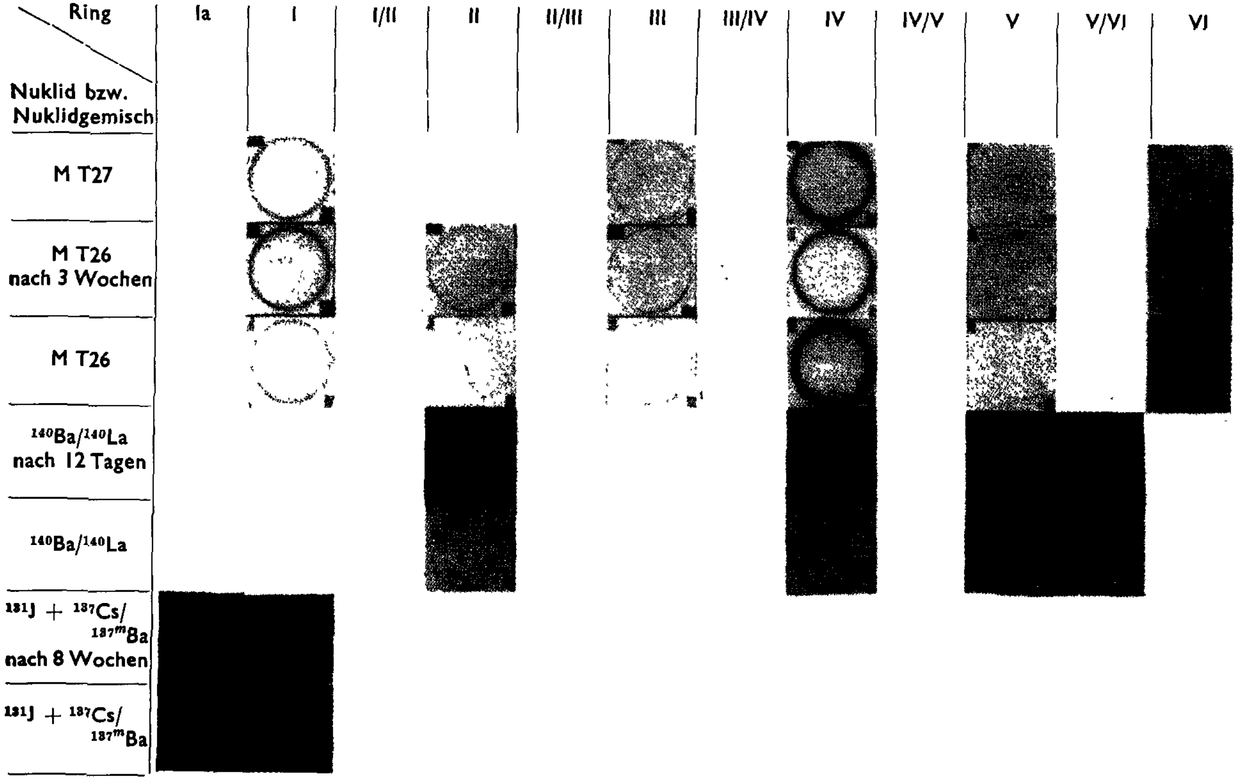

ABB. 3.—Autoradiogramme.

Teile der entwickelten Filmstreifen ausgeschnitten und in die Tabelle eingefügt, die eine eben noch sichtbare, ringförmige Schwärzung aufwiesen.

Wie man in Abb. 3 erkennen kann, ist nach Durchführung des Trennungsganges praktisch die gesamte Cäsium- und Jodaktivität in Ring I konzentriert, der 8 Wochen später (7 Halbwertszeiten von ^{131}J) nur noch ^{137}Cs/^{137m}Ba enthält. Badet man Ring I in salpetersaurer AgNO$_3$-Lösung, so bleibt nur das ^{131}J zurück (Ring Ia), welches in 8 Wochen zerfallen ist und auf dem Film keinen Ring mehr abbildet. In einem Versuch mit entsprechend hoher Ausgangsaktivität wurde der Abfall des in Ring Ia vorhandenen ^{131}J über einige Wochen hinweg verfolgt (s. Abb. 4). Vom Mutter-Tochter-System ^{140}Ba/^{140}La wird die Hauptmenge in Ring V konzentriert. Ein Teil des ^{140}La und geringe Mengen ^{140}Ba gelangen in den Ring IV, der 12 Tage (7 Halbwertszeiten des ^{140}La) nach erfolgter Trennung nur noch ein sehr schwaches Autoradiogramm liefert. In dieser Zeit ist in Ring V, desgl. auch in Ring II, in dem sich ein merklicher Anteil des ^{140}Ba befindet (vgl. Tab. 1), ^{140}La bis zum Gleichgewicht nachgewachsen. Die schwachen Abbildungen des Auswaschringes V/VI rühren von restlichem ^{140}Ba/^{140}La her. Die Untergrundschwärzungen der ^{140}Ba/^{140}La-Autoradiogramme unterscheiden sich nur deshalb so sehr voneinander, weil in einem Fall (nach 12 Tagen) ein frisch angesetzter Entwickler verwendet wurde. Ein solcher Unterschied in der Entwicklerwirksamkeit wäre für halbquantitative Schätzungen nicht mehr zulässig.[14]

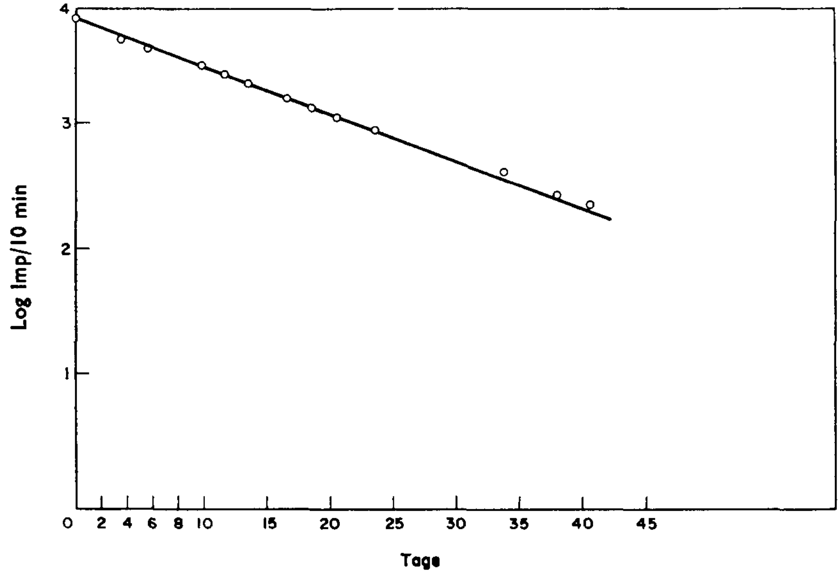

Abb. 4.—Abfallen der ^{131}J-Aktivät in Ring Ia.

Beim Nuklidgemisch MT26 ist besonders auf Ring II (^{90}Sr) zu achten, der unmittelbar nach der Trennung nur sehr schwach abbildet, 3 Wochen später (etwa 7 Halbwertszeiten des ^{90}Y) als Folge des nachgewachsenen ^{90}Y jedoch einen deutlichen schwarzen Ring liefert. In Ring IV, der ^{144}Ce/^{144}Pr, ^{91}Y, ^{90}Y sowie einen bedeutenden Anteil des ^{90}Sr enthält (vgl. Tab. 1) und deswegen ein besonders kräftiges Autoradiogramm ergibt, klingt die Aktivität des ^{90}Y entsprechend ab. Dieses Anwachsen der Aktivität in Ring II und Abklingen in Ring IV wird durch die Kurven in Abb. 5 veranschaulicht, die nach der Durchführung des Trennungsganges mit einer ^{90}Sr/^{90}Y-Lösung höherer Aktivitätskonzentration erhalten wurden. Auch beim Nuklidgemisch MT27, das kein ^{90}Sr/^{90}Y enthält (kein Autoradiogramm des Ringes II), bildet Ring IV sehr stark ab. Beiden Gemischen (MT26 und MT27) sind weiterhin die Autoradiogramme der Ringe I (^{137}Cs/^{137m}Ba), III (^{95}Zr/^{95}Nb) und VI (^{106}Ru/^{106}Rh) gemeinsam. Die geringen Schwärzungen, die Ring V liefert, rühren von restlicher Cer-, Yttrium- und (im Falle von MT26) Strontium-Aktivität her (vgl. Tab. 1).

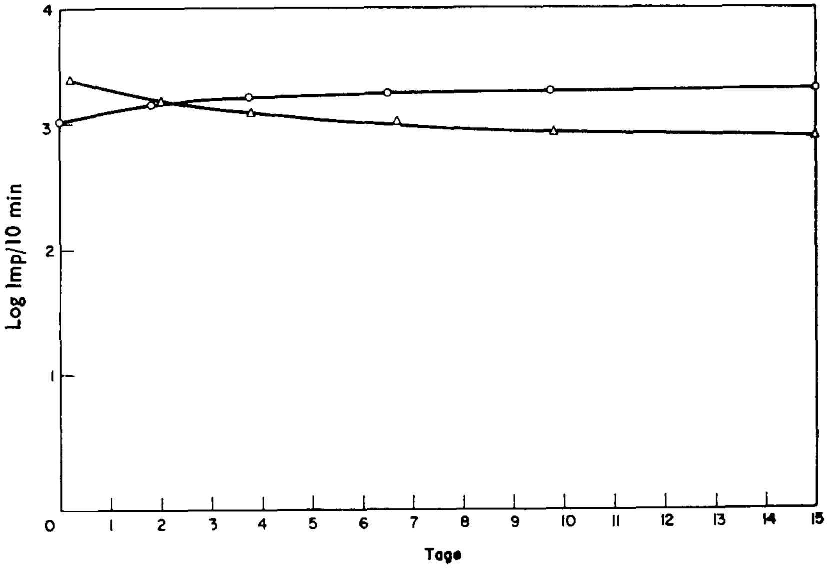

Abb. 5.—Nachwachsen der ^{90}Y-Aktivät in Ring II (○) und Abfallen in Ring IV (△).

DISKUSSION

Der beschriebene Trennungsgang soll als Modell für in der Praxis erforderliche Untersuchungen dienen. Obwohl die einzelnen Radionuklide nicht quantitativ voneinander getrennt werden konnten, ist es doch möglich, mit Hilfe der geschilderten Operationen in relativ kurzer Zeit und mit einfachen Mitteln erste Aussagen über Art und ungefähre Aktivität der in einer Probe vorhandenen Radioisotope zu machen. Die Durchführung des Trennungsganges, vom Auftragen des Probetropfens bis einschließlich Stufe VI gerechnet, erfordert etwa 6 Stunden Zeit. Allein die Hälfte hiervon wird für die beiden Druckfällungen benötigt und steht deshalb für andere Arbeiten zur Verfügung. Berücksichtigt man weiterhin, daß bequem mehrere Proben nebeneinander bearbeitet werden können, so verringert sich der effektive Zeitbedarf noch wesentlich.

Bei der Ausarbeitung dieses Trennungsganges wurden fertige Probelösungen mit definierten Trägerkonzentrationen eingesetzt. In der Praxis liegen jedoch stets Spuren radioaktiver Isotope in einem großen Ueberschuß inaktiven Materials vor, was Anreicherungen und Vortrennungen erforderlich macht. Durch Anwendung der Autoradiographie wird man aber wegen der Empfindlichkeit dieses Nachweisverfahrens nur geringe Substanzmengen aufarbeiten müssen.[17] Einen Weg zur Anreicherung von Radioisotopen aus wäßrigen Lösungen auf dem Ringofen zeigten Malissa und Loley;[17] das Aufschließen von Mikrogrammengen schwerlöslicher Proben unter Anwendung der Ringofenmethode wurde ebenfalls beschrieben.[18]

Die Auswertung der Autoradiogramme eines aufgetrennten Nuklidgemisches muß von der Tatsache ausgehen, daß einige Isotope in Ringe verschleppt werden können, in die sie theoretisch nicht gehören und hier Nuklide vortäuschen, die überhaupt nicht vorhanden sind (vgl. Tab. 1). Erst wenn man die ganze Serie der Autoradiogramme eines durchgeführten Trennungsganges betrachtet und womöglich noch die physikalischen Eigenschaften der Radionuklide (Halbwertszeit) zur Beurteilung heranzieht, können Entscheidungen über An- oder Abwesenheit bestimmter Isotope gefällt werden. So deutet z.B. eine schwache Abbildung des Ringes II auf ^{90}Sr oder verschlepptes ^{140}Ba hin. Handelt es sich um letzteres, so muß Ring V ein deutliches Autoradiogramm liefern. Liegt jedoch nur ^{90}Sr vor, so muß die von Ring II herrührende Schwärzung 3 Wochen nach der Trennung deutlich stärker sein als vorher. Will man ein schwaches Autoradiogramm des Ringes V nicht auf ^{140}Ba/^{140}La zurückführen sondern auf verschleppte Seltene Erden und Strontium, so muß Ring V einige Wochen später (Halbwertszeit des ^{140}Ba 12,8 d) immer noch sichtbar abbilden. Enthält die zu untersuchende Probe genügend hohe Aktivitäten, so kann man die voneinander getrennten Radioisotope eindeutig durch γ-Spektrometrie identifizieren, wie dies Hilton und Reed für die Abtrennung von ^{137}Cs/^{137m}Ba [19,20] sowie von ^{99}Mo/^{99m}Tc[21] aus bestrahltem Uran mit Hilfe der Ringofenmethode beschrieben haben.

Das bei der Spaltung von ^{235}U mit thermischen Neutronen gebildete Nuklidgemisch enthält neben den in diesem Trennungsgang berücksichtigten Radioisotopen noch eine Reihe anderer radioaktiver Spaltprodukte mittlerer bis langer Halbwertszeit, die sich chemisch gleich oder sehr ähnlich verhalten. So muß man z.B. mit der Anwesenheit von ^{89}Sr in Ring II oder von ^{141}Ce, ^{147}Pm und anderen Seltenen Erden in Ring IV rechnen. Nuklide wie ^{99}Mo/^{99m}Tc und ^{132}Te/^{132}J (Halbwertszeit jeweils $\approx$3 d) sowie Isotope mit noch kürzerer Halbwertszeit würden bei "jungen" Spaltproduktgemischen (Alter $<$20 d) von Bedeutung sein. Hingegen müßte das Verhalten von Uran- und Plutoniumisotopen, die im "Fallout" auftreten können, von natürlich vorhanden Radionukliden (^{226}Ra, ^{210}Pb) und von sekundär durch Neutroneneinwirkung induzierten Aktivitäten (Kobalt- und Wolframisotope, ^{54}Mn, ^{55}Fe, ^{24}Na, ^{204}Tl) im Trennungsgang noch untersucht und dieser gegebenenfalls entsprechend modifiziert werden.

Wie eben bereits angedeutet, variiert der Anteil der einzelnen Radionuklide an der Gesamaktivität eines Spaltproduktgemisches stark mit dessen Alter. Dieser Tatbestand ist nicht ohne Einfluß auf die Durchführung des Trennungsganges. Liegt z.B. ein Spaltproduktgemisch vor, das $>$150 d alt ist (MT26 entspricht etwa solch einem Gemisch), dann kann man ^{131}J und ^{140}Ba/^{140}La unberücksichtigt lassen (Anteil von ^{140}Ba/^{140}La an der Gesamtaktivität dann noch $\approx$0,2%)[22] und die Ausbeute beim Abtrennen des Radiostrontiums dadurch erhöhen, daß man den entsprechenden Trennungsschritt (II) wiederholt.

Will man sich auf die Abtrennung des einen oder anderen Isotops aus einem vorliegenden Nuklidgemisch beschränken, dann kann man den Trennungsgang so Modifizieren, daß sich die Aktivitäten der abgetrennten Isotope halbquantitativ durch

Autoradiographie[14,23–25] bestimmen lassen. Sind z.B. in Stufe I ^{137}Cs und evtl. vorhandenes ^{131}J praktisch quantitativ abgetrennt worden, dann können unmittelbar anschließend etwa 95% des ^{95}Zr/^{95}Nb ohne nennenswerte Kontaminerung durch andere Nuklide mit äthanolischer, essigsaurer NH_4F-Lösung aus dem Filterscheibchen in die Ringzone eines neuen Rundfilters gewaschen werden. Diese Operationen (einschließlich der H_2S-Druckfällung) beanspruchen 2–2½ Stunden Zeit. Hat man (nach Berücksichtigung einer evtl. noch vorhandenen Jodaktivität) die Aktivitäten von ^{137}Cs und ^{95}Zr/^{95}Nb autoradiographisch bestimmt, dann lassen sich aus dem Aktivitätsverhältnis möglicherweise Rückschlüsse auf das Alter des Spaltproduktgemisches ziehen.

An dieser Stelle möchten wir Herrn Professor Dr. W. Seelmann-Eggebert, dem Direktor des Instituts für Radiochemie der Kernreaktor Bau- und Betriebsgesellschaft m.b.H., Karlsruhe, für die Überlassung von Radio-Isotopen herzlich danken.

Summary—A qualitative separation procedure for uranium fission products of medium or long half-lives (isotopes of Cs, I, Sr, Ba, Zr, Nb, Ru, Y, rare earths) in a drop of solution, using the ring oven, is described. The test drop containing the radionuclides and submicrogram amounts of the corresponding carriers is spotted on a filter paper. Precipitation, dissolution, demasking and washing procedures are applied to wash out single isotopes or groups of isotopes from the central spot and concentrate them in different ring zones. The identification of the nuclides or groups of nuclides is by autoradiography of the individual rings. The yields of the various separation steps are shown in tabular form. The interpretation of the autoradiographs and possible uses of the separation are discussed.

Résumé—On décrit une technique de séparation qualitative de produits de fission de l'uranium de moyenne et longue demi-vie (isotopes de Cs, I, Sr, Ba, Zr, Nb, Ru, Y, terres rares) contenus dans une goutte de solution, par la technique du four annulaire. La goutte d'essai, contenant les radionucléides, et des quantités inférieures au microgramme des entraîneurs inactifs correspondants, est déposée sur un papier filtre circulaire. On applique ensuite les techniques de précipitation, dissolution, décomplexation et lavage pour entraîner les isotopes, seuls ou en groupe, à partir de la tache centrale, et les concentrer dans différentes zones annulaires. On identifie les nucléides ou groupes de nucléides par autoradiographie des anneaux individuels. Les produits des différents stades de la séparation sont présentés sous forme de tableau. On discute de l'interprétation des autoradiographies et des emplois possibles de cette séparation.

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UNE NOUVELLE MÉTHODE POUR LE DOSAGE GRAVIMÉTRIQUE DE L'URANIUM

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Résumé—Cette méthode pour le dosage gravimétrique de l'uranium est basée sur la précipitation des ions UO_2^{2+}, dans l'intervalle de pH 3–5, par une solution formée d'acide p-aminobenzoïque, de pyridine et d'eau: on obtient un précipité jaune, amorphe, facilement filtrable, $UO_2(H_2N—C_6H_4—COO)_2.2Py.2H_2O$, que l'on transforme pour le dosage de l'uranium, par calcination, en U_3O_8. Afin de vérifier l'efficacité de ce réactif, une série de dosages d'uranium effectuée comparativement avec NH_3 et l'oxine a montré que la nouvelle methode est plus avantageuse. Le dosage de l'uranium en presence de certains cations qui gênent la détermination se fait en masquant ceux-ci avec du complexon II dissous dans de l'eau et la pyridine.

On connaît une série de combinaisons complexes de l'uranium avec des substances organiques qui renferment dans leur molécule de l'azote, parmi lesquelles on en mentionne quelques-unes du type: $[UO_2R_2]^{2+}$,$[UO_2R.H_2O]^{2+}$, où R est une N-base organique.

De telles combinaisons ont été obtenues par Inghilleri et Gori[1] avec la quinoléine en milieu aqueux, par Inghilleri[2] avec un excès d'aniline dans de l'alcool et une solution concentrée de $UO_2(NO_3)_2$: $[UO_2(C_9H_7N)_2]^{2+}$; Anion = No_3^-, $CH_3—COO^-$, SO_4^{2-}, *etc.*[1] $[UO_2(C_6H_5NH_2)_2]^{2+}$; Anion = SO_4^{2-}, $CH_3—COO^-$, $C_2O_4^{2-}$.[2]

Des complexes similaires de l'uranium ont été synthétisés aussi par R. Răşcanu[3] avec de la pyridine (Py), de la quinoléine (Ch), de la quinaldine (Chd), etc.:

$$\left[UO_2\begin{matrix}Py\\Py\end{matrix}\right]^{2+};\ \left[UO_2\begin{matrix}Py\\H_2O\end{matrix}\right]^{2+};\ \left[UO_2\begin{matrix}Ch\\H_2O\end{matrix}\right]^{2+};\ \left[UO_2\begin{matrix}Chd\\H_2O\end{matrix}\right]^{2+}.$$

Compte tenu de la possibilité qu'a l'ion d'uranyle de former des combinaisons complexes avec les N-bases organiques, nous avons synthétisé un de ses sels avec la pyridine et l'acide p-aminobenzoïque.

Grâce à ses propriétés, ce complexe se prête très bien au dosage gravimétrique de l'uranium.

Il est bien connu que la plupart des réactions de dosage gravimétrique de l'uranium sont basées sur la formation des sels d'uranyle difficilement solubles, avec des réactifs organiques ou inorganiques, des sels que l'on calcine, l'uranium passant à U_3O_8, ou bien que l'on sèche et pèse tels quels.

La précipitation de l'uranium par l'hydroxyde d'ammonium sous forme de diuranate d'ammonium est une des méthodes ordinairement employées au dosage de l'uranium.[4]

L'hydroxyde d'ammonium employé pour la précipitation doit être filtré parce que, étant gardé dans des vases de verre, il contient toujours des inclusions qui renferment de la silice. On doit aussi le priver du carbonate et du bicarbonate qu'il contient en raison de l'absorption du bioxyde de carbone de l'air, car l'anion carbonique gêne la précipitation totale de l'uranium en formant des complexes solubles du type: $[UO_2(CO_3)_3]^{4-}$.

Cette précipitation a lieu à chaud et le précipité que l'on obtient est gélatineux et difficilement lavable, surtout lorsque la quantité d'uranium est grande. Cela augmente la durée de l'analyse et les résultats sont moins bons.

Des résultats satisfaisants dans le dosage gravimétrique de l'uranium sont obtenus en le précipitant par une solution de 8-oxy-quinoléine:[4] on obtient un précipité rouge-orange, facilement filtrable: $[UO_2(C_9H_6NO)_2] . C_9H_7NO$.

Nous mentionnons qu'avant de précipiter l'uranium par la 8-oxy-quinoléine, la solution qui le contient doit être chauffée à ébullition; et le précipité obtenu, n'est filtré qu'après refroidissement complet, ce qui provoque également une augmentation de la durée de l'analyse.

La méthode que nous proposons pour le dosage gravimétrique de l'uranium se distingue par sa simplicité et la commodité de son exécution, par la réduction de la durée de l'analyse (par rapport aux méthodes signalées), ainsi que par les résultats satisfaisants que l'on obtient.

Description de la substance

L'analysé du précipité que l'uranium forme avec la pyridine et l'acide p-aminobenzoïque, montre le rapport suivant entre composants:

$$1UO_2^{2+}: 2H_2N—C_6H_4—COO^-: 2Py: 2H_2O.$$

La substance est amorphe, de couleur jaune, très facilement filtrable, stable à l'air, soluble dans les acides, $CH_3—OH$, $C_2H_5—OH$, moins soluble dans l'eau et difficilement soluble dans l'éther et le chloroforme.

Lorsqu'il est chauffé, il présente une variation continue du poids en fonction de la température (jusqu'à 500°C) et de ce fait, l'uranium ne peut pas être dosé par le chauffage de la substance à l'étuve à une certaine température.

La limite de reconnaissance de l'uranium sur papier filtre avec ce réactif est de 1,36 μg.

Mode opératoire

Le réactif de précipitation est préparé de la manière suivante: à 3 g d'acide p-aminobenzoïque on ajoute 3 ml de pyridine, on mélange bien avec une baguette, ajoute 20 à 30 ml d'eau distillée, on chauffe faiblement le mélange (en agitant avec la baguette) jusqu'à ce que l'acide se dissolve, filtre et complète avec de l'eau jusqu'à 50 ml.

Le précipité du composé d'uranium s'obtient à la température ordinaire avec le réactif proposé, dans l'intervalle de pH 3–5.

A la solution du sel d'uranyle, qui contient 0,33 g U au maximum dans 60–120 ml, on ajoute par petites portions le réactif de précipitation, en mélangeant avec la baguette, jusqu'à ce que l'on observe qu'il ne se forme plus de précipité. On laisse le précipité se déposer (environ 2 à 3 minutes), on filtre sur papier filtre à bande blanche, puis on lave avec une petite quantité de solution (15 ml de réactif de précipitation + 85 ml d'eau), on le brûle et calcine à la température de 800 à 1050°C (l'uranium de la combinaison passe en U_3O_8). Le facteur de transformation est 0,848.

La réaction de précipitation de l'uranium, dans ces conditions de travail, n'est pas gênée par les éléments alcalins, alcalino-terreux, par les ions Mn^{2+}, Co^{2+}, Ni^{2+}, NO_3^-, Cl^-, $CH_3—COO^-$, SO_4^{2-}, par l'acide ascorbique, le complexon III, *etc.*; par contre, la détermination est gênée par les ions Zn^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Fe^{3+}, Cr^{3+}, Al^{3+}, PO_4^{3-}, AsO_4^{3-}, $C_2O_4^{2-}$, par l'acide citrique, *etc.*

La méthode a été vérifiée par une série de dosages d'uranium dans une solution de $UO_2(NO_3)_2$ de diverses concentrations, en dosant les mêmes quantités d'uranium comparativement par du NH_3 et de l'oxine (l'oxinate d'uranyle a été calciné en U_3O_8).

Dans le tableau I sont donnés les résultats obtenus.

Il ressort de ce tableau que le titre de la solution de nitrate d'uranyle, exprimé en uranium, est identique par sa détermination avec le réactif employé et l'oxine, mais plus faible par sa détermination avec l'hydroxyde d'ammonium.

TABLEAU I.—LES RÉSULTATS OBTENUS

No. crt.	No. ml	Réactif		Oxine		NH_3	
		U_3O_8	U	U_3O_8	U	U_3O_8	U
1	5	0,0476	0,0404	0,0474	0,0402	0,0470	0,0399
		0,0474	0,0402	0,0478	0,0405	0,0470	0,0399
		0,0480	0,0407	0,0478	0,0405	0,0474	0,0402
		0,0476	0,0404	0,0476	0,0404	0,0476	0,0404
2	10	0,0952	0,0807	0,0956	0,0811	0,0952	0,0807
		0,0952	0,0807	0,0956	0,0811	0,0948	0,0804
		0,0954	0,0809	0,0950	0,0806	0,0952	0,0807
		0,0956	0,0811	0,0950	0,0806	0,0944	0,0801
3	20	0,1906	0,1616	0,1906	0,1616	0,1900	0,1611
		0,1906	0,1616	0,1902	0,1613	0,1904	0,1615
		0,1904	0,1615	0,1908	0,1618	0,1900	0,1611
		0,1908	0,1618	0,1902	0,1613	0,1902	0,1613
4	30	0,2858	0,2424	0,2854	0,2420	0,2852	0,2419
		0,2862	0,2427	0,2862	0,2427	0,2850	0,2417
		0,2860	0,2425	0,2856	0,2422	0,2854	0,2420
		0,2856	0,2422	0,2862	0,2427	0,2856	0,2422
5	40	0,3808	0,3229	0,3812	0,3233	0,3798	0,3221
		0,3810	0,3231	0,3808	0,3229	0,3796	0,3219
		0,3810	0,3231	0,3814	0,3234	0,3804	0,3226
		0,3814	0,3234	0,3808	0,3229	0,3804	0,3226
			$T_U = 0,00808$		$T_U = 0,00808$		$T_U = 0,00805$

T_U = titre de la solution de $UO_2(NO_3)_2$ experimé en uranium.

Le principal inconvénient de la nouvelle méthode consiste dans le fait que la spécificité du réactif est faible.

Afin d'augmenter la sélectivité de la méthode nous avons employé le complexon II dissous dans de l'eau et la pyridine qui forme avec l'ion d'uranyle un complexe peu stable, et avec les cations gênants, des complexes suffisamment stables, qui demeurent dans la solution lors de la prêcipitation de l'uranium.

En ajoutant à la solution du sel d'uranyle différents cations au rapport 2:1, comparativement à la quantité d'uranium, et un excès de complexon II dissous dans l'eau avec de la pyridine, le dosage de l'uranium en présence de ceux-ci fournit des résultats très satisfaisants.

C'est ainsi qu'on a séparé et dosé l'uranium en présence de Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} (le rapport Fe: U a été de 20:1) et Th^{4+}, avec une erreur comprise entre $\pm 0,3\%$.

Les résultats obtenus pour le dosage de l'uranium en présence de Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+} et Ni^{2+} (au rapport de 2:1 comparativement à l'uranium, sans emploi du complexon), sont affectés par une erreur positive (maximum 0,3%), en raison de l'absorption de ces cations par le précipité.

Summary—A method for the gravimetric determination of uranium is based on the precipitation of the UO_2^{2+} ion, in the pH range 3–5, by a solution of *p*-aminobenzoic acid and pyridine in water. An amorphous yellow precipitate forms, which is easily filtered and has the composition $UO_2(H_2N—C_6H_4—COO)_2 \cdot 2Py \cdot 2H_2O$. This is ignited to U_3O_8. Comparative determinations with ammonia and with oxine indicate that the new method is superior to these. Certain ions which interfere with the determination can be masked with Complexone-II dissolved in pyridine-water.

Zusammenfassung—Eine Methode zur gravimetrischen Uranbestimmung beruht auf der Fällung des UO_2^{2+}-Ions mit einer Lösung von *p*-Aminobenzoesäure und Pyridin in Wasser bei Ph 3–5. Es bildet sich ein amorpher gelber Niederschlag, der sich leicht filtrieren läßt und die Zusammensetzung $UO_2(H_2N—C_6H_4—COO)_2 \cdot 2Py \cdot 2H_2O$ hat. Dieser wird zu U_3O_8 verglüht. Vergleichsbestimmungen mit Ammoniak und Oxin zeigten, daß die neue Methode besser ist. Einige störende Ionen können mit Komplexon II in Pyridin-Wasser maskiert werden.

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AKTIVIERUNGSANALYTISCHE BESTIMMUNG VON MOLYBDÄN IN WOLFRAM

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Zusammenfassung—Es wird ein Verfahren zur aktivierungsanalytischen Bestimmung von Molybdänspuren in Wolfram beschrieben, bei dem das aus Molybdän-99 entstehende Technetium-99m radiochemisch rein abgetrennt und in einem Bohrlochkristall-Szintillationszähler gemessen wird. Die Isolierung der Technetium-99m-Aktivität geschieht durch Pyridinextraktion und Anionenaustauschchromatographie. Mit dem Verfahren lassen sich noch etwa 10^{-8} g Molybdän bestimmen.

DIE Bestimmung von Molybdänspuren in Wolfram kann spektralanalytisch,[1–3] polarographisch[4–6] oder spektrophotometrisch[7–9] erfolgen. Die Nachweisgrenzen liegen bei 10^{-2} bis $10^{-3}\%$, solange die Probeneinwaagen kleiner als 1 g sind.

Modellversuche zur aktivierungsanalytischen Bestimmung von Molybdän in Wolfram ergaben brauchbare Ergebnisse bis zu Gehalten von $10^{-3}\%$ Molybdän.[10] Dabei zeigte sich, daß die Gewinnung einer radiochemisch reinen Molybdänaktivität wegen der gleichzeitig entstehenden sehr hohen Wolframaktivität und der chemischen Ähnlichkeit von Wolfram und Molybdän schwierig ist. Bei dieser Untersuchung wurde jedoch nicht berücksichtigt, daß außer den Wolfram- und Molybdänaktivitäten auch Rhenium- und Technetiumaktivitäten entstehen. In der vorliegenden Arbeit wurde deshalb untersucht, ob das aus Molybdän-99 entstehende Technetium-99m vollständig und radiochemisch rein von Makromengen Wolfram und extrem großen Wolframaktivitäten sowie von Molybdän-99 und Rhenium-186/188 abtrennbar und damit zur aktivierungsanalytischen Molybdänspurenbestimmung geeignet ist.

ABSCHÄTZUNG DER ENTSTEHENDEN AKTIVITÄTEN

Einen Überlick über die bei der Bestrahlung von Wolfram und Molybdän mit thermischen Neutronen entstehenden Nuklide und Aktivitäten gibt Tabelle I. Aus ihr geht hervor, daß nach einer hundertstündigen Aktivierung die entstandene Wolframaktivität bei gleicher Einwaage etwa hundertmal größer als die Molybdänaktivität ist. Da die Technetium-99m-Aktivität im Gleichgewicht etwa der Molybdän-99-Aktivität entspricht, beträgt das Aktivitätsverhältnis $A_W : A_{Mo-99} : A_{Tc-99m}$ bei einem Gehalt von $10^{-5}\%$ Molybdän etwa $10^9 : 1 : 1$.

TABELLE I—DIE BEI DER NEUTRONENAKTIVIERUNG VON WOLFRAM UND MOLYBDÄN ENTSTEHENDEN RADIOAKTIVEN NUKLIDE[13] (BESTRAHLUNGSZEIT 100 h, NEUTRONENFLUß 10^{13} n/sec . cm^2, EINWAAGE JE 100 mg W UND Mo)

Nuklid	Häufigkeit, %, oder Bildungsreaktion	b	Gebildetes Nuklid	Halbwertszeit	Aktivität, *Zerfälle/sec*	Zerfallsprodukt (Halbwertszeit)
W-180	0,135	30	W-181	140 d	$2{,}6 \,.\, 10^6$	Ta-181 (stabil)
			W-181m	14 μsec		
W-184	30,6	2,24	W-185	74 d	$7{,}2 \,.\, 10^7$	Re-185 (stabil)
			W-185m	1,7 min		
W-186	28,4	34	W-187	24 h	$3{,}0 \,.\, 10^{10}$	Re-187 (stabil)
W-187	W-186(n, γ)W-187	90	W-188	69 d	$1{,}0 \,.\, 10^5$	Re-188 (17 h)
						Re-188m (20 min)
Re-185	W-184(n, γ)W-185 $\xrightarrow{\beta^-}$ Re-185	120	Re-186	91 h	$4{,}0 \,.\, 10^8$	Os-186 (stabil)
Re-187	W-186(n, γ)W-187 $\xrightarrow{\beta^-}$ Re-187	69	Re-188	17 h	$3{,}6 \,.\, 10^6$	Os-188 (stabil)
			Re-188m	20 min		
Mo-92	15,86	0,003	Mo-93	10^4 a	$3{,}2 \,.\, 10^2$	Tc-93 (2,7 h)
			Mo-93m	6,8 h	$5{,}0 \,.\, 10^2$	Tc-93m (44 min)
Mo-98	23,75	0,51	Mo-99	67 h	$4{,}5 \,.\, 10^8$	Tc-99 ($2 \,.\, 10^5$ a)
						Tc-99m (6 h)
Mo-100	9,62	0,2	Mo-101	14,6 min	$1{,}2 \,.\, 10^6$	Tc-101 (14 min)

Außerdem entstehen bei der Aktivierung von Wolfram durch Sekundärreaktionen (Reaktion 1 und Reaktion 2) die radioaktiven Nuklide Rhenium-186 und Rhenium-188:

$$\begin{tikzcd}
\text{W-184} \arrow[r, "(n,\gamma)", "2{,}24\ b"'] & \text{W-185} \arrow[d, "\beta^-"', "74\ d"] & \\
& \text{Re-185} \arrow[r, "(n,\gamma)", "120\ b"'] & \text{Re-186} \arrow[d, "\beta^-{,}\gamma"', "91\ h"] \\
& & \text{Os-186 (stabil)}
\end{tikzcd} \qquad (1)$$

$$\begin{tikzcd}
\text{W-186} \arrow[r, "(n,\gamma)", "34\ b"'] & \text{W-187} \arrow[r, "(n,\gamma)", "90\ b"'] \arrow[d, "\beta^-{,}\gamma"', "24\ h"] & \text{W-188} \arrow[d, "\beta^-"', "69{,}5\ d"] \\
& \text{Re-187} \arrow[r, "(n,\gamma)", "69\ b"'] & \text{Re-188} \arrow[d, "\beta^-{,}\gamma"', "17\ h"] \\
& & \text{Os-188 (stabil)}
\end{tikzcd} \qquad (2)$$

deren Aktivitäten bei einer 100-h-Bestrahlung von 100 mg Wolfram $4 \cdot 10^3$ Re-186-Zerfälle/sec und $3{,}7 \cdot 10^6$ Re-188-Zerfälle/sec ergeben.

Die Schwierigkeiten, die bei der Bestimmung von 10^{-5}% Molybdän in 100 mg Wolfram durch das zusätzlich entstehende Rhenium-186 und Rhenium-188 bedingt sind, veranschaulicht Abbildung 1, in der die Abklingkurven der Rhenium- und Molybdän- bzw. Technetiumaktivitäten nach einer 100-h-Bestrahlung dargestellt sind. Modellversuche ergaben, daß die berechneten Rheniumaktivitäten[11,12] mit den experimentell ermittelten Werten annähernd übereinstimmen.

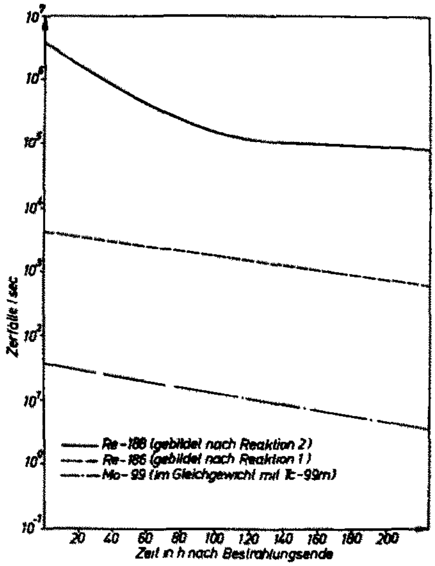

ABB. 1.—Abklingkurve der Rhenium- und Molybdänaktivitäten nach einer 100-Stunden-Bestrahlung von 100 mg Wolfram bzw. 0,01 μg Molybdän, $\phi = 10^{13}$ n/sec . cm².

PRINZIP UND SCHEMA DER TRENNUNG

Zur Abtrennung des Technetium-99m vom Wolfram ist die Extraktion von Pertechnetat aus alkalischer Lösung mit Pyridin geeignet.[14] Die durch Modellversuche für Pertechnetat-, Perrhenat- und Molybdatspuren in Gegenwart von 100 mg Wolfram ermittelten Verteilungskoeffizienten enthält Tabelle II. Man erkennt, daß das Technetium von Rhenium begleitet wird, und daß die von der organischen Phase aufgenommenen Wolfram- und Molybdänspuren durch Natronlauge auswaschbar sind, ohne daß dabei nennenswerte Technetiumverluste eintreten.

TABELLE II—VERTEILUNGSKOEFFIZIENTEN VON TECHNETIUM, RHENIUM, MOLYBDÄN UND WOLFRAM ZWISCHEN 4 n NATRONLAUGE UND PYRIDIN

Ion	Verteilungskoeffizient D	
	Literatur[14]	Nach eigenen Messungen*
TcO_4^-	778	830
ReO_4^-	225	620
MoO_4^{2-}	—	10^{-3}
WO_4^{2-}	—	10^{-4}

* Gemessen in Gegenwart von 100 mg inaktivem Wolfram (WO_4^{2-})

Unter den gewählten Arbeitsbedingungen wird durch Pyridin extraktion und dreimaliges Waschen der organischen Phase mit 4n Natronlauge eine Wolframabreicherung von etwa 10^7 erreicht. Die in der organischen Phase verbleibenden Wolframspuren sind durch mitgerissene Wassertröpfchen bedingt.

Zur Gewinnung von radiochemisch reinem Technetium müssen anschließend die im Pyridin verbliebenen Rhenium- und Wolframaktivitäten durch ein vielstufiges Trennverfahren entfernt werden. Bei Vorliegen einer wäßrigen Phase läßt sich eine Rhenium-Technetium-Trennung mit Hilfe eines Anionenaustauschers und einer ammoniumsulfat/-rhodanidhaltigen Lösung als Elutionsmittel durchführen.[15] Eigene Versuche ergaben, daß man die Anionenaustauschersäule auch direkt mit den im Pyridin enthaltenen Aktivitäten beladen kann, ohne daß Aktivitätsverluste auftreten. Eine anschließende Trennung von Wolfram, Rhenium und Technetium ist nach Veränderung einiger Versuchsbedingungen (Arbeitsvorschrift) auch bei extremen Aktivitätsverhältnissen möglich (Abbildung 2).

Zur Veranschaulichung ist das Trennschema für die Isolierung von radiochemisch reinem Technetium in Abbildung 3 dargestellt.

Eine modellmäßige Überprüfung des gesamten Verfahrens ergab, daß 96 bis 100 % des eingesetzten Technetiums in der Natriumperchloratfraktion zurückerhalten werden. Die Analyse ist also trägerfrei durchführbar.

ARBEITSVORSCHRIFT

0,1 g der zu analysierenden Wolframprobe und 1 mg metallisches Molybdän als Standard werden in einer Polystyrolkapsel im Reaktor 100 h mit einem Fluß von 10^{13} Neutronen/sec. cm^2 bestrahlt.

Die bestrahlte Probe wird in ca. 15 ml eines Gemisches aus 3 Teilen 40%iger Flußsäure und einem Teil konzentrierter Salpetersäure gelöst und die Lösung zur Trockne gedampft. Man löst den Rückstand in 10 ml 4 n Natronlauge und filtriert die Lösung durch ein Glaswollefilter in einen Schütteltrichter. Mit 2 ml Pyridin werden Pertechnetat und Perrhenat gemeinsam extrahiert. Wegen der hohen Aktivität der Matrix werden diese Operationen hinter einer Bleiabschirmung vorgenommen.

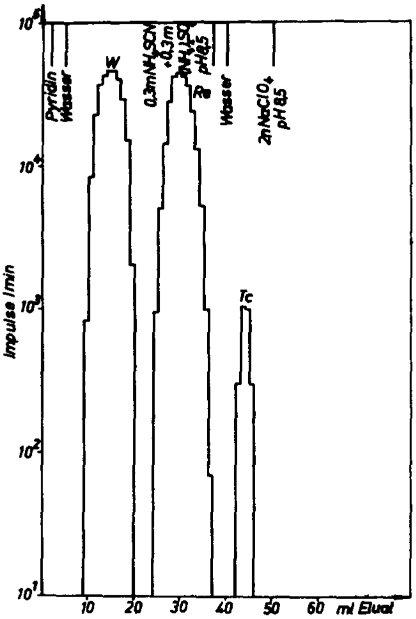

ABB. 2.—Elutionsdiagramm von Wolfram, Rhenium und Technetium aus einer Wolframprobe
(Molybdängehalt 1,4 ppm)

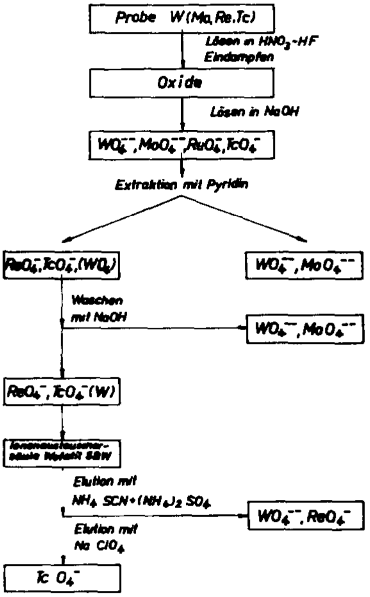

ABB. 3.—Schema zur Abtrennung des Technetiums von Wolfram, Molybdän und Rhenium

Zur weiteren Abreicherung des Wolframs wird die Pyridinphase dreimal mit je 5 ml 4 n Natronlauge gewaschen.

Anschließend gibt man die organische Phase auf eine mit dem Anionenaustauscher Wofatit SBW (Cl^--Form, Korngröße 0,09 bis 0,063 mm) gefüllte Säule von 30 cm Länge und 0,4 cm Durchmesser, wobei hier und im weiteren eine Flußgeschwindigkeit von 4 Tropfen/min eingehalten wird. Das auf der Säule zurückgebliebene Pyridin wird mit 3 ml Wasser ausgewaschen.

Zuerst werden die am Austauscher adsorbierten Wolfram- und Rheniumaktivitäten mit 32 ml einer auf pH 8,5 eingestellten Lösung, die jeweils 0,3 m an Ammoniumsulfat und Ammoniumrhodanid ist, eluiert. (Bei Benutzung von Dowex-1 X8 muß die Ammoniumsulfat- und Ammoniumrhodanidkonzentration je 0,4 m sein, da andernfalls die Aktivitätspeaks breiter werden und ein größeres Elutionsvolumen benötigt wird).

Zur Entfernung der auf der Säule verbliebenen Ammoniumionen wird mit 3 ml Wasser gewaschen und anschließend das Pertechnetat mit 2 n Natriumperchloratlösung (pH 8,5) eluiert. Das gesamte Technetium ist in etwa 4 ml Eluat enthalten. Die Aktivität der Pertechnetatfraktion wird in einem Bohrlochkristall-Szintillationszähler gemessen und eine Abklingkurve aufgenommen.

Der Molybdänstandard wird in 5 ml halbkonzentrierter Salpetersäure gelöst. Man dampft zur Trockne, nimmt den Rückstand in 100 ml 4 n Natronlauge auf und verwendet zur weiteren Verarbeitung, die analog der Analysenprobe erfolgt, ein Aliquot der Lösung.

Wegen der beim Lösen der Proben eintretenden Technetiumverluste darf ihre Weiterverarbeitung erst nach ca. 36 Stunden erfolgen, damit sich das Molybdän-99-Technetium-99-Gleichgewicht wieder einstellen kann.

BEWERTUNG DES VERFAHRENS

In Tabelle III sind die aktivierungsanalytisch bestimmten Molybdängehalte einiger Wolframproben den Resultaten spektralanalytischer Vergleichsanalysen gegenübergestellt. Die Übereinstimmung ist bei Proben mit verhältnismäßig hohen Molybdängehalten gut. Die Gehalte der Proben 3 bis 5 konnten bisher spektralanalytisch nicht erfaßt werden.

TABELLE III—ERGEBNISSE VON MOLYBDÄNBESTIMMUNGEN IN WOLFRAMPROBEN (MITTELWERTE AUS JEWEILS 3 BESTIMMUNGEN)

Probe	Aktivierungsanalyse, *ppm*	Spektralanalyse, *ppm*
1	87	90
2	43	46
3	15,2	nicht nachweisbar
4	8,0	nicht nachweisbar
5	1,4	nicht nachweisbar

Zur Ermittlung der Reproduzierbarkeit der Analysenwerte wurde der Variationskoeffizient des Verfahrens für zwei Konzentrationsbereiche berechnet.[16] Die erhaltenen Werte sind mit der Zahl der statistischen Freiheitsgrade in Tabelle IV aufgeführt.

TABELLE IV—REPRODUZIERBARKEIT DER AKTIVIERUNGSANALYTISCHEN MOLYBDÄNBESTIMMUNGEN IN WOLFRAM

Konzentrationsbereich des Molybdängehaltes, *ppm*	Variationskoeffizient, %	Zahl der Freiheitsgrade
1–10	9	8
10–100	4	9

Analysenproben mit ca. 10^{-5}% Molybdän standen bisher noch nicht zur Verfügung. Wie aber aus der Abklingkurve (Abb. 4) einer Technetiumaktivität, die aus einer Wolframprobe mit einem Gehalt von $1{,}4 \cdot 10^{-4}$% Molybdän isoliert wurde, hervorgeht, beträgt die Ausgangsaktivität ca. 5000 Imp/min und die radiochemische Reinheit ist besser als 99 %. Unter der Voraussetzung, daß zum sicheren Messen und Identifizieren eines Nuklids etwa 500 Imp/min notwendig sind, ergibt sich hieraus eine untere Bestimmungsgrenze von 10^{-8} g Molybdän. Bei einer Einwaage von 100 mg Probenmaterial entspricht dies ca. 10^{-5} % Molydbän.

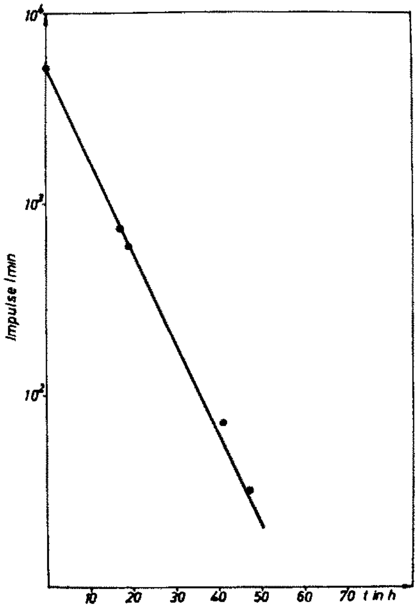

ABB. 4.—Abklingkurve einer aus einer Wolframprobe isolierten Technetiumaktivität (Molybdängehalt 1·4 ppm)

Das vorgeschlagene Trennverfahren ist außerdem zur aktivierungsanalytischen Bestimmung von Rheniumspuren geeignet, da, wie aus Abbildung 2 hervorgeht, eine in der Analysenprobe enthaltene Rheniumaktivität vom Ionenaustauscher als schmale Bande frei von Störungen und Verunreinigungen eluiert wird.

Summary—A method for the determination of traces of molybdenum in tungsten by activation analysis is described. The determination is done by measuring the activity of technetium-99m, daughter of molybdenum-99. Radiochemically pure technetium is separated from other radionuclides by pyridine extraction and anion-exchange chromatography. Amounts of 10^{-8} g of molybdenum can be determined.

Résumé—On décrit une méthode de dosage de traces de molybdène dans le tungstène par analyse par activation. Le dosage est effectué par la mesure de l'activité du technécium-99m, provenant du molybdène-99. Le technécium radiochimiquement pur est séparé des autres radionucléides par extraction à la pyridine et chromatographie d'échange anionique. On peut doser des quantités de molybdène de l'ordre de 10^{-8} g.

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SELECTIVE RETENTION OF ALKALI METALS ON CATION-EXCHANGE RESINS

RAPID SEPARATION OF ALKALI METALS FROM OTHER METALS*

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Summary—The alkali metals, as a group, can be rapidly separated from multivalent metals by batchwise precomplexing of the multivalent metals with EDTA at pH 8 and passing the solution through a cation resin in the tetramethylammonium ion form. After isolation of the alkali metals on the resin, they can be rapidly eluted as a group and concentrated. Separations of the alkali metals from the alkaline earths and cadmium are illustrated. Variables affecting the efficiency of alkali metal uptake have been studied in detail.

INTRODUCTION

THERE is a need for a simple, rapid method of separating the alkali metals, as a group, from other metal ions. In flame photometry, for example, many alkaline earths interfere with the analysis of the alkali metals,[1] and *vice versa*.[1,2]

The high selectivity of various inorganic ion-exchange crystals for certain alkali metals in acidic solutions is becoming well known, and has been used very successfully for the separation of individual alkali metals.[3–7] A group separation of the alkali metals from the alkaline earths has been worked out on the ammonium form of zirconium phosphate, but the ammonium form has essentially no selectivity left for the alkali metals, and they are eluted as a group, ahead of the alkaline earths.[3]

Likewise, in previously reported group separations of the alkali metals on organic ion-exchange resins, the heavier metals are preferentially held on the resin while the alkali metals are made to pass into the effluent. For example, Tsubota elutes sodium and potassium from a cation-exchange resin with dilute HCl or a formate buffer eluant, and then removed heavier metals with various formate buffer mixtures.[8] Schumacher preferentially eluted microgram amounts of potassium and rubidium from Dowex-50 ahead of the alkaline earths and rare earths.[9] Blaedel, Olsen and Buchanan held radiotracer amounts of most of the alkali metals on a cation resin while sequentially eluting groups of heavier metals, but the separation necessitated very low ionic strength eluants, and is applicable only to microgram amounts of metals.[10]

Anion-exchange resins have been used to separate the alkali metals from certain other metal ions. Samuelson and Sjöström used Dowex-2 anion-exchange resin in a mixture of EDTA and acetate forms to absorb calcium and magnesium from solutions containing sodium and potassium.[11] Samuelson, Sjöström and Forsblom separated the alkali metals from calcium, magnesium, vanadium(IV), iron(III), aluminium(III),

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copper(II), nickel(II), cobalt(II), manganese(II) and zinc(II) by passing solutions of these ions through a column of Dowex-2 in the EDTA, acetate, and oxalate forms. The alkali metals pass into the effluent while the multivalent ions are retained on the resin.[12] Although this is a satisfactory group separation, the alkali metals cannot be concentrated by this method.

In contrast, the procedure described in this paper retains the alkali metals on a cation-exchange resin and allows the other metal cations to pass through. Thus, even though the alkali metals ordinarily possess the weakest exchange affinity of all the metal ions,[13] and can readily be displaced by dilute hydrogen ion or ammonium ion,[10] the selectivity can be partially reversed by batchwise precomplexing of the multivalent cations with EDTA and passing this solution through a cation resin in the tetramethylammonium ion form. Variables affecting the efficiency of alkali metal uptake have been studied in detail.

EXPERIMENTAL

Apparatus and reagents

The *ion-exchange resin* used in most of this work was Baker Analyzed Dowex 50W-X8, 100–200 mesh, having a total exchange capacity of 1·8 meq/ml in the water-swollen hydrogen ion form. Baker Analyzed Dowex 50W-X12, 100–200 mesh, had a total exchange capacity of 2·2 meq/ml, and Dowex A-1 resin, used in preliminary studies, was obtained from the Dow Chemical Company and had a total exchange capacity of 0·66 meq/ml. The breakthrough capacity of the resin (the number of meq of ions that can be taken up quantitatively during column operations) varies with experimental conditions, and is expressed in this paper as the percentage of total exchange capacity. The resins were cleaned in large lots as described previously.[10]

The *glass columns* used to hold the resin were 20 cm long by 12 mm inside diameter, closed at the lower end by a coarse sintered-glass disk upon which the resin bed rested, and fitted at the top with a bowl 8 cm in diameter to hold eluants. A resin volume of 10·0 ml (H-form) was used in most of this work, giving a bed height of about 9·5 cm in the hydrogen ion form, and 10·2 cm in the tetramethylammonium ion form. The column free volume is about 3·8 ml.[14] Five-ml siphon pipettes, used to collect 5- or 10-ml fractions of column effluent, were obtained from the Ace Glass Company, Vineland, New Jersey, U.S.A. and were recalibrated under the conditions of use.

Reagent-grade EDTA (ethylenediaminetetra-acetic acid) was obtained in the acid form. *Tetramethylammonium hydroxide* was prepared according to the method of Peracchio and Meloche,[15] using purified silver oxide (Fisher Scientific Co.) and highest purity tetramethylammonium chloride (Eastman Organic Chemical Co.). Highest purity *tetraethylammonium hydroxide* was obtained as a 10% solution from Eastman Organic Chemical Co., but commercial tetramethylammonium hydroxide could not be used because the sodium ion content was over 0·05*M*. The nitrate or chloride salts of all metals were reagent-grade.

Procedure

Ten ml of Dowex 50W-X8 in the hydrogen ion from was converted to the tetramethylammonium ion form by passing 0·5–0·8*M* tetramethylammonium hydroxide through the column at a flow rate of about 1 ml/min until the effluent was basic to litmus; then the column was washed with 20 ml of water. In preliminary experiments in which effluent pH was plotted against effluent volume, using an apparatus described previously,[10] it was found that the column is completely converted with an equivalent amount of the reagent, indicating virtually 100% efficiency of conversion. When the conversion was attempted with 1·0*M* tetramethylammonium chloride, it was found that even a ten-fold excess was insufficient for quantitative conversion, as indicated by a slow rise of effluent pH. This finding is consistant with that of others.[16]

The sample solution, which may contain all the alkali metals at any concentration up to about 0·1*M*, and heavier metals up to a total concentration of about 0·05*M*, was made 2% in EDTA (0·068*M*) and adjusted to pH 8·0 with tetramethylammonium hydroxide. The sample solution was then passed continuously through the column at a flow rate of 1·0 ml/min and 5- or 10-ml fractions were collected until breakthrough equilibrium was achieved.

After washing the column with 20 ml of water, the alkali metals were eluted with 5*M* HCl, 2-ml fractions being collected in a graduated cylinder.

Analysis

A Beckman Model DU spectrophotometer with flame attachment was used for analysis of effluent fractions. An oxygen-hydrogen flame was used for barium, and an oxygen-acetylene flame was used for all other elements. At high concentrations, dilutions were performed to minimise self-absorption. To enhance barium readings, 1:1 dilutions with acetone were made. Standard solutions used for flame analysis contained the same concentration of EDTA as the effluent fraction analysed.

Because the flame photometric analysis of magnesium and cadmium is not very sensitive,[1] the behaviour of these elements was tested by running them individually, with only the alkali metals present, and effluent fractions were analysed by indirect titration of the excess EDTA with standard magnesium nitrate solution, using Eriochrome Black T indicator.[17] After elution of the resin with HCl, magnesium was qualitatively tested for with *p*-nitrobenzeneazoresorcinol,[18] and cadmium was tested for polarographically.

RESULTS AND DISCUSSION

Fig. 1 illustrates the separation that can be achieved when an ionic solution containing calcium, strontium, lithium, potassium, rubidium and caesium, each at a concentration of 0·010*M*, is made 2 % in EDTA at pH 8 with tetramethylammonium hydroxide and is passed continuously through 10 ml of Dowex 50W-X8 in the tetramethylammonium form at a flow rate of 1·0 ml/min. Calcium and strontium breakthrough immediately, and rapidly rise to influent concentration, and no leakage of the alkali metals occurs until over 80 ml of solution have passed. Thus, the first 80 ml can be collected free from all alkali metals. Magnesium, barium and cadmium, tested individually, behave similarly to calcium and strontium.

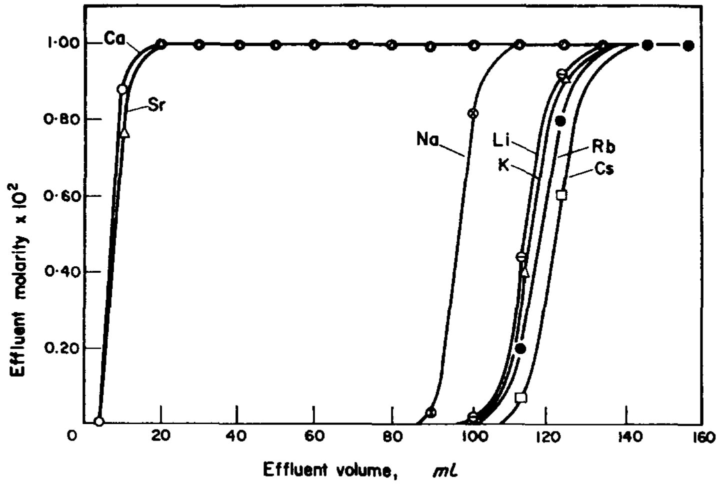

FIG. 1.—Breakthrough of $10^{-2}M$ Li, Na, K, Rb, Cs, Ca and Sr on 10·0 ml of Dowex 50W-X8, $(CH_3)_4N^+$ form.

After washing the column with 20 ml of water, 5*M* HCl can be used to elute the alkali metals rapidly from the resin, as illustrated in Fig. 2. Only the lithium and caesium curves are shown, because the curve for sodium is similar to that of lithium, and the curve for rubidium is almost identical to that of caesium, with the potassium curve comming in between. No calcium or strontium can be detected in the HCl fraction. In samples containing magnesium and barium, 0·5 % of the total magnesium and about 1 % of the total barium appear in the HCl fraction. Cadmium, like calcium and strontium, is quantitatively complexed by the EDTA, and does not appear in the

HCl fraction. The amount of magnesium and barium retained on the resin during the original passing of the sample solution is too small to give a measurable decrease in the flame analysis of the EDTA effluent, and likewise the contamination of the $5M$ HCl fraction is too small to interfere in the flame photometric analysis of the alkali metals. If it were desired to obtain the alkali metals completely free from magnesium and barium, this could be accomplished by elution of the column with $0{\cdot}1M$ HCl instead of $5M$ HCl. Three hundred ml of $0{\cdot}1M$ HCl were found to be sufficient to elute all the alkalies quantitatively*, leaving magnesium and barium on the resin from which they can be rapidly eluted with $5M$ HCl. No attempt was made to improve on these latter separation conditions.

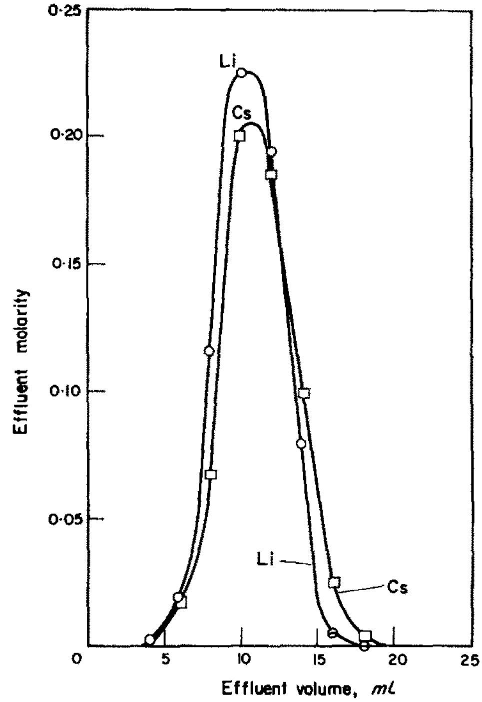

FIG. 2.—Elution of alkali metals with $5M$ HCl after passing $10^{-2}M$ alkali metals through 10·0 ml of Dowex 50W-X8 until breakthrough equilibrium.

It can be calculated from Fig. 1 that a total of 4·74 meq of alkali metals are quantitatively retained on the resin up to breakthrough of each of the ions. This represents 26% of the total exchange capacity of the resin. Since this breakthrough capacity is critically dependent upon a large number of variables, the next section is devoted to a study of these variables.

Conditions affecting breakthrough capacity

In most of the following breakthrough studies, lithium, sodium and potassium were chosen to be representative of all the alkalies, because rubidium and caesium can

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* Elution of the alkali metals with either $0{\cdot}10M$ HCl or $0{\cdot}05M$ HCl results in mutually-overlapping elution curves, indicating that the various alkali metals are probably retained in a somewhat random distribution on the resin, rather than in sharply-defined bands. No separation of the individual alkali metals can be expected by this technique because of the excessive loading of the resin.

be expected to show at least equal or greater uptake on the resin. Calcium was chosen to represent the alkaline earths because of its high sensitivity of detection with a flame photometer.[1]

Type of resin: Previous studies in this laboratory indicated that a rather high degree of selective retention of the alkali metals in the presence of other metal ions could be accomplished on Dowex A-1, a chelating resin, when the resin is used in the tetramethylammonium ion form and EDTA is used to complex the other metals into the anionic form.[19] To compare the breakthrough capacities of Dowex 50W-X8 and Dowex A-1, breakthrough curves were determined for each kind of resin using an influent solution containing 0·01*M* Li, Na, K and Ca, and 2% in EDTA at pH 7·0 with tetramethylammonium hydroxide.* The breakthrough capacity on Dowex A-1 was 8·0% of its total exchange capacity, whereas on Dowex 50W the breakthrough capacity was 26% of its total exchange capacity. It is interesting that in both runs the order of breakthrough is sodium, potassium, and then lithium. For Dowex A-1 this order has been explained on the basis of chelation of lithium by the iminodiacetic acid groups on the resin.[19] With Dowex 50W this explanation would not be valid, but no satisfactory explanation has yet been found. Because of the superior breakthrough capacity of Dowex 50W, it is used in all the studies that follow.

TABLE I.—EFFECT OF RESIN COUNTER ION ON ALKALI METAL BREAKTHROUGH CAPACITY

Influent: 0·0100*M* in Li^+, Na^+, K^+, Ca^{2+}; 2% in EDTA at pH 7·0 with hydroxide of counter ion;
Resin: Dowex 50W—X8, in counter ion form indicated;
Flow rate: 1·0 ml/min.

Counter ion	Breakthrough capacity (% of total capacity)
NH_4^+	5·6
$(CH_3)_4N^+$	26
$(C_2H_5)_4N^+$	28

Type of counter ion: Table I summarises the effect of using Dowex 50W-X8 in the ammonium ion and tetraethylammonium ion forms as compared to the tetramethylammonium ion form. It was of considerable interest to compare the effect of substituting ammonium ion in all places in the procedure where tetramethylammonium ion has been adopted because the ammonium ion form of the resin is commonly used in cation-exchange separations of metal ions using chelating agent eluants.[10,13] The relatively low efficiency of alkali metal retention in the presence of ammonium ion (5·6%) is in accord with the findings of others.[10] Thus, though it could have been predicted on the basis of steric considerations that the use of tetramethylammonium ion instead of ammonium ion would result in an improvement in the selective retention of the alkali metals, the magnitude of the improvement is remarkable. Using tetraethylammonium ion instead of tetramethylammonium ion could be expected to improve still further the relative affinity of the resin for the alkali metals. The small improvement over

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* Because Dowex A-1 is a weak acid resin and is subject to severe hydrolysis, it was necessary to make the sample solution for the Dowex A-1 experiment 0·01*M* in phosphoric acid before adjusting to pH 7 with tetramethylammonium hydroxide. With the phosphate buffer the effluent pH remained within 0·1 pH unit of 7; without the buffer the effluent pH rose to 10, and lithium and sodium leaked very early because of complexing by EDTA.[19]

tetramethylammonium ion that is found (28 % compared to 26 %) is probably attributable to slower rates of diffusion of the tetraethylammonium ion.[20] Slower column flow rates might appreciably improve the alkali retention when using tetraethylammonium ion, but this was not tried.

Degree of resin cross linkage and solution flow rates: Table II summarises the effects of using a higher degree of divinylbenzene (DVB) crosslinkage, and also shows the flow rate dependence of breakthrough capacity. When 10·0 ml of Dowex 50W-X12 is substituted for 10·0 ml of Dowex 50W-X8, the fastest flow obtainable without modifying the apparatus used was 0·30 ml/min, in contrast to the rate of 1·0 ml/min conveniently obtained for all other experiments. A significant improvement in breakthrough capacity is realised by using the higher degree of crosslinkage, in agreement with predictions based on steric effects and swelling pressures.[21] Because 0·30 ml/min is too slow to be convenient, flow rates were increased by attaching 60 cm of 2-mm (i.d.) capillary tubing below the columns to increase the total head of liquid. Thus, at 1·0 ml/min, the resin with 12 % DVB gives only a small improvement (29 % compared to 24 %) over the resin with 8 % DVB. Increasing the flow rate with Dowex-X8 likewise decreases the breakthrough capacity, but the dependence does not seem quite so marked as with the 12 % crosslinked resin. Dowex 50W-X8, operated at a flow rate of 1·0 ml/min, was chosen for all subsequent studies because of the simplicity of the column equipment and ease of obtaining the reproducible flow rate of 1·0 ml/min.

TABLE II.—EFFECTS OF DEGREE OF RESIN CROSSLINKAGE AND SOLUTION FLOW RATES ON ALKALI METAL BREAKTHROUGH CAPACITY

Influent: 0·0100*M* Li^+, Na^+, K^+; 0·050*M* Ca^{2+}; 2 % in EDTA at pH 7·0 with $(CH_3)_4NOH$;
Resin: Dowex 50W in $(CH_3)_4N^+$ form.

Flow rate, *ml/min*	Breakthrough capacity (% of total capacity) 8 % DVB	12 % DVB
0·30	—	40
1·0	24	29
2·5	19	—

TABLE III.—EFFECT OF CONCENTRATION OF EDTA AND CALCIUM ON ALKALI METAL BREAKTHROUGH CAPACITY

Influent: 0·0100*M* Li^+, Na^+, K^+; Ca^{2+} at concentration specified; EDTA at pH 7·0 with $(CH_3)_4NOH$;
Resin: Dowex 50W-X 8 in $(CH_3)_4N^+$ form;
Flow rate: 1·0 ml/min.

Concentration of EDTA, %, *w/v*	Concentration of Ca^{2+}, *mole/litre*	Breakthrough capacity (% of total capacity)
2·0	0·0100	26
2·0	0·050	24
3·0	0·050	18
4·5	0·110	9

Concentration of EDTA and concentration of chelated ions: The more EDTA contained in the sample solution, the greater is the concentration of multivalent metals that can be separated from the alkali metals. However, as can be seen from Table III, increasing the concentration of EDTA, and with it the concentration of tetramethylammonium ion, causes the efficiency of alkali metal uptake to decrease. This decrease can be qualitatively explained on the basis of the following equilibrium:

$$RSO_3N(CH_3)_4 + Na^+ \rightleftharpoons RSO_3Na + (CH_3)_4N^+.$$

Thus, as the concentration of tetramethylammonium ion increases, the alkali metal capacity should decrease.

Likewise, increasing the concentration of calcium ion tends to decrease the alkali metal breakthrough capacity, but the concentration dependence is much smaller than that of EDTA, because at pH 7 EDTA is predominantly[22] in the form HY^{3-}, and little extra tetramethylammonium hydroxide need be added to neutralise the hydrogen ion released in the chelation reaction.

The effect of concentration of multivalent ions on the extent of chelation is discussed in the next section.

pH and concentration of multivalent ions: Because EDTA complexes with lithium above pH 8·3 and with sodium above 9·0,[22,23] it was necessary to work at pH 8 or below. On the other hand, EDTA will not complex with many metal ions at low pH, and in addition, EDTA becomes rather insoluble below pH 4·5.[24] Therefore, the potentially useable pH range for this separation was pH 5–8, with the optimum pH being the lowest pH at which multivalent metal ions could be complexed quantitatively into the anionic form. The lower this pH, the better, because then the tetramethylammonium ion concentration would be at a minimum, and presumably the efficiency of alkali retention would be at a maximum. Because barium forms the weakest EDTA complex of all the multivalent metals,[25] it was chosen to determine the lower pH limit. An 0·050*M* barium ion solution was made 2% in EDTA and adjusted to the required pH with tetramethylammonium hydroxide. At pH 5 it was found that virtually all the barium ion was retained by the resin. At pH 7 the breakthrough effluent analysis indicated that approximately 80% of the barium was complexed into the anionic form, 20% being retained on the resin. At pH 8 the breakthrough effluent analysis indicated quantitative complexing of barium. However, elution of the resin with 5*M* HCl indicated that about 1–2% of the total barium had been retained by the resin during the breakthrough run. Higher pH's resulted in early breakthrough of lithium, and at pH 10 both lithium and sodium are complexed and reach influent concentration at around 25–30 ml. Even at pH 10 a trace of barium is retained on the resin.* Because negligible lithium complexing occurs at pH 8, and only a small amount of barium remains uncomplexed at this pH, pH 8 was chosen as the optimum pH for the separation. Tests with varying concentrations of barium revealed that the retention of barium (as revealed by a 5*M* HCl elution) drops to about 1% in samples containing 0·01*M* barium, and if 0·005*M* barium is used, only a trace (<0·5%) can be detected. The concentration level of strontium, which forms the second weakest EDTA complex of all the multivalent metals,[26] also effects the quantitativeness of its separation from the

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* Attempts were made to increase the stability of the barium-EDTA complex by working in 50% ethanol-water and 50% dioxan-water, but although the extent of complexing was increased, retention of traces of barium by the resin could not be prevented. Attempts were also made to complex barium quantitatively with DTPA (diethylenetriaminepenta-acetic acid), which forms a complex with barium that is over 100-fold stronger than the EDTA complex.[25] Although quantitative complexing of barium could be achieved at pH 10, lithium and sodium were likewise complexed at this pH, and so no further attempts were made.

alkali metals at pH 8. Whereas 0·01M strontium appears quantitatively complexed, 0·05M strontium is retained by the resin to the extent of about 2%. Thus, to keep the retention level of multivalent metal cations at 1% or below, the concentration of each of these ions, in general, should be 0·01M or below. Calcium, and metals forming more stable EDTA complexes than calcium, could probably be tolerated to the extent of about 0·05M, but the requirement of excess EDTA further restricts the total concentration of multivalent metals to about 0·05M when 2% EDTA is used.

Concentration of alkali metals: Table IV shows the effect of various concentration levels of alkali metals on the alkali metal breakthrough capacity. The sharp drop in breakthrough capacity at trace concentrations of the alkali metals is not surprising in view of the high ratio of tetramethylammonium ions to alkali metal ions at these concentrations. At $10^{-3}M$ alkali metals the ratio of tetramethylammonium ions to alkali metal ions is approximately 100:1, and at $10^{-4}M$ alkali metals the ratio is about 1000:1. These are rather startling competitive odds against the retention of the alkali metals, especially in view of the weakness with which the alkali metals are normally held. Nevertheless, the low breakthrough capacities at the $10^{-3}M$ and $10^{-4}M$ levels of alkali metals should not detract from the usefulness of this technique at low concentrations. It is still possible to achieve excellent separations of alkali metals from multivalent metals. For example, with a sample containing $10^{-4}M$ alkali metals under the conditions given in Table IV, over 140 ml of sample solution can be passed through 10 ml of Dowex 50W-X8 in the tetramethylammonium ion form before the first breakthrough of the alkali metals occurs. (Sodium breaks through at 144 ml, potassium at 188 ml and lithium at 278 ml.) After washing with 20 ml of water, 5M HCl elutes the retained alkali metals quantitatively in less than 20 ml, giving a peak concentration of each of the alkali metal ions of approximately $10^{-2}M$, representing a 100-fold increase in the sensitivity with which they can be detected flame photometrically. Over the 20-ml fraction, the average concentration of each of the alkali metals is $10^{-3}M$, representing a 10-fold concentration factor over the original sample.

TABLE IV.—EFFECT OF CONCENTRATION OF ALKALI METALS ON ALKALI METAL BREAKTHROUGH CAPACITY

Influent: 0·0100M Ca^{2+}; Li^+, Na^+, K^+ at concentration indicated; 2% EDTA at pH 8·0 with $(CH_3)_4NOH$;
Resin: Dowex 50W-X8 in $(CH_3)_4N^+$ form;
Flow rate: 1·0 ml/min.

Concentration of Li^+, Na^+, K^+, *mole/litre*	Breakthrough capacity (% of total capacity)
$1{\cdot}00 \times 10^{-1}$	49
$1{\cdot}00 \times 10^{-2}$	20
$1{\cdot}00 \times 10^{-3}$	3·2
$1{\cdot}00 \times 10^{-4}$	0·34

Length of the resin bed: Although the majority of the separations were made with 10·0 ml of resin, several runs were repeated with 5·0 and 15·0 ml of resin to test the effect of length of the resin bed on the alkali metal breakthrough capacity. In all cases the relative breakthrough capacity (percentage of total exchange capacity) remained the same within the accuracy and reproducibility of measuring breakthrough volumes (about ± 3 ml). Thus, the breakthrough capacity figures cited should be useful in estimating the amount of resin that should be used to isolate a given amount of alkali metals.

CONCLUSIONS

Results presented in this paper emphasise the separation of the alkali metals from the alkaline earths. Because other multivalent metals form even stronger EDTA complexes than do the alkaline earths,[26] the method described should be useful to separate a great many of these metals from the alkali metals, provided that an excess of EDTA is maintained. The separation of cadmium from the alkali metals is given as an example. The separation and isolation of the alkali group metals is simple and rapid and serves as a way of concentrating dilute solutions of these metals. The method is only useful for a separation of the alkali metals as a group. Further separation of the individual elements was not attempted, but should be possible using any of a number of separation procedures that have been devised.[3,13]

In this procedure the original sample solution is completely freed of alkali metals. If, for example, one were determining the alkaline earths by flame photometry, the complete removal of the alkali metals should contribute greatly to the ease and accuracy of the analysis. At the same time, the presence of EDTA in the sample solution should have the advantage of minimising anion interferences in the flame photometric analysis.[27]

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Zusammenfassung—Die Gruppe der Alkalimetalle kann von mehrwertigen Metallen schnell getrennt werden durch portionsweise Komplexbildung der mehrwertigen Metalle mit EDTA bei pH 8 und Passieren der Lösung durch einen Kationenaustauscher in der Tetramethylammonium-Form. Nach Isolierung der Alkalimetalle auf dem Harz kann die ganze Gruppe schnell eluiert und konzentriert werden. Trennungen der Alkalimetalle von Erdalkalien und Cadmium werden gezeigt. Bedingungen, die den Wirkungsgrad der Alkalimetallaufnahme beeinflussen, wurden im einzelnen untersucht.

Résumé—On peut séparer rapidement les métaux alcalins, en tant que groupe, des métaux polyvalents, en complexant au préalable l'ensemble de ceux-ci au moyen d'EDTA à pH 8, puis en passant la solution sur une résine cationique sous forme ion tétraméthylammonium. Après isolement des métaux alcalins sur la résine, on peut les éluer rapidement en tant que groupe et les concentrer. On présente, à titre d'exemple, des séparations des métaux alcalins d'alcalino-terreux et de cadmium. On a étudié en détail les variables affectant l'efficacité de l'absorption des métaux alcalins.

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DETERMINATION OF BERYLLIUM BY MEANS OF HEXAMMINECOBALT(III) CARBONATOBERYLLATE—II *

HIGH-PRECISION INDIRECT DETERMINATION OF BERYLLIUM BY TITRATION OF COBALT WITH EDTA

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Summary—A highly precise method of determining beryllium, based on the precipitation of hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate, is described. The complex is decomposed by fuming with sulphuric acid and the cobalt(II) produced determined by weight titration with standard 0·1*M* EDTA and back-titration with 0·01*M* cobalt(II). The titration is carried out at pH 8·5–9·0 in a potassium carbonate-bicarbonate buffer and in the presence of potassium thiocyanate, tetraphenylarsonium chloride and chloroform. The end-point is indicated by the appearance in the chloroform layer of the blue colour of the ion-association pair, tetraphenylarsonium tetrathiocyanatocobaltate(II). A precision of 0·02% has been obtained, which is much better than that possible with any other method for determining beryllium. There appears to be a negative bias not exceeding 0·1% which cannot yet be explained.

IN Part I[1] it was shown that the precipitate obtained when hexamminecobalt(III) chloride is added to a solution of beryllium in excess ammonium carbonate is hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate, which contains a variable amount or water depending on the humidity of the atmosphere with which the compound is in equilibrium. Also, it was shown that a reasonably reproducible composition, corresponding to the presence of about 11 molecules of water, could be assured by conditioning the precipitate at a definite relative humidity in the range 32–80%, but it was considered that for analyses of the highest precision it was best to avoid weighing a precipitate of non-stoichiometric composition. Consideration was therefore given to an indirect determination of beryllium based on evaluation of the cobalt in the precipitate and the development of a highly precise procedure of this kind is described below.

The determination of beryllium *via* the cobalt content of hexamminecobalt(III) carbonatoberyllate was described by Misumi and Taketatsu,[2] who decomposed the precipitate by heating with potassium hydroxide solution, dissolved the resulting cobalt hydroxide in acid and titrated the cobalt(II) with standard 0·01*M* EDTA using Murexide as indicator. The amounts of beryllium determined were 0·7–3·5 mg, corresponding to about 2·3–11·5 mg of cobalt. For high-precision work, quantities of about 50 mg of beryllium or 160 mg of cobalt are needed and under these conditions we found that the intensity of colour of the cobalt(II)-EDTA complex masks any indicator colour. Alternative methods of determining cobalt, including gravimetric techniques, were considered, but it was soon apparent that EDTA titration was the most promising field for study. Foster and Williams[3] showed that the best gravimetric technique is only capable of an accuracy of 0·1–0·2%. This involves the precipitation and weighing of $CoNH_4PO_4{\cdot}H_2O$ and the spectrophotometric determination of the unprecipitated cobalt in the filtrate.

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* Part I: see reference 1.

Titration of cobalt with EDTA

The high effective[4] stability constant of the cobalt(II)-EDTA complex, varying from about 10^{10} at pH 5 to 10^{16} at pH 10, ensures that the reaction between cobalt(II) and EDTA is stoichiometric in this pH range, and if a suitable method of equivalence point detection can be found it should be possible to carry out the titration very accurately. The best method of detecting the equivalence point in this case was that described by Cameron and Gibson.[5] These workers showed that cobalt may be determined by adding excess EDTA and back-titrating with cobalt in the presence of potassium thiocyanate, triphenylmethylarsonium chloride and chloroform. The end-point is indicated by the appearance in the chloroform layer of the blue colour of the extracted ion-association pair, triphenylmethylarsonium tetrathiocyanatocobaltate(II) $[(C_6H_5)_3CH_3As^+]_2[Co(CNS)_4{}^{2-}]$. Using 0·01*M* solutions they determined 1–6 mg of cobalt with an accuracy of about 0·5% at the higher level, but it appeared to us that much higher precision should be possible by the use of larger amounts of cobalt. We have found this to be the case and have used the method for titrating about 160 mg of cobalt, *i.e.*, the amount combined with about 50 mg of beryllium in the precipitate.

Cameron and Gibson showed that the $(C_6H_5)_4As^+$ and $(C_6H_5)_2(CH_3)_2As^+$ cations also give ion association complexes with $Co(CNS)_4{}^{2-}$ suitable for extractive end-point indication. They showed that end-points can be obtained over the pH range 5–10, but pointed out that a high pH is desirable to stabilise the cobalt-EDTA complex. They recommended an ammoniacal buffer with a pH of 9·3 and indicated the ranges of reagent concentrations—potassium thiocyanate, pH 9·3 buffer and 1% triphenylmethylarsonium chloride—that can be used.

In our work tetraphenylarsonium chloride was used because it was readily available. To avoid precipitation of beryllium in the titration an acetate buffer giving a pH of 5·5 was used initially. Later, to improve the sharpness of the end-point, consideration was given to possible ways of carrying out the titration at a higher pH while retaining beryllium in solution. A potassium carbonate–bicarbonate solution, giving a final pH of 8·5–9·0, was found to be suitable and was adopted; the end-point is considerably sharper under these conditions. An ammonium carbonate solution at a similar pH cannot be used because the quantity required to complex 50 mg of beryllium destroys the end-point completely. The ammonia concentration required is about 10 times that contained in the amount of buffer recommended by Cameron and Gibson for the cobalt titration and it appears that under these conditions ammino complexes are formed in preference to the $Co(CNS)_4{}^{2-}$ ion.

All titrations are carried out by weight using polythene ampoules, holding 50–60 g of solution, as weight burettes. The main titration is performed with 0·1 weight-molar EDTA and the small excess back-titrated with 0·01 weight-molar cobalt(II). To minimise pH changes in titration the EDTA solution is made up with sufficient sodium hydroxide to give the tetrasodium salt.

Conditions for precipitating hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate

To maintain beryllium in solution as the hexacarbonato-oxo-tetraberyllate anion a large excess of ammonium carbonate is required. Also, a high concentration of carbonate is needed to ensure the ready dissolution of the precipitate produced initially on adding ammonium carbonate to the beryllium solution. Now the hexamminecobalt(III) compound is appreciably soluble in solutions of electrolytes and this is noticeable in ammonium carbonate solutions of 10% or higher strength as are used in this determination. If a little hexamminecobalt(III) chloride solution is added to such a solution containing beryllium no precipitate is formed at first or, if any is produced locally, it redissolves. Dilution of the solution at this stage results in precipitation of the complex. If more precipitant is added to the solution without dilution the precipitate is formed fairly slowly and separates as coarse, easily filterable crystals. However, if precipitation is carried out from a solution more dilute than about 7% in ammonium carbonate, the precipitate is formed immediately in a very fine condition and tends to clog in filtration. There is, therefore, considerable advantage to be gained in carrying out the precipitation from strong ammonium carbonate solution. However, when the bulk of the precipitate has separated, it is necessary to dilute the solution to ensure complete precipitation of beryllium. This point was not appreciated when the work described in Part I was done and, as noted there, only 99·5–99·8% of the added beryllium was precipitated. In this connection it may be noted that in Pirtea's first paper[6] no mention of dilution is made although 2–10 g of solid ammonium carbonate are added to a solution of 5–50-ml volume. However, Pirtea and Constantinescu,[7] after the addition of the hexamminecobalt(III) chloride, prescribe dilution to a total salt concentration of 2–3%.

Because the method has been devised for application to metallic beryllium, most of the work has been carried out with 50-mg samples. For the determination of very much smaller amounts, the quantities of reagents can be scaled down. However, a few experiments have been carried out, using the same conditions of precipitation, but with variations of post-precipitation treatment, on 10- and 1-mg amounts of beryllium in order to determine whether precipitation is quantitative. It was as a result of these experiments that the shaking time of 1 hr was introduced as an additional precaution, to ensure establishment of equilibrium between solution and precipitate; in most of the work reported here the solution was merely allowed to stand for 1 hr after dilution with water.

Decomposition of the complex

It is necessary to convert the cobalt in the precipitate to cobalt(II) for titration with EDTA. The hexamminecobalt(III) complex is very stable and drastic treatment is necessary. Misumi and Taketatsu heated with potassium hydroxide, but this method is troublesome because of bumping and the precipitated cobalt hydroxide must be dissolved in acid. We have found that heating to fumes with sulphuric acid is more satisfactory and convenient, but this stage of the procedure is inevitably somewhat slow and needs to be carried out with care to ensure complete decomposition and avoidance of losses by spray. Because of the separation of beryllium and cobalt(II) sulphates a considerable excess of sulphuric acid is necessary to avoid spitting; the neutralisation of this excess acid with sodium hydroxide before adding the potassium carbonate-bicarbonate buffer is then necessary and this step accounts for about 75% of the total blank titration, which corresponds to 0·05–0·1% of beryllium on 50 mg.

EXPERIMENTAL

The optimum amount of beryllium for the determination is about 50 mg. This corresponds to about 1·3 g of precipitate and about 30 g of 0·1*M* EDTA. Increasing the weight of beryllium would mean increasing the amounts of reagents and volume of the solution and also prolong the time for filtration. Decreasing the amount would tend to reduce the accuracy of the determination by reducing the amount for titration. Fifty mg is rather a small weight of metal to weigh accurately and, even if this were not so, this amount may be unrepresentative of the sample. Consequently, it is necessary to make a solution of the metal of accurately known concentration and weigh out portions for analysis.

To reduce experimental errors it is desirable to minimise the number of transfers of material from one vessel to another and, in particular, to avoid the conventional transfer of the precipitate from beaker to filter. Therefore, a vessel was designed in which the precipitation, filtration, decomposition of the precipitate and final titration were all carried out. This consisted of a conical flask (*ca.* 200 ml) fitted with two necks opposite each other and each at an angle of about 25° with the vertical axis of the flask. One neck had a B10 ground glass socket and stopper. The other had a B24 socket to which was fitted either a stopper or a cone attached to a tube in which a 15-mm diameter X4 sintered glass disc was sealed. The other end of the glass tube was drawn down for connection to the vacuum line *via* rubber tubing. The glass joints could be held together as required by springs attached to glass lugs sealed to the flask, B10 stopper and B24 cone with filter.

For precipitation and filtration the vessel was used in the same manner as a micro-filter beaker. The precipitate was then washed back into the flask and dissolved by 20% v/v sulphuric acid forced back through the sinter by suction applied at the B10 neck. In the final titration of the cobalt the B10 stopper was held in position by the springs and the titrants added through the B24 neck.

The above apparatus was used for all the work described in this paper. More recently we have simplified the apparatus and now use an ordinary 500-ml stoppered conical flask with a B29 neck. Filtration is carried out by means of a filter stick, which is inserted into the flask when needed. The procedure as described below uses the simplified apparatus.

Reagents

All reagents must be of analytical reagent grade quality.

Ammonium carbonate-EDTA solution. Dissolve 250 g of ammonium carbonate and 4 g of disodium dihydrogen ethylenediaminetetra-acetate dihydrate by stirring with 120 ml of concentrated aqueous ammonia and 500 ml water. Dilute to 1 l.

5% *Hexamminecobalt*(III) *chloride solution*

Wash solutions. (a) 0·2% Hexamminecobalt(III) chloride solution; (b) 60% v/v ethanol and water

20% v/v *Sulphuric acid solution.*

25% w/v *Sodium hydroxide solution.*

Potassium carbonate-bicarbonate-thiocyanate solution. Dissolve 43 g of potassium carbonate, 123 g of potassium bicarbonate and 133 g of potassium thiocyanate in water and dilute to 1 l.

Acetate buffer (pH 4·5). Dissolve 136 g of hydrated sodium acetate in water, add 57 ml of glacial acetic acid and dilute to 1 l.

2% w/v *Tetraphenylarsonium chloride solution*

Dithizone solution. 0·005% in ethanol prepared freshly as required.

0·1*M EDTA solution* (*tetrasodium salt*). Dissolve 37·2 g of disodium dihydrogen ethylenediaminetetra-acetate dihydrate and 8·0 g of sodium hydroxide in water and dilute to 1 l. Standardise as described below. Store in a Polythene bottle.

0·01*M EDTA solution.* Weigh out about 5 g of 0·1*M* EDTA solution and dilute accurately to about 50 g.

0·01*M cobalt solution.* 0·28 g of cobalt sulphate heptahydrate dissolved in 100 ml of solution. Standardise as described below.

Apparatus

250-ml conical flasks with B24 ground glass necks and stoppers.

500-ml conical flasks with B29 ground glass necks and hollow stoppers.

Air-cooled reflux condensers with B24 cones.

Filter sticks. 15-mm diameter X4 disc, sealed into flared out end of glass tube (o.d. 6 mm); total length 15 cm.

2-oz Polythene ampoules with jets delivering not more than 0·02-g drops.

Procedure

Weigh out (to 0·01 mg) about 0·5 g of the beryllium sample and transfer it to a clean dry 250-ml conical flask with a B24 neck. The flask should previously have been weighed to the nearest 1 mg with its stopper present. Add a few ml of water, fit a reflux air-condenser to the flask and add 15 ml of concentrated hydrochloric acid, a few ml at a time, so that the reaction is always under control. When there is no further reaction add a few drops of concentrated nitric acid and heat until a clear solution is obtained.

Sometimes the solution remains cloudy because of undissolved beryllium oxide. In this case add 10 ml of concentrated sulphuric acid to the cooled solution, wash down the inside of the condenser and remove it from the flask. Carefully evaporate the solution without allowing it to boil by standing the flask on an asbestos-covered hot-plate. Dissolution of the oxide is normally complete by the time fumes of sulphuric acid appear, so, at this stage, remove the flask from the hot-plate and allow to cool. Dilute the solution by carefully adding 10 ml of water, cooling the flask at the same time.

Dilute to about 60 ml and add concentrated aqueous ammonia until a small permanent precipitate appears. Add 1*M* hydrochloric acid until a clear solution is obtained, being careful to ensure complete dissolution of any beryllium hydroxide adhering to the glass. Dilute to 70–90 ml, allow to come to room temperature, wipe dry the inside of the ground glass neck, stopper the flask and weigh it to the nearest 1 mg. Mix the contents of the flask thoroughly and transfer 50–60 g to a dry polythene ampoule.

Transfer 20 ml of ammonium carbonate-EDTA solution to a 500-ml conical flask with a B29 ground glass neck. Into this weigh out a quantity of beryllium solution containing about 0·05 g of beryllium, gently swirling the flask and contents all the time to help redissolve precipitated basic beryllium compounds. Heat to 60–70° for a few min, remove from the hot plate, and, after ensuring that all traces of precipitate have been dissolved, add 30 ml of 5% hexamminecobalt(III) chloride solution. Allow to stand for 5 min, add 100 ml of water, stopper the flask and agitate gently for 1 hr using a mechanical shaker. (*Note.* The shaking should be just sufficient to maintain the precipitate in suspension.)

Filter by suction through a filter-stick inserted into the flask and wash thoroughly with (a) 0·2% hexamminecobalt(III) chloride and (b) 60% ethanol, paying particular attention to the walls of the flask and breaking up the pad of precipitate two or three times during the ethanol washes. About four 10-ml portions of (a) and six 10-ml portions of (b) should be adequate. If hold-up of liquor inside the filter-stick exceeds about 1 ml, a further two 10-ml washes with 60% ethanol should be used to ensure complete removal of cobalt.

Remove the suction-tube from the filter-stick and add 10 ml of water and 5 ml of 20% v/v sulphuric acid to the contents of the flask. Cover the flask with a watch glass, mix the contents and add a further 20 ml of 20% v/v sulphuric acid when effervescence ceases. Heat until a clear solution is obtained, lift the filter-stick from the solution and wash it, collecting the rinsings in the main solution; to wash the inside, force portions of water through the sinter by means of a squeeze bulb.

Cover the flask with the watch glass and evaporate slowly until decomposition occurs and the orange solution turns dark red, indicating conversion of the cobalt to the bivalent state. When fumes of sulphuric acid are evolved copiously, cool the flask and carefully rinse the watch-glass and inside walls of the flask with a little water to wash back a small amount of spray. Again evaporate the solution to fumes and continue heating until a stage is reached at which most of the beryllium and cobalt sulphates have precipitated and the supernate is colourless. Cool, dilute carefully with 20 ml water and heat until a clear solution is obtained. Again cool.

Calculate the expected weight of 0·1*M* EDTA solution needed to complex the cobalt and add about 0·5% less than this from a polythene ampoule. Carefully neutralise the solution with 25% sodium hydroxide solution, continuing the addition until a slight permanent precipitate of beryllium hydroxide is produced; about 25 ml will be needed. Add 30 ml of potassium carbonate-bicarbonate-thiocyanate solution and warm until a clear solution is obtained. Cool to room temperature.

Add 5 ml of 2% tetraphenylarsonium chloride solution and 10 ml of chloroform, stopper the flask and shake once or twice. Carefully open the stopper to release the pressure and repeat the procedure until pressure is no longer generated. Then shake vigorously and invert the flask so that the chloroform layer runs into the hollow stopper and can be viewed against a white background. The layer should be blue, indicating excess untitrated cobalt. Titrate with 0·1*M* EDTA until the chloroform layer is colourless, shaking very thoroughly after each addition of titrant.

Back-titrate with 0·01*M* cobalt solution to the first appearance of blue in the chloroform layer. Less shaking is necessary in the back-titration because equilibrium is more quickly reached in the extraction of cobalt from the aqueous into the chloroform phase than *vice versa.*

Standardisation of solutions

Standardisation of 0·1*M EDTA against* 99·999% *zinc.* Cut a piece weighing 0·8–1·2 g, from a stick of 99·999% zinc and immerse it in 20% hydrochloric acid for a few min. Wash with water and acetone, dry and weigh to 0·01 mg.

Transfer the zinc to a weighed 250-ml conical flask with a B24 neck, add a few ml of water and fit an air-cooled reflux condenser. Add 5 ml of concentrated hydrochloric acid and warm until the zinc has completely dissolved (2–3 hr). Cool, add 6*M* aqueous ammonia until a permanent precipitate forms and redissolve by the dropwise addition of 1*M* hydrochloric acid. Cool and dilute to 70–90 g. Allow to come to room temperature, wipe dry the inside of the ground glass neck, stopper the flask and weigh it to the nearest 0·1 mg. Mix the contents of the flask thoroughly and transfer 50–60 g to a dry polythene ampoule. Calculate the molarity of the zinc solution.

Weigh out about 20 g of the 0·1*M* EDTA solution into a 250-ml conical flask and add 10 ml of acetate buffer (pH 4·5), 1 ml of 0·005% dithizone and 50 ml of ethanol. Titrate with zinc solution until the pale green colour changes to pink, then back-titrate with 0·01*M* EDTA.

Carry out a titration exactly as above but with 20 ml of water instead of 0·1*M* EDTA.

Let the molarities of the zinc and main EDTA (0·1*M* nominal) solutions be X and Y, respectively, and let 1 g of weak EDTA $\equiv \alpha$ g of main EDTA solution.

First titration: If E_1 g of main EDTA and e_1 g of weak EDTA require Z_1 g of zinc solution,

$$(E_1 + \alpha e_1)Y = Z_1X + \text{Blank}.$$

Second titration: If e_2 g of weak EDTA require Z_2 g of zinc solution,

$$\alpha e_2 Y = Z_2X + \text{Blank}$$

and

$$Y = \frac{(Z_1 - Z_2)X}{E_1 + \alpha(e_1 - e_2)}.$$

Standardisation of cobalt solution. Transfer 30 ml of potassium carbonate-bicarbonate-thiocyanate solution to a 500-ml glass-stoppered conical flask and add 50 ml of water. Weigh out about 1 g of 0·1*M* EDTA solution into the flask, add 5 ml of 2% tetraphenylarsonium chloride solution and 10 ml of chloroform, and titrate with the cobalt solution as already described for the beryllium determination. Similarly, titrate 1 or 2 drops (0·02–0·05 g) of 0·1*M* EDTA.

From the differences between the two titrations calculate the number of grams of EDTA equivalent to 1 g of cobalt solution (β). The blank from the potassium carbonate-bicarbonate-thiocyanate may be calculated to check reagent purity.

Determination of main titration blank. Transfer 25 ml of 25% sodium hydroxide to a 500-ml glass stoppered flask and carefully neutralise with 20% v/v sulphuric acid using Methyl Red as indicator. Make just alkaline with 2% alkali, added dropwise, cool and add 30 ml of potassium carbonate-bicarbonate-thiocyanate, 5 ml of 2% tetraphenylarsonium chloride and 10 ml of chloroform. Into the solution weigh out 0·05–0·1 g of 0·1*M* EDTA and titrate with the cobalt solution.

If E_3 g of Y*M* EDTA take C_3 g of cobalt solution,

$$E_3 = \text{Blank} + \beta C_3$$

and

$$\text{Blank} = E_3 - \beta C_3 = B.$$

Calculation of beryllium content of sample

Let the weight of beryllium metal taken = M g,
the total weight of metal solution = T g,
the weight of solution taken for analysis = S g,
the weight of Y*M* EDTA used = E g,
and the weight of cobalt solution = C g.

Hence: Beryllium in sample analysed $\equiv$ E g of Y*M* EDTA − C g of Cobalt solution − Blank
= (E − βC − B) g of Y*M* EDTA.

Because the precipitate contains 2 atoms of beryllium/atom of cobalt, and EDTA gives a 1:1 complex with cobalt:

$$\text{Equivalent weight of beryllium} = 9{\cdot}0122 \times 2 = 18{\cdot}0244.$$

A correction for buoyancy must be applied. The only weights affected are those of zinc and beryllium metal. Taking the densities of zinc and beryllium as 7·14 and 1·85, respectively, and the mean density of air as 0·00120, the correction factor becomes 0·99952.

Thus:

$$\text{Beryllium in sample} = \frac{18{\cdot}0244 \times 0{\cdot}99952\,\text{YT}(E - \beta C - B) \times 100}{1{,}000\,\text{MS}}\%$$

$$= \frac{1{\cdot}8016\,\text{YT}(E - \beta C - B)}{\text{MS}}\%.$$

The atomic weights used are based on the ^{12}C = 12 scale,[8] in which zinc = 65·37.

RESULTS

Cobalt titration at pH 5·5

In these determinations an acetate buffer was used, the other reagents being the same as in the recommended procedure. Five ml of glacial acetic acid were added to the solution and the pH adjusted to 5·5 with 6*M* aqueous ammonia. Although titrations were carried out by weight, as already described, the beryllium solution was prepared by dissolving a weighed portion of vacuum distilled beryllium metal in acid and making up to 1 l. in a calibrated volumetric flask. Determinations were then carried out on 50-ml portions of solution measured with a calibrated pipette.

Twenty determinations gave a mean value of 99·92% of beryllium and a standard deviation of 0·04%.

Cobalt titration at pH 8·5–9·0

Six different samples of beryllium metal were analysed as described in the recommended procedure and the results are given in Table I.

TABLE I.—DETERMINATION OF BERYLLIUM IN METAL SAMPLES BY THE PROPOSED METHOD

Sample	Be, % Individual results	Mean	Sum of impurities (C, O, Al, Cr, Cu, Fe, Mg, Mn, N, Ni, Si), %	Sum of Be content and impurities, %
Pechiney S.R.	99·69 99·75 99·74 99·72 99·71 99·73	99·72	0·07	99·79
Vacuum Distilled	99·90 99·89	99·90	—	99·90
A	98·36 98·36 98·44	98·39	1·47	99·86
B	98·21 98·17 98·20 98·19 98·21	98·20	1·66	99·86
C	98·59 98·60	98·60	—	—
D	98·93 98·93 98·90	98·92	0·88	99·80

Combining all the results in Table I the relative standard deviation is 0·02% for the method at the 50-mg level, *i.e.*, 0·01 mg of Be.

The results of the experiments with 10- and 1-mg amounts of beryllium are given in Table II. The figures in column 3 for the amounts of beryllium taken are calculated from the results obtained on the same beryllium metal solution at the 50-mg level.

DISCUSSION

The relative standard deviation of 0·02% calculated from the results of Table I shows that the method is highly precise—very much more so than any other method hitherto described for the determination of beryllium. It is, incidentally, interesting to note the high precision attainable in EDTA titrations when adequate equivalence-point indications are available. We obtained a relative standard deviation of 0·01% in the titration of zinc using dithizone as indicator. The precision of the cobalt titration was not determined separately but is included in the over-all figure of 0·02%.

As regards the accuracy of the method, this cannot be evaluated precisely but it will be noted from the last column of Table I that the sum of the beryllium content and principal impurities is less than 100%. The discrepancy varies between 0·1% and 0·2%, a variation much larger than the random error in the method and it is evident that part of the discrepancy at least must lie outside the beryllium determination; there will doubtless be some contribution from undetermined impurities and there may be some errors in those that have been determined. Even so, the results on the purest samples (Pechiney S.R. and the vacuum distilled) cannot be wholly accounted for on this basis. We believe that the vacuum distilled material is very close to 100·0% beryllium and that our result on this sample may therefore be 0·10% low. This appears to be the maximum systematic error in the method.

TABLE II.—EFFECT OF POST-PRECIPITATION TREATMENT ON RECOVERY OF SMALL AMOUNTS OF BERYLLIUM

Expt. no.	Post-precipitation treatment	Be taken, *mg*	Be found, *mg*	Error, *mg*
1	Stood for 1 hr	10·985	10·993	+0·008
2	Stood for 1 hr	0·993	0·921	−0·072
3	Stood for 1 hr	1·014	0·541	−0·473
4	Stood overnight	1·110	0·723	−0·387
5	Shaken for 1 hr	9·096	9·109	+0·013
6	Shaken for 1 hr	0·897	0·844	−0·053
7	Shaken for 1 hr and stood overnight	0·939	0·934	−0·005
8		1·068	1·048	−0·020

It is difficult to account for a systematic negative error of 0·1% and the first possibility to consider is incomplete precipitation of beryllium. This might arise in two ways (a) true solubility of the complex in the mother liquor, and (b) supersaturation because of non-establishment of equilibrium between precipitate and solution. The experiments using small amounts of beryllium (Table II) throw light on this question. The results of experiments 1 and 5 on about 10 mg of beryllium show slight positive errors and, at this level, no significant difference follows from shaking rather than standing for 1 hr. Therefore, we conclude that for 10 mg of beryllium and above, equilibrium is established very quickly after precipitation and dilution, and that the solubility of the complex in the mother liquor is negligible.

At this point one should take into account the uncertainty in the figure for the amount of beryllium taken arising from the fact that it is based on an analysis at the 50-mg level by the same method. If the method gives results 0·1% low, then we must increase the figures for beryllium taken by 0·1%. This has the effect of reducing the positive errors in experiments 1 and 5 to only −0·003 and +0·004 mg, respectively. The effect on the results with 1 mg of beryllium is 0·001 mg, which is quite negligible.

The results with 1-mg amounts of beryllium are obviously dependent on post-precipitation treatment and it is clear from experiments 2, 3 and 4 that standing without agitation is insufficient to establish equilibrium between precipitate and solution. In only one experiment, number 7, where shaking for 1 hr and standing overnight were employed, was equilibrium established, and in this case the result again shows that the true solubility of the complex in the mother liquor is negligible. Experiment 7 gave a result indicating not quite complete equilibrium conditions, while intermediate results were given in experiments 2 and 6.

One need not be surprised at the results using 1 mg of beryllium because, at this level, the ratio of surface area of precipitate to volume of solution is very low indeed, and the extreme conditions of these experiments would be avoided in normal analysis. It is clear from the results with 10-mg and 50-mg amounts that the procedure used involving standing 1 hr after precipitation is adequate. However, as an additional safeguard we have introduced a shaking for 1 hr after precipitation into the recommended procedure.

Another possible source of systematic error lies in the atomic weight of zinc, the standard used in the determination. Wichers[8] lists zinc among the elements whose atomic weights are of lower accuracy than the rest. He states "It is not possible to estimate the uncertainties in the atomic weights of these elements beyond saying that they do not exceed 0·05% and in a number of cases may be no more than 0·01%." In the case of zinc, the discrepancy that exists between the chemical atomic weight (65·370–65·376), which is that recommended, and that determined mass spectrometrically (65·387) is about 0·03%. However, the use of the mass-spectrometric atomic weight would make matters worse by decreasing the apparent beryllium content by 0·03%.

At the moment we cannot account for the apparent slight negative bias in the method, but, while its existence should not be overlooked, the error does not detract from the usefulness of the procedure.

Acknowledgement—Our thanks are due to Mr. D. J. Taylor for carrying out some of the determinations.

Zusammenfassung—Eine sehr genaue Methode zur Berylliumbestimmung auf Grund der Fällung von Hexamminkobalt(III)-hexacarbonato-oxo-tetraberyllat wird beschrieben. Der Komplex wird durch Abrauchen mit Schwefelsäure zersetzt und das gebildete Kobalt(II) durch Wägetitration mit eingestellter 0,1 m EDTA und Rücktitration mit 0,01 m Kobalt(II) bestimmt. Die Titration wird bei pH 8,5–9,0 in Kaliumcarbonat-Bicarbonat-Puffer und in Gegenwart von Kaliumrhodanid, Tetraphenylarsoniumchlorid und Chloroform ausgeführt. Der Endpunkt wird durch Erscheinen einer blauen Färbung in der Chloroformphase angezeigt, die von dem Ionenpaar Tetraphenylarsonium-tetrarhodanocobaltat(II) herrührt. Eine Genauigkeit von 0,02% wurde erreicht; sie ist viel besser als bei irgend einer anderen Bestimmungsmethode für Beryllium. Es scheint eine negative systematische Abweichung von höchstens 0,1% vorzuliegen, die noch nicht erklärbar ist.

Résumé—On décrit une méthode hautement précise de dosage du beryllium, basée sur la précipitation de l'hexacarbonato-oxo-tétraberyllate. Le complexe est décomposé par action de l'acide sulfurique, et le cobalt(II) produit est dosé par addition d'un excès de solution titrée 0,1 M d'EDTA, et titrage en retour par une solution 0,01 M de

cobalt(II). Le dosage est mené à pH 8,5–9,0 dans un tampon carbonate-bicarbonate de potassium, et en présence de sulfocyanure de potassium, chlorure de tétraphénylarsonium et chloroforme. Le point final est indiqué par l'apparition d'une coloration bleue dans la couche chloroformique, dûe à l'association ionique tétraphénylarsonium-tétrathiocyanatocobaltate(II). On a obtenu une précision de 0,02%, de beaucoup supérieure à celle observée avec n'importe quelle autre méthode de dosage du béryllium. Il semble y avoir un écart négatif n'excédant pas 0,1%, que l'on n'a encore pu expliquer.

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PRECIPITATION OF ZIRCONIUM TETRAMANDELATE FROM HOMOGENEOUS SOLUTION

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Summary—Hydroxypropyl mandelate has been found to be a satisfactory reagent for the *in situ* generation of mandelic acid for use in precipitation from homogeneous solution.

IN 1947 Kumins[1] proposed the use of mandelic acid as a highly selective reagent for the gravimetric determination of zirconium. There have been several subsequent investigations dealing with its use as a reagent for zirconium[2–8] and for the precipitation of scandium,[9] trace plutonium,[10] and the fractional separation of the rare earths.[11]

The present investigation was undertaken to explore the usefulness of hydroxypropyl mandelate as a reagent for the *in situ* generation of mandelic acid. Zirconium was chosen as the model ion to test the effectiveness of the reagent.

EXPERIMENTAL

Reagents

Zirconium solutions: A solution of zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$ (Fisher Scientific, Pittsburgh 19, Pennsylvania, U.S.A.), was prepared in 4*M* HCl, and the zirconium concentration was determined gravimetrically by precipitation as the hydroxide[1] and the mandelate.[1]

Mandelic acid solution: 160 g of mandelic acid (Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York, U.S.A.) were dissolved in water to prepare 1 litre of aqueous solution.

Hydroxypropyl mandelate: This ester (synthesised by Burdick and Jackson Laboratories, Muskegon, Michigan, U.S.A.) is presumed to be a mixture of the two isomers 2-hydroxy-1-propyl mandelate and 1-hydroxy-2-propyl mandelate. It was obtained as a thick viscous syrup which was subsequently diluted slightly with methanol to 88%(w/w) ester content, to afford a freely flowing syrup which was used as such in the analytical work.

All other chemicals were reagent-grade.

Procedure

Add sufficient HCl to 5–150 mg of zirconium in a 150-ml beaker to prepare 100 ml of a 5–6*M* acid solution. Add 10–12 g of hydroxypropyl mandelate syrup mixture with stirring. Cover the beaker with a watchglass and place on an electric hot-plate regulated to maintain a temperature of approximately 80° for 3 hr. The determination can be concluded by either of the following methods.

Method A: Filter the hot solution through a medium-porosity ignition crucible, washing the precipitate with no more than 150 ml of hot wash solution (5% mandelic acid and 2% HCl). Ignite the precipitate to 975°:

$$\text{Weight of } ZrO_2 \times 0{\cdot}7403 = \text{weight of Zr.}$$

Method B: Cool the solution to room temperature. Transfer and wash the precipitate with a saturated aqueous zirconium tetramandelate solution. Then wash with 30 ml of ethanol followed by 20 ml of ethyl ether. Dry to constant weight at 110° and weigh as the tetramandelate:

$$\text{Weight of } Zr(C_8H_7O_3)_4 \times 0{\cdot}1311 = \text{weight of Zr.}$$

RESULTS AND DISCUSSION

Initial studies with methyl mandelate as a generating reagent were unsuccessful, because of the limited solubility of the ester in water, whereas hydroxypropyl mandelate was found to be sufficiently soluble.

Preliminary investigations were undertaken to determine the appropriate concentration of hydroxypropyl mandelate, temperature of reaction and acidity which would result in quantitative separation of a precipitate with desirable physical characteristics.

TABLE I.—DETERMINATION OF ZIRCONIUM IN THE PRECIPITATE BY WEIGHING THE PRECIPITATE[a] AT 110° FOLLOWED BY ITS IGNITION AT 975°

Zr taken, *mg*	26·62		53·24		106·49	
Temperature, °*C*	110	975	110	975	110	975
Difference in Zr found, *mg*	−0·09 +0·02	±0·00 −0·04	+0·08 ±0·00 −0·04	+0·04 ±0·00 −0·04	+0·03 +0·03 −0·05	±0·00 ±0·00 −0·05

[a] The precipitates were filtered and washed according to Method B.

TABLE II.—PRECIPITATION OF ZIRCONIUM

Method	PFHS[a]	PFHS[b]	PFHS[a]	Conv.[a]	Conv.[b]
Zr taken, *mg*	5·12		10·24	26·62	
Difference in Zr found, *mg*	0·00 +0·12 −0·19	−0·11 −0·04 +0·05	0·00 +0·05 −0·22	−0·11 +0·22 0·00	0·00 +0·06 −0·11

Method	PFHS[a]	PFHS[b]	PFHS[a]	PFHS[b]	PFHS[a]	PFHS[a]
Zr taken, *mg*	25·61		51·22		102·44	153·66
Difference in Zr found, *mg*	0·00 +0·10 −0·07	+0·04 −0·03 +0·13	+0·19 −0·04 +0·48	+0·03 +0·05 +0·19	+0·22 −0·04 −0·14	−0·21 −0·04 0·00

[a] Weighed after ignition to 975° (*cf.* method A).
[b] Weighed after drying at 110°C (*cf.* method B).

The necessary conditions were met by (*a*) addition of sufficient reagent to effect a final solution 0·4–0·5M in mandelic acid, (*b*) heating the solution at 85° for 3 hr, and (*c*) precipitation in 5–6M HCl to avoid the formation of basic salts.[5]

The precipitate formed by PFHS can be dried and weighed at 110° or ignited to the oxide. Thermogravimetric analysis confirmed the use of 110° as a stable drying temperature. Tables I and II show the results obtained with zirconium alone.

Table II shows that quantitative results may be obtained with 5–150 mg of zirconium; larger quantities were not determined, and quantities less than 5 mg gave anomalous results.

Table III shows the separation of zirconium from iron, aluminium, titanium and thorium. The results indicate that there is little difference in the separations obtained

TABLE III.—SEPARATION OF ZIRCONIUM FROM DIVERSE IONS

Method	Conv.	PFHS	PFHS	Conv.	PFHS	PFHS	PFHS
Diverse Ion, *mg*	Fe(III)			Al(III)		Th(IV)	Ti(IV)
	280	280	80	80	80	80	75
Zr taken, *mg*	51·22	51·22	102·44	102·44	102·44	102·44	102·44
Difference in Zr found, *mg*	+1·42	+0·64	+0·03	+0·15	+0·15	+0·43	+0·32
	+0·58	+0·36	+0·05	+0·27	+0·08	+0·15	+0·16
	+0·64	+0·88	0·00	+0·08	−0·08	+0·15	+0·15

with the conventional and PFHS methods of precipitation; however, the PFHS method provides a precipitate with superior physical characteristics, which is far more easily filtered and washed than that obtained by conventional precipitation.

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Zusammenfassung—Hydroxypropylmandelat erwies sich als brauchbares Reagens zur in-situ-Bildung von Mandelsäure bei der Fällung aus homogener Lösung.

Résumé—On a trouvé que l'hydroxypropyl mandélate est un réactif satisfaisant pour la formation *in situ* d'acide mandélique utilisé dans la précipitation en milieu homogène.

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GRAVIMETRIC DETERMINATION OF RUBIDIUM AND CAESIUM WITH *N,N*-DIMETHYLETHANOLAMMONIUM OROTATE

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Summary—It has been shown that rubidium and caesium can be determined gravimetrically using *N,N*-dimethylethanolammonium orotate as precipitant. The composition and identity of the rubidium and caesium orotate, which were the precipitates utilised in the gravimetric methods developed, have been established by elemental analyses and the results confirm their purity.

SELLERI and Caldini[1] were able to determine sodium and potassium gravimetrically with *N,N*-dimethylethanolammonium orotate. These authors did not investigate the action of this reagent with rubidium and caesium. The present paper deals with its application to the determination of these elements.

Following the procedure of Selleri and Caldini[1] for the precipitation of caesium ions but using somewhat larger samples and filtering through a medium sintered glass crucible with suction, and washing twice with 2-ml portions of 70% methanol and twice more with 2-ml portions of 100% methanol, the results in Table I were obtained using caesium chloride for the determination of caesium.

TABLE I.—DETERMINATION OF CAESIUM

Sample no.	CsCl taken, *g*	Cs calc., *g*	Cs found, *g*	Cs found, %[a]	Error, %
1	0·2753	0·2167	0·2083	75·86	−3·90
2	0·2981	0·2346	0·2256	75·88	−3·87
3	0·3861	0·3039	0·2898	75·25	−4·67
4	0·4248	0·3344	0·3241	76·47	−3·12
5	0·5450	0·4291	0·4213	77·51	−1·81

[a] Theoretical Cs = 78·94%

The errors shown in Table I are all negative and the results are, therefore, low. This indicates: (1) Precipitation might be incomplete. (2) Improper washings may lead to loss of the caesium orotate obtained. To test whether the caesium orotate was precipitated completely or not, the metal was determined according to the above procedure but the precipitate was not washed. Table II shows the results obtained.

Because the results in Table II are positive and relatively high, the low results in Table I are attributed to improper washing and coprecipitation of reagent. Therefore, at this stage, the solubility of caesium orotate in water, 70% methanol and 100% methanol was determined.

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TABLE II.—DETERMINATION OF CAESIUM WITHOUT WASHING

Sample no.	CsCl taken, *g*	Cs calc., *g*	Cs found, *g*	Cs found, %[a]	Error, %
1	0·1800	0·1416	0·1434	79·90	+1·21
2	0·2155	0·1696	0·1415	80·76	+2·30

[a] Theoretical Cs = 78·94%

Determination of solubility of caesium orotate

Saturated solutions of caesium orotate in water, 70% methanol and 100% methanol were prepared by stirring an excess of the salt in the corresponding solvent for 2–3 hr using a magnetic stirrer. In the case of 70% methanol used as the solvent, the increase in temperature from mechanical stirring was minimised by placing the flask containing the solution over a cork ring; the flask was stoppered. After the saturated solutions were prepared, the excess of the salt was filtered off. An aliquot of the filtrate was evaporated almost to dryness, then further drying to constant weight performed at 100–110°. The solubilities (g/l.) at 20° are 30·82 for water, 3·83 for 70% methanol and 0·31 for 100% methanol.

From these figures some modification in the determination of caesium was found to be necessary.

Procedure for determination of caesium with N,N-dimethylethanolammonium orotate

The sample, containing 20–100 mg of caesium, is dissolved in the minimum amount of water to bring it into solution. The pH should be kept between 6 and 8 (at a lower pH the free orotic acid is formed, while at a higher pH the acidic imido groups may be attacked). An excess of the 0·1*M*

TABLE III.—DETERMINATION OF CAESIUM

Sample no.	$CsNO_3$ taken, *g*	Cs calc., *g*	Cs found, *g*	Cs found, %[a]	Error, %	Mean Error, %
1	0·0294	0·0200	0·0200	68·18	0·00	
2	0·0808	0·0549	0·0547	67·78	−0·58	−0.44
3	0·1082	0·0736	0·0731	67·68	−0·73	

[a] Theoretical Cs = 68·18%

Sample no.	CsBr taken, *g*	Cs calc., *g*	Cs found, *g*	Cs found, %[b]	Error, %	Mean error, %
1	0·0343	0·0209	0·0210	62·59	+0·23	
2	0·0428	0·0261	0·0262	62·35	+0·17	+0·30
3	0·0489	0·0298	0·0301	62·77	+0·51	

[b] Theoretical Cs = 62·45%

Sample no.	CsCl taken, *g*	Cs calc., *g*	Cs found, *g*	Cs found, %[c]	Error, %	Mean error, %
1	0·0751	0·0591	0·0589	78·72	−0·28	
2	0·0759	0·0597	0·0595	78·62	−0·41	
3	0·1085	0·0854	0·0850	78·63	−0·39	−0.17
4	0·1092	0·0859	0·0864	79·34	+0·50	
5	0·2357	0·1855	0·1850	78·72	−0·27	

[c] Theoretical Cs = 78·94%

reagent (*ca.* 25 ml), prepared according to Selleri and Caldini,[1] is added dropwise while the vessel containing the solution is gently swirled. Caesium orotate precipitates in a white crystalline form. The precipitated mixture is allowed to stand in the refrigerator (3°) for 2 hr (longer standing does no harm). The precipitate is then collected with suction on a medium or fine sintered glass crucible (medium sintered glass crucible is preferable because filtration is faster). The precipitate is washed three times with 2-ml portions of 100% methanol, then dried at about 105° to constant weight.

Results obtained following the above procedure using caesium nitrate, caesium bromide and caesium chloride samples were satisfactory and are shown in Table III.

When the same procedure was followed for the determination of rubidium in rubidium chloride, the results in Table IV were obtained.

The results in Table IV were all positive and relatively high because of coprecipitation of the precipitant. The solubility of rubidium orotate was, therefore, determined

TABLE IV.—DETERMINATION OF RUBIDIUM FROM RUBIDIUM CHLORIDE SOLUTION AFTER WASHING THREE TIMES WITH 2-ml PORTIONS OF 100% METHANOL

Sample no.	RbCl taken, *g*	Rb calc., *g*	Rb found, *g*	Rb found, %[a]	Error, %
1	0·0399	0·0279	0·0285	71·96	+1·81
2	0·0963	0·0675	0·0685	71·80	+1·58
3	0·1193	0·0836	0·0849	71·70	+1·44
4	0·1996	0·1400	0·1420	71·68	+1·41
5	0·2329	0·1633	0·1658	71·74	+1·49

[a] Theoretical Rb = 70·68%

TABLE V.—DETERMINATION OF RUBIDIUM

Sample no.	RbI taken, *g*	Rb calc., *g*	Rb found, *g*	Rb found, %[b]	Error, %	Mean error, %
1	0·0752	0·0302	0·0300	40·05	−0·47	
2	0·0957	0·0384	0·0385	40·40	+0·39	−0·03
3	0·1316	0·0528	0·0528	40·24	0·00	

[a] Theoretical Rb = 40·24%

Sample no.	RbCl taken, *g*	Rb calc., *g*	Rb found, *g*	Rb found, %[b]	Error, %	Mean error, %
1	0·0399	0·0279	0·0279	70·68	0·00	
2	0·0835	0·0585	0·0585	70·68	0·00	
3	0·0963	0·0675	0·0685	70·83	+0·21	+0·08
4	0·1051	0·0737	0·0739	70·84	+0·22	
5	0·1193	0·0836	70·68	70·68	0·00	

[b] Theoretical Rb = 70·68%

Sample no.	RbF taken, *g*	Rb calc., *g*	Rb found, *g*	Rb found, %[c]	Error, %	Mean error, %
1	0·0262	0·0207	0·0207	81·80	0·00	
2	0·0569	0·0449	0·0447	81·47	−0·42	−0·08
3	0·1616	0·1276	0·1278	81·95	+0·17	

[c] Theoretical Rb = 81·81%

by the method used previously for caesium orotate. The solubilities (g/l.) at 20° are: 5·59 for water, 0·49 for 70% methanol and 0·08 for 100% methanol. Because the solubility in 70% methanol is low, it could be used for washing and simultaneous removal of the coprecipitated material.

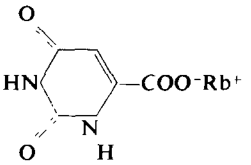
Procedure for determination of rubidium with N,N-dimethylethanolammonium orotate

The same procedure as detailed above (p. 106) for the determination of caesium is followed. Rubidium orotate precipitates in a milky form, the filtration of which is rapid at first but then slows down because of the firm packing of the precipitate. The precipitate is so fine that it passes even through an F-grade sintered glass crucible. It is, therefore, necessary that the filtration be as fast as possible and that is also the reason why a small amount of sample (containing 20–100 mg of rubidium) should be used for its determination. The precipitated rubidium orotate collected is washed first three times with 2-ml portions of 100% methanol followed by washing twice more with 2-ml portions of 70% methanol, then dried to constant weight at about 105°.

The results so obtained were very satisfactory (Table V) using rubidium iodide, rubidium chloride and rubidium fluoride as samples.

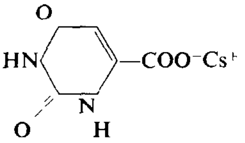
Properties and analyses of rubidium and caesium orotate

Rubidium Orotate



Molecular weight 240·57, white crystalline powder, insoluble in methanol, hydrochloric acid and aqueous ammonia.

Caesium Orotate



Molecular weight 288·00, white crystalline powder, very slightly soluble in methanol, insoluble in hydrochloric acid, soluble in aqueous ammonia.

Carbon and hydrogen were determined by combustion, nitrogen by the Kjeldahl method, caesium by fuming with concentrated sulphuric acid to Cs_2SO_4 and rubidium to Rb_2SO_4 (Table VI).

TABLE VI.—ANALYSIS OF CAESIUM AND RUBIDIUM OROTATES PREPARED BY THE PROPOSED METHODS FOR DETERMINATION OF CAESIUM AND RUBIDIUM

	C, %	H, %	N, %	Cs or Rb %
Caesium Orotate				
Calculated	20·85	1·04	9·73	46·15
Found	20·80	1·23	9·75	46·12
Rubidium Orotate				
Calculated	24·96	1·26	11·65	35·53
Found	24·93	1·43	11·61	35·51

The caesium and rubidium salts used were obtained from various companies who also provided the complete analyses of these salts.

The effect of *N*,*N*-dimethylethanolammonium orotate on different elements was tested qualitatively. It was found that the reagent forms a precipitate with Pb^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Pd^{2+}, Sn^{2+} and ZrO^{2+}. Therefore, these ions, together with Na^+ and K^+, interfere with the determination of rubidium and caesium. Because NH_4^+, Li^+, the alkaline earths, Fe^{3+}, Ni^{2+}, Co^{2+} and Cu^{2+} did not interfere in the determination of sodium and potassium,[1] it is inferred that they will not interfere in the determination of rubidium and caesium.

The particular advantage of the proposed method is its applicability for the separation of rubidium and caesium ions from ammonium ion. In practical analyses a separation of rubidium and caesium will have to precede their determination. This can be achieved by ion exchange.[2]

Zusammenfassung—Rubidium und Cäsium können gravimetrisch mit *N,N*-Dimethyläthanolammoniumorotat als Fällungsmittel bestimmt werden. Zusammensetzung und Identität der ausgefallenen Rubidium- und Cäsium-orotate wurden durch Gesamtanalysen festgestellt. Die Ergebnisse beweisen die Reinheit der Fällungen.

Résumé—On a montré que le rubidium et le césium peuvent être dosés gravimétriquement en utilisant, comme réactif de précipitation, l'orotate de *N,N*-diméthyléthanolammonium. On a établi, par des analyses complètes, la composition et l'identité des orotates de rubidium et de césium, qui sont les précipités utilisés dans la méthode gravimétrique développée, et les résultats confirment leur pureté.

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A COULOMETRIC TITRATOR USING POTENTIOMETRIC END-POINT DETERMINATION

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Summary—A coulometric titrator using operational amplifiers has been built and tested. A potentiometric titration can be made to a preset pH with a precision of ±0·05 pH unit, using glass and calomel electrodes. The electrolysis current is reduced near the end-point to avoid overtitration. If the solution has been overtitrated the current is reversed. The number of coulombs required during a titration is determined by integration of the current. 0·2–0·4 mmole of perchloric acid was titrated with a standard deviation of about 0·1%, and 0·2–0·8 mmole of benzoic acid with a standard deviation of 0·15%.

WHEN the end-point of a coulometric titration is determined potentiometrically, two pairs of electrodes are immersed in the same solution. The potentials of the indicating electrodes are different from the potential of the working electrode. The simultaneous operation of a pH-meter and a coulometer at different potentials, connected through the solution, is subject to several possible sources of error.

A current can flow between the chassis of the instruments. One path is through the solution, and the return path may be poor isolation to the line. This current will cause an erroneous reading of the pH-meter and it may also cause an error in the coulometric measurement.

Another source of error is the capacitance between the indicating and generating instrument systems. A change in potential of the systems relative to each other will require a current to charge this apparent capacitor. The response of the indicating system will be slow.

If two instruments are operated at different ground levels, only one of them can be connected to ground. The other instrument will pick up hum and noise. The disturbances will be most serious if the coulometric apparatus is grounded and the pH-meter has a floating ground.

In spite of these difficulties, many coulometric analyses have been proposed using the technique criticised above. The technique has even been recommended by some manufacturers. Of course, the effects can be reduced by great care in mounting, but the danger of erroneous results will always exist. The difficulties will be greater for a current source of high accuracy, because the circuitry will be more complex. Especially in non-aqueous solvents this technique has been found to give very erroneous results.

The easiest way to get rid of all these difficulties is to operate only one electrode system at one time. This method has been used by Smith and Taylor[1] and by the present author.[2] Both the generating and indicating electrodes were immersed in the solution, but a switch allowed only one of the electrode pairs to be connected to its instrument at any one time. The disadvantage of this method is that an analysis takes a very long time, and requires constant operator attendance.

Several instruments have been described which automatically perform a coulometric titration. A titration curve can be recorded when a constant current is passed through the solution, the end-point being determined graphically from the chart paper. Several titrators which shut off the current at the end-point have also been described in the literature. The number of coulombs is determined either by integration or by measuring the time of reagent generation. High impedance inputs are obtained by using a commercial pH-meter which actuates a relay,[3,4] or a recorder with a slave potentiometer.[5] Most of the titrators described are useful only for low impedance electrodes.[6–8] An interesting solution is presented by Burnett and Klaver.[9] The output of a pH-meter is fed into a magnetic amplifier which isolates the measuring circuit from the generating electrodes.

Information about the accuracy of the end-point determination is usually lacking in the literature. The overall accuracy seems to be less than what could be obtained by manual titration.

In this paper a titrator is described which measures the electrode signal directly, including the voltage to ground. The common mode voltage is cancelled in a differential amplifier, and the electrode potential minus a preset voltage is amplified and applied to the generating electrodes. When the electrode signal approaches the preset voltage the generating current will be reduced. If an overtitration has happened the current will reverse.

EXPERIMENTAL

Apparatus

Titrator. The input from the indicating electrode, *e.g.*, a glass electrode, is connected to the follower,* A1, which consists of an operational amplifier with extremely high input resistance (G. A. Philbrick Res., Inc., model P2), as shown in Fig. 1. The reference electrode is connected to a less expensive follower, A2, with a moderate input resistance (model P65).

The feed-back loop of A2 contains a 10-turn potentiometer over which 1·000 v is applied. The dial reads in mv. This voltage is obtained from a zener-stabilised supply floating with respect to ground; sign reversal is accomplished by a switch. The voltage set on this "set end-point"-potentiometer will cause a displacement of the output of A2 by the same amount. When the potential between the measuring electrodes equals the voltage set on the potentiometer, the output from the titrator will be zero; the titration will stop.

The outputs from the two followers are connected to a differential amplifier A3. In this amplifier only the difference between the two follower outputs will be amplified. The common part will be cancelled. This common voltage includes the voltage between the measuring electrode system and the generating electrode, the voltage drop over the current measuring resistor and the hum and noise. The magnitude of the common voltage must, for amplifier P55, be less than ±10 v, and it is cancelled to better than 0·1%. By using the amplifier P2 throughout it should be possible to get a still better performance. The common mode rejection of this amplifier is better than 0·0001% and the common voltage may be as large as ±200 v. However, the amplifier P55 was found to be sufficiently accurate for the present purpose. The common mode voltage is usually less than 2 v.

The output from A3 is connected to an amplifier A4, because the total amplification required is too large to be made in one step. A4 is also provided with a damping control for the system.

The response of a glass electrode will lag behind the actual pH in the solution. The time constant is of the order 10–25 sec. It can be reduced by etching the electrode in hydrofluoric acid. In the present investigation, however, unetched electrodes were used.

If no damping is provided, the titrator will shut off the current when the electrode voltage equals the set end-point potential. The solution is then already overtitrated. When the glass electrode then moves towards the correct value a back-titration will start resulting in a pH-oscillation. The oscillations may be quenched by reducing the gain of A4. The gain had to be reduced so much, however, that the end-point became ill defined.

The damping circuit R_1, R_2 and C_1 provides a damping against pH-oscillations by adding a

---

* A follower has a very high input resistance. The output is an accurate reproduction of the input voltage, *i.e.*, the gain is unity.

Fig. 1.
Schematic drawing of the coulometric titrator.

Operational amplifiers: G. A. Philbrick Res., Inc., Boston.

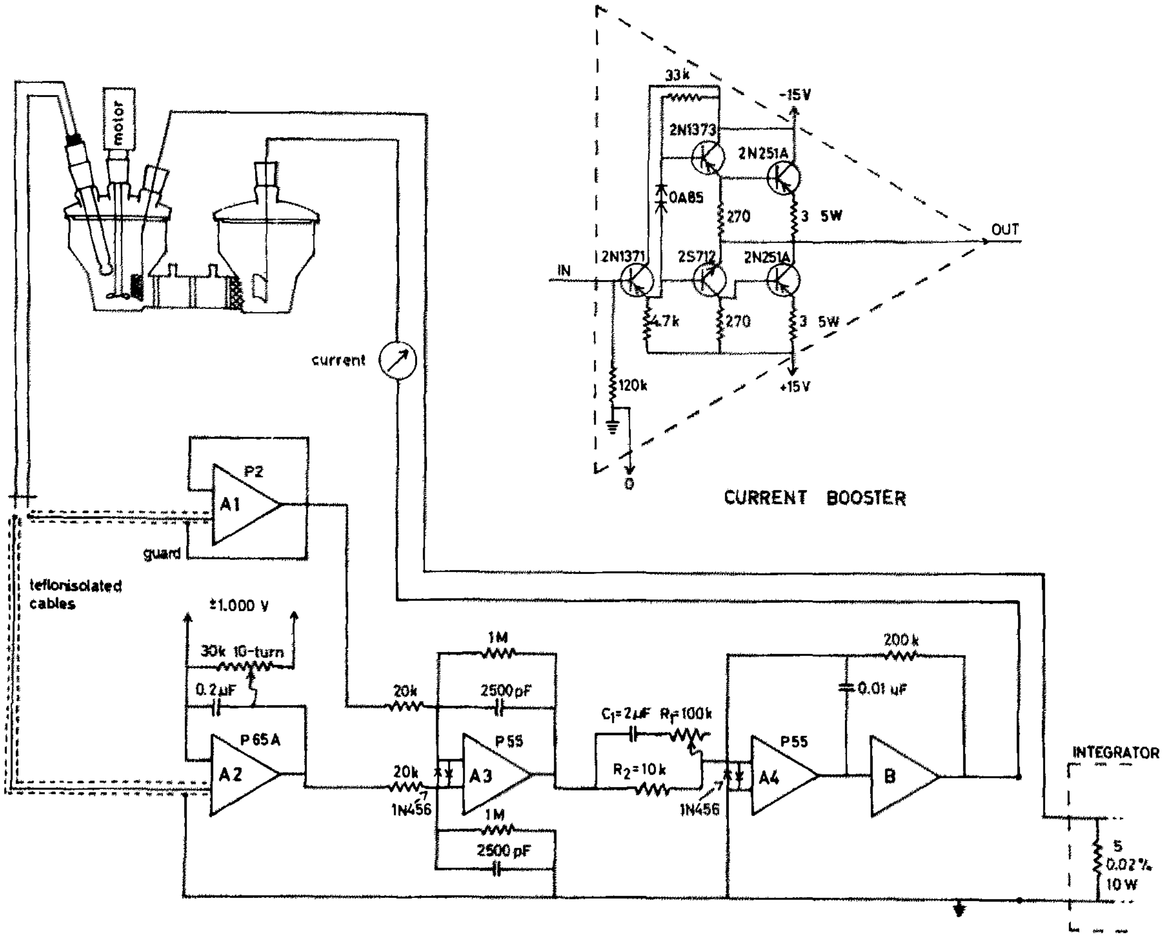
Transistors and diodes: Texas Instruments, Dallas 22, Texas, except the OA85 which are made by Phillips, Eindhoven.

Current is measured by a multipurpose instrument (Phillips).

The 10-turn potentiometer is a Helipot, model A., linearity 0·1% (Beckman Instruments).

Resistors are 0·05%, 1 w, except in the current booster where the resistors are 10%.

The booster is made as a plug-in unit on a printed-circuit card, 50 × 80 mm, with aluminum cooling fins.



derivative function to the signal. When the output voltage from A3 decreases, the decrease will be enhanced in the output of A4 because the derivative function has been added. The titration may stop or reverse. When the charge on C_1 leaks away through R_1 the titration will proceed again. During this time the glass electrode will have had time to move closer to the actual potential.

The amount of damping depends on the slope of the titration curve, on the time constant of the electrode and on the cell geometry. There will be a delay before the generated reagents will come to the electrode. This delay is an essential part of the damping system. It can be adjusted by moving the generating electrode to a new position and by varying the stirring rate. These parameters are adjusted, together with the potentiometer R_1, so that a titration of the solvent is critically or almost critically damped. This setting is then used for all types of titration. A damping system which is independent of electrode positions can be constructed, but it will make the apparatus more complicated.

A current booster is incorporated within the feedback path of A4. The booster shown in Fig. 1 is a modification of a circuit described by Towers.[10] This booster has a small quescent current but can deliver large peak currents. The maximum output voltage is ±12 v.

The bias adjustment for the amplifiers P55 must be provided externally. The potentiometer for bias adjustment of A3 had a sufficiently great range for compensation of the asymmetry potential of most of the glass electrodes used. The adjustment is made in the following way. The glass electrode is immersed in a buffer solution and the end-point potentiometer is set to a value corresponding to the pH of the buffer, *e.g.*, 0 mv for a buffer of pH 7·00. The auxiliary electrode is disconnected and a voltmeter is connected over the output terminals. The bias potentiometer is then adjusted until the voltmeter reads zero.

A zener shunt-stabilised power supply provides power for the operational amplifiers. Two power transistors regulate the power to the current booster, the transistor bases being connected to the zener diodes. The titrator is contained in an enclosure 32 × 20 × 16 cm.

Auxiliary equipment. Combined glass and calomel electrodes, Metrohm type EA121U or EA121X, were used. Type U is for general use in the range pH 0–14, the resistance being 400 MΩ. Type X is more resistant to physical shock, the pH-range is 0–11 and the resistance is also 400 MΩ. The reference electrode is in each case a saturated calomel electrode with a plugged tip.

The titration vessel consisted of two Metrohm EA615 joined by a tube containing two sintered-glass discs, as described earlier.[2] A silicic acid gel covered the glass filter disc in the auxiliary electrode compartment. The resistance of the cell was about 50 Ω when filled with 120 ml of saturated Na_2SO_4-solution. The maximum current is then of the order of 200 mA. When the current had decreased to zero the liquid in the compartments between the glass filter discs was transferred into the titration vessel by applying pressure with a pipette filler. A small suction was applied to fill the compartments again. The procedure was repreated once or twice more. A vigorous stream of CO_2-free air was blown over the liquid during the titration.

The titration current was integrated by a chopper-stabilised integrator with a precision of 3 parts in 10,000. The integrator was calibrated against voltage and time. "Taken" in the tables means the value obtained when dividing the weight of the substance by the formula weight. "Found" means the actual readings which are founded on standardisation against current and time. The tables thus provide an intercomparison between these two independent methods of standardising.

Reagents

Zone melted benzoic acid with a stated purity of 100.00% was used (Hopkin and Williams, Ltd., Benzoic acid P.V.S.). *Pro analysi* sodium carbonate was dried at 150°. Other reagents were of *pro analysi* quality.

Procedure

After a warm-up period of 10–15 min the noise of the titrator with the glass electrode connected was found to correspond to less than 0·01 pH-unit, and the drift over 15 hr to be less than 0·05 pH-unit. The measurement was taken with the glass electrode immersed in a phosphate buffer solution of pH 7·00. This solution had previously been used as a standard when the asymmetry potential of the electrode was compensated for. The drift of the operational amplifiers according to the manufacturer's specifications is equivalent to ±0·02 pH-unit in the worst case (per day and 5° in temperature change).

In order to determine the linearity, the buffer adjustment was done as above. The end-point potentiometer was then set at +15 mv (it had been set at 0 mv during the above adjustment). The titration started, and was allowed to go on until the current was less than 10 μA. The glass electrode was then connected to an expanded-scale pH-meter (Metrohm E-300) and the pH-value was noted. The pH-meter had previously been standardised against the same phosphate buffer solution.

RESULTS

Fig. 2 shows a plot of pH-values against the settings of the end-point potentiometer. First the values to the left of zero were measured in the direction from pH 7·00 towards higher pH-values. Then the titration was reversed and the points to the right of zero were taken in successive order. The points fall on two lines, depending on whether the titration is made upwards or downwards. This behaviour is partly caused by the hysteresis of the generating electrode. When base is generated, the platinum foil must be negative with respect to N.H.E., while it must be positive when acid is generated. The magnitude of the generating electrode hysteresis is thus the decomposition voltage of the solution divided by the loop gain, which was 1,000 times in the actual case.

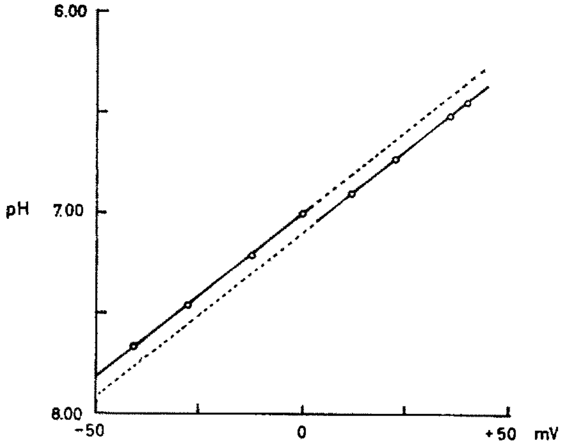


FIG. 2.—pH-values of the end-point in a phosphate buffer solution plotted *versus* the dial settings on the coulometric titrator.

Another contribution to the measured hysteresis will be derived from incomplete cancellation of the common mode voltage in A3. Depending on how the followers are connected to the differential amplifier it will add or subtract to the hysteresis of the generating electrode. If the connection is made as in Fig. 1, namely P2 to the "—" input of A3, it will be added, giving a higher total hysteresis. If the followers were connected for subtraction of the hysteresis effects an instability leading to oscillations would occur. The crossover distortion in the current booster might be another source of hysteresis. The two germanium diodes between the bases of the NPN and PNP transistors, together with the inclusion of the booster within the feed-back loop will reduce this contribution to a negligible value.

The slope of the lines in Fig. 2 is 60·3 mv/pH-unit as compared to the calculated 59·4 mv/pH-unit. A pH-unit is taken to be equal to the reading of the Metrohm E-300 meter pH-meter. The agreement between slopes found and calculated proves that the input resistance of the titrator is sufficiently high for the present purpose; it is of the order of 30,000 megohms.

Table I shows a set of coulometric titrations of perchloric acid to pH 7·00 in a medium of saturated Na_2SO_4. The anode was a silver foil, and sodium tetraphenylborate was added to the anode solution. The perchloric acid had previously been

TABLE I.—TITRATION OF PERCHLORIC ACID SOLUTION

Taken, *μmole*	Found, *μmole*	Taken, *μmole*	Found, *μmole*
202·4	202·5	404·9	405·2
	202·7		404·4
	202·2		404·4
	202·5		404·4
	202·4		404·9
	202·3		
	202·4		
Mean	202·4		404·6
Standard deviation	0·3		0·5
Deviation from taken	0%		−0·06%

standardised against sodium carbonate. The accuracy of the burette (Metrohm piston burette E 274) had been controlled by weighing.

Table II shows the results obtained when benzoic acid was titrated to pH 8·10. The weighings were made on a microbalance and the weight was corrected for air buoyancy. The benzoic acid was dissolved in a few ml of ethanol and washed into the titration vessel through one of the ground joints at the top. The medium was as described above. A titration was completed in 10–15 min.

TABLE II.—TITRATION OF BENZOIC ACID

Taken, *μmole*	Found, *μmole*	Deviation, %
390·6	390·7	+0·01
407·7	407·1	−0·15
400·5	399·8	−0·22
414·0	413·8	−0·06
415·3	415·5	+0·03
408·8	408·9	+0·02
884·8	883·3	−0·16
212·7	213·3	+0·26
Mean		−0·03
Standard deviation		0·15

In some cases the end-point setting may be calculated from tabulated pK-values. When this is impossible, a titration curve may be obtained from the titrator. The potential is set to a value on the early part of the titration curve, and the integral is noted when the current has ceased. The procedure is repeated for a number of points until the end-point is passed. The potential settings are then plotted *versus* the integrals. A titration curve of this type is shown in Fig. 3. This procedure is, of course, more time-consuming than direct titration to a calculated end-point. However, it will be useful when the conditions for a coulometric titration are evaluated and when more elaborate calculation, *e.g.*, derivation,[11] is necessary for location of the end-point.

DISCUSSION

The titrator itself can be reset with a reproducibility of the order of 0·01 pH-unit (0·6 mv). The hysteresis limits the over-all precision to about ±0·05 pH-unit (±3 mv). This precision was sufficient for the actual applications, especially because the electrodes in many cases limit the accuracy to a much lower value. The hysteresis can be reduced somewhat by employing a higher gain in the feedback loops, but then pH-oscillations are likely to occur in the titration of strong acids or bases. Substituting a P2 differential amplifier for the P55 will reduce the hysteresis to about ±0·02 pH-unit.*

The present titrator reverses the current if a small overtitration occurs. This technique is useful only when the electrode reactions are reversible. For reversible systems, however, the possibility of current reversal will reduce the titration time significantly. The precision will also be increased as compared with titrations with pH-control in only one direction. In regions of small buffer capacity a precision of 0·05 pH-unit will be difficult to attain without this positive control.

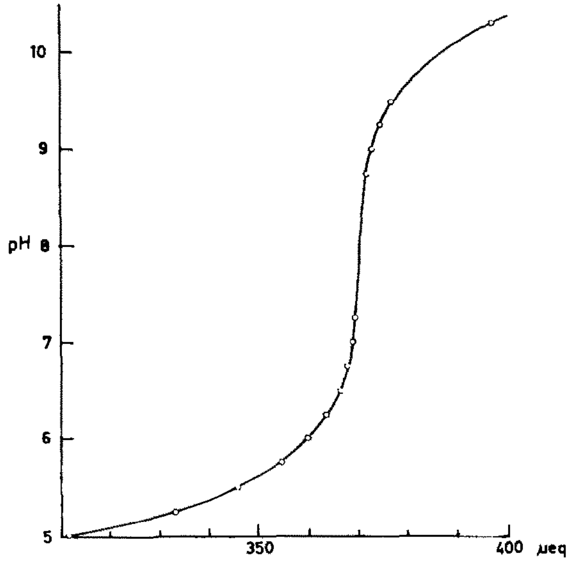


FIG. 3.—Titration of benzoic acid using the method described in the text. All points are corrected for the solvent base consumption.

The titrator has been tested only for acid and base titrations using glass and calomel electrodes. It can also be used in other types of titrations as well as with other electrodes.

Acknowledgements—The author thanks K. J. Karrman for his advice and interest. He also thanks Miss Karin Norberg for obtaining the results. This work was supported by grants from the Swedish Technical Research Council.

Zusammenfassung—Ein coulometrisches Titrationsgerät mit Servoverstärkung wurde gebaut und geprüft. Eine potentiometrische Titration kann bis zu einem vorher auf ±0,05 Einheiten festgelegten pH-Wert geführt werden, wobei zur Anzeige Glas- und Kalomelelektroden verwendet werden. Um Übertitrieren zu vermeiden, wird in der Nähe des Endpunktes der Elektrolysestrom verringert. Bei Übertitration wird der Strom umgepolt. Die zur Titration erforderliche Coulomb-Menge wird durch Integration des Stromes ermittelt. 0,2 bis 0,4 mMol Überchlorsäure wurden mit einer Standardabweichung von etwa 0,1 % und 0,2 bis 0,8 mMol Benzoesäure mit einer Standardabweichung von 0,15 % titriert.

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* An improved version of P2, called P2A, has just been made available by the manufacturer. A still higher input impedance and a lower drift should be obtained if the P2A is used.

Résumé—On a construit et expérimenté un appareil de titrage coulométrique utilisant des amplificateurs opérationnels. On peut effectuer un titrage potentiométrique, à un pH fixé au préalable avec une précision de ±0,05 unité pH, en utilisant des électrodes de verre et calomel. Au voisinage du point final, on a réduit le courant d'électrolyse afin d'éviter un surtitrage. Au cas où la solution est surtitrée, le courant s'inverse. Le nombre de coulombs nécessaire au cours d'un titrage a été déterminé par intégration du courant. On a dosé 0,2–0,4 mmole d'acide perchlorique avec un écart type d'environ 0,1 %, et 0,2–0,8 mmole d'acide benzoïque avec un écart type de 0,15 %.

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SHORT COMMUNICATIONS

Chromogenic reactions of titanium, zirconium and hafnium with Chrome Azurol S

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3″-SULPHO-2″,6″-DICHLORO-3,3′-DIMETHYL-4-HYDROXYFUCHSON-5,5′-DICARBOXYLIC acid, commonly known as Chrome Azurol S (CAS; Colour Index 43825), is one of the hydroxytriphenylmethane group of dyes which has been extensively studied in this laboratory as a chelating reagent.[1]

In the present communication, the formation of coloured chelates of titanium(IV), zirconium(IV) and hafnium(IV) with CAS are reported and suggestions made for use of CAS as a chromogenic reagent for these metals.

EXPERIMENTAL

Apparatus

Spectrophotometer. Absorbance were measured with a Unicam SP 500 spectrophotometer, using matched glass cells of 10-mm light path.

Colorimeter. Colorimetric measurements were made with a Klett Summerson photometric colorimeter (test tube model).

pH meter. pH measurements were made with a Leeds and Northrup pH meter operated on 220-V a.c. mains.

Reagents

Metal ions. Solutions of titanium chloride, zirconium oxychloride, and hafnium oxychloride were prepared and standardised by the usual methods. They were $0{\cdot}1M$ in hydrochloric acid and used fresh to avoid ageing effects. The titanium and zirconium salts were of B.D.H. analytical reagent grade and hafniumoxy chloride was obtained from Johnson and Matthey.

Chrome Azurol S. An aqueous stock solution of CAS was prepared by dissolving the B.D.H. indicator reagent in doubly-distilled water

pH control. An acetate buffer (pH 4·5) was used in the study of the titanium chelate, while in the other two systems the pH was adjusted to 2·0 by addition of acid or base.

Diverse ions. Solutions of diverse ions were prepared from reagent-grade chemicals.

Conditions of study

Measurements were performed in an air conditioned room at 25° ± 1°. The total volume of all the mixtures prepared for the measurements was 25 ml.

RESULTS

Effect of pH

The effect of pH on the complexes was studied and the pH range where λ_{max} remained constant was determined. This was the pH range of stability shown in Table I.

TABLE I.—EFFECT OF pH ON THE METAL CHELATES OF CAS

Chelate	pH range of stability
Ti–CAS	2·5–6·0
Zr–CAS	1·5–5·5
Hf–CAS	1·5–7·0

Nature of complexes

To determine the nature of the complex formed in solution, the modification of Job's method by Vosburgh and Cooper was employed.[2-4] Mixtures of the metal salts and CAS with varying metal:CAS ratio were prepared, the pH being kept constant. The absorbance of each mixture was measured at suitable wavelength intervals over the range 400–750 mμ. In each of the systems λ_{max} remained constant with the various compositions, showing that only a 1:1 complex is formed in each case under the conditions adopted. The mole ratio method[5] and the slope ratio method[6] were also used and confirmed the composition of the chelates. Fig. 1 shows typical results with the hafnium/CAS system.

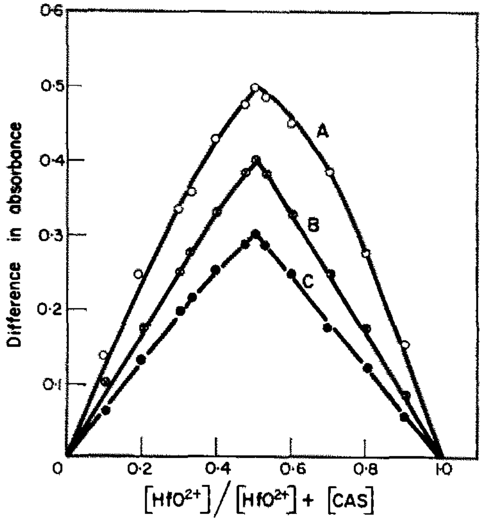

FIG. 1.—Composition of the Hf–CAS chelate by the method of continuous variations, using equimolecular solutions (pH 2·0; 550 mμ).
Concentrations of reactants:
A: 2·00 × $10^{-4}M$; B: 1·33 × $10^{-4}M$; C: 1·00 × $10^{-4}M$.

Evaluation of equilibrium constants

Two different methods were employed for determining the value of the equilibrium constant, K, at 25° and at the pH mentioned, of the complexes and the results are recorded in Table II ($\Delta G^\circ = -RT \ln K$, the terms having the usual meaning).

TABLE II—EQUILIBRIUM CONSTANTS AND FREE ENERGY CHANGES OF FORMATION OF THE METAL CHELATES OF CAS AT 25°

Chelate	pH	log K	ΔG°, *kcal*
Ti–CAS	4·5	4·2 ± 0·2	−5·8 ± 0·2[a]
		4·7 ± 0·2	−6·5 ± 0·2[b]
Zr–CAS	2·0	4·9 ± 0·1	−6·7 ± 0·2[a]
		5·0 ± 0·2	−6·8 ± 0·2[b]
Hf–CAS	2·0	4·7 ± 0·1	−6·5 ± 0·2[a]
		4·9 ± 0·1	−6·7 ± 0·1[b]

[a] By method of Dey *et al.*[7,8]
[b] By mole ratio method

Confirmity to Beer's law and sensitivity

The Sandell sensitivity[9] and ranges of adherence to Beer's law are given in Table III.

TABLE III.—RANGE OF ADHERENCE TO BEER'S LAW AND PHOTOMETRIC SENSITIVITY AT 25°

System	pH	Adherence to Beer's law, *ppm*	Wavelength, *mμ*	Sensitivity, *γ.cm*$^{-2}$
Ti–CAS	4·5	0·19–3·45	520	0·048
Zr–CAS	2·0	0·18–6·50	530	0·091
Hf–CAS	2·0	0·48–13·00	510	0·178

Effect of diverse ions

The effect of several ions on the colour reaction was studied. It was found that Be(II), Al(III), Cu(II), Sc(III), Y(III), V(V), Fe(III), Th(IV), U(VI), Pd(II), fluoride, borate, carbonate, citrate, tartrate and oxalate interfere at all concentrations. Mg(II), Ca(II), Sr(II), Ba(II), Tl(I), Pb(II), As(III), Bi(III), Se(IV), Te(IV), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), Cr(III), Mo(VI), Mn(II), Co(II), Ni(II), Ru(III), Rh(III), Pt(IV), chloride, bromide, iodide, chlorate, nitrate, thiocyanate, sulphate and thiosulphate must not exceed 60 ppm in the case of Ti(IV) and 30 ppm in the case of Zr(IV) and Hf(IV).

Acknowledgement—The authors thank the Council of Scientific and Industrial Research, New Delhi, for awarding a fellowship to one of them (S. D. B.).

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Summary—The chromogenic reactions of titanium(IV), zirconium(IV) and hafnium(IV) with Chrome Azurol S have been investigated. The conditions for formation of coloured 1:1 chelates have been established and the adherence to Beer's law ascertained. An interference study has been made.

Zusammenfassung—Die Farbreaktionen von Titan(IV), Zirkonium(IV) und Hafnium(IV) mit Chromazurol S wurden untersucht. Die Bedingungen zur Bildung farbiger 1:1-Komplexe wurden ermittelt und die Gültigkeit des Beerschen Gesetzes gesichert. Auch Störungen wurden geprüft.

Résumé—On a étudié les réactions chromogènes des titane(IV), zirconium(IV) et hafnium(IV) avec le chrome azurol S. On a établi les conditions de formation des chélates colorés 1:1, et montré que la loi de Beer est suivie. On a procédé à une étude des interférences.

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A method for increasing the reproducibility of chromatographic parameters in thin-layer chromatography

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WHEN the parameters (R_f and R_M) obtained from chromatographic separations are to be used for comparative purposes, it is essential that there is reproducibility of these parameters from separation to separation. In separations on paper, if all extra-molecular factors are standardised, it is possible to have R_f-values reproducible to ±0·01 R_f unit.[1,2]

In separations using thin-layer techniques it has been stated[3] that a reproducibility of ±0·03 R_f unit is generally acceptable. Brenner *et al.*[4] obtained a reproducibility of better than ±0·03 R_f unit, quoting ±0.016 R_f unit for ascending development. To obtain the reproducibility necessary for molecular structure studies, it is important that all extra-molecular factors be standardised.

Bark and Graham[2] have shown that among the extra-molecular factors which are important is the standardisation of the stationary support. In thin-layer chromatography (TLC) involving the use of non-polar eluents and polar substrates, this standardisation is achieved by controlling the activation of the layers and the amount of 'deactivation' during the time the plate is being loaded with the compounds to be chromatographed. It is usual to activate the adsorbent layers used for TLC by heating the prepared plate to 110° for silica gel and alumina, 100° for cellulose and 80° for polyamides, all for periods up to 30 min. The plates are then cooled in a desiccator to prevent uptake of water vapour from the laboratory atmosphere. It is considered that one of the most important causes of deactivation of polar substrates is the adsorption of polar water molecules onto the active sites of the substrates during exposure to air. It is possible to minimise the deactivation by loading in a dry box, but in many laboratories this is not feasible and, in consequence, a random degree of deactivation results. It is possible both to standardise and to reduce the degree of deactivation by loading the plate in a very short time, which is standardised. This standardisation has been achieved with the apparatus described below.

A second source of deactivation of the substrate is the sorption of water vapour by the substrate from the air in the tank during the elution of the chromatogram. The larger the tank in which the elution is carried out, the more serious will be the error from this source. Further, it is more difficult to obtain saturation of the atmosphere of large tanks. To reduce errors from this source we have used a modified Davies-type[5] saturation chamber throughout this work.

EXPERIMENTAL

A rubber policeman is shortened to a length of 1 cm, a hole pierced in the closed end and a Microcap disposable pipette* inserted through the hole.

A strip of Scotch tape is placed on the underside of a Shandon spotting template.† The former is pierced with a needle to give a small hole, wide enough to permit the insertion of the micropipette, coinciding with the centre of the hole in the spotting template.

Each pipette and policeman is positioned in the template and the amount of pipette protruding is adjusted in the following way. A glass plate, on which rests a feeler gauge of the same thickness as the applied layer, is placed below the pipettes. Each pipette is then pressed until it touches the feeler gauge. Thus, all the pipettes are aligned horizontally and this ensures minimum optimum contact to be made with the stationary phase during transfer of the solutions from the pipettes.

Standard plates (20 × 20 cm) are capable of holding 19 spots of the same or different samples. Where the adsorbent is removed from the edges of the plate to enable the plates to be used in a saturation chamber of the type described by Davies,[5] the number of samples is reduced to 17 per plate.

Drainage of the sample solutions from the pipette is negligible, thus enabling the 17 pipettes to be individually filled and positioned in the template before the activated plate is taken from the desiccator.

After taking the plate from storage it is laid on strips of Scotch tape, the template quickly aligned with the plate and each pipette discharged by capillary action by being brought into contact with the sorbent surface as a result of gentle finger pressure on the top of the template, thus pressing the pipettes on to the chromoplates. This causes all the pipettes to touch simultaneously the stationary phase coating the plate. Because of the careful alignment of the micropipettes to the thickness of the applied layer, little or no disturbance of the adsorbent surface occurs during the application of

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* Manufactured by Drummond Scientific Company, Broomall, Pa., U.S.A., and available from Shandon Scientific Company Ltd.

† Shandon Scientific Company, Ltd., 65 Pound Lane, London N.W. 10, England.

the samples. Hence, distortion of the spots caused by holes in the surface of the adsorbent is kept to a minimum.

After the spotting of the plates, a glass former surrounding three sides of the plate is placed in position and a cellulose wick positioned along the fourth. A glass cover plate is placed on top of the former and the Scotch tape tightly drawn over the plate to form the saturation chamber. This is then placed in a polythene bag* into which is also placed the eluent, and the bag is closed by folding the open end upon itself and sealing the fold with polythene adhesive tape. Hence, a saturation chamber within a saturation chamber is obtained.

The use of the cellulose wick ensures rapid saturation of the small space inside the inner saturation chamber by increasing the surface area over which the eluent can evaporate. In addition, we have observed that certain sorbents, particularly polyamides, tend to crack on being wetted with solvent and cause a ragged eluent front on the chromatogram. This is entirely prevented by the method described.

The over-all time taken for removal of the plate from storage, spotting of the samples and placing of the plate in the saturation chamber is less than 1 min and with only a little practice can be standardised to within a few seconds of a predetermined time, say 45 sec. Hence, standardisation and minimum deactivation are achieved.

A comparison of some results obtained by individual and template spotting of sample solutions is given in Table I.

TABLE I.—R_f-VALUES FOR THREE DYES[a] USING INDIVIDUAL AND TEMPLATE SPOTTING

	Individual spotting[b]			Template spotting[b]		
	Dye 1[c]	Dye 2[d]	Dye 3[e]	Dye 1[c]	Dye 2[d]	Dye 3[e]
Highest value	0·39	0·46	0·61	0·34	0·42	0·59
Lowest value	0·33	0·41	0·56	0·32	0·40	0·58
Mean value	0·36	0·44	0·58	0·33	0·41	0·58
Standard deviation × 10^{-2}	1·40	1·26	1·22	0·53	0·53	0·10

[a] The dyes were obtained in benzene solution from E. Merck, Darmstadt, Germany; they were diluted 1:1 with benzene before application.

[b] Results obtained from two runs each of 17 sample spots of the dyes.

[c] Sudan Red G: C.I. 12150.

[d] Indophenol Blue: C.I. 49700.

[e] Butter Yellow (*p*-dimethylazobenzene).

Washed plates were coated with a 0·25-mm layer of silica gel (35 g of Merck Silica Gel (G) slurried with 65 ml of deionised water). The plates were air dried overnight (12 hr) and activated by heating at 110° for 30 min, then allowed to cool in a desiccator over molecular sieve (B.D.H. Ltd., England, Type 5A). After loading two plates by individual spotting and two by the template method, with 1-μl aliquots of a solution containing 3 dyestuffs, one plate of each type was placed in the saturation chamber and eluted with a mixture of light petroleum spirit and diethyl ether [70% v/v light petroleum spirit (boiling range 40°–60°) and 30% v/v diethyl ether].

The two sets of plates were eluted until the solvent fronts had moved the same distance from the loading lines (15 cm). Dyestuffs were used so that no detection of separated components by spraying of the chromatogram was necessary; any movement of the components during spraying was thus avoided.

The results are given in Table I.

DISCUSSION

In these and in all other cases where this technique has been used, it has been found that where polar substrates have been used the R_f-values obtained with individual spotting are higher than those obtained by simultaneous spotting. This is to be expected because the number of active sites on the individually spotted plates is less than on the simultaneously spotted plates and hence the effective

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* It is realised that significant amounts of plasticisers used in the manufacture of such polythene may be leached out with some solvent systems used in TLC. This would alter the composition of the chromatographic system and the behaviour of the compounds being chromatographed. A comparison of the results obtained in an all glass-saturation chamber and those reported in the present paper showed no significant differences. However, the possibility of composition changes because of the dissolution of plasticisers must always be considered.

polarity of the surface is reduced. This will result in the substance being chromatographed being relatively more positioned in the non-polar phase (the eluent) and hence the R_f-value will be greater. This is in accordance with the Consden-Gordon-Martin equation relating R_f and partition[6] and is expected if the chromatographic mechanism is essentially adsorption onto a polar surface. There is also greater variation in the range of R_f-values recorded for a particular compound, the standard deviation for the individually spotted materials being at least twice that for the simultaneously spotted materials. From a consideration of the results obtained by simultaneous spotting, it can be seen that this method, when used under the conditions suggested for standardisation of extra-molecular factors,[1,2] enables results to be obtained within ±0·01 R_f unit, which is acceptable for comparison purposes.

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Summary—A technique is described for the simultaneous multiple spotting of thin-layer chromatographic plates. When used in conjunction with a modified saturation chamber, it enables standardisation of important extra-molecular factors to be made. A mixture of three dyestuffs has been spotted individually and by the described technique under identical conditions. The results show that simultaneous multiple spotting gives the lesser variation in R_f-values, the reproducibility being ±0.01 R_f-unit.

Zusammenfassung—Ein Verfahren zur gleichzeitigen Aufbringung mehrerer Flecke auf Dünnschicht-Chromatographieplatten wird beschrieben. In Verbindung mit einer modifizierten Sättigungskammer erlaubt es Standardisierung wichtiger extramolekularer Faktoren. Flecke aus einer Mischung dreier Farbstoffe wurden einzeln und mittels des beschriebenen Verfahrens unter einheitlichen Bedingungen aufgebracht. Die Ergebnisse zeigen, daß gleichzeitiges Aufbringen mehrerer Flecke geringere Variationen in den R_f-Werten liefert; die Reproduzierbarkeit beträgt ±0,01 R_f-Einheiten.

Résumé—On décrit une technique de dépôt simultané multiple sur les plaques de chromatographie en couche mince. Elle permet, lorsqu'on l'utilise conjointement à une chambre de saturation modifiée, la normalisation d'importants facteurs extra-moléculaires. Dans des conditions identiques, on a déposé un mélange de trois colorants, individuellement et selon la technique décrite. Les résultats montrent que le dépôt simultané multiple conduit aux plus faibles variations des valeurs de R_f, la reproductibilité étant de ±0,01 unité R_f.

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Ultraviolet spectra of some piaselenol derivatives*

(*Received* 17 *April* 1964. *Accepted* 24 *October* 1964)

Aromatic 1,2-diamines react with selenous acid to form piaselenol derivatives. The reaction, which is quantitative, serves for the spectrophotometric determination of selenium. Thus, it has been reported[1] that 1,2-phenylenediamine is an excellent reagent for selenium. Several 4-substituted

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* Read at the 36th Chûgoku–Shikoku Local Meeting of the Chemical Society of Japan, Okayama, May, 1962.

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Ultraviolet spectra of some piaselenol derivatives*

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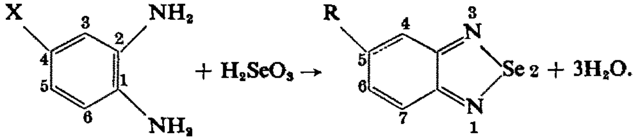
1,2-phenylenediamines have now been investigated to ascertain if they provide an increased sensitivity:



EXPERIMENTAL

Synthesis of piaselenol derivatives

The 4-substituted 1,2-phenylenediamines were dissolved in dilute hydrochloric acid and the equivalent amounts of selenous acid added at room temperature. The piaselenol derivatives, which precipitated immediately, were filtered and washed with a small amount of water, then twice recrystallised from aqueous alcohol.

Ultraviolet spectra of piaselenol derivatives

The piaselenol derivatives were dissolved in toluene so as to give 5·00 × $10^{-5}M$ solutions. The absorption spectra of these solutions over the range 280–400 mμ were observed with a Shimadzu QR-50 spectrophotometer, using 1-cm cells (Table I).

DISCUSSION

In Fig. 1 the maximum wave numbers of the 5-substituted piaselenol derivatives are *versus* $\sigma_m + \sigma_p$ of Hammett's substituent constants, because the 5-substituent is affected through the nitrogen atoms at the *m*- and *p*-positions. Sawicki and Carr[3] determined the ultraviolet spectra of some piaselenol derivatives in 95% ethanol. The wave numbers are greater in ethanol than in toluene. Furthermore, while the absorption curves show some inflection in ethanol, little or no inflection is shown in toluene, except in the case of the 5-methoxy- and 5-ethoxypiaselenol derivatives. The difference seems to derive from the difference in polarity of the two solvents. No connection was found between the substituent and the molar extinction. The present investigation shows that 3,4-dichloro-1,2-phenylenediamine should be the most sensitive reagent for selenium, because the extinction of 4,5-dichloropiaselenol is the highest of the piaselenol derivatives studied.

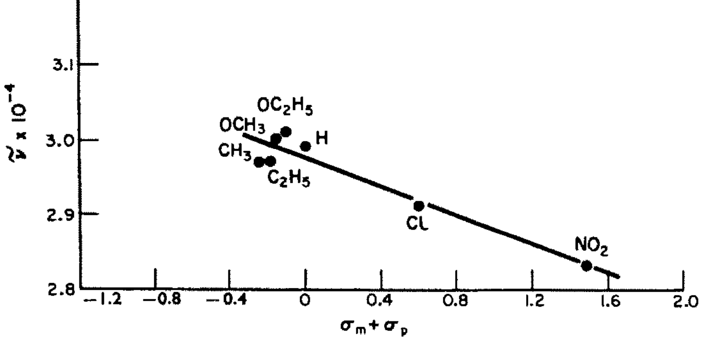


FIG. 1.—Plot of maximum wave numbers of 5-substituted piaselenol derivatives against $\sigma_m + \sigma_p$ of Hammett's substituent constants.

Acknowledgement—The authors wish to express their sincere thanks to Dr. R. L. Clark of Merck Sharp and Dohme International for a generous gift of 4-nitro-, 4-methyl-, 3,4-dichloro-, 4-chloro-, 4-ethoxy- and 4-ethyl-1,2-phenylenediamine.

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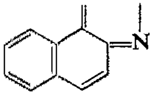
TABLE I

Piaselenol derivative	λ_{max}, *mμ*	$\bar{\nu} \times 10^{-4}$, *cm*$^{-1}$	E_{max}	$\varepsilon_{max} \times 10^{-4}$	M.p, °*C*	
					Found	Literature
Piaselenol (I)	334	2·99	0·851	1·70	74°	76° (3)
5-NO_2—I	353	2·83	0·757	1·51	220°–221°	223°–224° (2)
5-Cl—I	344	2·91	0·873	1·75	119°–119·5°	118°–119° (2)
5-CH_3—I	337	2·97	0·827	1·65	72°–73·5°	72°–73° (3)
5-C_2H_5—I	337	2·97	0·870	1·74	72°–73·5°	
5-CH_3O—I	333	3·00	0·559	1·12	108°–111°	110°–111° (2)
5-C_2H_5O—I	332	3·01	0·564	1·13	99·5°–102·5°	103°–104° (4)
4,5-di Cl—I	354	2·82	0·996	1·99	162°–164°	
	361	2·77	0·640	1·28	127·5°–128·5°	128°–129° (3)

Summary—Some 4-substituted 1,2-phenylenediamines have been investigated to ascertain if they provide an increased sensitivity over 1,2-phenylenediamine for the spectrophotometric determination of selenium (IV). 3,4-Dichloro-1,2-phenylenediamine appears to be the most sensitive of the reagents studied.

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Talanta, 1965, Vol. 12, pp. 129 to 131. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Specific and selective reactions

SIR,

Although the terms *specific* and *selective* date from many years ago, it is now generally conceded that there is no such thing as a *specific reagent* and, therefore, one always speaks of a *specific reaction.* The term *selective reagent* is still widely used, but requires some qualification; nebulous terms, such as *very selective, highly selective, non-selective, moderately selective,* which are used have little meaning, and there is a definite need for selectivity to be clarified in some way.

A possible simple approach would be to use a Selectivity Index Number. Thus, if only one ion responded to the reaction in the most favourable circumstances possible, the reagent would have a Selectivity Number of I. If two ions responded to the reaction, the reagent would have a Selectivity Number of II. Perhaps three to five responses would be given a Selectivity Number of III and so on. Obviously, as the Selectivity Index increased it would be necessary to include more ions in the group. It would not be necessary to have more than about six or seven groups because after a few groups the term selectivity would become meaningless. If the selectivity of a reagent were enhanced by the discovery of some new masking reagent, it would be promoted to a higher group. A reagent which has a Selectivity Number of I would be regarded as providing a specific reaction.

This suggestion was made to my friend Professor Louis Gordon at the Case Institute of Technology, Cleveland, Ohio, U.S.A., who was sufficiently interested to hold a Seminar Discussion on the topic. The result of this led to a proposal that the term specific and selective be abandoned and that a tabular list of properties be attached to reagents. However, this suggestion, useful though it be, does not solve the problem. For example, when one is lecturing to undergraduate classes and the properties of a reagent are mentioned in passing, one does not want to supply every minute detail, but only to give a qualitative indication of the properties of the reagent: the Selectivity Index would serve this purpose.

I have also held a Seminar with my own research students to which some of my former students were invited. As a result of this Dr. D. Betteridge has made a proposal which goes much further than mine. A full description of Dr. Betteridge's suggestion is contained in the following letter.

The Betteridge proposal gives at a glance a remarkable amount of information and is well worth further discussion. It incorporates the idea of the Selectivity Index, hence one could still use this term when making passing reference to a reagent. Dr. Betteridge's expansion of the idea could be used where more information is required.

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11 *November* 1964

Selectivity index

SIR,

The Selectivity Index Number suggested by Professor R. Belcher is a simple way of making such nebulous terms as *highly selective* more precise. Because it is the reaction rather than the reagent to which the term *specific* applies, it seems desirable to extend the idea of a Selectivity Index Number to give a Selectivity Index to a reaction of analytical interest. This letter proposes such a symbol, which will be called a Selectivity Index.

The index should contain the following information:

(1) The particular type of analytical reaction for which the reagent is to be used, *e.g.*, gravimetric, spectrophotometric, *etc.*;
(2) a semi-quantitative measure of selectivity;
(3) pH;
(4) the masking reagent, if one is used;
(5) the element which is most usefully determined by the reaction.

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LETTERS TO THE EDITOR

Specific and selective reactions

SIR,

Although the terms *specific* and *selective* date from many years ago, it is now generally conceded that there is no such thing as a *specific reagent* and, therefore, one always speaks of a *specific reaction*. The term *selective reagent* is still widely used, but requires some qualification; nebulous terms, such as *very selective*, *highly selective*, *non-selective*, *moderately selective*, which are used have little meaning, and there is a definite need for selectivity to be clarified in some way.

A possible simple approach would be to use a Selectivity Index Number. Thus, if only one ion responded to the reaction in the most favourable circumstances possible, the reagent would have a Selectivity Number of I. If two ions responded to the reaction, the reagent would have a Selectivity Number of II. Perhaps three to five responses would be given a Selectivity Number of III and so on. Obviously, as the Selectivity Index increased it would be necessary to include more ions in the group. It would not be necessary to have more than about six or seven groups because after a few groups the term selectivity would become meaningless. If the selectivity of a reagent were enhanced by the discovery of some new masking reagent, it would be promoted to a higher group. A reagent which has a Selectivity Number of I would be regarded as providing a specific reaction.

This suggestion was made to my friend Professor Louis Gordon at the Case Institute of Technology, Cleveland, Ohio, U.S.A., who was sufficiently interested to hold a Seminar Discussion on the topic. The result of this led to a proposal that the term specific and selective be abandoned and that a tabular list of properties be attached to reagents. However, this suggestion, useful though it be, does not solve the problem. For example, when one is lecturing to undergraduate classes and the properties of a reagent are mentioned in passing, one does not want to supply every minute detail, but only to give a qualitative indication of the properties of the reagent: the Selectivity Index would serve this purpose.

I have also held a Seminar with my own research students to which some of my former students were invited. As a result of this Dr. D. Betteridge has made a proposal which goes much further than mine. A full description of Dr. Betteridge's suggestion is contained in the following letter.

The Betteridge proposal gives at a glance a remarkable amount of information and is well worth further discussion. It incorporates the idea of the Selectivity Index, hence one could still use this term when making passing reference to a reagent. Dr. Betteridge's expansion of the idea could be used where more information is required.

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11 *November* 1964

Selectivity index

SIR,

The Selectivity Index Number suggested by Professor R. Belcher is a simple way of making such nebulous terms as *highly selective* more precise. Because it is the reaction rather than the reagent to which the term *specific* applies, it seems desirable to extend the idea of a Selectivity Index Number to give a Selectivity Index to a reaction of analytical interest. This letter proposes such a symbol, which will be called a Selectivity Index.

The index should contain the following information:

(1) The particular type of analytical reaction for which the reagent is to be used, *e.g.*, gravimetric, spectrophotometric, *etc.*;
(2) a semi-quantitative measure of selectivity;
(3) pH;
(4) the masking reagent, if one is used;
(5) the element which is most usefully determined by the reaction.

Additionally, it should be simple to comprehend and possible to print.

The most natural symbol is one analogous with the symbol for an isotope. The proposed modification is

$${}^{\text{selectivity group}}_{\text{pH}}\times^{\text{useful reaction}}_{\text{masking agent}}$$

where × = a letter to describe the analytical use to which the reagent is being put,
selectivity group = a letter to describe the degree of selectivity,
pH = pH range,
and masking agent = masking agent, if any.

These will be discussed, then examples of use will be given.

Type of analytical reaction

The type of reaction must be specified because the selectivity and the conditions of reaction may vary with the use. For example, 1,10-phenanthroline is less selective when used as a masking agent than as a spectrophotometric reagent. The conditions required to effect a precipitation may differ from those needed in an extraction, so the two cases should be noted separately.

It should be possible to indicate by a capital letter, or a capital letter and a small letter, the types of reaction most commonly used. The following tentative list is proposed:

G = gravimetric
S = spectrophotometric
E = extractant
M = masking reagent
F = fluorimetric
T = titrant
Sx = spectrophotometric after extraction
I = indicator
Q = qualitative
N = nephelometric

Selectivity group

A semi-quantitative assessment of selectivity can be made as suggested above by placing reagents into groups according to the number of ions with which they react. These groups could then be represented by a number or a letter, known as the Selectivity Index, which would replace such qualifiers of *selective* as *very, highly, non-, moderately, etc.* For clarity in the final symbol it is suggested that greek letters rather than numerals be used:

Number of ions with which reagent reacts	Index
1	α
2–3	β
4–6	γ
7–10	δ
10	ε

Numbers could be used if preferred, but to avoid confusion with the pH number, roman numerals must be used. For teaching purposes, where excessive detail is to be avoided, the index could be reduced to, for example, ${}^{\alpha}X$.

pH

As one of the most important variables in an analytical reaction, the pH must be specified.

Masking reagents

Most masking reagents can be abbreviated[1]; because they are widely used to enhance selectivity, their presence must be specified.

Usefulness of reaction

If the reagent falls in group α or β, any ion of special interest could be noted. If it so happened that a reagent was in group ε but differentiated between two similar ions, *e.g.*, rubidium and caesium, this could be noted. This is a useful feature of the symbol because in the example cited it would be a simple matter to remove other interfering ions before the addition of the reagent.

Examples

A few random examples are now given to illustrate the use of the symbol:

dimethylglyoxime	α Pd G 1	α Ni G 4–10 NH_3	α Ni Sx 7–10 NH_3
4-(-2-pyridylazo)resorcinol	ε I 3–10	α Bi I 1–2 HNO_3	β Nb S 6 EDTA
Alizarin Fluorine Blue	γ Pb I 4	α F 5 4–5 Ce	

Discussion

In essence the proposed symbol gives an abstract of the reaction and specifies, rather crudely, the selectivity under a given set of conditions. It cannot, of course, replace the literature or give full details, but it serves as a useful guide and it does place the emphasis on the reaction rather than the reagent.

There are several limitations. The extent of a reaction is not only dependent on pH but also on the reagent concentration. However, whilst the $[H^+]$ may vary by a factor of 10^{14}, the reagent concentration is usually of the order of 0·1–0·01M. Similarly, the per cent extracted at a given pH and reagent concentration will vary with the solvent used and it is impossible to specify all the possible solvents. This again is usually a second order consideration. In any case, most of these objections can be made against current descriptions of selectivity and in practice are not serious.

The specifying of a useful reaction is both a strength and a weakness. If several useful reactions are known the choice may be subjective rather than objective. On the other hand, the proposed symbol does embody masking reagents where the usefulness may be measured by the number of ions with which the reagent does not react and for which the normal terms of selectivity are not suited.

The advantages of the symbol are that it is simple, small, easily comprehensible and printable and that it contains most of the information of analytical importance.

Corollaries

For a Selectivity Index to be meaningful a large number of ions must be examined. Therefore, if a proposal were made about the use of the term *selectivity*, it would be logical to draw up a minimum list of ions which must be examined before making any claims about selectivity. This would end such claims as a "specific reagent for copper, which is not affected by sodium, potassium and nitrate ions in a thousand-fold excess"!

The degree of acceptable interference should be standardised so as to make selectivity groupings meaningful. Here again, there is a wide view of what constitutes an acceptable interference, but a standard guide would have a practical use. A working definition follows. An ion shall be called an interference if, when present in a 100-fold (molar) excess, it shall cause an error of greater than 0·5% in a gravimetric or titrimetric procedure or greater than 5% in other procedures.

D. Betteridge

Department of Chemistry
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Singleton Park
Swansea, Wales

11 *November* 1964

REFERENCE

[1] *Handbook of Analytical Chemistry*, ed. L. Meites. McGraw-Hill Book Co., Inc., New York, 1963.

EDITORIAL NOTE

The Editor-in-Chief has been asked by the authors to emphasise that the above ideas are purely tentative and that the purpose of the letters is to invite criticism and further suggestions. *Talanta* is willing to publish letters from other people who now wish to make a contribution to this subject.

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TALANTA MEDAL

The Editorial Board of *Talanta* has pleasure in announcing that, with the approval of the Advisory Board, the third award of the Talanta Medal [see *Talanta*, 1964, **11** (4), xi] has been made to

PROFESSOR I. P. ALIMARIN

of the Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow.

Professor Alimarin's scientific activities range over an extraordinarily wide field of analytical chemistry, from the investigation of new organic reagents (especially for photometric purposes), through the application of separation methods such as ion exchange or solvent extraction, to ultramicro analysis. His work on the analysis of the rarer elements, especially niobium and tantalum, is worthy of special attention in this connection. However, he has also made essential contributions to the determination of zirconium and scandium. In recent years he has devoted himself to the application of radioactive isotopes to analytical chemistry.

Outside the U.S.S.R., Professor Alimarin has become known also through his publications on the qualitative microanalysis of minerals and ores, his textbook of semimicro qualitative analysis and his monograph on inorganic ultramicro analysis. In this very field of ultramicro analysis, he has laid the groundwork for wider application by his introduction of electrochemical indicator methods.

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AUTOMATIC AMPEROMETRIC TITRATIONS USING A MERCURY CATHODE*

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(*Received* 19 *March* 1964. *Accepted* 25 *August* 1964)

Summary—An apparatus for performing automatic amperometric titrations is described which uses a stationary mercury electrode as well as the twin platinum electrode system. The titration of sulphate with lead nitrate is given in detail. Quantities as low as 0·001 mmole of sulphate can be determined. Titrations of lead with sulphate, nickel with dimethylglyoxime, lead with dichromate and iodine with thiosulphate are discussed. Results are presented to show the precision and accuracy for inorganic sulphates and organic sulphur compounds.

INTRODUCTION

AMPEROMETRIC titrations do not represent a new technique; the principle was first proposed by Salomon[1] in 1897. The titration of sulphate with lead ion which was reported by Majer[2] in 1936 is representative of this type of analysis. The titration itself, however, is slow and tedious, requiring many manipulations, *e.g.*, the manual addition of titrant, purging and stirring after each addition, and measuring the current to obtain each point on the graph. In all probability, because of these drawbacks, this precise and accurate technique has not found wide use in industry. Therefore, it becomes advantageous to render the titration automatic, thus increasing the speed with which each titration may be made. Several papers have been published describing automatic amperometric titrations in which solid indicator electrodes were employed. In this type of determination the burette delivers the titrant at a definite flow rate to a stirred solution of the sample. (Coulometric generation of reagent might be substituted for a burette.) A recorder attached to the output of the electrodes will plot a continuous curve. Murayama[3] has converted the titration of mercaptans with silver nitrate, using a rotating platinum electrode, into a patented recording titrator. Juliard[4] determines small quantities of chloride automatically using a pretreated silver cathode and utilising mechanical stirring. Commercial units are available for performing, automatically, the titration of small quantities of water by Karl Fischer reagent, employing a set of twin platinum electrodes. Gonzales Barredo[5] reports the automatic titration of arsenic trioxide with potassium bromate using a rotating platinum electrode.

No mention has been found in the literature of an automatic titration using a mercury cathode. The oscillating current of the dropping mercury electrode (DME), in addition to the sensitivity of the drop to stirring of the solution, makes it unsuitable for automatic titration.

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* Paper presented on 5 March 1963 at Pittsburgh Conference on Analytical Chemistry.

The mercury cathode, however, offers the advantage of hydrogen overvoltage. This is the reason why the DME finds such a wide variety of uses in polarography and why it would be favourable to apply this type of electrode (*i.e.*, a mercury cathode) to amperometric titrations. The purpose of this paper is to report our examination of this application.

EXPERIMENTAL

Apparatus

The apparatus consists of a JKM constant-rate syringe drive using a 50-ml Luer-type syringe; a Leeds and Northrup Electrochemograph, Type E (automatic recording polarograph); a silver-silver chloride reference electrode with 1*M* lithium chloride as the salt bridge; and a stationary mercury-pool electrode which will be described in detail later.

Nitrogen was used to purge the solution and also provides stirring during the titration.

Procedure

A titration is run in the following manner: the solution is purged with nitrogen to remove traces of oxygen. The electrodes are immersed in the solution along with the delivery tip of the syringe. A suitable potential is placed between the electrodes. In the case of the titration of sulphate with lead the potential can be between −0·6 and −1·2 V. The bubbling of nitrogen is continued, to provide stirring. The chart drive on the polarograph is then turned on, and the syringe drive is started when the pen of the recorder passes a reference line on the chart paper. The end-point is indicated by a sharp rise in the flow of current in the case of the titration of sulphate with lead. The titration is continued until somewhat past the end-point.

Mercury cathode

A detailed diagram of the mercury pool electrode is shown in Fig. 1. The electrode consists of levelling bulb filled with mercury at (1), which is connected with Tygon tubing to a stopcock at (2). A piece of platinum wire is sealed into the glass below the stopcock at point (3), providing the necessary electrical contact. The reservoir and stopcock assembly are connected to the electrode [designated as point (4)] by a short length of Tygon tubing.

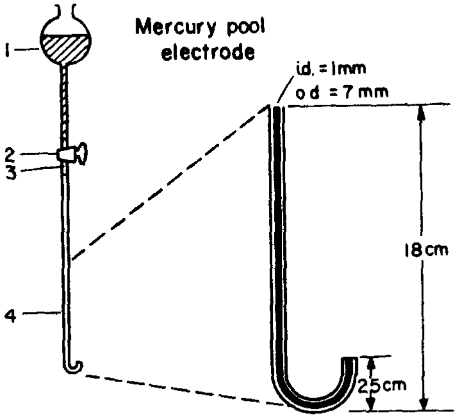

FIG. 1.—Mercury-pool electrode.

The dimensions of the electrode are given in the enlarged drawing to the right in Fig. 1. The optimum i.d. of the capillary was found to be about 1 mm; the other measurements are not critical, and can be varied as conditions require.

As can be seen in Fig. 1, the short end of the electrode is formed into a small cup. The pool of mercury which rests in this cup can be renewed by opening the attached stopcock should contamination be suspected. Contamination is not a problem in all titrations; for example, ten samples of

0·1 mmole of H_2SO_4 in 100 ml of methanol were titrated in succession on the same pool of mercury without distortion of the curve or the end-point. Distortion of the curve was noticed when the pool was made too large. Fig. 2 shows the optimum size of pool, *i.e.*, one in which the top of the pool is at a level with the edge of the cup. A much larger pool has the tendency to shake, resulting in undesirable fluctuations in current. The tubing between the stopcock and the electrode is fitted with an adjustable pinch clamp which allows easy adjustment of the pool size.

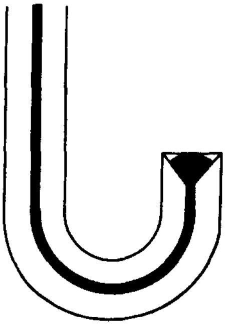

FIG. 2.—Details of mercury pool.

Determination of sulphur by Parr bomb

Most of the work done by this method involved the titration of sulphate with lead nitrate, with methanol or ethanol as the solvent. Standard H_2SO_4 was used for preparing the calibration curves. Solutions of lead nitrate were used as the titrant. Some typical results can be seen in Table I.

TABLE I.—AMPEROMETRIC TITRATION OF SO_4^{2-} WITH $Pb(NO_3)_2$

C.R. = 10 μA full-scale
Damping = 2
Titrant: Approx. 1·0*M* $Pb(NO_3)_2$

Sulphur in approx. 75 ml of methanol, *mmole*	Chart divisions
0·940	96
1·880	199
2·820	290
3·760	410

C.R. = 1 μA full-scale
Damping = 3
Titrant: Approx. 0·002*M* $Pb(NO_3)_2$

Sulphur in approx. 75 ml of methanol, *mmole*	Chart divisions
0·001	26
0·002	54
0·003	78
0·004	106

In order to test the applicability of this type of titration to the analysis of organic sulphur-containing compounds, three standards were chosen. In each case the compound was an Eastman white-label reagent.

The sample was ignited in a Parr oxygen bomb using distilled water as the absorbing solution. The sample was diluted with methanol and titrated as described above. The final concentration of methanol was *ca.* 90%. The samples were also analysed by an alternative method using the Dietert furnace[6] followed by titration with barium perchlorate. The results appear in Table II.

TABLE II.—DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS USING AUTOMATIC AMPEROMETRIC TITRATION AND ALTERNATE MANUAL TITRIMETRIC METHOD

Compound	Sulphur, %		
	Theory	Parr bomb	Dieter furnace
Thiourea	42·0	42·2	42·2
		42·0	42·9
Diphenylthiocarbazone	12·5	12·6	12·6
		12·7	12·3
N-Ethyl-*p*-toluenesulphonamide	16·1	16·7	15·5
		16·8	15·8

Known quantities of diphenylthiocarbazone were mixed with dextrose to produce mixtures containing 0·12% and 0·012% of sulphur. These were determined by Parr bomb ignition, and the results of these analyses are shown in Table III.

Twenty-three samples of nitrocellulose-type materials were analysed for sulphur content by this method. Ten of the samples showed a sulphur content of from 0·01 to 0·11%. The standard deviation between duplicates was 0·01. The remaining thirteen samples contained from 0·14 to 0·51% of sulphur and gave a standard deviation of 0·022.

TABLE III.—DETERMINATION OF SULPHUR IN A MIXTURE OF DIPHENYLTHIOCARBAZONE AND DEXTROSE

Mixture	Theory, %	Found, %
1	0·12	0·10
		0·12
2	0·012	0·012
		0·010

Determination of sulphur by oxygen flask ignition technique

The method of Gildenberg,[7] using the oxygen flask method of ignition, was employed to determine sulphur in 2-benzyl-2-thiopseudo urea hydrochloride. The absorbing solution was diluted with ethanol and titrated. Both manual and automatic titrations were applied to the analysis and no significant difference was noted between the results. The concentration of alcohol was about 75%.

Titration of lead

The reverse titration, *i.e.*, the titration of lead ion with sulphate, a titration in which the current decreases to a minimum and levels off past the end-point, was also attempted. In this case the curves were not well defined and the end-point was not reproducible.

Lead ion may be titrated using this electrode system at an applied potential of zero volts, with potassium dichromate. At this potential lead is not reduced, but dichromate is reduced. An advantage of this titration is that it does not require the removal of oxygen from the solution.

If the potential is increased to −0·6 V, both lead and dichromate are reduced at the cathode. The titration of dichromate with lead was also found to give satisfactory results.

In each case calibration curves were run. The precision was as good as the sulphate-lead titration. Nitrogen provided the stirring, and acted as the purging agent where necessary.

Titration of nickel with dimethylglyoxine

The titration of nickel ion with dimethylglyoxime was attempted using this electrode system, without success. Presumably the precipitation reaction does not take place fast enough for this type of titration to be performed automatically. The results were highly erratic.

Iodine-thiosulphate titration using twin platinum electrodes

In order to test the entire titration system, using other electrodes, twin platinum electrodes were substituted and the iodine-thiosulphate titration was studied. Fig. 3 shows the graph of the titration of thiosulphate with iodine. Here current does not flow until there is an excess of iodine. Fig. 4 shows the reverse titration, *i.e.*, iodine with thiosulphate.

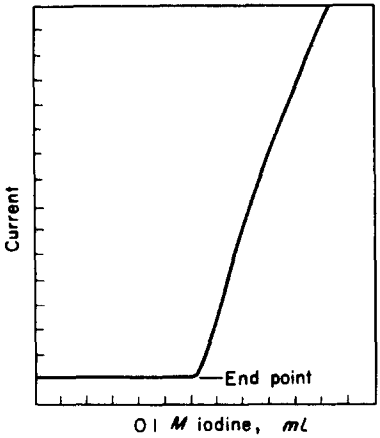

FIG. 3.—Titration of thiosulphate with iodine using twin platinum electrodes (C.R. = 5; damping = 2; voltage = −0·10)

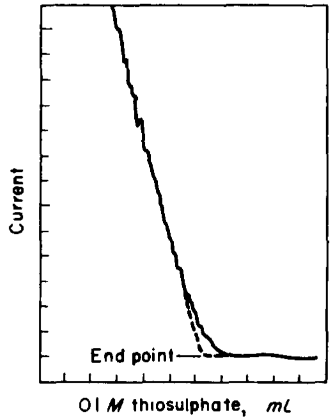

FIG. 4.—Titration of iodine with thiosulphate using twin platinum electrodes (C.R. = 5; damping = 2; voltage = −0·10)

Zusammenfassung—Ein Gerät zur automatischen amperometrischen Titration mit stationärer Quecksilberelektrode und mit zwei Platinelektroden wird beschrieben. Die Titration von Sulfat mit Bleinitrat wird im einzelnen beschrieben. Es kann bis herunter zu 0,001 mMol Sulfat bestimmt werden. Die Titration von Blei mit Sulfat, von Nickel mit Dimethylglyoxim, von Blei mit Dichromat und von Jod mit Thiosulfat wird diskutiert. Angegebene Daten belegen Genauigkeit und Richtigkeit in der Bestimmung anorganischer Sulfate und organischer Schwefelverbindungen.

Résumé—On décrit un appareil pour dosages ampérométriques automatiques. Il utilise une électrode stationnaire de mercure, aussi bien que le système à électrodes de platine couplées. On décrit en détail le dosage des sulfates au moyen de nitrate de plomb. On peut doser des quantités de sulfate aussi faibles que 0,001 millimole. On discute des dosages de plomb au moyen de sulfate, nickel au moyen de diméthylglyoxime, plomb au moyen de bichromate et iode au moyen d'hyposulfite. On présente des données montrant la précision et la justesse dans le cas de sulfates inorganiques et de composés organo-sulfurés.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—II*

CHELATOMETRIC DETERMINATION OF THALLIUM(III) USING AN INDICATION SYSTEM OF TWO PLATINUM ELECTRODES

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(*Received* 30 *June* 1964. *Accepted* 1 *October* 1964)

Summary—Amperometric detection of the end-point, using two identical platinum electrodes at a constant applied potential, has been investigated for the chelatometric determination of thallium(III). It is possible to titrate thallium with 0·005–0·05*M* EDTA solution at an applied potential of 0·2–1·8 V. The optimum pH is 1–2, and in the presence of fluoride ion as a masking agent the determination is then highly selective.

PREVIOUSLY, we have used biamperometric detection of the end-point of a chelatometric titration[1,2] for the determination of iron(III) in the presence of iron(II) in metallurgical materials.[3] Good results have now been obtained for the determination of thallium(III). As in the case of the amperometric determination of iron, unsatisfactory results were obtained from the interpretation of potential-current titration curves. Again it appears that the electrode process differs when the applied potential is changed and when it is kept constant.

In this paper are presented empirical results which enable the elaboration of an analytical procedure for a highly selective and accurate determination of thallium by EDTA biamperometric titration.

EXPERIMENTAL

Reagents

0·05M EDTA solution. Standardised by titration against lead nitrate. A 0·005*M* solution was prepared by suitable dilution.

Standard 0·05M thallium(III) nitrate solution. Prepared by dissolving 44·446 g of $TlNO_3.3H_2O$ in a minimum of water followed by a two-fold evaporation to dryness with 50 ml of *aqua regia*. After addition of a few ml of nitric acid (1:1) to the residue, a solution of thallic salt was obtained and this was diluted to 2000 ml with water. A 0·005*M* solution was prepared by suitable dilution.

1M Buffer solutions. Prepared from 1*M* trichlor- and monochloracetic acids and acetic acid by neutralisation with aqueous ammonia (1:2) under electrometric pH control.

All other solutions were prepared from reagent-grade chemicals and standardised by recommended procedures.

Apparatus

A "dead-stop" instrument was used for the biamperometric titrations with a micro ammeter (0–05 μA) or the current was measured with an electronic polarograph (Polarecord E 261, Metro-ohm, Switzerland). The indicator electrodes were two identical platinum plates (5 × 6 × 0·2 mm). pH was measured with an electronic pH meter (Multoskop V, Lab. potřeby, Prague, Czechslovakia)

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* Part I: see reference 2.

and a glass electrode. The titrations were carried out with an automatic burette (motor-driven hypodermic syringe) reading to ±0·005 ml.

Procedure

To a known amount of thallium(III) nitrate (0·05 or 0·005*M* solution) were added 10 ml of 1*M* buffer solution and a known amount of 1*M* nitric acid, followed by any compound whose influence on the titration was being studied (see later). After dilution to 100 ml the resulting solution was titrated with 0·05 or 0·005*M* EDTA solution at a suitable applied potential. During the titration the solution was stirred with a propeller (1500 rpm). After each addition of the titrant the value of the current was read, stabilisation of the current being practically instantaneous. Quantitative evaluation of the titrations was carried out graphically. All results presented in this paper are an arithmetical mean of three determinations.

RESULTS AND DISCUSSION

Influence of pH

In buffered solutions of pH 1·6–3·8 the pH has no influence on the titration. Titrations at a pH higher than 3·8 showed results which are analytically without value. This is because in this pH range the competitive complex formation of the acetate buffer solutions used influences the measured current (very small current before starting the titration). The titration is even possible in dilute nitric acid solution, but only at a concentration of 25 ml of 1*M* nitric acid/100 ml is the detection of the end-point sufficiently reliable (see Fig. 1). With respect to the selectivity of the determination, which increases with decreasing pH, the titrations were carried out in solutions of pH 1·6 (a buffer solution of 0·1*M* trichloracetic acid partially neutralised with aqeuous ammonia, which has a minimum complex forming ability). A detailed study of all equilibria taking place in the studied system had shown that a minimum error for the chelometric titration of thallium is obtained at pH 1·7.[4]

Influence of applied potential

The applied potential has practically no influence on the amperometric determination of thallium, which was also the case in the amperometric determination of iron with two polarisable platinum electrodes. Fig. 2 shows that the value of the applied potential influences the absolute value of the current in particular stages of the titration. By using a sufficiently sensitive galvanometer it is possible to titrate thallium even at a relatively low applied potential (Fig. 3).

Titration of thallium with 0·005*M* EDTA at various applied potentials is shown in Fig. 4, the optimum course of the titration curve being at an applied potential of 1·2 V, where detection of the equivalence point is very sharp. At a higher applied potential the absolute values of the current are higher, but the relative changes of the current are not so expressive as at a potential of 1·2 V.

Influence of stirring, temperature and question of passivation of electrodes

The course of titration is not influenced by the intensity of stirring if the solution in the neighbourhood of the electrodes is stirred intensively (more than 500 rpm).

Under the described conditions, stabilisation of the current during the titrations proceeds satisfactorily, and formation of the complex of thallium with EDTA is also rapid enough. Temperature does not influence these phenomena and under the described conditions the titration can be carried out at room temperature.

When the titration is repeated many times, no accumulation of solid products of the electrode reaction occurs on the surface of the electrode.

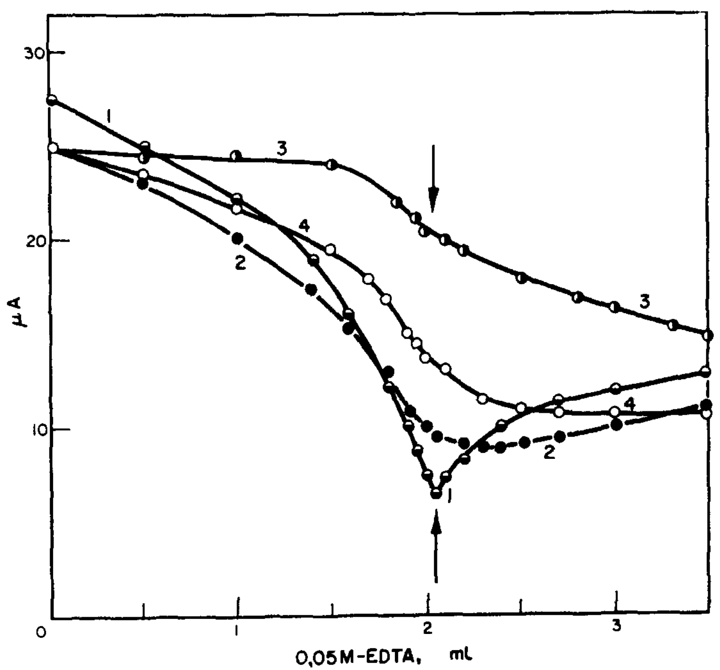

FIG. 1.—Influence of concentration of nitric acid on titration of thallium(III) using 0·05*M* EDTA solution:

1. 25 ml of 1*M* HNO_3; 3. 75 ml of 1*M* HNO_3;
2. 50 ml of 1*M* HNO_3; 4. 100 ml of 1*M* HNO_3.

[2 ml of 0·05*M* $Tl(NO_3)_3$; applied potential: 1·2 V; total volume: 100 ml]

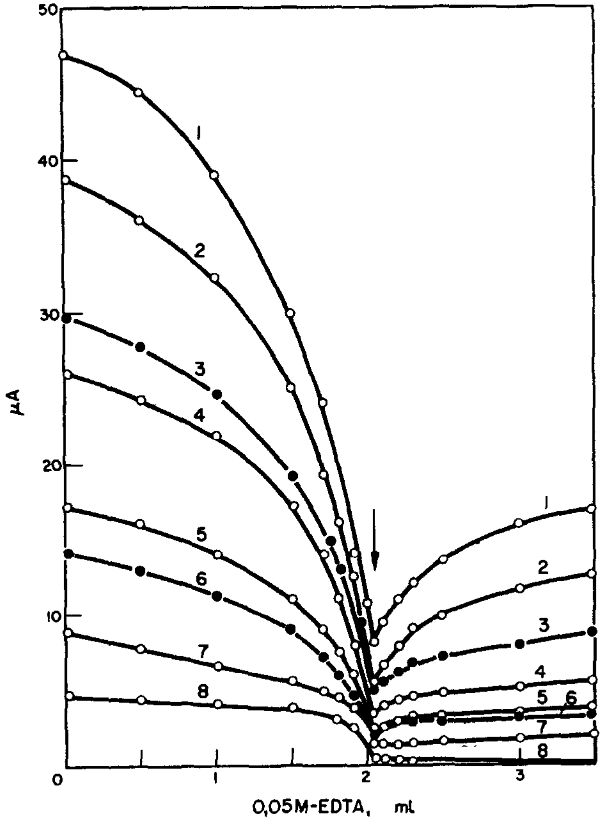

FIG. 2.—Influence of applied potential (0·7–1·5 V) on titration of thallium(III) using 0·05*M* EDTA solution:

1. 1·5 V; 3. 1·3 V; 5. 1·1 V; 7. 0·9 V;
2. 1·4 V; 4. 1·2 V; 6. 1·0 V; 8. 0·7 V.

[2 ml of 0·05*M* $Tl(NO_3)_3$; 10 ml of 1*M* buffer solution (pH 3·1); total volume 100 ml]

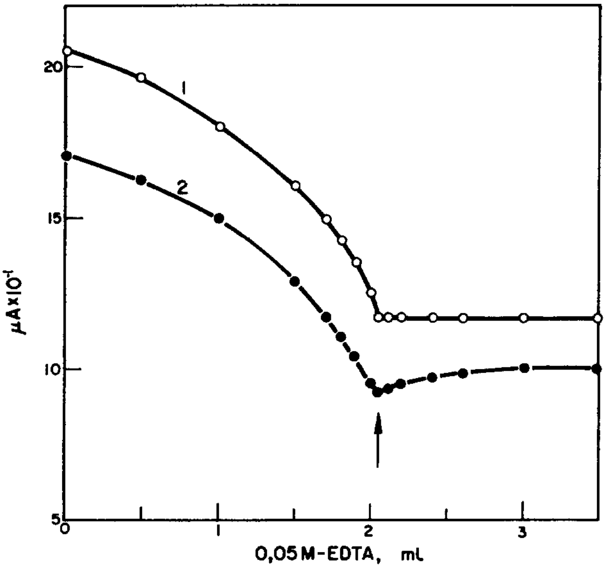

FIG. 3.—Influence of applied potential (0·2–0·4 V) on titration of thallium(III) using 0·05*M* EDTA solution:

1. 0·4 V; 2. 0·2 V.

[2 ml of 0·05*M* Tl(NO$_3$)$_3$; 10 ml of 1*M* buffer solution (pH 3·1); total volume: 100 ml]

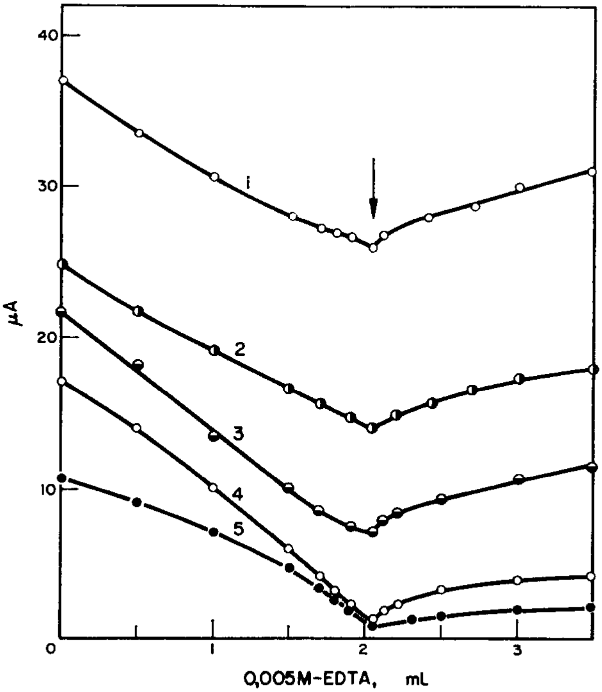

FIG. 4.—Influence of applied potential (1·1–1·8 V) on titration of thallium(III) using 0·005*M* EDTA solution:

1. 1·8 V; 2. 1·6 V; 3. 1·5 V; 4. 1·2 V; 5. 1·1 V.

[2 ml of 0·005*M* Tl(NO$_3$)$_3$; pH: 1·6; total volume: 100 ml]

Sensitivity and accuracy

A series of titrations of thallium (0·5–4·08 mg) was carried out with 0·005*M* EDTA solution at an applied potential of 1·2 V and pH 1·6. The error was found to be 1 % rel. In Fig. 5 are shown the titration curves for the amperometric titration of 5·1–40·8 mg of thallium; the mean error in this case was not greater than 0·3 % rel.

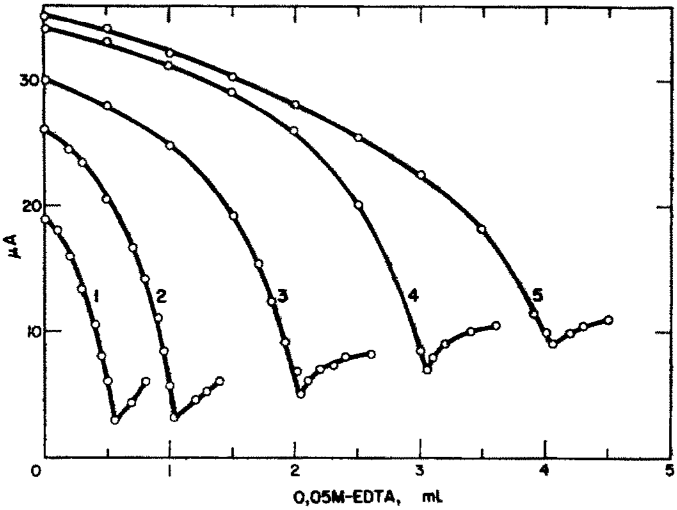

Fig. 5.—Titration of thallium(III) using 0·05*M* EDTA:

1. 5·1 mg of Tl; 2. 10·2 mg of Tl;
3. 20·4 mg of Tl; 4. 30·6 mg of Tl;
5. 40·8 mg of Tl.

[0·5–4 ml of 0·05*M* $Tl(NO_3)_3$; 10 ml of 1*M* buffer solution (pH 1·6); applied potential: 1·2 V; total volume: 100 ml]

Selectivity

The biamperometric determination of thallium is highly selective. Bivalent metals do not interfere with the determination. A series of determinations of thallium (20·4 mg) was made at an applied potential of 1·2 V and pH 1·6 with an error not greater than ±0·5 % rel. These determinations were carried out in the presence of cadmium (560 mg), zinc (650 mg), nickel (230 mg), copper (155 mg), cobalt (160 mg) and uranium(VI) (360 mg). The given amounts of metals are not the maximum possible amounts which do not interfere; they merely illustrate the selectivity of the determination. The following metals and anions do not interfere even in high concentrations: alkali metals, alkaline earth metals, beryllium, manganese, chromium, titanium, silver, nitrate, perchlorate and fluoride. Chloride interferes if present in a concentration greater than 0·1*M*. Bromide and iodide interfere even in small concentrations because they form stable complexes with thallium.

Masking of interfering elements with fluoride ion

The possibility of the determination of thallium in the presence of fluoride ion was used for masking some interfering elements (those which are otherwise simultaneously titrated with EDTA).

Procedure. Thallium(III) (2·04 mg in 100 ml) was titrated with 0·005*M* EDTA solution under optimum conditions (pH 1·6; applied potential 1·2 V). For the screening of interfering elements 10–15 ml of 1*M* sodium fluoride solution/100 ml were used. Any partially soluble fluoride compounds formed with the masked elements do not influence the course of the titration (unlike in a visual EDTA titration).

Under these conditions, for example, thallium (116 mg) was determined in the presence of scandium (110 mg), zirconium (45 mg), lanthanum (70 mg), praseodymium (75 mg), aluminium (130 mg) and tin(IV) (60 mg) with an error ±0·6% rel. Also in this case the given amounts are not the maximum permissible. This problem is being studied in detail and results will be published later.

Determination of thallium in presence of iron

No direct chelometric determination of thallium in the presence of iron has previously been described.[5] In the absence of a masking agent iron is titrated together with thallium. It is well known that the masking of iron with fluoride against EDTA is impossible in an acidic medium. In the case of aluminium masking with fluoride is possible; this phenomenon has been used for the chelometric determination of these two metals.[6] Quantitative precipitation of the anionic fluoride complex of iron(III) as $Na_3Fe_6F_6$ only takes place in solutions containing a great excess of sodium ions.[7] For the formation of FeF_6^{3-} in an acidic medium an excess of fluoride should also be present.

For the screening of 30 mg of iron in the titration of 2·04 mg of thallium, the following procedure gave good results:

To a mixture of the metals 10 ml of 1*M* buffer solution (pH 1·6) were added, followed by 20 ml of 1*M* sodium fluoride solution, the pH of which was previously adjusted to 1·6 with 1*M* nitric acid. After the addition of 5 g of sodium nitrate the solution was diluted to 100 ml. In 5 min the precipitation of Na_3FeF_6 is quantitative and the solution can be titrated with 0·005*M* EDTA solution. The mean error of such a determination is ±0·50% rel.

Influence of gallium and indium

Because these elements are very similar in their chemical properties, their influence on the titration of thallium can be evaluated according to the values of their instability constants with EDTA: $pK_{Ga} = 20{\cdot}3$, $pK_{In} = 24{\cdot}95$ and $pK_{Tl(III)} = 22{\cdot}5$. This shows that indium will interfere even at very small concentrations. On the other hand, in the case of gallium one would expect interference only at a higher concentration.

Experiments have shown that very small quantities of indium are actually titrated together with the thallium(III) by EDTA, and gallium interferes only at higher concentrations. Thallium(III) (2·04 mg) was determined in the presence of a maximum of 17 mg of gallium with an error not exceeding ±1% rel. At a higher concentration of gallium detection of the end-point of the titration is not sharp, and there is a significant positive error.

Analytical application

The biamperometric chelometric titration of thallium with two indicator platinum electrodes is very selective and can be used for the determination of thallium in various materials, including some metals, such as zinc and cadmium, which contain only small amounts of thallium. Procedures for the analysis of individual materials will be published later.

Acknowledgement—The authors wish to express their appreciation to Dr. M. Kopanica for his valuable comments and discussion.

Zusammenfassung—Die Anwendung einer amperometrischen Endpunktbestimmung mittels zweier identischer Platinelektroden bei konstantem Potential in der komplexometrischen Bestimmung von Thallium(III) wurde untersucht. Es ist möglich Thallium mit einer 0,005–0,05*M* EDTA-Lösung und einem angelegten Potential von 0,2–1,8 V zu titrieren. Bei dem optimalen pH 1–2 und in Gegenwart von Fluoridionen ist die Bestimmung sehr selektiv.

Résumé—On a étudié, dans le dosage chélatométrique du thallium(III), la détection ampérométrique du point de virage, en employant deux électrodes de platine identiques, à potentiel appliqué constant. On peut doser le thallium au moyen d'une solution d'EDTA 0,005–0,05*M*, avec un potentiel appliqué de 0,2–1,8 V. Le pH optimal est 1–2, et en présence d'ion fluor agissant comme agent dissimulant, le dosage devient hautement sélectif.

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ANODIC STRIPPING COULOMETRY OF GOLD USING THE GLASSY CARBON ELECTRODE

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Summary—A glassy carbon electrode is used for the anodic stripping coulometric determination of gold; the polishing procedure and the usefulness of the electrode are shown. The effect of chloride ion in the stripping process of gold is discussed.

ANODIC stripping procedures are eminently suitable for the micro determination of metallic ions, because the ions can be collected on the electrode surface before the determination. Because suitable electrode materials have not been found previously, the method could not be applied to the micro determination of noble metals.

While the authors' investigation was in process, Jacobs[1] developed a determination of silver and gold by using a carbon paste electrode.[2] Although this was the first investigation into the determination of noble metals using an anodic stripping method, the electrode is very difficult to produce, and training for several days is necessary to obtain reproducible results. Recently, Yamada and coworkers[3] produced "glassy carbon", which is made from pure carbon and has a very compact surface similar to glass. The hardness is 5–6 (mohs), and the density is about 1·5. It can be polished with chromium(III) oxide emulsion by the same method as is used for the preparation of steel samples for microscopic observation. The polished surface of the glassy carbon electrode is suitable for the deposition of metal, and to obtain reproducible stripping curves.

The effect of anions in the electrolyte is very important in the anodic stripping process of noble metals, but was not mentioned by Jacobs.[1] Because of the high dissolution potentials of the noble metals plated on the electrode, the evolution of oxygen precedes the dissolution of the metals, and the oxidation of water makes it impossible to obtain the dissolution curves. This difficulty can be overcome by the addition to the electrolyte of any anion which decreases the oxidation potentials of metals on the electrode surface.

Micro amounts of gold can be successfully determined by anodic stripping coulometry using the glassy carbon electrode. The determination of micro amounts of silver has not been investigated, here, because this element has already been determined by stripping analysis using a platinum electrode.[4,5]

EXPERIMENTAL

Apparatus

Polarograph. A polarographic instrument produced by Yanagimoto MFG. Co. (Type PA-102) is used to provide the redissolution potential for the plated metal, and for recording the dissolution current. The total resistance of the potentiometer drum of this instrument is 200 Ω and the speed of

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potential change is 200 mV/min. The sensitivity of the recorder was kept at 0·400 μA/mm during this investigation (full scale = 80 μA; input impedance = 5 KΩ).

Electrode. A carbon rod (5 mm diameter and 100 mm long) made glassy by heating at 2000° is used as a working electrode. The sides of the electrode are covered with epoxy resin, and the surface of the end is polished for work with gold. Polishing of the electrode is necessary in order to obtain reproducible results. It is polished first with a series of emery papers of increasing fineness, then with chromium(III) oxide suspension on a rotary table polisher. With this treatment a glossy surface can be obtained. This process is nearly the same as the polishing of samples of steel for microscopic examination, and the electrode surface thus produced gives reproducible results in the determination of gold. Finally, the prepared surface of the electrode is washed with aqueous ammonia, and rinsed thoroughly with water; the electrode is then ready to use. If fatty materials are on the surface of the electrode they must be removed. The electrode can be renewed by washing with *aqua regia*, polishing with chromium(III) oxide and washing with aqueous ammonia.

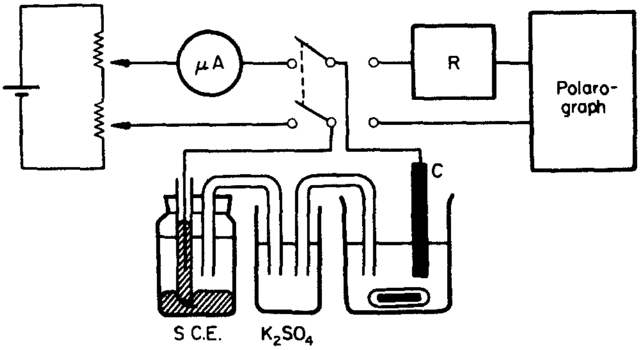

FIG. 1.—Apparatus:
R: recorder,
μA: 100-μA meter,
C: glassy carbon electrode.

The cell is similar to a weighing bottle, and is 35 mm in diameter and 50 mm in height. A magnetic stirrer is used for stirring the electrolyte, and the temperature of the electrolyte is thermostatted to 30°.

A schematic diagram of the apparatus is shown in Fig. 1. The potentiometer-type circuit is conveniently used for the constant potential electro deposition of gold.

Reagents

All chemicals are of reagent grade, and are used without further purification except hydrochloric and nitric acids, which are purified by distillation.

Standard gold solution. Prepared[6] by dissolving a weighed amount of pure gold (99·99%) with *aqua regia*, and evaporating the solution to small volume (not to dryness). Add hydrochloric acid and again evaporate the solution to a small volume; repeat the addition of hydrochloric acid and the evaporation until the solution is free from nitric acid. Dilute the solution with water to a definite volume.

Procedure

Because of the better reproducibility of the results, anodic stripping coulometry is preferable to anodic stripping voltammetry. The following procedure was adopted in the present work.

A known volume of gold solution (containing 1–2 μg of gold) is placed in the cell, and a measured volume of perchloric acid is added. In order to expel chloride, evaporate the solution until it fumes. Cool and dilute with water to 15 ml. Place the cell in the thermostat and connect up the apparatus as shown in Fig. 1.

Electrolyse the solution at constant potential (0·4 V *vs.* S.C.E.). Electrolyse for a definite time, then add 1·5 ml of 0·1*M* hydrochloric acid to the electrolyte. Stop the stirrer, then turn the switch to the position of polarograph, and strip the gold deposit anodically, the potential of the electrode being scanned from 0·5 to 1·3 V *vs.* S.C.E.

A blank experiment must be performed in exactly the same way as above. The areas beneath the curves obtained both by stripping the gold deposit and by the blank experiment are measured with a planimeter.

RESULTS AND DISCUSSION

Electrolyte

In order to investigate the effect of chloride ion in.the electrolyte, perchloric acid was used as the supporting electrolyte. It is also suitable for the analysis of samples containing silver.

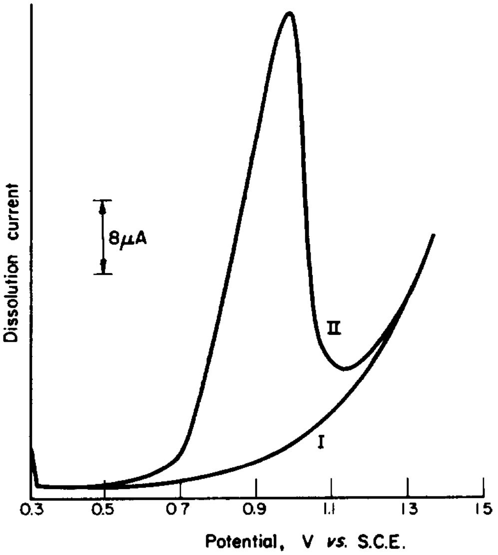

FIG. 2.—Dissolution curve.

The various standard potentials between gold and gold ions are:[7]

$$\mathrm{Au^+ + e \rightleftharpoons Au} \qquad E^\circ = 1{\cdot}68\ \mathrm{V} \qquad (1)$$

$$\mathrm{Au^{3+} + 3e \rightleftharpoons Au} \qquad E^\circ = 1{\cdot}50\ \mathrm{V} \qquad (2)$$

$$\mathrm{AuCl + e \rightleftharpoons Au + Cl^-} \qquad E^\circ = 1{\cdot}17\ \mathrm{V} \qquad (3)$$

$$\mathrm{AuCl_4^- + 3e \rightleftharpoons Au + 4Cl^-} \qquad E^\circ = 1{\cdot}00\ \mathrm{V} \qquad (4)$$

Because the standard oxidation potential of water is 0·45 V lower than E° in reaction (1), and 0·27 V lower than E° in reaction (2), oxygen may be produced on the anode surface before the dissolution of gold, so that gold(I) or gold(III) ions cannot be obtained by the anodic dissolution process. Also, because the standard potentials of reactions (3) and (4) are, respectively, 0·06 V and 0·23 V lower than that of the oxidation of water, the anodic stripping curve will be obtainable in electrolytes containing chloride ion. With the experimental conditions used in Jacob's paper,[1] a considerable amount of chloride ion from the standard solution of gold was contained in the electrolyte.

Preliminary experiments showed that the dissolution curve of gold was not obtained with an electrolyte free from chloride ion and that the curve was similar to that of the blank experiment (curve I in Fig. 2). The effect of the concentrations of chloride ion and of perchloric acid on the dissolution curve of gold are shown in Table I. The form of and hence the area under the dissolution curve are slightly changed by the

TABLE I.—EFFECT OF THE CONCENTRATION OF HYDROCHLORIC AND PERCHLORIC ACIDS IN THE ELECTROLYTE

$HClO_4$, *M*	HCl, *M*	Dissolution curve area, *cm*^{2}
1·0	0·001	10·6
1·0	0·01	27·1
1·0	0·05	25·2
1·0	0·1	22·1
0·5	0·01	30·5
0·1	0·01	17·0

Au: 13·0 μg; time of plating: 60 min.

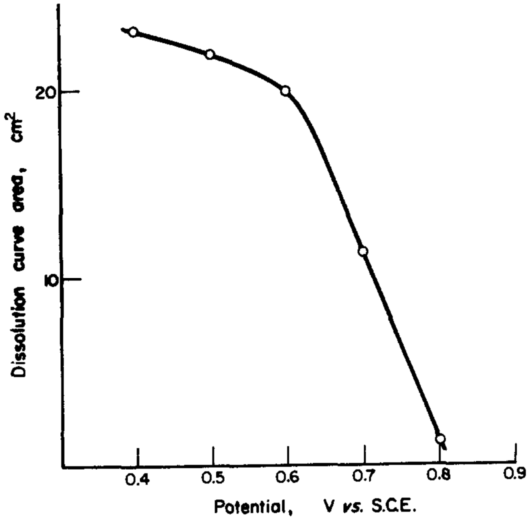

FIG. 3.—Plating potential *vs.* dissolution-curve area.

concentrations of hydrochloric and perchloric acids. The results given in Table I show that the optimum concentrations of hydrochloric and perchloric acids are 0·01*M* and 0·5*M*, respectively.

Plating potential

According to experiments using controlled potential electrolysis for the determination of macro amounts of gold, the value of 0·70 V *vs.* S.C.E. was preferred in 0·7*M* nitric acid media,[8] and 0·60 V in 0·3*M* hydrochloric acid containing 0·14*M* hydroxylamine hydrochloride. For the micro determination of gold, however, the potential should be lowered for successful deposition.[8]

Harrar and Stephens[9] have recently reported that a potential of 0·48 V *vs.* S.C.E. was preferable in 0·5*M* hydrochloric acid solution for the determination of milligram amounts of gold. Fig. 3 shows the dissolution-curve area as a function of the potential of the cathode. From these results, cathode potentials less than 0·6 V *vs.* S.C.E. are suitable for the deposition of gold, so that 0·4 V *vs.* S.C.E. is preferred as the cathode potential in this investigation. The potential should be lowered for the analysis of more dilute solutions.[1]

Time of electrodeposition

The dissolution-curve area depends largely on the time of electrodeposition of gold, and the relation between the area and the time is illustrated in Fig. 4. The curve shows that the electrodeposition of gold on the cathode is not complete even after electrolysis for 6 hr. The deposition time must, therefore, be closely controlled.

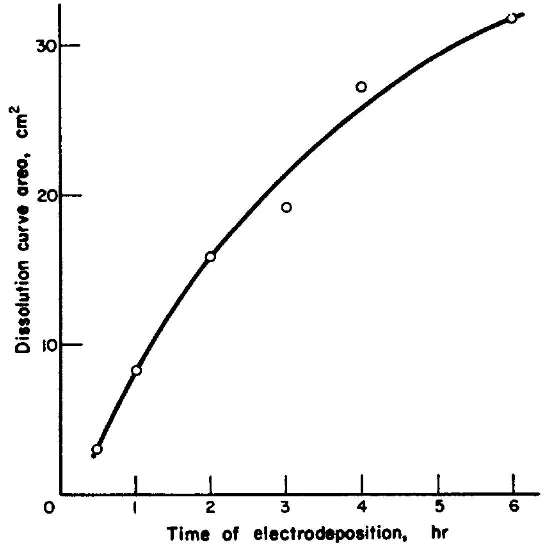

FIG. 4.—Time interval of electrodeposition *vs.* dissolution-curve area.

Recently, Lingane[10] investigated the equilibrium between tetrachlorogold(III) ion and gold in hydrochloric acid media, and proved the reaction

$$AuCl_4^- + 2Au + 2Cl^- \rightleftharpoons 3AuCl_2^-.$$

The number of coulombs calculated from the dissolution-curve area after electrodeposition for 6 hr is, however, larger than that calculated stoichiometrically from reaction (3). Considering the slow rate of the reaction studies by Lingane, it may be supposed that reaction (4) is preferred in this stripping process.

Dissolution-curve area as a function of amount of gold (Calibration curve)

A calibration curve of dissolution-curve area as a function of the amount of gold present in the electrolyte. The following experimental conditions were used: potential of the cathode: 0·4 V *vs.* S.C.E.; concentrations of perchloric acid and hydrochloric acid: 0·5*M* and 0·01*M*, respectively; time of electrodeposition: 2 hr. Other conditions were as used previously. The calibration curve was a straight line, over the range of at least 1 to 10 μg of gold, with a slope of 3·2 $cm^2 \cdot \mu g^{-1}$.

Zusammenfassung—Der Nutzen der glasigen Kohlenstoffelektrode bei der anodischen "stripping"-Coulometrie von Gold wurde gezeigt und der zugehörige Polierprozeß beschrieben. Auch der Einfluß von Chlorid beim "stripping"-Prozeß von Gold wurde diskutiert.

Résumé—On établit la technique de polissage de l'électrode de carbone vitrifié, ainsi que son activité, lorsqu'on l'utilise pour le dosage coulométrique anodique par dissolution de l'or. On discute aussi de l'effet de l'ion chlore sur le processus de dissolution de l'or.

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APPLICATION OF STEADY-STATE CONTROLLED-POTENTIAL COULOMETRY TO THE STUDY OF HOMOGENEOUS SOLUTION REACTIONS*

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Summary—The use of steady-state controlled-potential electrolysis in the investigation of the kinetics of redox reactions has been examined with regard to theory, instrumentation, experimental variables and types of systems amenable to study. The method is precise, allows the evaluation of rate constants over a range of many orders of magnitude to a maximum of about 10^5 mole^{-1}. sec^{-1}, and may be especially useful in the investigation of systems in which one of the reactants is unstable and can be generated at an electrode.

INFORMATION regarding the kinetics of a reaction can be useful in choosing optimum experimental conditions for carrying out that reaction. The application of controlled-potential electrolysis in the investigation of the kinetics of homogeneous solution reactions has been approached through the relationship between kinetic parameters and the apparent extent of oxidation or reduction during electrolysis,[1-4] and the relationship between kinetic parameters and the steady state current obtained during an electrolysis opposed by a chemical regeneration of the electroactive material in the bulk of the solution.[5,6] This paper examines the basic principles and experimental limitations of the latter approach.

THEORY

If a bulk electrolysis is carried out on a substance, A, to yield a product, B, at an electrode whose potential is maintained constant and under limiting current conditions, the current will decay exponentially with time, according to $i = i_0 e^{-\lambda t}$, where i_0 is the current at time zero and λ is a constant depending upon prevailing mass transfer conditions, cell geometry, solution volume, electrode area and stirring.[7]

If, however, the electroactive species, A, is regenerated by a chemical reaction between the electrolysis product and some species, C, in the bulk of the solution ($B + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + D$), the current, after an initial decay, will attain some steady-state value (Fig. 1). This steady-state current, which results when the rates of the electrochemical process and the chemical reactions in the bulk of the solution become equal, can be used to obtain information about the kinetic parameters of the chemical reaction. The relationship between the steady-state current, i_{ss}, and the rate of the

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chemical reaction is shown by the following.

The rate of the electrode reaction is given by

$$\frac{d(A)}{dt} = \lambda(A) = \frac{i}{nFV} \tag{1}$$

where A is the concentration of the electroactive species, i the electrolysis current, n the electron change, F the faraday and V the volume of solution in the electrolysis cell. The rate of the chemical reaction, for simple kinetics, is given by

$$\frac{d(B)}{dt} = -k(B)^x(C)^y \tag{2}$$

If electrolysis is begun with only A and C present, the rate of the electrolysis reaction will decrease as time passes, because of a decrease in the bulk concentration of A, and the rate of the chemical reaction will increase because of an increase in the bulk concentration of B. Eventually, a situation will be reached in which the rates of the two reactions become equal, *i.e.*, $\frac{d(A)}{dt} = \frac{d(B)}{dt}$, and the electrolysis current, now a steady-state current, attains a constant value.

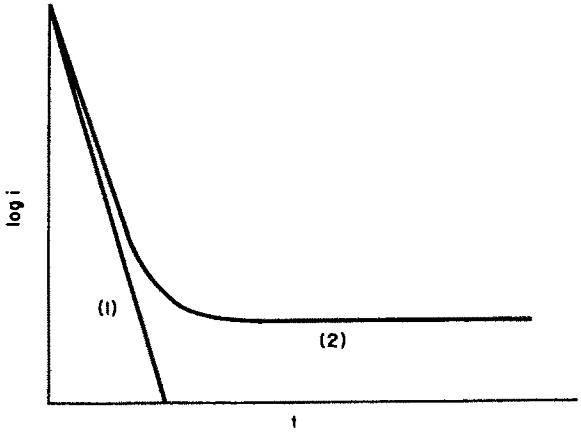

FIG. 1.—Reaction schemes:—

(1) $A \xrightarrow{\pm ne^-} B$

(2) $A \xrightarrow{\pm ne^-} B$; $B + C \rightarrow A + D$

Before steady-state is reached, $\frac{d(B)}{dt}$ is given by

$$\frac{d(B)}{dt} = -k_1(B)^x(C)^y + k_{-1}(A)^m(D)^n + \lambda(A),$$

where k_1 and k_{-1} are the forward and backward rate constants for the chemical reaction taking place in the bulk of the solution. At steady state, $\frac{d(B)}{dt} = 0$, and for a chemical system in which the contribution from the back reaction is negligible, we have

$$k_1(B)^x(C)^y = \lambda(A) \tag{3}$$

and from (1), (2), and (3),

$$\frac{i_{ss}}{nFV} = k_1(B)^x(C)^y = \frac{d(B)}{dt}$$

a relationship between the steady-state current and the rate of the chemical reaction. The effect of the various reactants and products, A, B, C and D, on the rate of the chemical reaction can be tested by varying their steady-state concentrations and observing the corresponding variation in steady-state current.

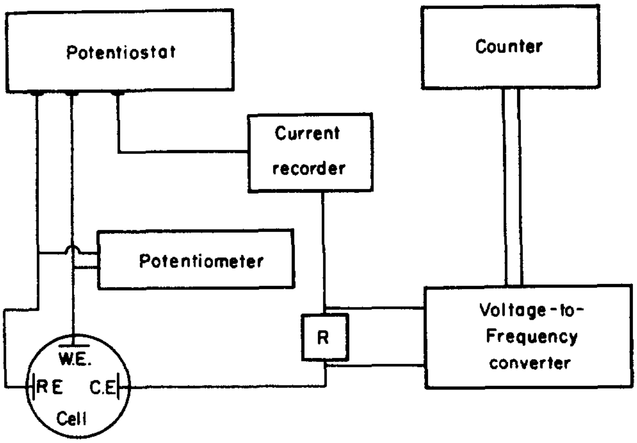

FIG. 2.—Diagrammatic representation of experimental arrangement.

INSTRUMENTATION

A scheme of the type of experimental arrangement used is shown in Fig. 2. A potentiostat is used to maintain the potential of the working electrode constant. The control potential should be monitored with a high-impedance voltmeter so that loss of potential control arising from resistance limitations, for example, can be observed. The electrolysis current may be followed with either an ammeter or a recorder. A recorder is preferred because it shows any spurious change in current which might not otherwise be observed. The recorder resistance should be low in order to minimise *iR* loss in this part of the circuit. The pen speed of the recorder is unimportant except in cases where steady-state is reached very rapidly.

Cell design

An electrolysis cell of the type described by Meites[8] may be used. In the cases where potential control is very important, however, *i.e.*, where potential gradients cannot be tolerated, a cell with maximum symmetry should be used. (The problem of potential gradients has been discussed by Booman and Holbrook,[9] who report potential gradients up to 125 mV at 40 mA across a 4-cm diameter mercury pool electrode with poor working counter electrode geometry.)

For electrolyses in which a high mass transfer coefficient is required (for study of systems in which the chemical reaction is fast), a cell such as that described by Bard[7] may be used. This small volume cell makes use of ultrasonic stirring and has been shown to yield a mass transfer coefficient as high as 0.1 sec^{-1}.

PRACTICAL CONSIDERATIONS

The steady-state concentration of reactants may be estimated from the current-concentration relationship, spectrophotometrically, and/or from the amount of reactant added to the cell.

The steady-state concentration of the electrode product may be estimated from the electrolysis current-electroactive species concentration relationship in the following manner. The electrolysis current is proportional to the concentration of the electroactive species at any time, *i.e.*, $i_t = k'(\mathrm{A})$. The proportionality constant, k', may be determined from $i_0 = k'(\mathrm{A})_0$, where i_0 is the initial current obtained by extrapolation to time zero, and $(\mathrm{A})_0$ is the initial concentration, which is known from the amount of A added to the cell and the cell volume. The concentration of A at steady-state is i_{SS}/k', and, because $(\mathrm{A})_0 = (\mathrm{A})_{\mathrm{SS}} + (\mathrm{B})_{\mathrm{SS}}$ (for the simple case),

$$(\mathrm{B})_{\mathrm{SS}} = (\mathrm{A})_0 - (\mathrm{A})_{\mathrm{SS}} \tag{4}$$

The steady-state concentration of the electrolysis product may in some cases be estimated by direct measurement or by measurement of $(\mathrm{A})_{\mathrm{SS}}$ and relationship (4). For the slow reactions, concentrations can be measured by a sampling technique. For faster reactions, in which the concentrations may change significantly during the time required for sampling and measurement, it may be possible to make use of a flow technique in which the test solution is circulated through a spectrophotometer cell or another type of appropriate detector (NMR, ESR, *etc.*)

The steady-state concentration of other reactants, *e.g.*, C, can be estimated from the amount of C added to the cell, because its concentration is so chosen that it cannot change significantly during the electrolysis.

DISCUSSION

"Steady-state" controlled-potential electrolysis should be applicable to the investigation of the kinetics of any redox reaction which is part of a cycle involving regeneration of the electroactive species by chemical reaction provided that (1) the system meets certain electrochemical requirements, and (2) the rate constant does not exceed a certain value.

The main electrochemical requirement is that only one species be electroactive at the controlled potential. This species, of course, will be that which is regenerated by the chemical reaction in the bulk of the solution. If this condition is not met, species C, which reacts with the electrolysis product B, regenerating A, will also be consumed at the electrode. The electrolysis current will continue to fall as both A and C are consumed, and a steady-state situation will not be reached. When one considers the standard potentials of the redox couples involved in a chemical reaction, it is obvious that, if both couples are reversible, more than one species will be electroactive at the controlled-potential, *i.e.*, if C is capable of oxidising B ($\mathrm{C} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{D}$), the electrolysis product of A, the standard potential of the couple $\mathrm{C} + ne^- \rightarrow \mathrm{D}$ must be more positive than that of $\mathrm{A} + ne^- \rightarrow \mathrm{B}$, so that C will also be reduced at the controlled potential where A is reduced. Thus, it can be seen that the couple involving the species which regenerates the electroactive species must be irreversible. This requirement is obviously a limitation of the number of reactions which can be investigated by the controlled potential electrolysis method, but may be overcome to some extent by masking techniques.

The smallest rate constant which can be investigated by this method is probably limited by the experimenter's ability to distinguish between background and steady-state currents. The maximum rate constant which can be measured is limited by the requirement that there be an initial decay of current before the steady-state is attained.

This condition ensures that the chemical reaction is taking place homogeneously in the bulk of the solution, not just in the region of the electrode surface, and that the current is a measure of the rate of the chemical reaction. This condition may or may not be attainable for a given reaction, depending on mass transfer conditions and reactant concentrations. A large mass transfer coefficient, λ, is desirable when studying fast reactions. With optimum cell geometry and good stirring, λ values as high as $0{\cdot}1\ \mathrm{sec}^{-1}$ can be attained.[7] Reactant concentrations should be such that measurable values of i_0 and i_{ss} are obtained and if a colorimetric method is to be used to measure steady-state concentration, high enough to give a measurable absorbance. Concentrations should also be such that the steady-state concentration does not change significantly, *i.e.*, $> 1\,\%$, during the steady-state measurement. A relationship for the maximum rate constant which can be investigated for a given set of mass transfer and reactant concentrations conditions is given below.

At steady-state for a second order reaction,

$$\frac{i_{ss}}{nFV} = \frac{\mathrm{d(B)}}{\mathrm{d}t} = \frac{\mathrm{d(A)}}{\mathrm{d}t} = \lambda(\mathrm{A}) = k(\mathrm{B})(\mathrm{C})$$

or

$$k = \frac{\lambda(\mathrm{A})}{(\mathrm{B})(\mathrm{C})}\,.$$

Recalling the requirement that the current must decay before steady-state is reached and that this decay be at least 1 % of the initial current,

$$\frac{(\mathrm{A})}{(\mathrm{B})} = \frac{0{\cdot}99(\mathrm{A})_0}{0{\cdot}01(\mathrm{A})_0} = 10^2 \text{ and } k = \frac{\lambda(100)}{(\mathrm{C})}\,.$$

λ and C should be chosen so that the conditions outlined above (measurable current and concentration and no change in concentration during the steady-state measurement) are met. The maximum rate constant which can be investigated by this method is $\simeq 10^5\,M^{-1}.\,\mathrm{sec}^{-1}$, corresponding to a situation where $\lambda = 0{\cdot}1\ \mathrm{sec}^{-1}$, cell volume $= 5$ ml, $n = 1$, $(\mathrm{A})_0 = 10^{-6}\,F$, and $\mathrm{C} = 10^{-4}\,F$. Under these conditions, assuming $i_{ss} = 99\,\%\,i_0$, i_{ss} will be about $50\,\mu\mathrm{A}(nFV\lambda\mathrm{C})$. Steady-state should be reached in about 1 sec $\left(\frac{i}{i_0} = \mathrm{e}^{-0.1t} = \frac{99}{100}\right)$, and (C) should decrease less than 1 % in 10 sec $\left(\frac{\mathrm{d(C)}}{\mathrm{d}t} \times \mathrm{d}t = 10^5 \times 10^{-6} \times 10^{-4} \times 10 = 10^{-6}\right)$.

The method has been shown to give rate constants with a precision of ± 3 %.[10] More rigid control of such variables as cell temperature and reactant concentrations should result in even better precision.

Acknowledgement—The financial support of the Laboratory for Research on the Structure of Matter is gratefully acknowledged.

Zusammenfassung—Theorie, Instrumentierung, experimentelle Variable und Anwendungsbereich der stationären Elektrolyse bei kontrolliertem Potential bei kinetischen Untersuchungen von Redoxreaktionen wurden untersucht. Die Methode ist genau, gestattet die Bestimmung von Geschwindigkeitskonstanten über viele Größenordnungen bis maximal etwa $10^5\ \mathrm{mol}^{-1}.\ \mathrm{sec}^{-1}$ und kann sich besonders nützlich erweisen bei der Untersuchung von Systemen, in denen einer der Reaktanten unbeständig ist und an einer Elektrode erzeugt werden kann.

Résumé—On a examiné l'emploi de l'électrolyse à potentiel contrôlé et régime constant dans les recherches sur la cinétique des réactions redox, aux points de vue théorie, instrumentation, variables expérimentales, et types de systèmes susceptibles d'être étudiés. La méthode est précise, permet l'évaluation des constantes de vitesse dans un très grand domaine d'ordres de grandeur, jusqu'à un maximum d'environ 10^5 mole^{-1}. sec^{-1}, et peut être spécialement utile dans l'étude de systèmes dans lesquels l'un des réactifs est instable et peut être généré à une électrode.

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SELECTIVE SPOT TESTS FOR GLYOXAL, PYRUVIC AND LACTIC ACID

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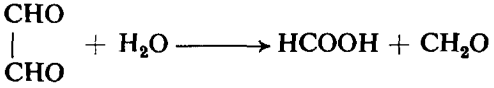
Summary—Glyoxal and pyruvic acid can be transformed, through known condensation reactions with ammonia or β-naphthylamine, into compounds which contain a tertiary nitrogen. These condensation products show the Ohkuma colour reaction when treated with a mixture of acetic anhydride and citric acid. Selective spot tests for glyoxal and pyruvic acid have been developed on this basis. Lactic acid can be detected after oxidative transformation into pyruvic acid.

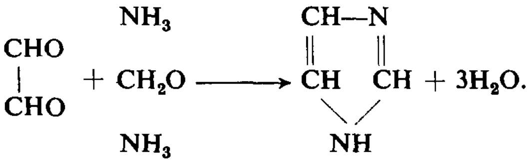
Ohkuma[1] has described a sensitive test for tertiary amines (bases or salts) based on the development of a red, violet or blue colour by heating with a mixture of acetic anhydride and citric acid. The mechanism of this colour reaction is not yet known.

Experiments have shown that the colour test may be used to identify the occurrence of such reactions, leading to the formation of tertiary amines.[2] The participants in the pertinent reactions may thus also be detected. This is illustrated by the tests described here for glyoxal, pyruvic and lactic acid.

Glyoxal combines with ammonia to give the heterocyclic compound glyoxaline (imidazole). The mechanism of the reaction is uncertain; it has been suggested[3] that one molecule of glyoxal breaks down into formic acid and formaldehyde, and the latter, together with ammonia, reacts with glyoxal. The underlying reactions therefore would be:



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array} + H_2O \longrightarrow HCOOH + CH_2O$$



Glyoxaline, being a tertiary amine, gives a positive response to the Ohkuma test. The above transformations thus permit the detection of glyoxal in the absence of tertiary amines (*Procedure* 1).

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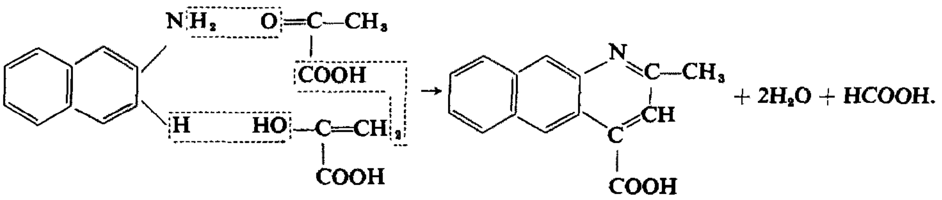
When pyruvic acid is present, a modification of the test is necessary, because this acid, treated with ammonia, yields uvitonic acid,[4] which likewise contains a tertiary nitrogen atom and therefore shows the Ohkuma colour reaction. As described below, pyruvic acid can be detected by a specific test with β-naphthylamine (*Procedure* 2). When this test gives a positive response, and glyoxal is to be detected, use may be made of the fact that in contrast to the ammonium salt of uvitonic acid, the glyoxaline formed is soluble in ether (*Procedure* 3).

Pyruvic acid condenses with β-naphthylamine as follows:[5]



The α-methyl-β-naphthocinchonic acid formed contains a tertiary nitrogen atom, thus showing the Ohkuma colour reaction. The above condensation seems to be specific for pyruvic acid and permits its sensitive detection.

Lactic acid is easily oxidised to pyruvic acid:

$$CH_3CHOHCOOH + [O] \rightarrow CH_3COCOOH + H_2O.$$

It was found that this oxidation, carried out with lead dioxide and followed by the pyruvic acid test, described above, can be applied for the detection of lactic acid (*Procedure* 4) in the absence of pyruvic acid and/or tertiary amines.

Procedure 1: *Detection of glyoxal*

In a micro test-tube 1 drop of the diluted test solution (not more concentrated than 5%) is mixed with 1 drop of conc. ammonia solution, then evaporated to dryness. To the residue a few crystals of citric acid and 2 drops of acetic anhydride are added. The bottom of the tube is then immersed in a water-bath heated to 80–85°. A positive response is indicated by the appearance of a violet colour within 5–10 min. A blank test with the citric acid–acetic anhydride mixture is advisable.

Limit of identification: 1 μg of glyoxal.

Under the conditions described here neither biacetyl nor other 1,2-dioxy compounds react.

Procedure 2: *Detection of pyruvic acid*

In a micro test-tube 1 drop of the test solution is mixed with 1 drop of a 2·5% ethanolic solution of β-naphthylamine. After 10–15 min the mixture is evaporated to dryness, and the residue is heated for 5 min at 120°. The further treatment with acetic anhydride and citric acid is the same as in *Procedure* 1.

Limit of identification: 0·2 μg of pyruvic acid.

Procedure 3: *Detection of glyoxal in the presence of pyruvic acid*

In a micro test-tube 1 drop of the test solution is mixed with 1 drop of conc. ammonia solution, then evaporated to dryness. To the residue some drops of ether are added to extract the glyoxaline formed. After shaking and allowing to stand for some min, the clear ether solution is transferred to another micro test-tube and then evaporated. The further treatment with acetic anhydride and citric acid is the same as in *Procedure* 1.

This method is not only recommended if glyoxal is to be detected in the presence of pyruvic acid, but also when a coloured residue remains after treatment of the sample with ammonia, and subsequent evaporation.

Limit of identification: 10 μg of glyoxal.

Procedure 4: *Detection of lactic acid*

In a micro centrifuge-tube 1 drop of the test solution is mixed with 1 mg of lead dioxide and heated on the water-bath for 15 min. After addition of 3 drops of water and centrifugation, the clear liquid is transferred to a micro test-tube. The remainder of the procedure is the same as in *Procedure* 2.

Limit of identification: 10 μg of lactic acid.

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Zusammenfassung—Glyoxal und Brenztraubensäure können durch bekannte Kondensationsreaktionen mit Ammoniak oder β-Naphthylamin in Verbindungen umgewandelt werden, die ein tertiäres N-Atom enthalten. Diese Kondensationsprodukte zeigen die Ohkuma-Farbreaktion mit einer Mischung von Acetanhydrid und Zitronensäure. Auf dieser Grundlage wurden selektive Tüpfelproben für Glyoxal und Brenztraubensäure entwickelt. Milchsäure kann nach Oxydation zu Brenztraubensäure nachgewiesen werden.

Résumé—On peut transformer le glyoxal et l'acide pyruvique en composés qui renferment un atome d'azote tertiaire, au moyen des réactions de condensation connues avec l'ammoniaque ou la β-naphtylamine. Ces condensats donnent la réaction colorée d'Ohkuma lorsqu'on les traite par un mélange d'anhydride acétique et d'acide citrique. Sur cette base, on a mis au point des essais à la touche sélectifs pour le glyoxal et l'acide pyruvique. On peut déceler l'acide lactique après l'avoir transformé en acide pyruvique par oxydation.

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ANALYSIS OF COLUMN EFFLUENTS BY CONTROLLED-POTENTIAL COULOMETRY

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Summary—A cell for the coulometric analysis of flowing solutions at controlled electrode potentials has been developed and tested. It is shown that it is rapid enough to allow analysis of chromatographic fractions with a half width of 1 min or more. The cell is generally applicable because the counter electrode is separated from the working electrode. Analysis of chromatographic fractions has been performed with a standard deviation of less than 1% for silver and less than 2% for copper.

THE instrumentation and experimental procedure for electrolysis by controlled electrode potential have been refined in recent years.[1,2] The analysis time is usually 10–15 min, but high speed electrolysis cells have also been designed.[3] Controlled potential coulometry should be very useful in analysing column effluents and process streams, provided that the cell response is rapid. This paper is concerned with the development of a cell suitable for analysis of flowing solutions.

Coulson and Cavanagh[4] have described a coulometric titrator for the analysis of chloride in conjunction with gas chromatography. A coulometric titrator for acidic and basic components of a gas stream has been described by Burnett and Klaver.[5] Eckfeldt[6] has described a cell for analysis of flowing solutions. He applied a measured potential between a working gold electrode and a reference electrode. The hold-up volume of the cell was only 1·5 ml and the response was very fast. The content of the cell was electrolysed in about 1 min. The cell described by Eckfeldt is unsuitable for large currents; he usually operated at less than 1 mA. The deviations from the theoretical current were also rather large at high flow rates.

Polarographic analysis of column effluents and process streams has been investigated by several authors[7–11] and cells with very small hold-up volumes have been constructed.[12]

There appears to be no reference in the literature to the application of controlled-potential coulometry in analysing flowing solutions.

EXPERIMENTAL

Apparatus

Coulometer. The general principles, described by Kelley, Jones and Fisher,[2] were followed in the construction of a controlled potential coulometer. However, transistor operational amplifiers (G. A. Philbrick, type P 65A) were used instead of vacuum tube amplifiers. The transistor amplifiers are not very sensitive to variations of the supply voltages so a simple zener stabilisation of the power supply could be used. In this way the construction is greatly simplified and the apparatus is smaller and less costly. The performance is comparable to that of the vacuum tube counterpart; 500 mA could be delivered at 30 V and up to 1 A at lower output voltages.

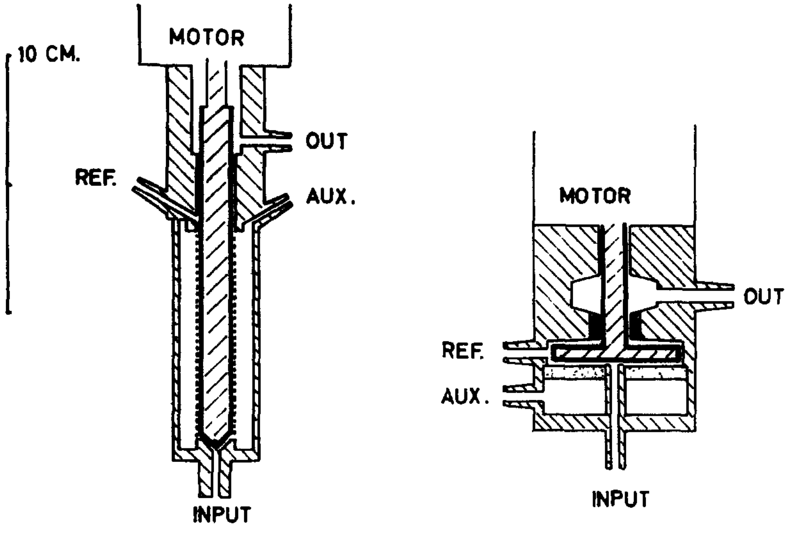
The voltage developed over a standard resistor in series with the cell is a measure of the current and thus of the concentration of electroactive species in the cell. The current was continuously monitored by a recorder. The number of coulombs consumed in the cell reaction was determined by integration of the current, using an integrator made according to the description given by Booman[1] and by Kelley, Jones and Fisher.[2]

Cells

For a reaction limited by the rate of mass transfer to the electrode the electrolysis current decays[3] according to

$$i_t = i_0 e^{-pt} \tag{1}$$

$$p = f(A, 1/V, m) \tag{2}$$



CELL 2 CELL 3

FIG. 1.—Sections showing *Cell* 2 and *Cell* 3:

········	dialysis tubing,	▨	platinum,
□	sintered glass,	▧	perspex.

where i_t is the current at time t, i_0 the initial current, V is the solution volume, A is the electrode area and m is a mass transfer constant with units of cm. sec^{-1}. A high value of the constant p indicates a high speed of the electrolysis. Several cells have been constructed in order to get a cell with a large p-value.

Cell 1. Platinum gauze was tightly packed in a Teflon tube into which the reference electrode and the auxiliary electrode protruded. The area to volume ratio of this cell was very large. The size of the mass transfer constant, m, was dependent on the flow rate, being mainly determined by diffusion at low flow rates. At practical flow rates, about 1 ml/min, it was found that only 1–3 % of the eluted fractions were electrolysed.

Cell 2. A platinised rotating cylinder constituted the working electrode. The auxiliary electrode was separated from the flowing solution by a dialysis tube slightly larger than the rotating electrode. A schematic drawing of the cell is shown in Fig. 1.

This cell was more efficient than *Cell* 1; at 1 ml/min, 4–6% of the electroactive species were electrolysed in the cell. Both the rotating electrode and the dialysis tubing had low-friction surfaces. The diameter of the rotating electrode was rather small, giving a low linear speed. These effects combined to give a low mass transfer rate.

Cell 3. A rotating platinum disc was used in the next cell (Fig. 1). The auxiliary electrode was separated from the flowing solution by a sintered glass disc. At 1 ml/min about 50% of the eluted fraction was electrolysed by this cell. The improvement is caused by the higher linear speed at the disc periphery and by the turbulence caused by the rough surface of the sintered glass disc.

Cell 4. This cell was similar to *Cell* 3 except that the solid platinum surfaces were replaced by several discs made from platinum gauze. This increased the efficiency to a practical value. A detailed drawing of the cell is shown in Fig. 2 and a description is given below. The results presented in the following are all obtained by this cell unless otherwise stated.

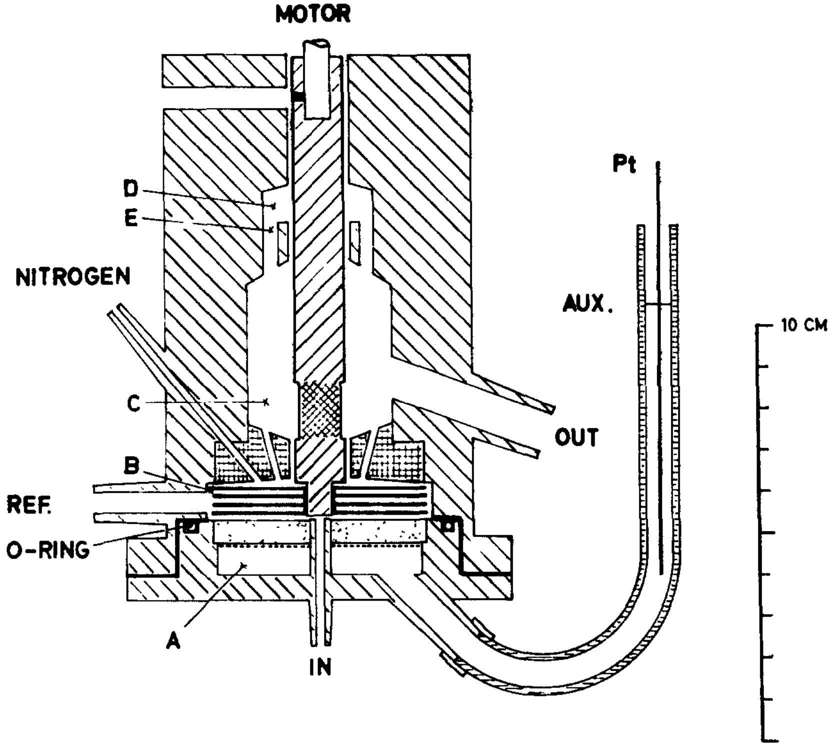


FIG. 2.—Section of *Cell* 4:

······ dialysis tubing,
⬚ sintered glass,
☐ perspex,
▨ bakelite,
▦ nylon,
▩ platinum gauze,
▤ glass.

The main body of the cell was made from solid Perspex (methacrylate), into which a nylon disc was pressfitted. The auxiliary electrode forms the bottom of the cell. The auxiliary and working electrodes are separated by a sintered glass disc glued into the perspex. All seals were made with glue except the connection between the main body and the auxiliary electrode, which was sealed by an O-ring. It would be of advantage to make the bottom from a more heat-resistant material than perspex if agar-agar gel is settled by heating the cell.

The rotating electrode consisted of 3 or 4 platinum gauze discs (0·1 mm wires, 0·5 mm apart), separated by 1-mm platinum rings and fastened to a bakelite axis connected to the motor axis. The motor speed was 2600 rpm. Electrical connection to the rotating electrode was made by a mercury contact at the top of the motor and the motor axis was connected to the platinum gauze by a platinum wire inside the bakelite axis. A post electrolyser gauze was wound on the axis at a height corresponding to the bottom of chamber C.

The rotation of the inner electrode causes a strong pressure towards the periphery of the cell.

All gas bubbles are removed from the periphery and an empty space is formed in the centre. The volume contained in a working cell, 19 ml, is, thus, somewhat smaller than the geometrical volume. The reference electrodes must be able to withstand the pressure; commercial saturated calomel electrodes with asbestos plugs in the tip have been found to be adequate.

The bottom of the electrolysis chamber, B, was made from a sintered glass disc of medium porosity. A dialysis tube was cut open and glued to the back of the sintered glass disc. The auxiliary electrode chamber was then filled with agar-agar gel or silicic acid gel up to near the auxiliary platinum electrode. This arrangement prevented the flowing solution from being pressed into the auxiliary electrode chamber. The gel, especially the narrow connection to the side tube, is responsible for most of the IR-drop of the cell. The resistance of the cell is about 200–400 Ω. A small stream of nitrogen can be introduced into the cell during reduction to displace the oxygen in the cell, but the purging of the column effluent must be arranged externally.

The liquid introduced into the cell through the input in the centre of the sintered glass disc is mixed with the solution in chamber B. Excess liquid is drained up into the drain chamber C. Any splashings in this chamber are returned except that which goes along the axis. To prevent this liquid from passing into the motor a trap, D, is made which empties back to C through two holes, E. When a few ml of liquid have been collected in chamber C, it will drain through the outlet.

The cell was cleaned occasionally in nitric acid; 10–25 analyses could be made before cleaning was necessary.

RESULTS

Rate of electrolysis

In order to get a measure of the efficiency of the cells the procedure given by Bard[3] was followed. A solution of copper sulphate was placed in the cell and the coulometer switched on. The reduction was performed at −500 mV *versus* S.C.E. in a medium of sodium sulphate. The current-time curve was recorded. Log current was then plotted *versus* time to yield an almost straight line. From the slope of this line the value of p in equations (1) and (2) may be calculated. For *Cell* 3 the p-values ranged between 0·014 $\sec^{-1}$ and 0·026 $\sec^{-1}$; *Cell* 4 gave p-values between 0·10 $\sec^{-1}$ and up to 0·18 $\sec^{-1}$. These values can be compared to that of about 0·1 $\sec.^{-1}$ found by Bard for a cell using nitrogen and ultrasonic stirring. The cell described by Eckfeldt[6] had a speed similar to that described by Bard.

Output concentration

The input stream will be mixed with the liquid in the cell in such a way that most of the electrolysis will occur at the lowest platinum gauze disc. The other discs will then be responsible for less and less of the total electrolysis. This behaviour may be visualised if a fraction of copper sulphate is passed through the cell and the copper plating on the bright platinum is inspected. The mixing between chamber B and chamber C is rather low. A post-electrolyser gauze placed in the drain chamber C will thus further reduce the output concentration of electroactive substance. It is difficult to measure the efficiency of this gauze because of the spread in p-values, but a slight plating of copper indicates that some electrolysis will take place at the gauze.

In order to determine the concentration in the drain the flow rate is varied while the amount of copper(II) ion introduced into the cell per second is kept constant ($1{\cdot}5 \times 10^{-7}$ mole/sec). The concentration of copper(II) in the drain is measured spectrophotometrically by the diethyldithiocarbamate method. The results show that the percentage of unreduced copper(II) is linearly dependent upon the flow rate. At flow rates lower than 1 ml/min, less than 0·5% will pass the cell unreduced; at a rate of 10 ml/min, 5% will pass the cell unreduced.

The percentage recovery of chromatographic fractions containing about 120 μmole of silver nitrate was determined as a function of the flow rate. A linear relationship was found with 100% recovery for zero flow rate and 94% recovery at a rate of 10 ml/min.

Both the silver and copper were reduced at —500 mV *versus* S.C.E. in a slightly acid 0·5*M* sodium sulphate medium.

Analysis of chromatographic fractions

Samples of copper(II) sulphate and silver nitrate were put on a 15-cm long column made from an inert material (fire brick of 35 mesh). In this way an elution curve of correct form and short retention time was obtained. The results are shown in Table I.

TABLE I.—REDUCTION OF A CHROMATOGRAPHIC FRACTION PASSING THE CELL AT A FLOW RATE OF 0·8 ML/MIN.

Substance	Found, *μmole*	Recovery, %	Mean value, %
Cu^{2+}	153·1	102·0	
	153·8	102·5	
	147·2	98·2	100·9
Cu^{2+}	75·1	100·1	
	74·9	99·9	100·0
Ag^{+}	150·3	100·2	
	147·9	98·6	
	150·1	100·1	
	149·2	99·5	
	150·8	100·5	99·8

The reduction was performed at —500 mV *versus* S.C.E. in a medium 0·5*M* in sodium sulphate and 0·2*M* in sulphuric acid. A recording of the current when two fractions pass the cell is shown in Fig. 3.

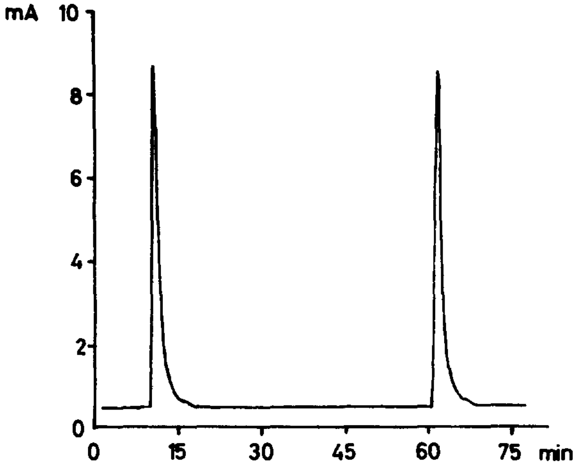


FIG. 3.—Recordings of the current when two consecutive fractions, each containing 12 μmole of silver, are passed through the cell.

Stripping analysis

In order to investigate the possibility of analysing very dilute process streams, amounts of copper(II) varying between 6 and 150 μmole were diluted to 1000 ml. The solution was passed through the cell at 9·5 ml/min. The reduction was performed at

-600 mV *versus* S.C.E. in the same medium as above. Direct measurement of the number of coulombs required for reduction is not feasible because the background current is larger than the Faradaic current. Instead, the deposited copper was reoxidised at -10 mV *versus* S.C.E. The number of coulombs required for the reoxidation was measured and the results are shown in Table II. At this flow rate some of the copper will pass the cell unreduced. A correction is taken from a graph of percentage of copper passing through the cell unreduced as a function of the flow rate, and added to the measured value. The accuracy is less than for the direct analysis of more concentrated chromatographic peaks, but the results demonstrate that the cell will operate satisfactorily down to very dilute concentrations.

TABLE II.—REOXIDATION OF COPPER DEPOSITED FROM 1000 ML OF SOLUTION

Copper taken,			Corrected
μmole	*μg/ml*	Recovery, %	recovery, %
150	9·54	98·4	103·2
45	2·86	92·8	97·6
6	0·37	83·3	88·1

Background current

The magnitude of the background current depends on the acidity of the medium, the amount of impurities in the electrolyte and on the reduction potential. The background current was integrated for some time after each analysis. A correction was computed and subtracted from the total integral. This correction, usually less than 10%, is one of the main sources of error in this type of analysis.

In some cases a bucking voltage was applied in series with the integrator input, and it was adjusted so that the integrator input was zero just before the chromatographic fraction arrived at the cell. This procedure eliminated the calculation of a correction.

Distortion of peaks

All cells which have limited response time will cause distortion of chromatographic peaks. The magnitude of this distortion may be calculated in the following way.

A peak of the shape $\Phi(t)$ is introduced into the cell volume ω at a flow rate of n ml/sec. The substance in the cell is removed by electrolysis at a rate of $y \cdot p$, where y is the cell concentration, and p and t are defined by equations (1) and (2). If the amount of substance lost through the drain is neglected, the change in cell concentration is

$$\frac{dy}{dt} = \Phi(t)\frac{n}{\omega} - y \cdot p \qquad (3)$$

This equation is similar to that derived by Vandenheuvel[13] for the effect of post-column dead space. Equation (3) was solved for $\Phi(t)$ equal to the normal distribution function. The maximum of the function y, will occur later than the maximum of $\Phi(t)$. This delay or error in retention time was calculated as a percentage of the half bandwidth, a, of the elution curve $\Phi(t)$ and plotted *versus* the half width in Fig. 4. The maximum height of the y-function is lower than the maximum of $\Phi(t)$. The difference is calculated as a percentage of the maximum height of $\Phi(t)$ and also plotted *versus* *a* in Fig. 4. From the graph it is seen that the error in most cases can be neglected if *a* is about 1 min, *i.e.*, if the chromatographic peak is eluted in 2 min or longer time.

DISCUSSION

Bard[3] found that the plots of log current *versus* time were non-linear near zero time, indicating a more rapid electrolysis at the start. The cell used in the present investigation yielded log current-time plots which were usually linear over the whole range. On the other hand, the slope of lines from different runs were scattered over a wide range. For a given substance the slope depends on the medium and the applied potential. The speed of the electrolyses at different potentials is well pictured by the polarographic wave. A high diffusion current corresponds to a high speed electrolysis. Thus, it should be advantageous to operate at high potentials. A compromise must, however, be found because high potentials will give rise to large background currents.

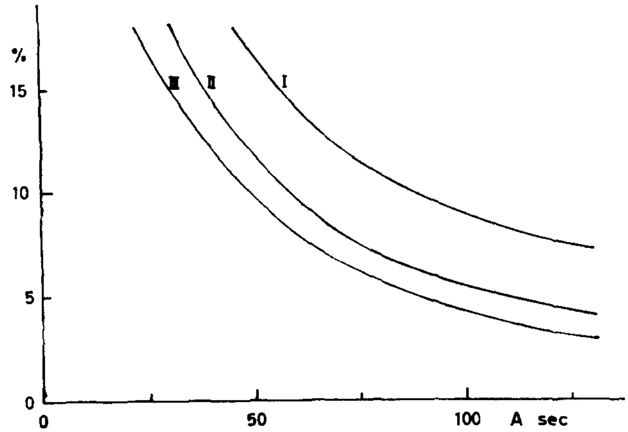


Fig. 4.—Relative increase in retention time and relative decrease in peak height plotted versus the half peak width (*a*):

I Relative increase in retention time for p = 0·1.
II Relative decrease in peak height for p = 0·2.
III Relative increase in retention time for p = 0·2.

The accuracy which can be obtained by use of this coulometric cell compares favourably with that of polarographic methods and also with the accuracy obtained by Eckfeldt.[6] The flow sensitivity is rather low and there is no temperature dependence. The accuracy is, however, much less than that obtained in ordinary coulometric analysis. The main source of error is the correction for the background current. If all the substance had been in the cell at the start the analysis would have been completed in about 1 min, but the chromatographic peak will last for much longer time, perhaps 10–15 min. This length of time will give rise to a background current correction which may exceed 10% of the measured integral. The background current may be reduced by purification of the solvent. Even *pro analysi* quality electrolytes contain sufficient quantities of reducible substances to cause a significant increase in the background current. The amount of oxidisable substances is usually smaller.

Errors may also arise because some substance is lost in the drain. Usually the flow rate is known approximately, and it is then possible to calculate a correction. There may still be some uncertainty, of course, but this source of error is easier to control than the error in the background correction.

The diaphragm cell described in this paper is generally applicable. In some cases the counter electrode can be kept in the same solution as the working electrode, which simplifies the construction because the bottom of the electrolysis chamber can be made from the counter electrode material. The resistance of such a simplified cell will be very low.

The supporting electrolyte can often be present in the column effluent. When this is impossible, the electrolyte can be added via a T-junction at the cell inlet.

Acknowledgement—The author thanks Professor K. J. Karrman for his advice and interest. This work was supported by grants from the Swedish Technical Research Council.

Zusammenfassung—Eine Zelle zur coulometrischen Analyse strömende Lösungen bei kontrollierten Elektrodenpotentialen wurde entwickelt und geprüft. Es wird gezeigt, daß sie schnell genug arbeitet, um die Analyse chromatographischer Fraktionen mit einer Halbwertsbreite von einer Minute und darüber zu ermöglichen. Die Zelle ist allgemein anwendbar, da die Gegenelektrode räumlich von der Arbeitselektrode getrennt ist. Die Analyse von chromatographischen Fraktionen wurde durchgeführt und ergab eine Standardabweichung von weniger als 1% für Silber und weniger als 2% für Kupfer.

Résumé—On a élaboré et expérimenté une cellule pour l'analyse de solutions en mouvement par coulométrie à potentiel d'électrode contrôlé. On montre qu'elle est suffisamment rapide pour permettre l'analyse de fractions chromatographiques. La cellule est d'une application générale car la contre-électrode est séparée de l'électrode de travail. On a effectué l'analyse de fractions chromatographiques avec un écart type inférieur à 1% pour l'argent et à 2% pour le cuivre.

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ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—III*

EINFLUSS DES ALKOHOL-WASSER-VERHÄLTNISSES AUF DEN SORPTIONSVORGANG

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Zusammenfassung—Bei der Untersuchung von wasserhaltigen Alkoholen [Methanol, Äthanol, Propanol-(1), Propanol-(2), Butanol-(1)] konnte festgestellt werden, daß durch trockene Cellulose Wasser aus den Lösungen aufgenommen wird. Beim wasserarmen Methanol wird allerdings bevorzugt der Alkohol gebunden. Durch Adsorptionsversuche über die Gasphase konnte gezeigt werden, daß je nach Alkoholart und Wassergehalt verschiedene Mengen der beiden Komponenten von der Cellulose adsorbiert werden. Zwischen dem Molekulargewicht (bzw. der Dielektrizitätskonstanten) und der von der Cellulose adsorbierten Menge Alkohol bestehen enge Beziehungen. Die Versuche bestätigen, daß am Aufbau der stationären Phase alle Komponenten des Fließmittels beteiligt sind.

IN der 2. Mitteilung[1] war bei der Untersuchung des Verhaltens verschiedener Alkohole gegenüber Cellulosepulver mit unterschiedlichem Wassergehalt die Vermutung geäußert worden, daß bei gegebenem Wassergehalt der Cellulose die Zusammensetzung der flüssigen Phase entscheidet in welchem Umfang Wasser bzw. Alkohol von der Cellulose gebunden wird.

Die folgenden Versuchsreihen sollten der weiteren Aufklärung dieses Vorganges dienen.

EINFLUSS DES ALKOHOL-WASSER-VERHÄLTNISSES

Versuchsanordnung

Für die Versuche wurden die früher[1] beschriebenen Säulen verwendet. Das benutzte Cellulosepulver (Whatman Standard Grade) war bei 110° getrocknet worden.

Den Wassergehalt der Lösungen bestimmten wir wieder durch Titration mit Karl-Fischer-Lösung.

Die untersuchten Alkohol-Wasser-Gemische sind in Tabelle I zusammengestellt.

In den Abbildungen 1–5 sind die Elutionskurven von einigen der untersuchten Mischungen dargestellt. Die Diagramme selbst lassen allerdings untereinander nur einen halbquantitativen Vergleich zu, da die Titer der verwendeten Karl-Fischer-Lösung etwas unterschiedlich waren.

Wie die Abbildung 1 zeigt, wird aus allen Mischungen mit einem Wassergehalt

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* I. und II. Mitteilung siehe Literatur.

TABELLE I.—ZUSAMMENSETZUNG DER UNTERSUCHTEN ALKOHOL-WASSER-GEMISCHE

Nr. der Kurve in der Abb.	Wassergehalt in %				
	Methanol	Äthanol	Propanol-(1)	Propanol-(2)	Butanol-(1)
1	0,73	0,65	1,02	0,94	1,16
2	3,09	1,13	3,03	3,04	2,87
3	4,35	2,78	5,27	3,65	5,84
4	5,54	3,88	7,79	6,29	7,76
5	8,78	5,52			
6	11,88				
	1,31	7,06	12,02	10,77	4,28
		10,46			11,70

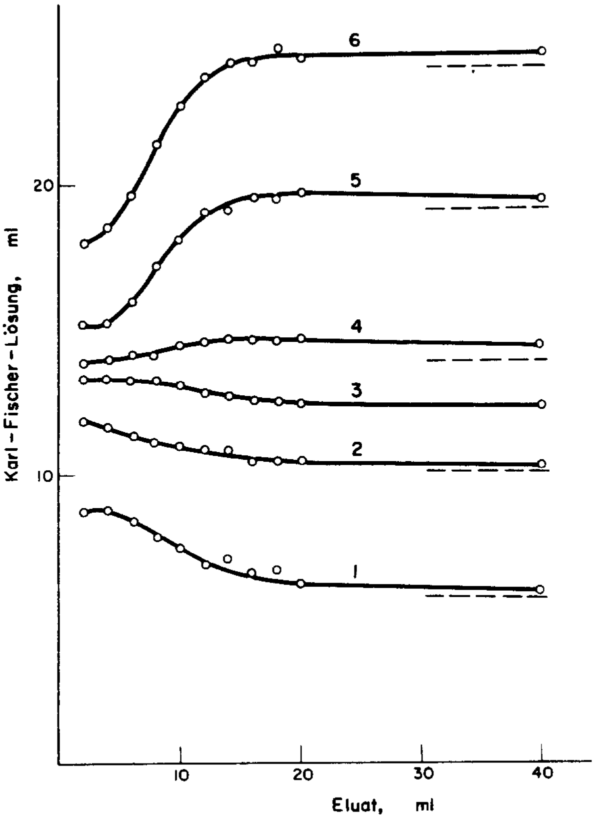

ABB. 1.—Änderung des Wassergehalts im Filtrat: System Methanol-Wasser.

von <5% (Kurven 1–3) von der trockenen Cellulose bevorzugt Methanol aufgenommen. Bei höherem Wassergehalt und bei allen anderen geprüften Gemischen (Abb. 2–5) wird—in Übereinstimmung mit der bisher üblichen Vorstellung über den Aufbau der stationären Phase—in erster Linie Wasser von der Cellulose bis zu einem Gleichgewichtszustand gebunden.

Aus den erhaltenen Meßwerten läßt sich berechnen, wieviel Gramm Wasser von den 35 g Cellulosepulver bis zur Einstellung des Gleichgewichts gebunden werden. Die Ergebnisse sind in Abbildung 6 graphisch dargestellt.

Das Diagramm läßt eine praktisch lineare Abhängigkeit zwischen dem Wassergehalt der verwendeten Alkohole und der von der trockenen Cellulose gebundenen Wassermenge erkennen. Da man aber annehmen muß, daß die von der Cellulose festgehaltene Flüssigkeitsmenge (= stationäre Phase) zumindest bei ein- und demselben Alkohol etwa gleich ist, muß man wohl auch diese Meßergebnisse als Bestätigung für den komplexen Aufbau der stationären Phase ansehen. Nach der unterschiedlichen Steilheit zu schließen, nimmt dabei der Alkoholgehalt der stationären Phase mit steigendem Molekulargewicht der Alkohole ab.

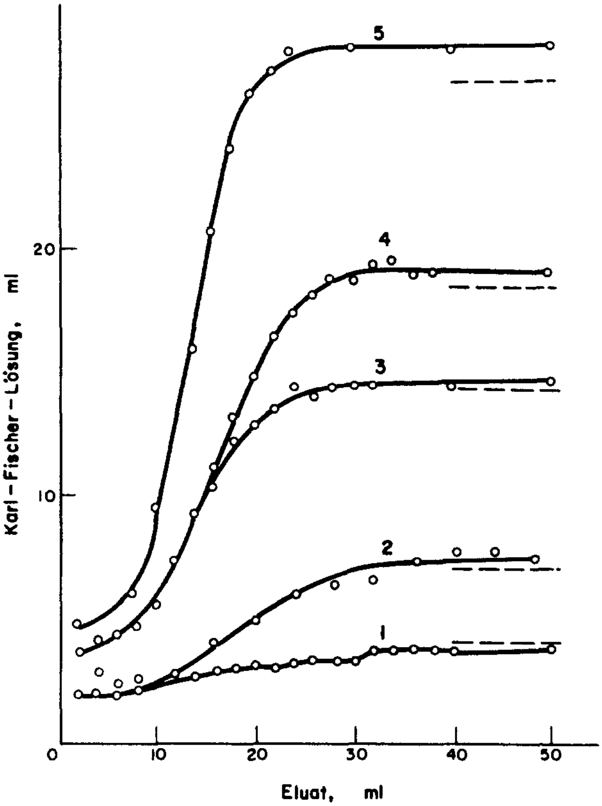

ABB. 2.—Änderung des Wassergehalts im Filtrat System Äthanol-Wasser.

Die Abbildung zeigt auch, daß das Methanol keine Sonderstellung einnimmt. Wenigstens beim Äthanol ist bei sehr geringem Wassergehalt noch eine bevorzugte Aufnahme des Alkohols zu erwarten. Allerdings ist für den Beweis dieser Annahme wegen der Hygroskopizität der Cellulose ein ziemlich hoher experimenteller Aufwand erforderlich, der sich in vorliegendem Zusammenhang nicht lohnt.

Wie das Bild noch erwarten läßt, müssen Alkohol-Wasser-Mischungen, die auf einer Parallele zur Abszisse liegen an Cellulosepulver mit gleichem Wassergehalt auch die gleiche Wassermenge abgeben.

Um diese Feststellung zu überprüfen, wurden Säulen, die mit lufttrockener—d.h. noch wasserhaltiger—Cellulose gefüllt waren, mit Mischungen von Äthanol, Propanol-(1), Propanol-(2) und Butanol-(1) behandelt. Der Wassergehalt der

Gemische und die bis zur Einstellung des Gleichgewichts vom Cellulosepulver aufgenommene Wassermenge sind in Tabelle II enthalten.

Wie die Übersicht zeigt, liegen die gefundenen Werte so dicht beieinander, daß man wohl auch diese Ergebnisse als Bestätigung der aufgestellten Arbeitshypothese ansehen kann.

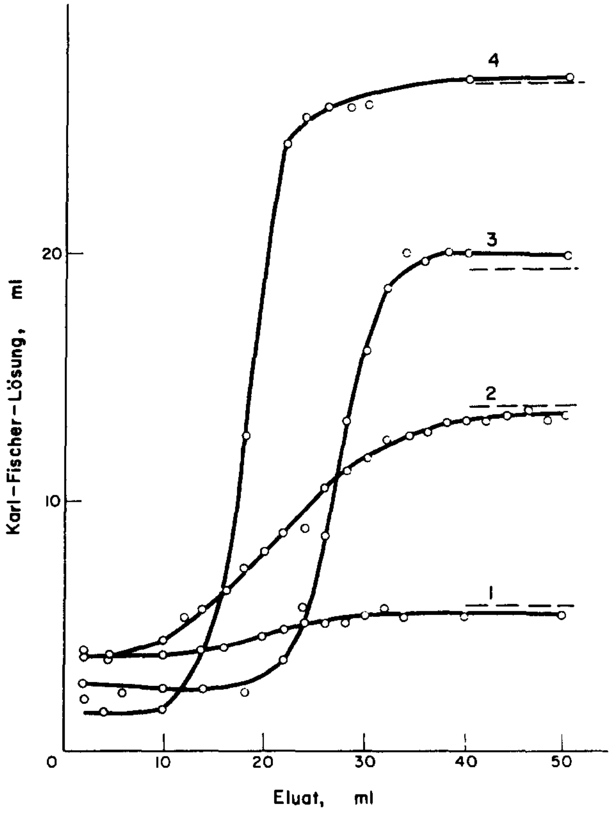

ABB. 3.—Änderung des Wassergehalts im Filtrat: System Propanol-(1)-Wasser.

SORPTION VON ALKOHOL UND WASSER AUS DER GASPHASE

Es war nun interessant einmal zu prüfen, wie sich Cellulosepulver verhält, das nur den Lösungsmitteldämpfen ausgesetzt worden ist. Von den papierchromatographischen Trennungen her ist doch bekannt, daß mit Fließmitteldämpfen gesättigtes Papier oft andere (bessere) Trennergebnisse liefert als unbehandeltes.

Da eine exakte Analyse der Zusammensetzung des Dampfraumes nicht durchgeführt worden ist, können die zu beschreibenden Versuche natürlich nur qualitativen Charakter haben.

Die für die Versuche angewandten Alkohol-Wasser-Gemische hatten folgende Zusammensetzung:

Methanol	0,94% H_2O	Propanol-(2)	1,75% H_2O
Äthanol	6,88% H_2O	Butanol-(1)	0,36% H_2O
Propanol-(1)	0,95% H_2O	Butanol-(2)	1,17% H_2O

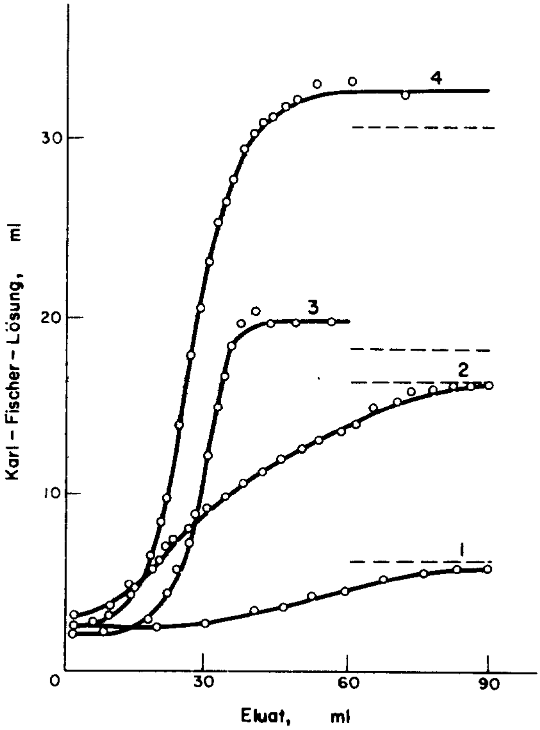

Abb. 4.—Änderung des Wassergehalts im Filtrat: System Propanol-(2)-Wasser.

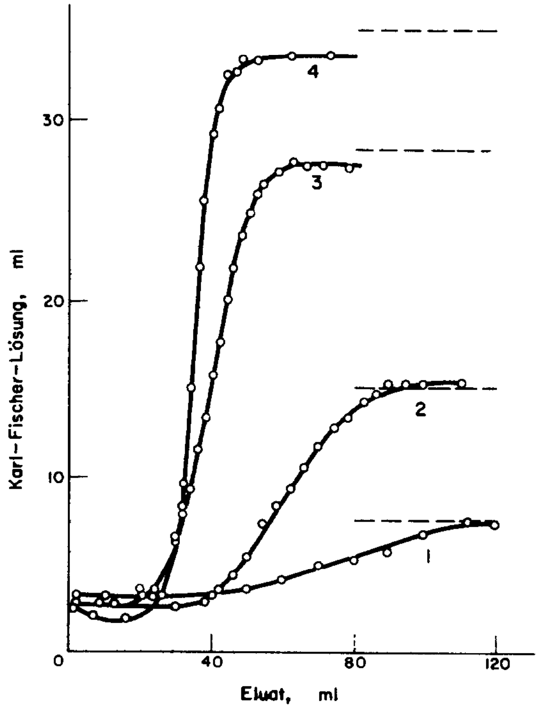

Abb. 5.—Änderung des Wassergehalts im Filtrat: System Butanol-(1)-Wasser.

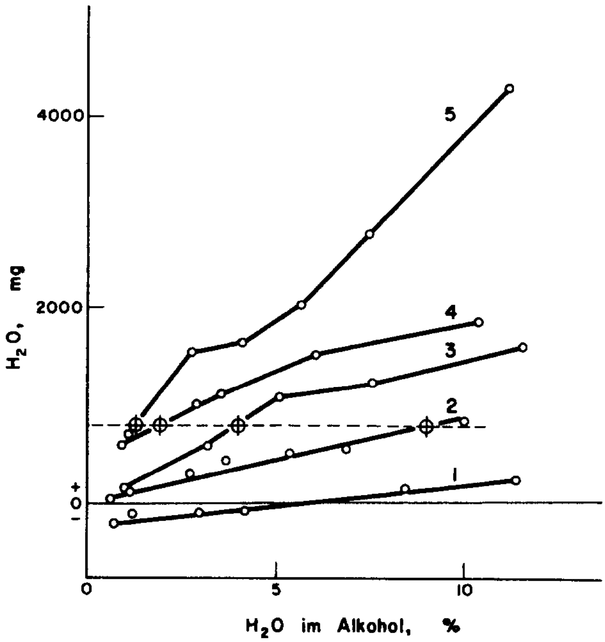

ABB. 6.—Abhängigkeit der von der Cellulose gebundenen Wassermenge vom Wassergehalt der Alkohole:

Kurve 1: Methanol,
Kurve 2: Äthanol,
Kurve 3: Propanol-(1),
Kurve 4: Propanol-(2),
Kurve 5: Butanol-(1).

TABELLE II.—WASSERABGABE VON ALKOHOL-WASSER-TESTMISCHUNGEN

Alkohol	H_2O, %	aufgenommenes H_2O, *g*
Äthanol	9,4	0,410
Propanol-(1)	4,2	0,440
Propanol-(2)	2,1	0,280
Butanol-(1)	1,4	0,310

Versuchsanordnung

Etwa 3–4 ml der Alkohole, sowie reines Wasser wurden in Wägegläser von 55 × 35 mm gegeben, in denen je ein weiteres Wägeglas 40 × 30 mm stand, das etwa 1 g (genau gewogen) getrocknetes Cellulosepulver enthielt. Das große Wägeglas wurde sorgfältig verschlossen und bei 19°C ±1 grd aufbewahrt. Die Massezunahme je 1,00 g Cellulose nach 11 Tagen ist für die einzelnen Proben in Tabelle III zusammengestellt.

Die Übersicht zeigt, daß die Massezunahme im allgemeinen mit der Dielektrizitätskonstanten der Substanzen fällt. Der schwankende Wassergehalt der Gemische scheint dabei die Meßwerte nur in untergeordnetem Maße zu beeinflussen.

Für die Beurteilung des chromatographischen Trennprozesses war aber außerdem wichtig, in welchem Verhältnis Alkohol und Wasser von der Cellulose aufgenommen worden waren.

Zu diesem Zwecke wurden weitere Proben von *ca.* 1 g Cellulosepulver (genau gewogen) 96 Std. über den auf Seite 172 angegeben Alkohol-Wasser-Gemischen aufbewahrt und wieder die Massezunahme bestimmt. Daraufhin wurden die Proben sofort in 10 ml Methanol von bekanntem Wassergehalt übertragen und mit Karl-Fischer-Lösung titriert. Die Meßergebnisse sind in Tabelle IV zusammengestellt.

TABELLE III.—MASSEZUNAHME [IN g] VON 1 g CELLULOSEPULVER AUS DEM ALKOHOL-WASSER-DAMPFRAUM

Wasser	Methanol	Äthanol	Propanol-(1)	Propanol-(2)	Butanol-(1)	Butanol-(2)
0,2054	0,1317	0,1036	0,0849	0,0816	0,0496	0,0423

Nach unserer Erfahrung ist der Sättigungszustand der Cellulose nach 96 Std. nahezu erreicht, so daß die Werte der Tabellen III und IV ohne Bedenken miteinander verglichen werden können.* Aus den Versuchen ist zu erkennen, daß die Massezunahme der Cellulose nicht allein auf eine Erhöhung des Wassergehalts zurückgeführt werden kann. Bei allen untersuchten Gemischen sind sowohl Wasser wie auch Alkohol von der Cellulose adsorbiert worden. Dabei ist allerdings festzustellen, daß mit fallender Dielektrizitätskonstante der Alkohole im allgemeinen deren Aufnahme durch die Cellulose erheblich zurückgeht (Verhältnis etwa 10:1), während die Masse des gebundenen Wassers etwa im Verhältnis 1:3 von Methanol bis zum Butanol ansteigt. Wenn die bisherigen Meßergebnisse auch eine quantitative Auswertung noch nicht gestatten, so sprechen sie doch ebenfalls für den Aufbau der stationären Phase aus allen Komponenten des Fließmittels.

TABELLE IV.—ZUSAMMENSETZUNG DES AN DIE CELLULOSE GEBUNDENEN ALKOHOL-WASSER-GEMISCHES

Fließmittel	Massezunahme, *g*	H_2O, *g*	Alkohol, %
Wasser	0,1733	0,1732	
	0,1762	0,1759	
Methanol	0,1227	0,0106	91,4
	0,1155	0,0113	90,2
Äthanol	0,1030	0,0296	71,3
	0,0933	0,0252	73,0
Propanol-(1)	0,0687	0,0221	67,8
	0,0682	0,0208	69,5
Propanol-(2)	0,0670	0,0278	58,5
	0,0594	0,0287	51,7
Butanol-(1)	0,0310	0,0278	10,3
	0,0311	0,0305	2,0
Butanol-(2)	0,0431	0,0331	23,2
	0,0428	0,0349	18,4

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* Die erhaltenen Meßwerte werden von vielen Faktoren, wie Eigenschaften der Cellulose, Luftdruck, Luftfeuchtigkeit, usw. beeinflußt. Wir glauben, daß es für den vorliegenden Zusammenhang nicht erforderlich ist die Arbeitsbedingungen so auszudehnen, daß der Einfluß dieser Größen ausgeschlossen wird.

Summary—When water: alcohol mixtures (methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol) are passed through dry cellulose, water is preferentially adsorbed except in the case of methanol low in water content, where there is preferential adsorption of the alcohol. Gas-phase experiments show that the relative amounts of the two components adsorbed on the cellulose depend both on the nature of the alcohol and on the alcohol: water ratio. A close relationship exists between the molecular weight (or the dielectric constant) and the amount of alcohol adsorbed. It has been confirmed that all the components of a liquid mixture take part in constituting the stationary phase.

Résumé—Lorsqu'on passe des mélanges eau-alcool (méthanol, éthanol, propane-1-ol, propane-2-ol, butane-1-ol) sur de la cellulose sèche, l'eau est adsorbée de façon préférentielle, sauf dans le cas du méthanol à faible teneur en eau, où il y a adsorption préférentielle de l'alcool. Les expériences en phase gazeuse montrent que les quantités relatives des deux constituants adsorbés sur la cellulose dépendent à la fois de la nature de l'alcool et du rapport alcool:eau. Il existe une relation étroite entre le poids moléculaire (ou la constante diélectrique) de l'alcool et sa quantité adsorbée. On a confirmé que tous les constituants d'un mélange liquide participent à la constitution de la phase stationnaire.

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SHORT COMMUNICATIONS

Analysis of metal chelates—III: Simultaneous determination by a.c. polarography of copper and nickel in copper-contaminated nickel dimethylglyoximate

(*Received* 11 *June* 1964. *Accepted* 11 *October* 1964)

THE reaction of nickel and dimethylglyoxime has been widely used for the gravimetric determination of nickel since 1905.[1] Dimethylglyoxime is a highly selective reagent for nickel and the conventional gravimetric procedure is generally satisfactory. However, some diverse ions, such as iron(III), cobalt(II), copper(II), coprecipitate with nickel dimethylglyoximate. The coprecipitated ions may be determined spectrophotometrically after tedious treatment of the precipitate.[2]

The present investigation has been made to determine simultaneously the content of nickel and copper in copper-contaminated nickel dimethylglyoximate by a.c. polarography.

EXPERIMENTAL

Reagents

0·1M Solutions of nickel sulphate and copper sulphate. Prepared from the guaranteed grade salts and standardised by titration against a standard solution of EDTA.

1% Dimethylglyoxime solution. Prepared from guaranteed grade reagent by dissolution in ethanol.

20% Potassium sodium tartrate solution. Prepared from guaranteed grade reagent.

Other materials used were all guaranteed grade.

Apparatus

A Yanagimoto (Kyoto, Japan) a.c. polarograph, Model PA-102, was used for the determination of nickel and copper. This instrument is based on the a.c. bridge polarograph.[3] All measurements were made against the mercury pool.

Procedure

Simultaneous determination of nickel and copper. A slightly acidic solution, containing 1–30 mg of nickel, 32·5 mg of copper, 5 ml of 20% potassium sodium tartrate solution and 2 g of ammonium chloride in 200 ml of solution, was adjusted to pH 7–7·5 by the addition of dilute aqueous ammonia. After heating the solution to 80°, 1% dimethylglyoxime solution (6 ml for each 10 mg of nickel) was added with continuous stirring. The precipitate was filtered on a sintered glass filter, then washed with hot water. It was dissolved in 10 ml of 6*M* hydrochloric acid and diluted with water to about 200 ml. This solution was evaporated to dryness on a hot-plate, 50 ml of water added and again evaporated to dryness. The residue was dissolved in 2 ml of 6*M* hydrochloric acid and 4 ml of 20% potassium sodium tartrate solution added, followed by dilution to 50 ml in a volumetric flask. An aliquot of the solution was transferred to a polarographic cell and hydrogen bubbled through for 10 min. The a.c. polarograms were taken in the voltage range of −0·1 to −0·4 V for copper and −0·95 to −1·3 V for nickel at 25°. The calibration curve of nickel was obtained from the wave height at the maximum of the polarogram.

Calibration curve for copper. 59·5 mg of nickel were precipitated as nickel dimethylglyoximate and the precipitate treated as mentioned above, except that the residue from the evaporation was dissolved in water to make 100 ml without using hydrochloric acid. To each 25 ml of this solution 0·1–0·7 mg of copper, 2 ml of 6*M* hydrochloric acid and 4 ml of 20% potassium sodium tartrate solution were added, followed by dilution with water to 50 ml in a volumetric flask. The copper was determined by a.c. polarography as described above, and the calibration curve obtained from the wave height at the maximum of the polarogram.

RESULTS AND DISCUSSION

In general, nickel does not give good a.c. polarographic waves because of the irreversibility of nickel in most media.[4] It gives a well defined a.c. polarographic wave at a potential of about −1·4 V in a supporting electrolyte containing only cyanide.[5,6] Although nickel does not give a reversible wave in the supporting electrolyte of hydrochloric acid and potassium sodium tartrate solution used here, the a.c. polarographic wave height, obtained from the nickel solution containing a relatively large amount of nickel, is linear with concentration. On the other hand, copper gives a well defined a.c. polarographic wave. It was because of the small amount of copper to be determined in the presence of a large amount of nickel, that the authors decided to use a.c. polarography. The polarogram obtained is illustrated in Fig. 1. The maxima of the a.c. polarograms of copper and nickel appeared at −0·25 V and 1·15 V, respectively.

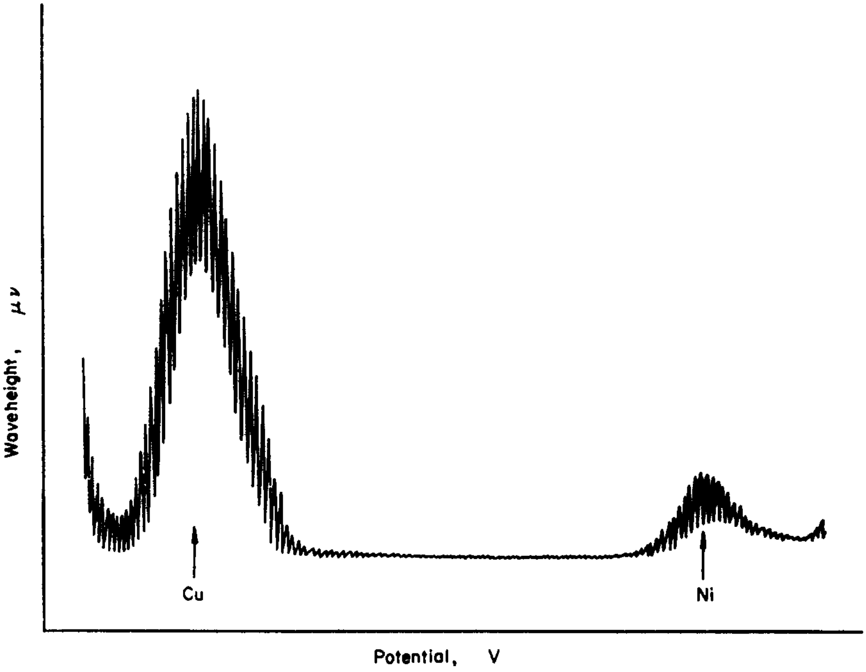

Fig. 1.—A.C. polarograms of copper and nickel.

Nickel was precipitated in the presence and absence of copper as described under *Experimental*, but the calibration curve was the same in both cases. Nickel can be determined in the range 1–20 mg/50 ml of solution (0·4–7·0 × $10^{-3}M$), and copper in the range 0·05–0·5 mg/50 ml of solution (0·2–2·0 × $10^{-4}M$).

The procedures developed were applied to the determination of copper coprecipitated with various quantities of nickel dimethylglyoximate itself precipitated by the conventional method (Table I).

TABLE I.—COPRECIPITATION OF COPPER WITH VARIOUS QUANTITIES OF NICKEL DIMETHYLGLYOXIMATE

Ni taken, *mg*	Cu taken, *mg*	Cu copptd., *mg*
5·96	32·5	0·034
8·93	32·5	0·19
11·91	32·5	0·11
14·89	32·5	0·16
17·87	32·5	0·20
23·82	32·5	0·20
26·79	32·5	0·23
29·78	32·5	0·24

The present procedures are being used in a study of the coprecipitation of copper during the precipitation of nickel dimethylglyoximate from homogeneous solution using biacetyl as the source of dimethylglyoxime.[2]

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Résumé—Lorsqu'on précipite le diméthylglyoximate de nickel en présence de cuivre, une petite quantité de celui-ci coprécipite. Le dosage simultané de cette petite quantité de cuivre et de la quantité importante de nickel a été réalisé par polarographie en courant alternatif.

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5,5′-Thiodisalicylic acid as an analytical reagent

(*Received* 16 *July* 1964. *Accepted* 2 *October* 1964)

In our search for new and sensitive absorptiometric procedures for the determination of small amounts of rhodium and palladium, we have made a thorough study of some of the compounds containing the active sulphydryl (—SH) group. We have been able to work out spectrophotometric procedures for determining rhodium and palladium individually and simultaneously using 2-diethylaminoethanethiol hydrochloride.[1,2]

During the course of these investigations it was observed that 5,5′-thiodisalicylic acid (TDSA) forms coloured complexes in solution with rhodium(III), palladium(II), iron(III), ruthenium(III) and uranium(VI), and precipitates with a few other metals including the lanthanons. It seemed profitable to carry out a detailed study of these complex-forming reactions, and to explore their possible applications in analysis. Some preliminary results of these studies are reported in this communication.

EXPERIMENTAL

Apparatus and reagents

The spectra of the solutions were obtained using a Beckman DK-1 recording spectrophotometer and all other absorbance measurements were performed with a Beckman DU spectrophotometer. Far ultraviolet silica cells of 10-mm path length were used.

pH measurements were carried out with a Beckman Zeromatic pH meter equipped with micro glass and calomel electrodes.

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pH measurements were carried out with a Beckman Zeromatic pH meter equipped with micro glass and calomel electrodes.

Stock solutions of the metals were prepared from analytical-grade reagents, and were standardised by well known methods.

3·06 g of reagent-grade 5,5′-thiodisalicylic acid (Eastman Organic Chemicals) were dissolved in 50 ml of an aqueous solution containing an exactly equivalent amount of sodium hydroxide, and the contents were made up to 100 ml with a sodium acetate-hydrochloric acid buffer of pH 5·0.

TABLE I.—REACTIONS OF 5,5′-THIODISALICYLIC ACID WITH INORGANIC CATIONS

Ion	Used as	Colour (at pH 5, unless otherwise stated)	Optimum pH range (approx.)	Remarks
Au(III)	$HAuCl_4$	Slightly yellow colour	6·0–8·0	Deepens above pH 7
UO_2(II)	$UO_2(NO_3)_2 \cdot 6H_2O$	Orange-red colour	4·0–6·5	Extractable into tributyl phosphate
In(III)	$InCl_3$	White ppt.	4·5–6·0	—
Ce(III)	$Ce_2(SO_4)_3 \cdot 4H_2O$	White ppt.	5·0–7·0	Precipitation is quantitative
Ce(IV)	$Ce(HSO_4)_4$	White ppt.	5·0–7·0	Precipitation is quantitative
Rare earths(III)	Chlorides	White ppt.	5·0–7·0	Precipitation is quantitative
Pb(II)	$Pb(NO_3)_2$	White ppt.	4·0–6·0	Precipitation is quantitative
Th(IV)	$ThCl_4$	White ppt.	5·0–7·0	Precipitation is quantitative
ZrO(II)	$ZrOCl_2 \cdot 8H_2O$	White ppt.	4·5–6·5	Precipitation is quantitative
Mo(VI)	$(NH_4)_2MoO_4$	Yellow colour at pH 4	3·5–5·0	Not very sensitive
Cu(II)	$CuSO_4 \cdot 5H_2O$	Yellowish colour above pH 5	5·0–7·0	Not very sensitive
Fe(II)	$FeSO_4 \cdot 7H_2O$	Purple colour	4·5–6·5	Colour development slow in cold, hastened on heating — purple lake in concd. solutions
Fe(III)	$FeCl_3 \cdot 6H_2O$	Deep purple colour	4·5–6·5	Colour development slow in cold, hastened on heating — purple lake in concd. solutions
Ru(III)	$RuCl_3$	Purple colour	4·5–6·0	Colour development hastened on heating
Rh(III)	$RhCl_3$	Orange-yellow colour	4·0–7·0	Maximum colour development requires 30 min heating on a steam bath
Pd(II)	$PdCl_2$	Orange-red colour	4·5–6·5	—

Procedure

For observing the colour reactions, a suitable aliquot of the metal ion was taken in a 25-ml volumetric flask and 5 ml of the sodium acetate-hydrochloric acid buffer of pH 5·0 were added, followed by 2 ml of the reagent solution. The mixtures were allowed to stand, and were warmed, if necessary. The volume was finally raised to 25 ml with distilled water, and the spectra of the solutions were recorded. Precipitate-forming reactions were observed in a similar way.

RESULTS

Reactions of 5,5′-thiodisalicylic acid with metal ions

The complex-forming reactions of 5,5′-thiodisalicylic acid with various metal ions are described in Table I. The acid itself is insoluble in water, but dissolves in ethanol. However, the sodium salt is soluble in water and is very stable above pH 4.

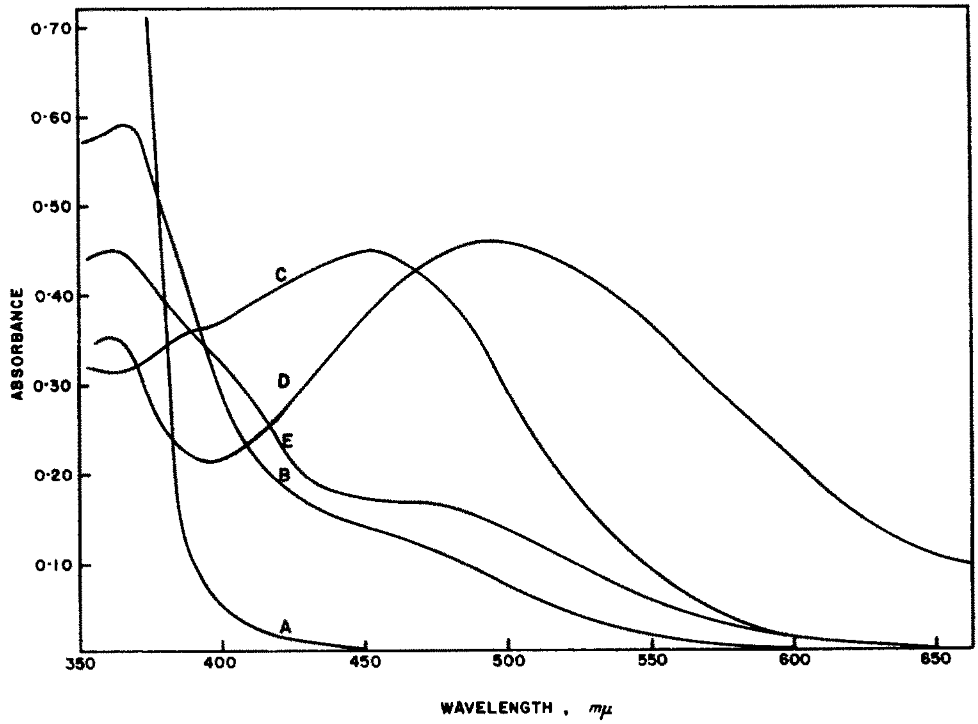


Fig. 1.—Absorbance curves of TDSA and its rhodium(III), palladium(II), iron(III) and uranyl(II) complexes:

A	reagent alone, 2·8 mg/ml;
B	12·35 ppm of Rh(III);
C	4·26 ppm of Pd(II);
D	8·98 ppm of Fe(III);
E	92·4 ppm of UO_2(II).

The reactions with Au(III), Cu(II) and Mo(VI) are not very sensitive, though they can be used at a macro level. In the case of gold(III), the colour deepens above pH 7, but the metal ion has a tendency to hydrolyse above this pH. The colour reactions with rhodium(III), palladium(II), iron(III), ruthenium(III) and uranyl(II) are fairly sensitive. Iron(III) forms purple lakes in concentrated solutions. Indium(III), zirconyl(II), lead(II), thorium(IV), cerium and other rare earths form white to slightly pinkish-white precipitates with the reagent.

In the case of rhodium(III), iron(III) and ruthenium(III), colour formation at room temperature is slow, but if the solutions are heated on a steam bath for from 10 to 30 min, full colour development occurs.

Absorbance curves of complexes

Fig. 1 shows the absorbance curves of the reagent and its rhodium, palladium, iron and uranyl complexes. The reagent has significant absorption below 360 mμ, but does not absorb appreciably above 400 mμ. The palladium complex shows a pronounced maximum at 452 mμ. The rhodium complex does not show any sharp peaks in the visible region, but there is a slight peak at 365 mμ, and measurements may be carried out fairly accurately at this wavelength against reagent blanks. A slight shoulder appears around 465 mμ. The uranyl complex shows absorption maxima at 365 and 455 mμ, and measurements may be performed accurately at or around 380 mμ. The iron complex shows maximum absorption at 498 mμ.

Molar absorptivities and sensitivity

Table II describes the absorption maxima, molar absorptivities and the sensitivities of the iron(III), palladium(II), rhodium(III) and uranyl(II) complexes. The sensitivity is expressed in μg/cm^2 of the metal ion that give an absorbance of 0·001 unit.

TABLE II.—ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF METAL-THIODISALICYLATE COMPLEXES

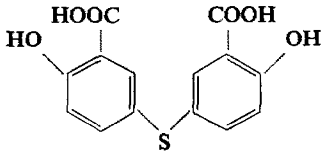
Complex	Concentration, *ppm*	λ_{max}, *mμ*	Absorbance, A_{max}	Molar absorptivity, ϵ_{max}	Sensitivity, *μg/cm^2*
Fe(III)-TDSA	8·98	498	0·460	2·86 × 10^3	0·0195
Pd(II)-TDSA	4·26	452	0·449	1·12 × 10^4	0·0095
Rh(III)-TDSA	12·35	365	0·592	4·93 × 10^3	0·0208
UO$_2$(II)-TDSA	92·4	365 455	0·450 0·172	1·16 × 10^3 4·4 × 10^2	0·2056 0·5368

Extraction studies

An attempt was made to examine the possibility of extracting the soluble complexes into organic solvents. Only the uranyl complex seemed to extract quantitatively into tributyl phosphate; others showed no tendency to extract. This would imply that the uranyl complex species is neutral and the other complexes are ionic in nature. The solvents studied included chloroform, carbon tetrachloride, benzene, toluene, cyclohexane, butanol, *etc.*

DISCUSSION

The reagent, 5,5′-thiodisalicylic acid:



as may be seen from its structure, offers favourable sites for complex formation with metal-ions, the presence of sulphur enhancing the activity of the molecule as a whole. The colour formation with metal ions and the precipitates formed are quantitative, and preliminary investigations show that the reagent can be utilised for the absorptiometric and gravimetric determination of various metal ions including the rare earths. Studies on the effects of certain variables on these systems and on the characteristics of the complexes formed with respect to their composition and stability, as well as further studies on the analytical applications of these complex forming reactions, are in progress.

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Summary—The reactions of 5,5′-thiodisalicylic acid with various metal ions have been studied. The reagent produces coloured complexes with Rh(III), Pd(II), Fe(III), Ru(III) and UO_2(II), and precipitates with Pb(II), ZrO(II), In(III), Th(IV), Ce(III), Ce(IV) and the rare earths under suitable conditions. The reagent shows promise as a spectrophotometric as well as a gravimetric reagent for various metal ions.

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Mechanism of the oxidation of sulphite by permanganate in the presence of iodine monochloride

(*Received* 8 *September* 1964. *Accepted* 30 *October* 1964)

DURING a kinetic study involving sulphite ion, none of the known methods for determination of sulphite was found suitable. In an attempt to use permanganate for a direct titration, a number of useful observations were made which have been helpful in arriving at a mechanism of the reaction.

Formation of dithionate ion[1-8] has been the main reason for the low results during attempts to determine sulphite or sulphurous acid with permanganate. This ion resists oxidation even by strong oxidising agents. However, good results have been found when the oxidation of sulphite is carried out in an alkaline medium.[1-8]

The possibility of determining sulphite by permanganate alone in an acidic medium has been completely investigated, but without success. A preliminary study indicated that

1. With increase in hydrogen ion concentration, more permanganate is consumed.
2. Prior heating of the sulphite solution does not improve the results.[9]
3. The results are no better in the presence of manganese(II), iron(II), iron(III) or copper(II), all of which are known to catalyse many reactions and are said[10] to help decomposition of the sulphite.
4. At lower temperatures (*ca.* 10°) permanganate is consumed.
5. In view of there being a standard iodimetric method,[11] it was thought that iodide, if added initially, may be oxidised to iodine (by the permanganate) which may oxidise the sulphite, giving back iodide. This catalytic activity of iodide was not observed.

Having failed to determine sulphite by permanganate alone, the well-known method involving the use of iodine monochloride was employed and satisfactory results comparable to standard methods[12,13] were obtained. However, the new method has no advantage over that involving iodate.[13]

Summary—The reactions of 5,5′-thiodisalicylic acid with various metal ions have been studied. The reagent produces coloured complexes with Rh(III), Pd(II), Fe(III), Ru(III) and UO_2(II), and precipitates with Pb(II), ZrO(II), In(III), Th(IV), Ce(III), Ce(IV) and the rare earths under suitable conditions. The reagent shows promise as a spectrophotometric as well as a gravimetric reagent for various metal ions.

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EXPERIMENTAL

Reagents

All the chemicals used were either B.D.H. (analytical grade) or E. Merck (guaranteed reagent). Sodium sulphite was of May and Baker quality. Sulphite solutions are very susceptible to air oxidation,[13] but one of the organic compounds, sucrose,[14] ethanol[15] or glycerol,[16,17] may be used to check this tendency. In dilute solutions these do no react with the permanganate nor do they complicate titrations using iodine monochloride.

Iodine monochloride was prepared in the usual way.[18] It was standardised iodometrically and approximately 0·1*N* solutions were prepared by diluting it with 4*M* hydrochloric acid. Permanganate solution was prepared and stored in the usual manner. The sulphite solution was standardised iodometrically.[13]

Procedure

To 25 ml of concentrated hydrochloric acid, 20 ml of water and 2 ml of iodine monochloride (*ca.* 0·1*N*) in a conical flask, are added 10, 5 or 2 ml of sulphite solution (*ca.* 0·1*N*). The iodine monochloride is instantaneously used up. Permanganate is run in from a 10-ml burette. In the beginning the permanganate is decolourised, then the characteristic orange colour of iodine appears. The addition of permanganate is continued until this orange colour is converted to a light yellow which matches the colour of a comparison solution consisting of concentrated hydrochloric acid, water and iodine monochloride in the proportions mentioned above. Alternatively, carbon tetrachloride may also be used.[19] However, continued and vigorous shaking is essential in this procedure, which is a disadvantage.

The amount of iodine monochloride initially to be added, depends on the concentrations of sulphite and hydrogen ions. There is no harm in adding more than a minimum quantity (Table II). In such cases the reaction mixture may not be colourless after the addition of the monochloride; even then, however, permanganate is added until the original light yellow colour matching a comparison solution is obtained.

TABLE I

$KMnO_4$, *N*	$Na_2(S_2)O_3$, *ml*	Sulphite, *g*	$KMnO_4$ required, *ml*	Sulphite found *g*	Sulphite found %	Sulphite stabilised by
0·1031	20	0·200	30·11	0·19556	97·78	Sucrose (2% by weight)
	10	0·100	15·05	0·09774	97·74	
	5	0·050	7·52	0·04884	97·68	
	2	0·020	3·01	0·01955	97·75	
	1	0·0100	1·50	0·009742	97·42	
0·1041	20	0·200	29·71	0·19492	97·46	Ethanol (2% by volume)
	10	0·100	14·85	0·09745	97·45	
	5	0·050	7·43	0·04876	97·52	
	2	0·020	2·97	0·01949	97·45	
	1	0·010	1·49	0·009777	97·77	
0·1052	20	0·200	29·49	0·19556	97·78	Glycerol (2% by volume)
	10	0·100	14·74	0·09775	97·74	
	5	0·050	7·38	0·04894	97·80	
	2	0·020	2·94	0·01949	97·48	
	1	0·010	1·47	0·009748	97·48	

Concentration of sulphite: 10 g/l.; iodometric assay of sulphite: 97·64%.

DISCUSSION

A few results for sulphite using the iodine monochloride procedure are given in Table I. Results with sulphurous acid are similar and have not been included.

Iodine monochloride has been considered as a catalyst in many oxidation processes.[20,21] The role of iodine monochloride in the present method is slightly different, because a minimum quantity is essential for a successful titration (Table III). Here it is not a catalyst but a pre-oxidiser.

TABLE II

0·1*N* ICl,	0·1031*N* KMnO$_4$,	Sulphite found[a]	
ml	*ml*	*g*	%
2	7·50	0·04871	97·42
4	7·51	0·04877	97·55
6	7·50	0·04871	97·42
8	7·52	0·04884	97·68
10	7·51	0·04877	97·55
12	7·50	0·04871	97·42

[a] Concentration of sulphite: 10 g/l. (stabilised by sucrose); volume of sulphite used: 5 ml; iodometric assay of sulphite: 97·64%.

TABLE III

Apparent end-point with KMnO$_4$ alone, *ml of KMnO$_4$*[a]	10% sulphite solution, ml	0·1*N* ICl,[b] *ml*	Appearance of orange colour, *ml of KMnO$_4$*[a]	Final end-point, *ml of KMnO$_4$*[a]	Difference of columns 1 and 4 for minimum ICl
2·41	2	1·50	1·35	2·80	
		1·00	1·81	2·80	
		0·90	1·91	2·80	
		0·80	2·01	2·80	0·40
		0·70	2·07	2·77	
		0·60	2·14	2·75	
		0·40	2·34	2·74	
6·45	5	2·00	5·07	7·04	
		1·50	5·50	7·045	
		1·40	5·59	7·05	
		1·30	5·70	7.04	
		1·20	5·73	7·045	0·72
		1·10	5·79	6·87	
		1·00	5·85	6·75	
13·24	10	2·00	12·10	14·05	
		1·90	12·15	14·06	
		1·80	12·16	14·05	1·08
		1·70	12·19	13·86	
		1·50	12·25	13·76	
		1·40	12·32	13·63	

[a] 0·1003*N*

[b] Minimum quantity of ICl underlined

Aqueous solutions of sulphite are known to possess a number of species of quadrivalent sulphur amongst which bisulphite and pyrosulphite are important.[22] There is spectroscopic evidence for the following equilibria:

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^{2-}$$

$$2\ HSO_3^{2-} \rightleftharpoons H_2O + S_2O_5^{2-}.$$

It is difficult to say which of these species are completely oxidised to sulphate and which gives dithionate when titrated with permanganate alone. The following facts have to be considered for the discussion of a mechanism of reaction:

(1) Iodine monochloride is not a catalyst.

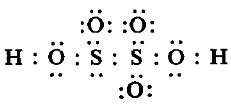
(2) With a minimum quantity or more of iodine monochloride-treated sulphite solutions, permanganate does not give dithionate ion.

(3) Iodine monochloride does not oxidise dithionic acid.

It appears that there is a particular species of quadrivalent sulphur which alone is oxidised to dithionate by permanganate and this is removed by prior treatment of the sulphite solution with iodine monochloride.

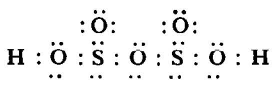
It has been found that permanganate-treated sulphite solutions to the apparent end-point (appearance of colour due to iodine), do not reduce iodine, iodine monochloride or iodate, obviously because dithionate ion is formed which is not oxidised further. On the other hand, all of them oxidise sulphite quantitatively to sulphate and no dithionate is formed. It is clear that dithionate does not exist with sulphite solutions and that it is formed only when sulphite solution is treated with permanganate in the absence of iodine monochloride.

Dilute solutions of sulphite, from cryoscopic evidence,[23] have mostly bisulphite and a small percentage of pyrosulphite ions. The structure of pyrosulphite ion has been differently reported



$$\mathrm{H : \ddot{O} : \overset{:\ddot{O}:}{\ddot{S}} : \underset{:\ddot{O}:}{\overset{:\ddot{O}:}{\ddot{S}}} : \ddot{O} : H}$$

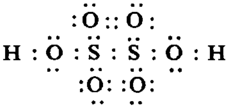
(I)



$$\mathrm{H : \ddot{O} : \overset{:\ddot{O}:}{\ddot{S}} : \ddot{O} : \overset{:\ddot{O}:}{\ddot{S}} : \ddot{O} : H}$$

(II)

In structure (I) the S—S and S—O bond distances are 2·18 and 1·46 Å, respectively.[24] Structure (II) involves S—S and S—O bond distances of 2·209 and 1·499 Å, respectively.[25] The dithionate ion has the following structure,[26] the S—S and S—O distances being 2·16 and 1·45 Å, respectively:



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The oxidation of pyrosulphite (I) to dithionate can be easily understood on the basis of the similarity of the structures. It has been said earlier that one of the species of quadrivalent sulphur is oxidised to dithionate by the permanganate, but it is at the same time oxidised to sulphate by iodine monochloride. This seems to be unlikely in view of iodine monochloride being a less powerful oxidant than the permanganate.

Therefore, it appears that a small percentage of pyrosulphite exists in the two forms [structures (I) and (II)] in an equilibrium which is rapid and that iodine monochloride can oxidise only the second form, whereas permanganate can oxidise both or rather the first form selectively because dithionate ion is produced. This equilibrium, as other equilibria in sulphite solutions, must depend on the concentrations of sulphite and hydrogen ions. A similar situation of structures has also been reported for[27] hyposulphurous acid.

Satisfactory results would be obtained only when all the pyrosulphite, through conversion to form (II), is oxidised by iodine monochloride to sulphate before any permanganate is added. The necessity of a minimum quantity of iodine monochloride in the suggested method points to the requirement of complete oxidation of pyrosulphite. It may be seen from Table III that this minimum quantity is not in proportion to different volumes of sulphite solutions titrated, because the amount of pyrosulphite formed depends on the concentrations of sulphite and hydrogen ions. It is for this reason that this minimum quantity is slightly more even for the same concentrations of sulphite and hydrogen ions, if the order of mixing iodine monochloride and sulphite is reversed. If a slight excess of the former is used, any order of mixing gives satisfactory results.

In the present method, first iodine monochloride oxidises pyrosulphite and if present in excess other quadrivalent sulphur species are also oxidised. Iodine monochloride is thus reduced to iodide. Permanganate run from the burette now oxidises the remaining quadrivalent sulphur species to the sexavalent state. The completion of this stage is marked by the appearance of the yellow or orange colour of iodine. Further additions of permanganate liberate more iodine. When iodide is completely oxidised to iodine, further oxidation to iodine monochloride starts. This stage and the end-point of the titration are marked by the complete conversion of iodine to iodine monochloride. The end-point is fairly sharp.

The volumes of permanganate consumed at the first end-point and the true end-point are shown in Table III; the end-point with permanganate alone (without using iodine monochloride) is shown in column 1. It may be seen that the sum of columns 3 and 4 is always approximately equal to column 5, which proves what has been said above. Further, the difference of columns 1 and 4 for the minimum quantity (underlined) of iodine monochloride, is found to be approximately one half the minimum quantity of the latter. This further lends evidence to the formation of dithionate from pyrosulphate. If one considers sulphite solutions consisting of pyrosulphite and sulphite (including all quadrivalent species of sulphur except pyrosulphite) and their separate permanganate equivalents on oxidation to sulphate to be x and y, column 1 will give $(x/2 + y)$ ml of permanganate because pyrosulphite is oxidised only to the quinquevalent state. Column 4 gives y values because all pyrosulphite has been oxidised by prior addition of iodine monochloride. The difference of columns 1 and 4 is $x/2$, which is approximately half of column 3 (true, of course, only for minimum quantity of iodine monochloride). The figures given in column 3 of Table III are a rough guide to the above line of reasoning because iodine monochloride may also oxidise other species in addition to pyrosulphite.

Iodine, on the basis of the iodometric determination of sulphite, may be expected to be able to oxidise pyrosulphite ion and, therefore, an attempt was made to use it as a catalyst or a pre-oxidiser in place of iodine monochloride. It does react, but the results are always low. It apppears that iodine reacts first with sulphite and then with pyrosulphite or rather the fraction of the latter oxidised is small. Hence, some pyrosulphite remains and these solutions on further oxidation with permanganate will give lower results.

Though a method using permanganate has been worked out, it is not an independent method. Hendrixson[6] very truly observed that any attempt to determine sulphite by permanganate in a direct titration would prove futile. A truly permanganate method would be one in which permanganate itself oxidises all quadrivalent sulphur species to the sexavalent state.

Acknowledgement—One of us (H. G. S. S.) is thankful to the C.S.I.R., India, for an award of a Junior Research Fellowship and a grant. We also thank Professor R. C. Mehrotra for his encouragement and interest.

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Summary—A mechanism for the oxidation of sulphite or sulphurous acid by permanganate in the presence of iodine monochloride has been suggested. The mechanism requires a minimum quantity of iodine monochloride as a pre-oxidiser. Complete oxidation of sulphite to sulphate by permanganate alone is not possible under any conditions.

Zusammenfassung—Ein Mechanismus für die Oxydation von Sulfit oder schwefliger Säure durch Permanganat in Gegenwart von Jodmonochlorid wurde vorgeschlagen. Der Mechanismus erfordert eine Mindestmenge Jodmonochlorid zur Voroxydation. Die völlige Oxydation von Sulfit durch Permanganat allein ist unter keinen Bedingungen möglich.

Résumé—On suggère un mécanisme pour l'oxydation des sulfites ou de l'acide sulfureux au moyen de permanganate en présence de monochlorure d'iode. Le mécanisme nécessite une quantité minimale de monochlorure d'iode, en tant que pré-oxydant. Quelles que soient les conditions, l'oxydation complète du sulfite par le permanganate seul n'est pas possible.

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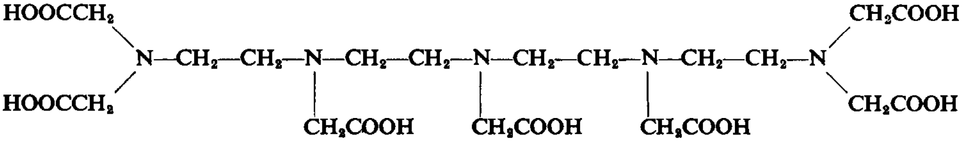
LETTERS TO THE EDITOR

Tetraethylenepentamine-N,N,N′,N″,N‴,N⁗,N⁗′-hepta-acetic acid as a titrimetric reagent

SIR,

OF the polyaminopolycarboxylic acids containing more than four carboxymethyl groups, only diethylenetriamine-N,N,N′,N″,N″-penta-acetic acid (DTPA) has been thoroughly studied[1] and proposed for some complexometric titrations.[2-4] More recently, it has been found that triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid (TTHA) shows a different behaviour in comparison with EDTA or DCTA as regards complex formation. With most bivalent cations this acid forms 2:1 complexes (with the exception of manganese), but it forms normal 1:1 complexes with tervalent and quadrivalent metals (with the exception of gallium).[5] Also, some interesting displacement reactions between EDTA and TTHA complexes have been discovered. These effects have been utilised for complexometric determinations where EDTA or DCTA are inapplicable, *e.g.*, for the determination of mixtures of thorium and lanthanum,[4] mixtures of thorium and scandium,[6] mixtures of gallium and indium,[7] *etc.*

It seemed of interest to us to study from the analytical point of view a new polyaminocarboxylic acid containing five nitrogen atoms, tetraethylenepentamine-N,N,N′,N″,N‴,N⁗,N⁗-hepta-acetic acid (TPHA):



synthesised recently in the laboratories of Geigy Chemical Company (Basel, Switzerland) from tetraethylenepentamine and iminodiacetic acid (99·5% purity). It was expected that polynuclear complexes would be formed under various conditions.

TABLE I

Metal	Back-titrant	pH	Indicator[a]	Complex	Comments
Al	Pb	5–5·5	XO	2:1	Good end-point; complex formed in cold even in presence of 10 g of KNO$_3$
Th	direct	3–4	XO	2:1	Very good end-point; reversible
Pb	direct	5–5·5	XO	2:1	Very good end-point
Zn	direct	5–5·5	XO	2:1	Good end-point
Cd	direct	5–5·5	XO	2:1	Adequate end-point
Ni	Pb	5–5·5	XO	2:1	Good end-point
Bi	direct	1–2	XO	Formation of 1:1 and 2:1 complexes uncertain	Unfit for use
	Th	3–4	XO		
La[b]	direct	5·5–6	MTB	1:1?	Very bad end-point
Cr	Pb	5–6	XO	2:1	Adequate end-point
Ca	direct	NH$_4$OH 1:2	MTB	2:1	Adequate end-point; back-titration with Ca not good
Mg	direct	10	MTB	2:1	Very poor
Mn	direct	NH$_4$OH 1:2	MTB	2:1	Adequate end-point

[a] XO = Xylenol Orange, MTB = Methylthymol Blue.

[b] Sc, Ce, Nd and Pr behave similarly to La; it is also impossible to titrate Fe.

Only sufficient sample was available for some exploratory titrations. The acid is soluble in water with a slight cloudiness and has a slight undefined odour. The pH of a 0·05*M* solution is about 3. We prepared a 0·05*M* solution of the sodium salt by neutralisation with sodium hydroxide to pH 6. All titrations were performed with the usual metallochromic indicators in different media as previously described for TTHA.[5] Our results are summarised in Table I.

The results of the exploratory experiments show that, with a few exceptions, TPHA is not a suitable titrant under normal experimental conditions (in aqueous solutions). Because of the small quantity of sample available, it was not possible to study the compound as a masking agent in gravimetry, colorimetry, polarography, *etc.*

The authors thank Dr. K. Krebser (Geigy Chemical Company, Basel, Switzerland) for his interest and for providing the sample of tetraethylenepentaminehepta-acetic acid.

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16 *September* 1964

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[6] *Idem*, *ibid.*, 1964, **11**, 1545.
[7] *Idem*, *ibid.*, 1964, **11**, 1319.

Interlingua

SENIOR,

Io rende gratias a vos pro le permission de publicar un littera in interlingua. Io spera que vos e le tote lectores de Talanta pote leger lo sin difficultate.

Pro illustrar le simplicitate de iste lingua artificial, vamos comparar le conjugation del tempore presente del verbo *to be* in anglese e in interlingua:

I am	*io esse*
you are	*tu esse*
he is	*ille esse*
we are	*nos esse*
you are	*vos esse*
they are	*illes esse*

Si le comparation esseva inter interlingua e germano, espaniol, italiano, or francese, le avantage de interlingua esserea etiam major. De plus, le tote verbos de interlingua forma le altere tempores per un methodo perfectemente regular. Per exemplo:

Infinitive	*to speak, write, hear*	*parlar*	*scriber*	*audir*
Present	*I speak, etc.*	*io parla*	*io scribe*	*io audi*
Past	*I spoke, etc.*	*io parlava*	*io scribeva*	*io audiva*
Future	*I shall speak, etc.*	*io parlara*	*io scribera*	*io audira*
Conditional	*I would speak, etc.*	*io parlarea*	*io scriberea*	*io audirea*

Le nomines e le adjectivos esse equalmente simple.

Io cree que le majoria del chemistas pote ja leger interlingua. Post alicun horas de studiar, poterean alsi scriber lo. Le problemas del communication inter le chemistas del varie nationes esserea multo simplificate si le chemistas scriberea lor articulos e lor libros in interlingua. On pote emer dictionarios e grammaticas a Storm Publishers, 80 E. 11th St., New York, N.Y., U.S.A.

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Sincermente,
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Dr. Rieman wrote the letter here published, and sent with it a translation. However, because I myself found little difficulty in understanding his letter, and feel, like him, that the readers of *Talanta* will follow it easily, I did not arrange for publication of the translation.

I would still be interested to know the extent to which an artificial language could cope with the highly specialised requirements of a scientific vocabulary. For instance (I quote from a recent paper in *Talanta*) "... a new analytical tool is introduced for the analysis of fluorescent molecules—quenchofluorescence analysis. This field of research will have far-reaching ramifications in organic trace analysis. Analytical use is made of the quenching effect in spectrophotofluorometry. Compounds such as anthracene, phenanthrene, pyrene, benz(*a*)anthracene, benzo(*a*)pyrene, perylene, *etc.*, have been found to be non-fluorescent in nitromethane solution, but hydrocarbons containing the fluoranthenic ring are fluorescent."

Because the decision about future communications in Interlingua now rests with you, I look forward with some interest to your reaction.

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The Queen's University
Belfast, Northern Ireland.
22 *November* 1964

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DERIVATIVES OF 2-(2-THIAZOLYLAZO)PHENOL AS ANALYTICAL REAGENTS—VII*

SPECTROPHOTOMETRIC DETERMINATION OF ZINC WITH 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

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(*Received* 5 *March* 1964. *Accepted* 12 *October* 1964)

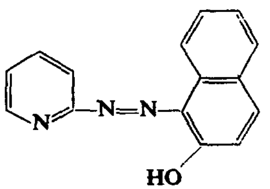
Summary—The spectrophotometric determination of trace amounts of zinc using derivatives of 2-(2-thiazolylazo)phenol has been studied. With zinc these compounds form blue or red-violet chelates, which are mostly extractable with chloroform to give solutions exhibiting an absorption maximum near 600 mμ. 1-(2-Thiazolylazo)-2-naphthol (NT) is recommended for the determination of zinc down to 0·1 μg Sandell's expression of the sensitivity is 0·0013 μg of zinc/cm^2. The interference of 29 cations and 11 anions has been examined in the presence and absence of ammonium citrate and demethylglyoxime. Mercury(II), manganese(II), cadmium(II), uranium(VI), EDTA, cyanide and pyrophosphate interfere, but mercury(II) and manganese(II) can be masked by the addition of thiosulphate and periodate, respectively. NT has been applied to the determination of zinc in thorium oxide and magnesium.

INTRODUCTION

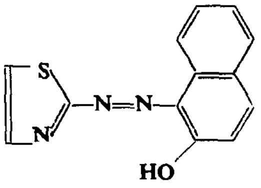
1-(2-Pyridylazo)-2-naphthol, synthesised by Chichibabin[1] and applied to the spectrophotometric determination of metals by Cheng and Bray,[2] possesses useful analytical properties. By replacement of the pyridine ring in 1-(2-pyridylazo)-2-naphthol with a thiazole ring it should also be possible to obtain a chelating property.

Because 2-aminothiazole is easier to diazotise and to couple with phenol than is 2-aminopyridine, the preparation of 2-(2-thiazolylazo)phenol is very easy and it is obtained in good yield and in excellent purity. 2-(2-Thiazolylazo)phenol behaves as a weaker and more selective chelating agent than 2-(2-pyridylazo)phenol,[7] because thiazole is a weaker base than pyridine.

The author has already reported on the preparation of 2-(2-hydroxy-5-methoxyphenylazo)-4-methylthiazole (MMT)[3a] and some derivatives of 2-(2-thiazolylazo)-phenol[3b] and their analytical applications to the determination of copper,[4a,5a]



1-(2-pyridylazo)-2-naphthol
(PAN)



1-(2-thiazolylazo)-2-naphthol
(NT)

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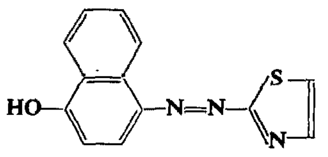
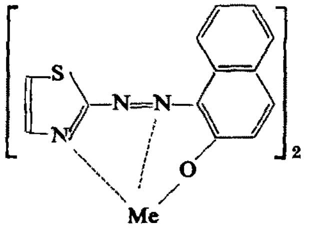
* Part VI: see reference 7.



4-(2-thiazolylazo)-1-naphthol



NT-metal chelate
(Me=Cu^{2+},Ni^{2+},Co^{2+},Zn^{2+})

nickel[4c,5b,6] and cobalt;[4c,5c,5d] MMT has also been applied to the determination of zinc[4b] and iron.[4d] The stability constants of the metal chelates of the 2-(2-thiazolylazo)phenol compounds have been evaluated[7] and the infrared absorption spectra of the 2-(2-thiazolylazo)phenol compounds and their metal chelates recorded.[8]

In the present paper, the spectrophotometric determination of trace amounts of zinc with eleven derivatives of 2-(2-thiazolylazo)phenol (Table I) is reported. Of these derivatives, 1-(2-thiazolylazo)-2-naphthol (NT) is recommended for the determination of zinc.

As expected from its higher pK_a value, NT is a stronger chelating agent than MMT. Furthermore, NT forms more extractable chelates than MMT because of its higher molecular weight and having no polar group in the molecule.

4-(2-Thiazolylazo)-1-naphthol has also been prepared[14] and applied to the determination of palladium.[15] The donor atoms of this reagent are one of the nitrogens of the azo group and the nitrogen of the thiazole ring, so that a different reactivity towards metal ions than that of NT would be expected. Thus, in practice, zinc forms a weak chelate with this reagent.

EXPERIMENTAL

Reagents

Standard zinc solution. 0·6538 g of high purity zinc was dissolved in nitric acid (1 + 1), 10 ml of perchloric acid added and the solution evaporated until fumes of perchloric acid appeared. After cooling, the solution was diluted to 1 litre with water. The concentration of the resulting solution was $10^{-2}M$. Less concentrated solutions were prepared by appropriate dilution of this stock solution.

$10^{-3}M$ *Reagent solutions.* The 2-(2-thiazolylazo)phenolic compounds[3a,3b] were dissolved in methyl alcohol (MT, HMT, RT, HCT and DMT), water(SNT) or dioxan(NT, MNT, BNT, PNT and HNT).

Buffer solution. 34 g of sodium acetate trihydrate and 12 g of borax were dissolved in 1 litre of water, and the pH of the solution adjusted to a desired value with dilute hydrochloric acid.

Chloroform. "Guaranteed grade" reagent was redistilled.

Other reagents were of "guaranteed grade" quality.

Apparatus

pH Measurements were made with a Horiba glass electrode pH meter Model M3. The measurements of absorption spectra and absorbance were made with a Cary Model 14 spectrophotometer using 1-cm matched silica cells.

RESULTS AND DISCUSSION

Selection of solvent for extraction

Under optimum conditions, the orange 2-(2-thiazolylazo)phenolic compounds gave the following colour changes with zinc ion: to intense reddish-violet (reagents 1–5 and 11), red (reagent 8) and blue (reagents 6, 7, 9 and 10).

TABLE I.—DERIVATIVES OF 2-(2-THIAZOLYLAZO)PHENOL STUDIED

Reagent no.	Abbreviation	Chemical name
1	NT	1-(2-thiazolylazo)-2-naphthol
2	MNT	1-(4-methyl-2-thiazolylazo)-2-naphthol
3	BNT	1-(2-benzothiazolylazo)-2-naphthol
4	PNT	1-(4-phenyl-2-thiazolylazo)-2-naphthol
5	HNT	1-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-2-naphthol
6	MT	2-(2-thiazolylazo)-4-methoxyphenol
7	HMT	2-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-4-methoxyphenol
8	RT	4-(2-thiazolylazo)resorcinol
9	HCT	2-(4,5,6,7-tetrahydrobenzo-2-thiazolylazo)-4-methylphenol
10	DMT	2-(2-thiazolylazo)-4,6-dimethylphenol
11	SNT	1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid

With the exception of RT and SNT, the zinc chelates were only slightly soluble in water. To test their solubility in organic solvents, a mixture of each reagent and zinc ion was shaken with benzene, chloroform, carbon tetrachloride, isoamyl alcohol or methyl isobutyl ketone (MIBK). In general, chloroform, isoamyl alcohol and MIBK were excellent extractants for all of the zinc chelates, whereas benzene and carbon tetrachloride were not. The zinc chelates of reagents 1–5 and 11 were almost insoluble in water and only slightly soluble in organic solvents, especially the chelates of BNT and HNT, but could be very efficiently extracted with chloroform. When the chelates of HCT and DMT were extracted with chloroform the extracts were green, indicating the chelates to be partially dissociated. All of the zinc chelates should be extracted from aqueous solution of high pH because their stability constants were not very large.[7] At high pH, however, the reagents were ionised in aqueous solution. When isoamyl alcohol was used as extractant, the ionised reagents were also extracted into the isoamyl alcohol phase and gave a high and fluctuating blank value. Therefore, isoamyl alcohol is not a suitable extractant. MIBK is unsuitable because it is relatively miscible with water. Chloroform is the most suitable extractant.

Absorption spectra of zinc chelates

Copper is known to form two types of chelate:[4a,5a] one in which the metal to reagent is in a 1:1 ratio and the other in a 1:2 ratio. A similar occurrence was expected in the case of the zinc chelates. Therefore, absorption spectra were measured with solutions containing an excess of zinc in one case and an excess of reagent in the other case.

One ml of $10^{-3}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were added to 10 ml of buffer solution and adjusted to the optimum pH (Table II). The mixture was diluted to about 25 ml with water and twice extracted with a few ml of chloroform. The combined extracts were diluted to 25 ml with chloroform and the absorption spectra measured over the range 350–750 mμ, using chloroform as reference solution. The absorption spectra of the zinc chelates of RT and SNT were measured under the same conditions except that water was used as the solvent.

The results are shown in Figs. 1 and 2. As the molecular weight of the 2-(2-thiazolylazo)phenolic compound increased, the molecular extinction coefficient increased and the maximum absorption also shifted to a longer wavelength. The molecular extinction coefficient of PNT was, however, smaller than the expected value. This is believed to be caused by a steric effect of the 4-phenyl group in PNT.

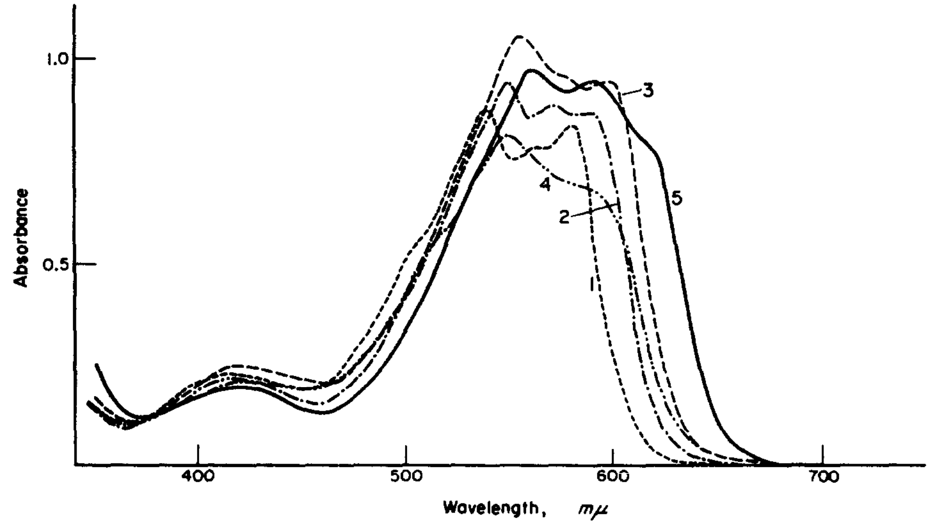


FIG. 1.—Absorption spectra of zinc chelates in chloroform:
1—NT, 3—BNT,
2—MNT, 4—PNT,
5—HNT.

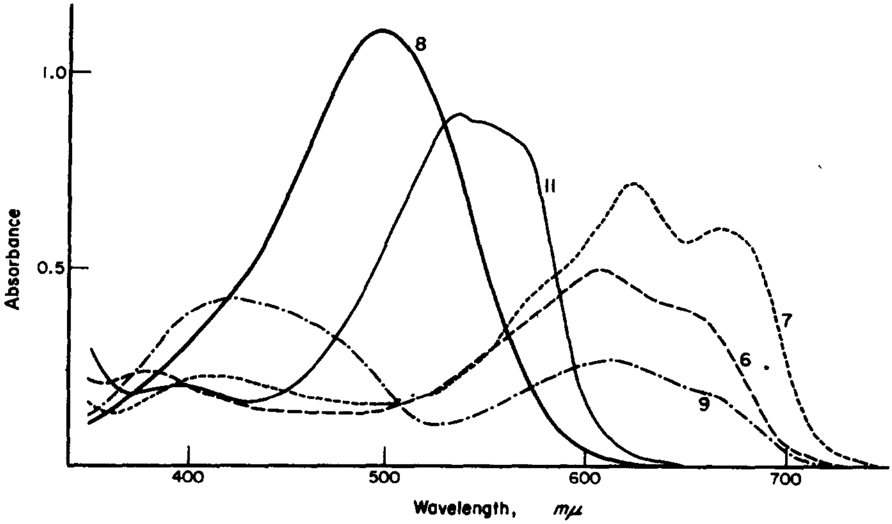


FIG. 2.—Absorption spectra of zinc chelates in chloroform or aqueous solution
6—MT, 7—HMT, 8—RT, 9—HCT, 11—SNT.

The absorption spectra of the chelates of NT, MNT, HNT, BNT and PNT had up to three maxima in the range 500–600 mμ, and were similar to the spectra of the nickel chelates.[4b,5b] The zinc chelate of HCT exhibited a high maximum at about 400 mμ. This is caused by free HCT produced by dissociation of the chelate under these conditions.

In the presence of a large excess of reagent, the absorption spectra of the chelates could not be measured accurately because of the absorption of the reagents themselves. Because the stability constants (log $K_1 . K_2$) were 12–15,[7] dissociation of the chelates was negligible as long as the concentration of the reagents exceeded that of the zinc. The remaining reagent concentration could then be calculated by assuming that a 1:1 or 1:2 chelate was formed. The absorption spectra of the zinc chelates could, therefore, be estimated by recording the spectra against the reagent solution with a concentration calculated as above.

To 10 ml of buffer solution with the optimum pH (Table II), 1 ml of $10^{-4}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were added. The mixture was diluted to about 25 ml with water and treated with 10 ml of chloroform. The absorption spectrum of the chloroform extract was measured against a reference solution prepared as follows. To 10 ml of buffer solution, 0·9 ml (for a 1:1 chelate) or 0·8 ml (for a 1:2 chelate) of $10^{-3}M$ reagent solution was added, and the mixture shaken with 10 ml of chloroform. The chelates of RT and SNT were investigated in aqueous solution.

A mixture of 5 ml of buffer solution, 1 ml of RT or 2 ml of SNT solution and 1 ml (or 2 ml in the case of SNT) of $10^{-4}M$ zinc solution was diluted to 10 ml with water. Absorption spectra were measured against the reagent.

The results are shown in Figs. 3, 4 and 5. Each of the absorption spectra in Fig. 3 is assumed to be that of a 1:2 chelate and is similar to the absorption spectra obtained with an excess of zinc (Fig. 1). From their absorption spectra and absorbances, it appears that the extracted chelates were 1:2 chelates. If the composition of the chelate of RT was assumed to be 1:1 (Fig. 4, curve 8a), the absorption spectrum was negative at about 400 mμ. This shows that the concentration of the reference solution was too high. When the composition of the chelate was assumed to be 1:2 (Fig. 4, curve 8b), the absorption spectrum was normal and resembled that obtained if excess of zinc was present (Fig. 2, curve 8).

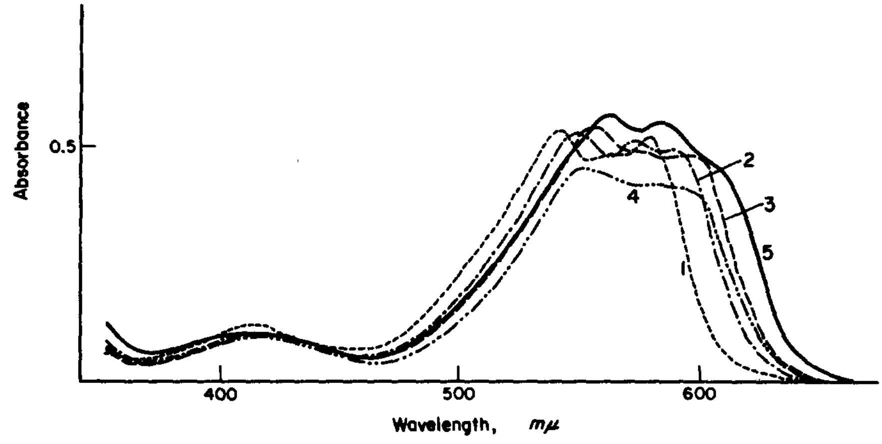


Fig. 3.—Absorption spectra of zinc chelates in chloroform:
1—NT, 3—BNT,
2—MNT, 4—PNT,
5—HNT.

In the case of the chelate of HCT (Fig. 4, curve 9), the absorption spectrum at wavelengths longer than 500 mμ was similar to the spectrum obtained when excess of zinc was present, but the absorbance near 400 mμ was high. This shows that the formation of a 1:2 chelate was more favourable in the presence of excess of reagent than in the presence of excess of zinc.

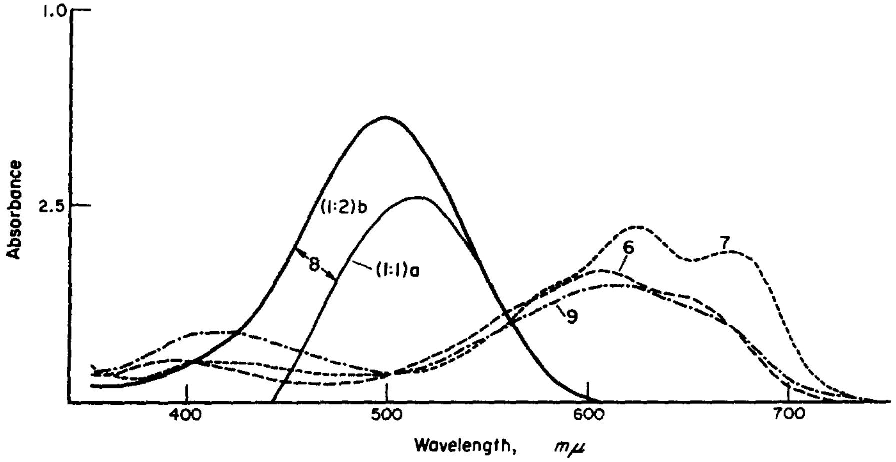


FIG. 4.—Absorption spectra of zinc chelates in chloroform or aqueous solution:
6—MT, 8—RT,
7—HMT, 9—HCT.

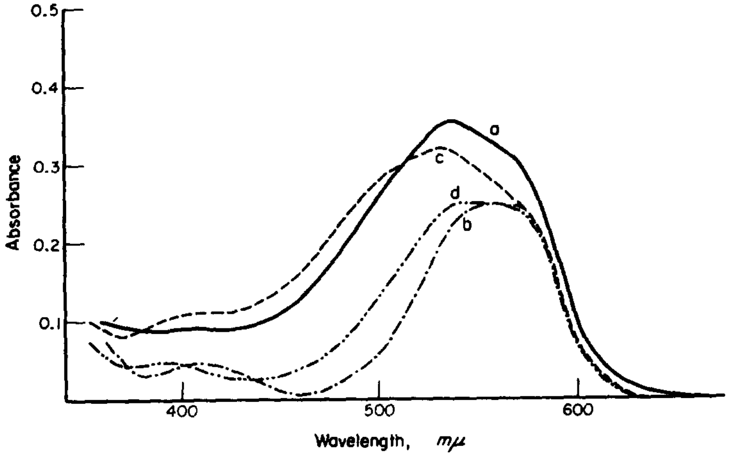


FIG. 5.—Absorption spectra of SNT-zinc chelate in aqueous solution:
a—pH 8·0, 1:2; b—pH 8·0, 1:1; c—pH 6·5, 1:2; d—pH 6·5, 1:1.

In the case of the chelate of SNT, when a 1:2 chelate was assumed to be present at pH 6·5, the absorption spectrum (Fig. 5, curve c) appeared to be that of the reagent alone. When the chelate was assumed to be 1:1 (Fig. 5, curve d), the measured spectrum resembled that obtained when excess of zinc was present. From these results, it is thought that a 1:1 chelate predominates, while a 1:2 chelate is formed slightly at higher pH.

The results of the measurements of absorption spectra in the presence of excess of zinc are summarised in Table II.

Effect of pH

For evaluation of the optimum pH for determination of zinc, the effect of pH on the absorbance and on the absorption spectrum of the chelates was studied.

TABLE II.—PROPERTIES OF THE 2-(2-THIAZOLYLAZO)PHENOL REAGENTS AND THEIR ZINC CHELATES

Reagent	Absorption maxima,[a] mμ		Colour of chelate	Optimum pH	Optimum wavelength, mμ	Isosbestic point, mμ
	Reagent	Chelate				
NT	485	581, 563, 535, 416	red-violet	8·0	581	508
MNT	493	591, 572, 550, 416	red-violet	8·0	591	516
BNT	490	596, 575, 559, 423	red-violet	8·0	596	517
PNT	500	552, 417	red-violet	8·0	600	523
HNT	502	584, 563, 417	red-violet	8·0	610	526
MT	481, 365	610, 369	blue	9·0	610	534
HMT	485, 402	670, 624, 415	blue	8·5	624	533
RT[b]	489 (pH 5·98)	500	red	7·5	560	471
HCT	454, 432	612[c]	blue	9·0	612	513
DMT	455, 373	605[c]	blue	—	605	—
SNT[b]	445 (pH 5·39)	550, 525, 394	red-violet	6·5	570 or 590	503

[a] Chloroform solution.
[b] Aqueous solution.
[c] Absorption maximum near 400 mμ uncertain.

One ml of $10^{-4}M$ zinc solution and 1 ml of $10^{-3}M$ reagent solution were diluted to 10 ml and the pH adjusted to a value in the range 5·5–9·3. The mixture was allowed to stand for about 15 min, then shaken with 10 ml of chloroform. The absorption spectrum of the chloroform extract was measured over the range 500–750 mμ against chloroform. In the case of RT and SNT, 5 ml of buffer solution were used; each mixture was diluted to 10 ml with water and the spectrum measured against water.

The absorption spectrum was not observed to change over the pH range 5·5–9·3, so that obviously only one type of chelate is formed. The zinc chelate of SNT having a 1:2 ratio of zinc to SNT was assumed to be formed at high pH. The red shift of the chelate was not so large, while the influence of pH was so great in the spectrum of the reagent that the accurate determination of spectra of the chelates was impossible, and the formation of a 1:2 chelate was questionable.

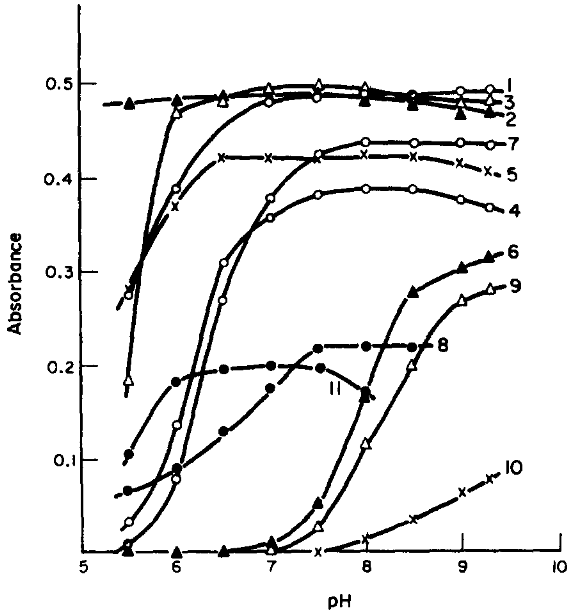


FIG. 6.—Relationship between absorbance of zinc chelates and pH:

1—NT,	6—MT,
2—MNT,	7—HMT,
3—BNT,	8—RT,
4—PNT,	9—HCT,
5—HNT,	10—DMT,

11—SNT.

The effect of pH on the extraction of zinc is shown in Fig. 6. MT, HCT and DMT do not give constant absorbances in the pH ranges studied here. The extraction of zinc with MNT, NT, HNT and BNT is complete over a wide range of pH. Because the reagent absorbance of PNT and HNT is high, a wavelength longer than the absorption maxima of their chelates is selected for the determination of absorbance.

The reactivity of DMT with zinc is small, so that DMT is not used for subsequent experiments. The optimum pH and wavelength for the determination of zinc are shown in Table II.

Composition of chelates

The method of continuous variation[9] was employed to elucidate the composition of the chelates, presumed to be 1:2 from the results of the measurements of absorption spectra described above.

Solutions for the spectrophotometric measurements were prepared as follows. Each separatory funnel contained the reagent ($2 \times 10^{-4}M$) and zinc solution ($2 \times 10^{-4}M$) in different proportions, but the volume of each combined solution was held at 3·0 ml. After adjusting the solution to the optimum pH (Table II) with 10 ml of buffer solution, the mixture was extracted with 10 ml of chloroform. The absorption spectra of the chloroform extracts were measured against chloroform over the range 500–750 mμ.

For RT and SNT, 5 ml of buffer solution were used. The mixtures were diluted to 10 ml with water and the absorption spectra of the solutions measured against water.

The value Y (Fig. 7) was calculated at the various wavelengths from the difference in absorbance of the chelate and estimated amount of free reagent. The necessary curves were obtained by plotting the composition of the solution expressed as mole fraction of zinc.

All of the curves exhibit a distinct maximum or minimum at 0·33 mole fraction, corresponding to a mole ratio of 1:2, but in the case of the SNT chelate, the curves indicate the formation of a 1:1 chelate at pH 6·5 and 8·0. Dissociation of the chelates of MT, SNT, RT and HCT was relatively high. Examples of the curves are shown in Fig. 7.

Isosbestic point

If the chelate formed had a 1:1 or 1:2 combining ratio, the absorption spectra of the zinc and reagent system would give an isosbestic point. To determine the isosbestic point, the following solutions were prepared.

To 10 ml (5 ml for SNT and RT) of buffer solution which had been adjusted to the optimum pH (Table II), 2 ml of $2 \times 10^{-4}M$ reagent solution and 0–0·8 ml of $2 \times 10^{-4}M$ zinc solution were added. The mixture was extracted with 10 ml of chloroform (or diluted to 10 ml with water for SNT and RT). The absorption spectra were measured over the range 500–750 mμ.

All of the absorption spectra have an isosbestic point in the range measured (Table II). The occurrence of an isosbestic point indicates that there is only one kind of chelate, in which the ratio of zinc to reagent is 1:1 for SNT and 1:2 for the other reagents.

Relationship between reagent concentration and absorbance of chelate

The following experiments were undertaken to obtain the optimum amount of the various reagents, and from these results, the molecular extinction coefficient of the chelates were calculated.

One ml of $10^{-4}M$ zinc solution was added to a mixture of 10 ml of buffer solution at the optimum pH (Table II) and 0·5–4·0 ml of $10^{-3}M$ reagent solution. The mixture was allowed to stand for about 15 min, then extracted three times with 3 ml of chloroform. The combined extracts were diluted to 10 ml with chloroform in a 10-ml calibrated flask. The absorbance of the extract was measured at the optimum wavelength (Table II) against chloroform as reference. The blank absorbance of the reagent was measured under the same conditions. The difference between the absorbance of the chelate and the blank corresponds to the chelate absorbance. In this case, the decrease in absorbance of the reagent because of chelate formation was assumed to be negligible. For RT and SNT, 5 ml of buffer solution were used and the absorbance was measured in aqueous solution, the other conditions being the same as described above.

The results are shown in Table III. The MT and HCT chelates did not give a constant absorbance in the range of reagent concentration studied. One ml of reagent solution is sufficient for complete formation of the chelate with 1 ml of $10^{-4}M$ zinc solution, whereas RT and SNT require 2 ml of reagent solution to produce a constant absorbance. The molecular extinction coefficients of PNT, RT and SNT were large at the wavelength measured.

From the sensitivity and reagent absorbance data in Table III and the known order[7] of the stability constants (log $K_1.K_2$) in 50% v/v dioxan-water (NT > HMT > HCT > DMT > MT), NT, BNT and HMT are the most suitable of the compounds for determination of zinc. However, because NT is the easiest of these reagents to synthesise and there is no difference in their chelating action towards other metals, further experiments were carried out with NT only.

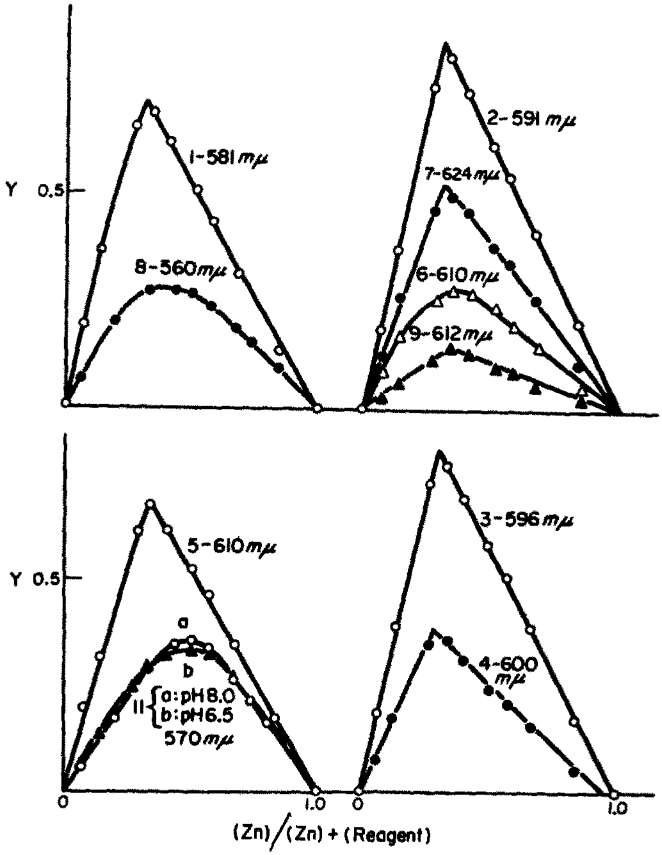


FIG. 7.—Continuous variation plots for zinc chelates:

1—NT,
2—MNT,
3—BNT,
4—PNT,
5—HNT,
6—MT,
7—HMT,
8—RT,
9—HCT,
11—SNT.

Effect of foreign ions and masking agents

NT reacts with many other metals under the conditions used to form its zinc chelate. The following metals (μg) gave an absorbance corresponding to 1 μg of

TABLE III.—RELATIONSHIP BETWEEN REAGENT CONCENTRATION AND ABSORBANCE OF THEIR ZINC CHELATE

Reagent		Absorbance									
		NT	MNT	BNT	PNT	HNT	MT	HMT	RT	HCT	SNT
Wavelength, *mμ*		581	591	596	600	610	610	624	560	612	590
Reagent added, *ml*	0·5	0·476[a]	0·463	0·514	0·359[a]	0·400[a]	0·218	0·455	0·203[a]	0·291	0·092[a]
	1·0	0·507	0·458	0·527	0·395	0·418	0·319	0·453	0·218[a]	0·313	0·107[a]
	2·0	0·500	0·460	0·528	0·391	0·412	0·340	0·461	0·227[a]	0·327	0·111
	3·0	0·498	0·461	0·532	0·399	0·415	0·353	0·454	0·231	0·331	0·118
	4·0	0·502	0·461	0·532	0·396	0·418	0·388	0·456	0·231	0·346	0·117
Molecular extinction coefficient ($\times 10^4$)		5·02	4·61	5·29	3·95	4·16	—	4·56	2·31	—	1·15
Absorbance of reagent at $10^{-4}M$		0·007	0·009	0·006	0·035	0·007	0·006	0·005	0·052	0·004	0·060

[a] Discarded.

zinc: cobalt(II) (1·3), cobalt(III) (9·8), nickel(II) (1·2), iron(II) (3·4), iron(III) (9·5), copper(II) (1·6), cadmium(II) (2·8), manganese(II) (1·3), mercury(II) (15) and indium(III) (38). A detailed study of cation interference was not carried out at this stage because the above results indicated the great need for separations or masking before zinc could be determined with NT.

The extraction curves of some chelates of NT in the absence of masking agents are shown in Fig. 8. The following did not interfere with the determination of zinc under the conditions indicated in the *Recommended procedure*: thiosulphate, citrate, acetate, oxalate and dimethylglyoxime (Table IV). Large amounts of hydrogen peroxide and periodate gave rise to low results by oxidation of the reagent. EDTA, cyanide and pyrophosphate prevented the reaction. Chloride, sulphate and nitrate were without effect up to at least 500 mg.

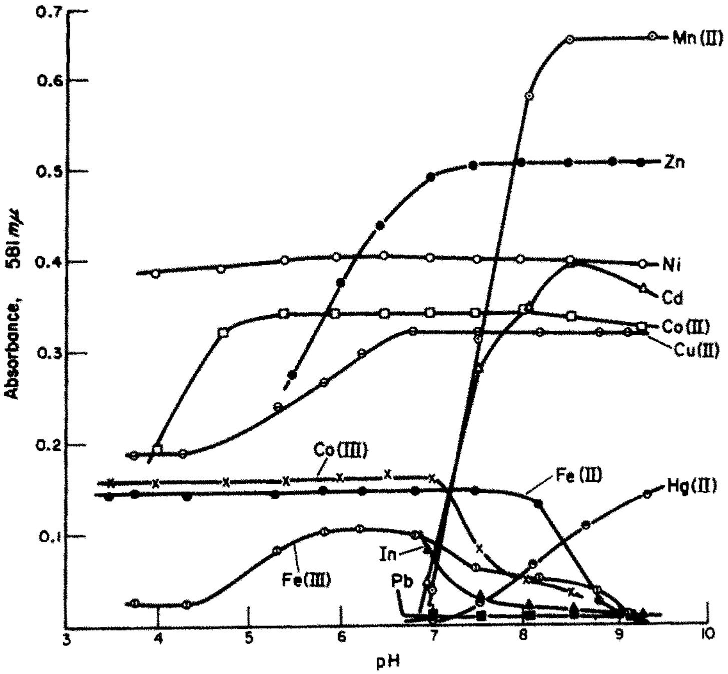


FIG. 8.—Extraction curves of some NT chelates
(Mn—10 μg; Zn—6·54 μg; Ni—5·87 μg; Cd—10 μg; Co—5·89 μg; Fe—5·58 μg; Cu—6·35 μg; Hg—10 μg; In—10 μg; Pb—20 μg)

Dimethylglyoxime forms more stable chelates with iron, nickel, cobalt and copper than does NT, while it has no effect on the reaction between zinc and NT. Therefore, dimethylglyoxime is expected to be an excellent masking agent in the determination of zinc. If the pH was more alkaline than 7·5, the presence of 5 mg of dimethylglyoxime and 100 mg of ammonium citrate did not interfere (Table V). The ammonium citrate prevented the precipitation of some metals.

In the interference studies of various cations, the foreign ions were added under the same conditions as in the *Recommended procedure* (*i.e.*, dimethylglyoxime and ammonium citrate present as masking agents) and their effect noted (Table VI).

TABLE IV.—ANION INTERFERENCE

Anion, *mg*[a]		Zn found,[b] *μg*
Sodium thiosulphate	100	6·5
Sodium citrate	100	6·4
Ammonium citrate	10	6·5
	50	6·5
	100	6·6
	200	6·4
Sodium acetate	100	6·5
Ammonium oxalate	10	6·5
Sodium pyrophosphate	100	0·0
Potassium periodate	7	6·0
0·7% solution	2 drops	6·5
Potassium cyanide	100	0·0
Hydrogen peroxide	100	5·8
	50	5·9
$10^{-2}M$ EDTA	1 ml	0·0
Dimethylglyoxime	5	6·5
	10	6·5

[a] Anhydrous.
[b] 6·54 *μg* of zinc present.

TABLE V.—EFFECT OF CITRATE AND DIMETHYLGLYOXIME

Masking agent,	*mg*	Zn found,[a] *μg*					
Ammonium citrate	100	pH	6·96	7·50	8·10	8·52	9·33
		Absorbance	0·472	0·502	0·502	0·505	0·499
Dimethylglyoxime	5	pH	6·95	7·55	8·00	8·50	9·33
		Absorbance	0·391	0·498	0·506	0·506	0·506
Ammonium citrate	100	pH	7·00	7·50	8·00	8·52	8·95
Dimethylglyoxime	5	Absorbance	0·471	0·500	0·503	0·506	0·504

[a] 6·54 *μg* of zinc present.

Mercury(II), bismuth(III), manganese(II), cadmium(II) and uranium(VI) cause interference. Moderate amounts of sodium, potassium and ammonium do not interfere. The chelates of bismuth and mercury are partially decomposed when they are extracted. The latter can be masked with thiosulphate. Bismuth decreases the absorbance, but can be tolerated up to 50 μg. Manganese forms a coloured chelate which is extracted under the conditions used for determining zinc, but its interference up to 50 μg is readily overcome by the addition of 2 drops of 0·7% potassium periodate solution before the addition of NT. Although the interference of uranium is relatively small, cadmium interferes seriously. A special separation step must be introduced if cadmium is present, such as anion exchange and dithizone extraction separation.[10]

Other experimental variables

The reaction time for chelate formation was tested under the conditions specified in the *Recommended procedure*. The chelate was formed quantitatively within 5 min and no further increase in absorbance was noted up to at least 20 min in the presence

TABLE VI.—CATION INTERFERENCE

Cation, μg	Zn found,[a] μg	Cation, μg	Zn found,[a] μg
Ni^{2+} 50	6·3	Cu^{2+} 50	6·5
100	6·5	100	6·5
Co^{2+} 50	6·5	Ca^{2+} 100	6·5
100	6·4	Mg^{2+} 100	6·5
Co^{3+}[b] 100	6·5	Al^{3+} 100	6·5
Fe^{2+} 100	6·5	Zr^{4+} 100	6·4
Fe^{3+} 50	6·4	Ce^{4+} 100	6·4
100	6·4	UO_2^{2+} 100	7·1
Hg^{2+} 50	7·1	La^{3+} 100	6·4
100	6·5[b]	Mo^{6+} 100	6·4
In^{3+} 50	6·7	W^{6+} 100	6·6
Pb^{2+} 200	6·5	Sb^{5+} 100	6·4
Mn^{2+} 50	13·3	Sn^{4+} 100	6·3
50	6·7[c]	Pd^{2+} 100	6·6
100	15·3	Bi^{3+} 50	6·2
Cd^{2+} 2	7·7	100	5·4
5	9·3	Cr^{3+} 100	6·5
10	10·6	V^{5+} 100	6·7

[a] 6·54 μg of zinc present.
[b] 100 mg of sodium thiosulphate added.
[c] 2 drops of 0·7% potassium periodate added.

or absence of masking agents. A 10-min reaction time is recommended simply to allow a margin of safety. The extracted zinc chelate of NT was stable and no change in the absorbance was observed for at least 1 hr.

Chloroform often contains oxidising substances produced by its own decomposition. If such chloroform was used for the extraction, the absorbance of the chelate showed a 2% decrease over 10 min and this tendency was remarkable at low pH. In this case, good results can be obtained by shaking the chloroform with ascorbic acid solution and water. Redistillation is then unnecessary.

The chelate was rapidly and quantitatively extracted into chloroform in a single equilibration by shaking about 50 times by hand. The reagent solution must be added to the buffered zinc solution. Because of precipitation of the reagent in aqueous solution, a sufficient excess of reagent does not remain in solution to give a rapid and quantitative reaction if it is added before the buffer solution.

The chelate solution was found to follow Beer's law over the range 0·1–8·0 μg of zinc using the *Recommended procedure*. The Sandell expression of sensitivity was found to be 0·0013 μg of zinc/cm^2 compared with 0·0016 for dithizone and 0·003 for Zincon.[11]

Recommended procedure

Transfer test solution containing 0·1 – 8 μg of zinc to a 50-ml beaker. Add 10 ml of buffer solution and 1 ml of 10% ammonium citrate solution. Adjust the pH to 8, then transfer to a 50-ml separatory funnel. Dilute to 20–30 ml with water. Add 0·5 ml of 1% alcoholic dimethylglyoxime solution and 1 ml of $10^{-3}M$ NT solution. Stand for 10 min. Add 10 ml of chloroform and shake vigorously about 50 times by hand. Drain the chloroform phase into a 1-cm cell through a small absorbent cotton plug to remove droplets of water. Measure the absorbance at 581 mμ against chloroform. Run a blank experiment through the entire procedure and subtract the blank from the absorbance of the sample. Establish the amount of zinc from a calibration curve obtained with known amounts of zinc treated as above.

Determination of zinc in thorium oxide and magnesium

The *Recommended method* was tested by analysing samples of thorium oxide and magnesium and compared with other procedures for the determination of zinc. Using the dithizone extraction method, a preliminary separation was necessary. Zinc dithizonate was extracted from a buffered ammonium citrate solution of thorium oxide at pH 8·3 with a benzene solution of dithizone and from a sodium thiosulphate-acetate solution of magnesium at pH 5·5 with a carbon tetrachloride solution of dithizone. The extracts were then shaken with $0 \cdot 1M$ hydrochloric acid to obtain zinc in the aqueous phase. The results are shown in Table VII: there is a good agreement between the new method and the other procedures.

TABLE VII.—DETERMINATION OF ZINC IN THORIUM OXIDE AND MAGNESIUM USING NT[a]

Sample	Zinc, %	
	Present	Found
Thorium oxide	0·00028[b]	0·00028 ± 0·00003
Magnesium	0·022[c]	0·022 ± 0·0004

[a] Each value is the average of 5 determinations.

[b] Dithizone extraction-dithizone (photometric) method:[12] 2·8 ± 0·2 ppm; dithizone extraction-polarographic method:[12] 2·8 ± 0·1 ppm; anion exchange-dithizone (photometric) method:[12] 2·6 ± 0·3 ppm; anion exchange-polarographic method:[12] 2·9 ± 0·3 ppm.

[c] Japan Industrial Standard Method:[13] 0·022%; dithizone extraction-polarographic method:[12] 0·022%.

Zusammenfassung—Die spektralphotometrische Bestimmung von Zinkspuren mit Derivaten von 2-(2-Thiazolylazo-)phenol wurde untersucht. Mit Zink bilden diese Verbindungen blaue oder rotviolette Chelate, die sich meist mit Chloroform extrahieren lassen. Es entstehen Lösungen mit einem Absorptionsmaximum in der Nähe von 600 mμ. 1-(2-Thiazolylazo-)-2-naphthol (NT) wird zur Zinkbestimmung bis herunter zu 0,1 μg empfohlen. Die Empfindlichkeit nach Sandell ist 0,0013 μg Zink pro cm^2. Die Störung von 29 Kationen und 11 Anionen wurde mit und ohne Gegenwart von Ammoniumcitrat und Dimethylglyoxim geprüft. Quecksilber(II), Mangan(II), Cadmium(II), Uran(VI), EDTA, Cyanid und Pyrophosphat stören, doch können Quecksilber(II) und Mangan(II) durch Thiosulfat bzw. Perjodat maskiert werden. NT wurde zur Zinkbestimmung in Thoriumoxyd und in Magnesium verwendet.

Résumé—On a étudié le dosage spectrophotométrique de traces de zinc au moyen de dérivés du 2-(2-thiazolylazo) phénol. Ces composés forment avec le zinc des chélates bleus ou rouge-violets qui sont pour la plupart extractibles au chloroforme, donnant des solutions qui présentent un maximum d'absorption voisin de 600 mμ. On recommande le 1-(2-thiazolylazo)-2-naphtol (NT) pour le dosage du zinc jusqu'à 0,1 μg (limite inférieure). L'expression de la sensibilité selon Sandell est de 0,0013 μg de zinc/cm^2. On a étudié l'interférence de 29 cations et 11 anions en présence et en l'absence de citrate d'ammonium et de diméthylglyoxime. Les mercure(II), manganèse(II), cadmium(II), uranium(VI), EDTA, cyanure et pyrophosphate interfèrent, mais on peut dissimuler les mercure(II) et manganèse(II) par addition, respectivement, d'hyposulfite et de periodate. On a appliqué (NT) au dosage du zinc dans l'oxyde de thorium et dans le magnésium.

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SOME 4-SUBSTITUTED *o*-PHENYLENEDIAMINES AS REAGENTS FOR SELENIUM*

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Summary—*o*-Phenylenediamine and its 4-substituted derivatives, 4-methyl-*o*-phenylenediamine, 4-chloro-*o*-phenylenediamine and 4-nitro-*o*-phenylenediamine, all react with selenous acid in acid solution to form benzoselenadiazoles, which can be extracted into toluene. The distribution ratio, wavelength of maximum extinction, molar extinction coefficient and optimum conditions of formation have been studied for each benzoselenadiazole. Iron(III) and molybdenum(VI) interfere in the determination of selenium with these reagents, but the interference can be overcome by EDTA in both cases. Vanadium(V) interferes only in the case of the 4-chloro- and 4-nitro-*o*-phenylenediamines, and EDTA does not eliminate this interference.

INTRODUCTION

SINCE Hoste and Gillis[1,2] proposed 3,3′-diaminobenzidine as a specific reagent for selenium, this reagent has found several analytical applications.[3–7] It has also been employed for the fluorimetric determination of trace amounts of selenium.[8,9] Recently, Parker and Harvey[10] have proposed 2,3-diaminonaphthalene as an excellent fluorimetric reagent for selenium. The use of the reagent in gravimetry and photometry of selenium has also been attempted.[11] *o*-Phenylenediamine has been the subject of several investigations.[12–14] The reaction of 4-dimethylamino-*o*-phenylenediamine with selenous acid has also been described[15,16] and the reagent has found an application in the determination of selenous acid.[17]

In this paper, critical studies are presented on the suitability of some commercially available 4-substituted *o*-phenylenediamines as reagents for selenium.

EXPERIMENTAL

Reagents

0·5% *o-Phenylenediamine hydrochloride solution*
0·5% 4-*Methyl-o-phenylenediamine hydrochloride solution*
0·5% 4-*Chloro-o-phenylenediamine hydrochloride solution*
0·6% 4-*Nitro-o-phenylenediamine hydrochloride solution*

One ml of each solution corresponds to about a 100-times molar excess for 20 μg of selenium. The solutions can be stored for a few days in a refrigerator. The 4-nitro-*o*-phenylenediamine is so stable that the solution can be used without any difficulty after standing for more than 1 week at room temperature.

All the reagents are commercially available (Tokyo Chemical Industry Co., Ltd., Japan). The commercial products can be purified as follows: Prepare a hot saturated solution of the relevant amine hydrochloride containing sodium bisulphite and Norit "SX-II" (N. V. Norit-Vereeniging,

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* Presented before the 12th Annual Meeting of the Japan Society for Analytical Chemistry, Kanazawa, on 9th October, 1963.

Netherlands). Filter and add concentrated hydrochloric acid to the cooled filtrate. Filter the resulting crystals of amine hydrochloride and wash with a small amount of water. Store the purified material in a vacuum desiccator. Reagents thus obtained can be stored without any deterioration for more than 1 year.

Stock selenium solution (1 mg of Se/ml). Dissolve 2·20 g of anhydrous sodium selenite in 1 litre of 0·1*M* hydrochloric acid. Standardise the solution iodimetrically. A working solution of 5·00 μg of Se/ml is prepared by suitably diluting the stock solution with 0·1*M* hydrochloric acid.

Hydrochloric acid, reagent grade

2·5M and 1M formic acid

0·1M EDTA solution

Toluene, reagent grade or redistilled

Anhydrous sodium sulphate. Metallic impurities are removed by repeatedly washing a column of reagent grade anhydrous sodium sulphate with a chloroform solution of 8-hydroxyquinoline. The purified reagent is dried and stored in a well-stoppered bottle.

Apparatus

Hitachi EPS-2 auto-recording spectrophotometer

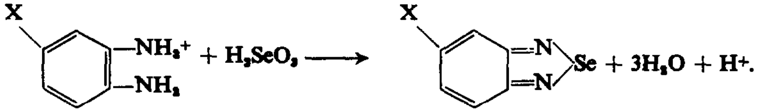
Beckman Model DU spectrophotometer with 1-cm Pyrex and silica cells

Toyo-Roshi Model GB glass-electrode pH meter

Horiba Model P glass-electrode pH meter

RESULTS AND DISCUSSION

4-Substituted *o*-phenylenediamines react with selenous acid to form 5-substituted benzoselenadiazoles as exemplified below:



5-X-2, 1, 3-
benzoselenadiazole

Spectral characteristics

Twenty μg of selenium are taken in a 100-ml separatory funnel. The solution is diluted with 0·1*M* hydrochloric acid to 24 ml and 1 ml of *o*-diamine reagent solution added. After standing for 2 hr, the benzoselenadiazole formed is extracted with exactly 10 ml of toluene, the funnel being shaken for 5 min on a shaker. After complete separation of the two phases, the aqueous layer is drawn off and the toluene layer washed once with 10 ml of 0·1*M* hydrochloric acid. The absorption curves of the benzoselenadiazoles are recorded on the toluene solution thus obtained over the wavelength range from 300 to 420 mμ (Fig. 1). In Fig. 2 are given the absorption curves of the *o*-diamine reagents themselves in toluene.

As shown in Fig. 1, absorption maxima are found at wavelengths of 335, 337, 341 and 350 mμ for benzoselenadiazole, 5-methyl-benzoselenadiazole, 5-chloro-benzoselenadiazole and 5-nitro-benzoselenadiazole, respectively. Thus, the substitution of CH_3-, Cl- and NO_2-groups at the 5-position of benzoselenadiazole and 4-position of *o*-phenylenediamine shifts the absorption maximum to a longer wavelength, in accordance with previous observations on mono-substituted benzenes.[18] Although the absorption curves of 4-nitro-*o*-phenylenediamine and 5-nitro-benzoselenadiazole overlap considerably, the reagent can be effectively eliminated by washing once with 0·1*M* hydrochloric acid, while the 5-nitro-benzoselenadiazole is quantitatively retained in toluene (see the subsequent section).

Effect of pH

The benzoselenadiazoles have been formed at 20° and various pH. After standing for 2 hr, the product is extracted with 10 ml of toluene at the same pH and the extract washed once with 0·1*M*

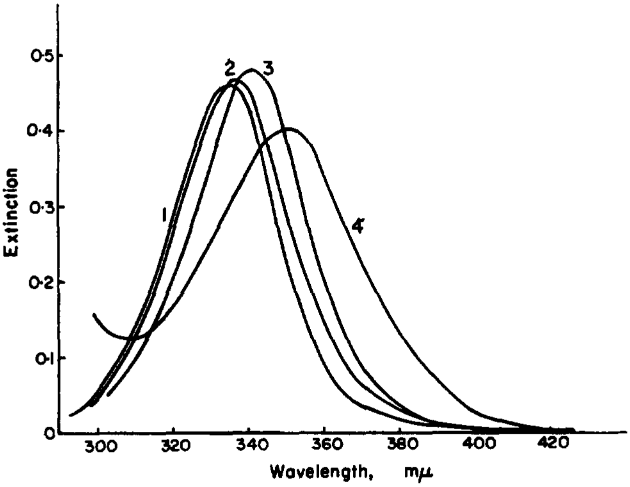


FIG. 1.—Absorption curves of the 5-substituted benzoselenadiazoles:
1: 2,1,3-benzoselenadiazole;
2: 5-methyl-2,1,3-benzoselenadiazole;
3: 5-chloro-2,1,3-benzoselenadiazole;
4: 5-nitro-2,1,3-benzoselenadiazole.

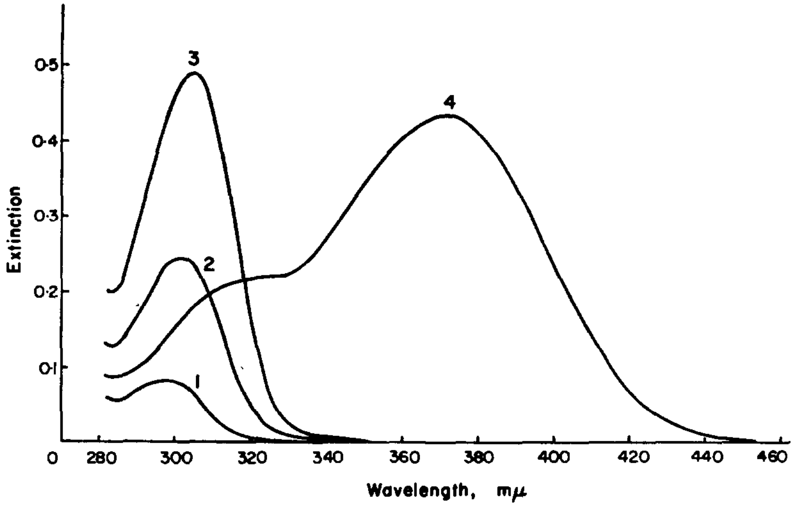


FIG. 2.—Absorption curves of the 4-substituted *o*-phenylenediamines:
1: *o*-phenylenediamine;
2: 4-methyl-*o*-phenylenediamine;
3: 4-chloro-*o*-phenylenediamine;
4: 4-nitro-*o*-phenylenediamine.
(2 μmole of relevant *o*-phenylenediamine extracted at pH 10·1–10·3)

hydrochloric acid. The extinction of the toluene extract is measured at the relevant maximum wavelength using toluene as reference (Fig. 3). The extinction thus obtained is a measure of the extent of reaction at each pH.

As shown in Fig. 3, constant extinctions are obtained over the range of pH 1–2·5 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while the pH ranges of constant extinction are <2·3 and <2 for 4-chloro- and 4-nitro-*o*-phenylenediamines, respectively.

The acid dissociation constants of the *o*-diamine dihydrochlorides were determined spectrophotometrically. The pK-values decrease with increasing electron-withdrawing power of the substituent at the 4-position (Table I). Hence, the results given in Fig. 3 are reasonably explained, if undissociated selenous acid (pK$_1$: 6·60, pK$_2$: 2·57[19]) and singly protonated *o*-diamine are assumed to be concerned in the formation of benzoselenadiazole.*

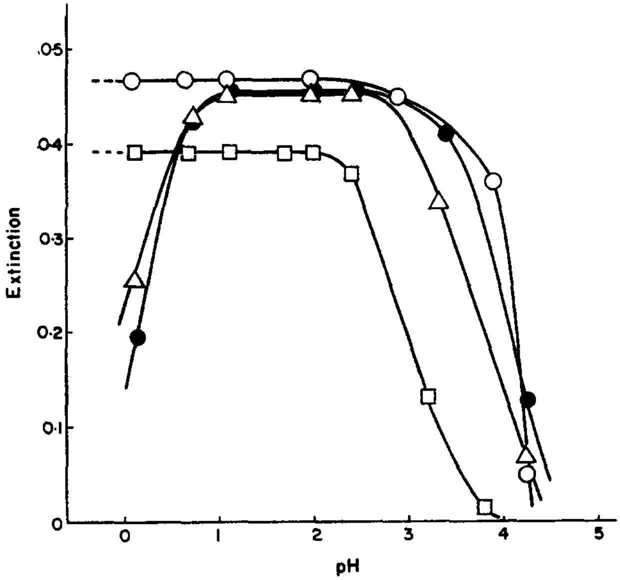


FIG. 3.—Effect of pH on formation of the 5-substituted benzoselenadiazoles:
—△— *o*-phenylenediamine;
—●— 4-methyl-*o*-phenylenediamine;
—○— 4-chloro-*o*-phenylenediamine;
—□— 4-nitro-*o*-phenylenediamine.

Time required for full coloration

The time required for quantitative formation of benzoselenadiazole has been critically examined for each *o*-diamine at 20 ± 1° (Fig. 4). The reaction rate is greater at pH 2 than at pH 1 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while for 4-chloro- and 4-nitro-*o*-phenylenediamines the rate is greater at pH 1 than at pH 2. These results can be easily accounted for by taking into account the following facts: the concentration of reactive singly protonated species is higher at

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* Detailed results on the kinetics of these reactions will be published elsewhere. A kinetic study of the reaction of selenous acid with *o*-phenylenediamine[11] was found while we were preparing this manuscript.

TABLE I.—pK-VALUES OF THE *o*-DIAMINE DIHYDROCHLORIDES (20°; IONIC STRENGTH μ = 1·0)

o-Diamine	pK$_1$	pK$_2$[a]
o-Phenylenediamine	4·85(4·57,[20] 4·58[21])	0·88(1·36,[20] 2·01[21])
4-Methyl-*o*-phenylenediamine	5·24	1·27
4-Chloro-*o*-phenylenediamine	4·04	—0·14
4-Nitro-*o*-phenylenediamine	2·85	—

[a] $K_2 = \frac{C_{HCl}[HA^+]}{[H_2A^{2+}]}$, where total concentration of HCl and free amine are denoted as C_{HCl} and A, respectively.

pH 2 than at pH 1 for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, while the reverse situation holds in the case of the other two *o*-diamines (*cf.* pK-values listed in Table I). Anyhow, 2–2·5 hr are sufficient at 20° for full coloration in all cases. As expected, heating hastens the reaction and 5 min are sufficient for full coloration in

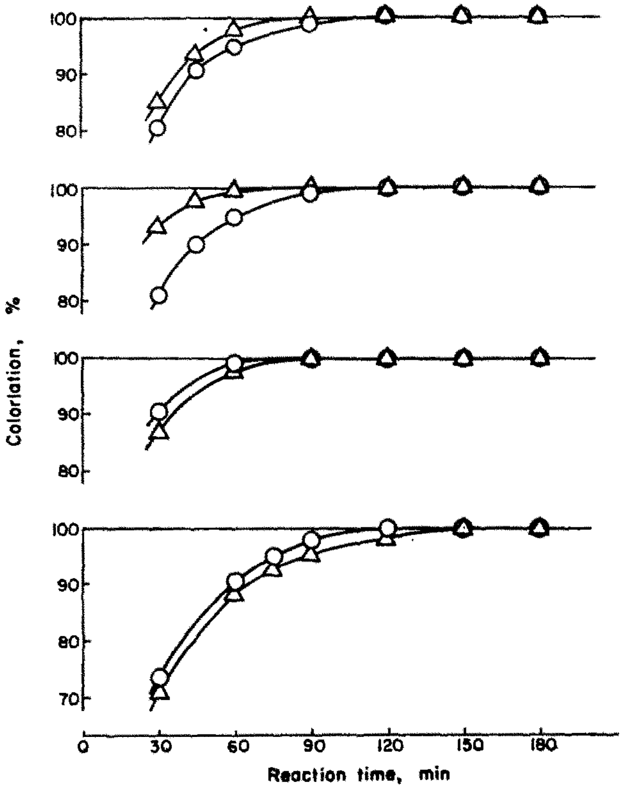

FIG. 4.—Effect of time on maximum formation of the 5-substituted benzoselenadiazoles:

1: *o*-phenylenediamine;
2: 4-methyl-*o*-phenylenediamine;
3: 4-chloro-*o*-phenylenediamine;
4: 4-nitro-*o*-phenylenediamine;
—○— pH 1; —△— pH 2.

a boiling water-bath. The benzoselenadiazoles thus formed are stable indefinitely in toluene and no change of extinction is observed even after standing for more than 10 days at room temperature.

Comparison of molar extinction coefficients and distribution ratios

The molar extinction coefficients of the benzoselenadiazoles are given in Table II. In the same table are also listed the distribution ratios. Because the distribution ratios are too high to measure after only one equilibration of the aqueous and organic phases, 10 ml of toluene containing benzoselenadiazole of known extinction are equilibrated 10 times with 50 ml of aqueous phase saturated with toluene. The distribution ratio can then be easily calculated from the decrease in extinction. As shown in Table II, the molar extinction coefficients are satisfactorily high in all cases and the distribution ratio is sufficiently high for all but *o*-phenylenediamine. The 4-methyl- and 4-chloro-*o*-phenylenediamines are excellent as regards sensitivity as well as in the distribution ratio of the corresponding 5-substituted benzoselenadiazoles.

As observed earlier for aniline and 8-hydroxyquinoline derivatives,[23,24,25] substitution of chlorine at the 4-position of *o*-phenylenediamine most favours the extractability of the resulting benzoselenadiazole. Enhancement of distribution ratio of the 5-substituted benzoselenadiazoles is in the following order:

$$\text{H—} < \text{NO}_2\text{—} < \text{CH}_3\text{—} < \text{Cl—}.$$

Beer's law is obeyed over the range 0–25 μg of selenium/10 ml of toluene for all of the three 4-substituted *o*-phenylenediamines.

TABLE II.—MOLAR EXTINCTION COEFFICIENT AND DISTRIBUTION RATIO OF THE 5-SUBSTITUTED BENZOSELENADIAZOLES

Benzoselenadiazole	Molar extinction coefficient	Distribution ratio[a]	
		pH 1	pH 2
2,1,3-Benzoselenadiazole	17750	149	154
5-Methyl-2,1,3-benzoselenadiazole	17900	657	657
5-Chloro-2,1,3-benzoselenadiazole	18400	2580	2580
5-Nitro-2,1,3-benzoselenadiazole	15460	367	367

[a] The experimental values were recalculated to get values for a 1:1 volume ratio of the aqueous and organic phases and only the chargeless benzoselenadiazole exists in both phases under these experimental conditions. Therefore, these values can be regarded as partition coefficients.

Interference studies

The following elements or compounds do not interfere with the determination of 20 μg of selenium at least up to the specified amount (reaction carried out in 0·1*M* hydrochloric acid unless otherwise noted): aluminium(III) (100 mg), arsenic(III) (1 mg), arsenic(V) (1 mg), barium(II) (400 mg), cadmium(II) (150 mg), calcium(II) (100 mg), chromium(III) (0·05 mg), cobalt(II) (50 mg), copper(II) (10 mg), lead(II) (300 mg, used as nitrate in 0·1*M* formic acid), magnesium(II) (250 mg), manganese(II) (10 mg), nickel(II) (50 mg), tin(II) (0·1 mg), zinc(II) (100 mg), iodide (10 mg), sodium chloride (0·5 g), potassium chloride (0·5 g), potassium chlorate (0·5 g), ammonium sulphate (1 g), sodium nitrate (0·5 g), potassium dihydrogen phosphate (0·5 g), potassium bromide (0·5 g), tartaric acid (150 mg), oxalic acid (1 g).

When antimony or bismuth is present, it is recommended that the 4-chloro- or 4-nitro-derivative be employed and the reaction carried out in 1–2*M* hydrochloric acid. The presence of 150 mg of antimony(III) and 100 mg of bismuth(III) is then without influence.

Iron(III) interferes in all cases, an orange product being formed both at pH 1 and 2. In the case of *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, the colored products extracted in toluene can be completely removed by washing once with 0·1*M* hydrochloric acid and no interference is then appreciable for about 1 mg of iron(III). With 10 mg of iron(III), however, a negative interference is observed. The toluene extracts for 4-chloro- and 4-nitro-*o*-phenylenediamines in the presence of iron(III) show a yellowish shade even after washing with 0·1*M* hydrochloric acid and positive interference results regardless of the quantities of iron(III). Because the formation of stable protonated diamine is more appreciable at pH 1 than at pH 2, the interference of iron(III) is greater at pH 2 than at pH 1. The interference of iron(III) can, however, be effectively eliminated by EDTA (Table III).

TABLE III.—EFFECT OF IRON(III) ON THE DETERMINATION OF 20 μg OF SELENIUM (pH 1)

Fe^{III} added, *mg*	0·1*M* EDTA added, *ml*	Extinction			
		o-Phenylene-diamine	4-Methyl-*o*-phenylene-diamine	4-Chloro-*o*-phenylene-diamine	4-Nitro-*o*-phenylene-diamine
None		0·450	0·453	0·467	0·393
0·4		0·446	0·453	0·496	0·593
0·4		0·450	—	0·490	0·562
1		0·450	0·457	0·586	—
1[a]		0·448	0·454	—	—
1	1	—	—	0·468	0·392
1[a]	1	—	—	0·854	1·12
10		0·077	0·073	2·2	1·95
10		0·096	0·077	—	—
10[a]		0·012	0·024		
10	5	0·450	0·454	0·468	0·395
10[a]	5	0·447	0·454	0·469	0·392
10	10	0·453	0·452	0·467	0·393

[a] pH 2

Molybdenum(VI) gives rise to a negative interference probably because of consumption of the reagent. This interference can also be suppressed by EDTA.

Vanadium(V) also forms yellowish products in aqueous solution at pH 1 and 2; for *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, vanadium does not interfere if the toluene layer is washed once with 0·1*M* hydrochloric acid. For 4-chloro- and 4-nitro-*o*-phenylenediamines, although 60 μg of vanadium(V) have no effect on the determination of selenium, 1·36 mg cause a positive interference, giving rise to a violet or yellow coloration in the toluene which cannot be eliminated by washing. Neither a higher acidity (1*M* hydrochloric acid) nor EDTA eliminates the interference from vanadium (Table IV).

TABLE IV.—EFFECT OF VANADIUM(V) ON THE DETERMINATION OF 20 μg OF SELENIUM (pH 1)

V^V added, *mg*	$0 \cdot 1M$ EDTA added, *ml*	Extinction			
		o-Phenylene-diamine	4-Methyl-*o*-phenylene-diamine	4-Chloro-*o*-phenylene-diamine	4-Nitro-*o*-phenylene-diamine
None		0·450	0·453	0·467	0·393
0·03		0·450	0·453	0·467	0·423
0·06		—	0·453	0·468	0·430
0·06	1	—	0·450	0·468	0·477
0·12		0·444	—	—	—
0·12	1	0·449	—	—	—
1·36		0·450	0·455	0·645	0·505
1·36[a]		0·450	0·450	1·04	1·12
1·36	2	0·448	0·446	0·649	1·37
1·36[a]	2	0·447	0·447	0·559	1·42
1·36	5	0·450	0·449	0·601	1·61

[a] pH 2

More than 0·1 mg of tin(IV) or chromium(III) gives rise to a negative interference in all cases and neither higher acidity (1*M* hydrochloric acid nor the addition of EDTA is effective in the suppression of the interference. However these elements can be easily separated from selenium as oxinates.

CONCLUSION

o-Phenylenediamine and 4-methyl-*o*-phenylenediamine can be regarded as highly selective reagents for the determination of selenium when used with EDTA. Of these, the latter is the better because of the higher distribution ratio of 5-methylbenzoselenadiazole. If iron(III), vanadium(V), tin(IV) and chromium(III) are separated by extraction as 8-hydroxyquinolates from a slightly acidic medium (*ca.* pH 4), the other two reagents, 4-chloro- and 4-nitro-*o*-phenylenediamine, can also be used successfully. These two *o*-diamines, in particular the latter, can be very conveniently employed for the determination of selenium in strongly acidic solution, *e.g.*, the determination of selenium(VI) after reduction to the quadrivalent state in concentrated hydrochloric acid. Thus, taking into consideration the above findings, one can choose one of the four *o*-diamines to suit a particular problem.

Zusammenfassung—*o*-Phenylendiamin und seine 4-substituierten Derivate 4-Methyl-, 4-Chlor- und 4-Nitro-*o*-phenylendiamin reagieren alle mit seleniger Säure in saurer Lösung zu Benzoselenadiazolen, die in Toluol extrahiert werden können. Verteilungsverhältnis, Absorptionsmaximum, molarer Extinktionskoeffizient und optimale Bildungsbedingungen fur jedes Benzoselenadizaol wurden ermittelt. Eisen(III) und Molybdän(VI) stören die Selenbestimmung mit diesen Reagentien, die Störung kann jedoch in beiden Fällen durch EDTA beseitigt werden. Vanadium(V) stört nur im Falle der 4-Chlor-und 4-Nitro-*o*-phenylendiamine, und diese Störung läßt sich mit EDTA nicht beseitigen.

Résumé—L'*o*-phénylènediamine et ses dérivés 4-substitués, 4 méthyl-*o*-phénylènediamine, 4-chloro-*o*-phénylènediamine et 4-nitro-*o*-phénylènediamine, réagissent tous avec l'acide sélénieux en solution acide pour former des benzosélénodiazoles, extractibles au toluène. Pour chaque benzosélénodiazole, on a étudié le coefficient de partage, la longueur d'onde du maximum d'extinction, le coefficient d'extinction moléculaire et les conditions optimales de formation. Le fer(III) et le molybdène(VI) interfèrent dans le dosage du sélénium au moyen de ces réactifs, mais cette interférence peut être éliminée dans les deux cas au moyen d'EDTA. Le vanadium(V) n'interfère qu'avec les 4-chloro- et 4-nitro-*o*-phénylènediamines, et l'EDTA n'élimine pas cette interférence.

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NEUTRON-ACTIVATION ANALYSIS OF COPPER IN LEAD

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Summary—Submicrogram quantities of copper were determined in lead samples using neutron-activation analysis. The chemical separation of copper was performed by extraction with 2,2′-diquinolyl (cuproïne) in isoamyl alcohol. No minor or trace constituents in the lead samples interfere with the copper determinations.

INTRODUCTION

ALTHOUGH copper is a common constituent of lead, a neutron-activation analysis of this element in a lead matrix has hitherto never been developed. Copper has been determined in various other materials[1–7] using a separation as CuCNS or CuS. Non-destructive gamma-spectrometric copper determinations have been performed by Cosgrove and Morrison[8] using decay measurements of the 0·51-MeV annihilation radiation of ^{64}Cu. Chinaglia[9] and Petit and Engelmann[10] used a rather specific ^{64}Cu determination based on the coincidence measurement of the two annihilation quanta. Other isotopes yielding β^+ radiation can, however, interfere with the ^{64}Cu determination. Activation analyses based on irradiations with a Van de Graaff accelerator neutron source have been made by Guinn and Wagner.[11]

In this paper a copper determination in lead using ^{64}Cu is described. A specific chemical separation procedure is used, based on the extraction of the ^{64}Cu-2,2′-diquinolyl complex in isoamyl alcohol according to Hoste.[12]

NUCLEAR PROPERTIES

^{64}Cu ($t_{\frac{1}{2}}$ = 12·8 hr) formed by neutron irradiation with an activation cross-section of 3·0 b predominantly gives rise to annihilation radiation. A low-intensity γ-ray of 1·34 MeV is valueless for a gamma spectrometric determination, in the presence of a mixture of radioisotopes from other contaminants of the lead samples, although the matrix itself is quite inert for neutron irradiation. Table I gives a survey of the nuclear values for most of the common minor and trace constituents of lead.

If a chemical separation of copper is used, none of these elements can interfere with the copper determination. The ^{64}Zn (n,p)^{64}Cu reaction with a cross-section of 22 mb can give rise to an interference, which was experimentally determined for irradiations in the BR-1 reactor at a neutron flux of 8 × 10^{11} neutrons . cm^{-2} . sec^{-1}. For a concentration of 100 ppm of zinc, the error in the determination of 1 ppm of copper was only 3%. The use of more thermalised irradiation positions of the reactor can further reduce this error to a significant degree if required.

Neutron shadowing effects in the copper standards were avoided by the use of dilute copper solutions in quartz ampoules. As can be seen from Table II, the specific activity of copper remains unaffected by self-shadowing up to concentrations of 7 mg of copper in 250 μl of water (irradiation at 8 × 10^{11} neutrons . cm^{-2} . sec^{-1} in BR-1).

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TABLE I.—RADIONUCLIDES PRODUCED FROM TRACE AND MINOR CONSTITUENTS OF LEAD ALLOYS BY IRRADIATION WITH THERMAL NEUTRONS

Element	Target nuclide	Isotopic abundance, %	Isotopic activation cross section, *barns*	Product on thermal neutron irradiation	Half-life	γ-radiation and energy, *MeV*
Cu	^{63}Cu	70·13	3·0	^{64}Cu	12·8 hr	0·511; 1·34
	^{65}Cu	29·87	0·65	^{66}Cu	5·1 min	0·83; 1·04
As	^{75}As	100	4·3	^{76}As	26·5 hr	0·55; 0·64; 1·20; 1·78; 2·10; 2·80
Sb	^{121}Sb	56	3·7	^{122}Sb	2·8 d	0·566; 0·686; 1·137 1·256
	^{121}Sb	56	1·3	^{122m}Sb	3·5 min	0·060; 0·075
	^{123}Sb	44	1·1	^{124}Sb	61 d	0·603; 0·641; 0·716 1·68; 2·09
	^{123}Sb	44	0·013	^{124m_1}Sb	1·3 min	0·012
	^{123}Sb	44	0·013	^{124m_2}Sb	21 min	0·018
Ag	^{107}Ag	51·9	23	^{108}Ag	2·3 min	0·430; 0·511; 0·600 0·630
	^{109}Ag	48·1	54	^{110}Ag	24 sec	0·660; 0·720; 0·810 0·880; 0·940
	^{109}Ag	48·1	1·4	^{110m}Ag	270 d	0·656; 0·681; 0·706 0·764; 0·884; 0·940 1·38; 1·48
Zn	^{64}Zn	50·9	0·25	^{65}Zn	254 d	0·511; 1·11
	^{68}Zn	17·4	0·62	^{69m}Zn	13·8 hr	0·438
Sn	^{112}Sn	1·1	0·013	^{113}Sn	112 d	0·260; 0·392
	^{116}Sn	15·5	0·001	^{117m}Sn	14 d	0·161; 0·320
	^{122}Sn	5·5	0·007	^{123}Sn	40 min	0·153
	^{124}Sn	6·8	0·01	^{125m}Sn	9·5 min	0·326
Na	^{23}Na	100	0·54	^{24}Na	14·8 hr	1·38; 2·76

TABLE II.—NEUTRON SELF-SHADOWING

Weight of copper, *mg/250 μl*	Count rate, *c/m*	Relative specific activity, *c/m. mg*
17·322	296,470	17,115
6·929	119,740	17,470
1·732	30,537	17,730
0·693	11,955	17,426
0·173	3,005	17,630

EXPERIMENTAL

Chemical separation of copper traces from lead

The extraction of the copper-2,2′-diquinolyl complex in isoamyl alcohol can be used for the detection and the determination of trace amounts of copper. The yield is *ca.* 99% in the presence of gram amounts of lead for an isoamyl alcohol-water volume ratio of 1:3·5. As appears from Table III, the extraction is practically quantitative for 100 μg-amounts of copper when 10 ml of a 0·02% 2,2′-diquinolyl solution is used. Two successive extractions ensure a quantitative recovery from the aqueous phase.

The influence of arsenic, antimony, zinc, bismuth and silver was carefully investigated using tracers of these elements. None of these common contaminants of lead is extracted together with copper, or gives rise to a measurable interference.

TABLE III.—COPPER EXTRACTION

Cu carrier, *µg*	Extraction, %
10	99·1
15	99·8
20	99·0
40	99·0
55	99·0
68	99·5
85	99·2
170	98·5
340	73

Procedure

Lead samples of *ca.* 1 g are sealed in quartz ampoules and are irradiated in the BR-1 reactor at a neutron flux of 8 × 10^{11} neutrons.cm^{-2}. sec^{-1}. The irradiated samples are dissolved in 30 ml of 1*M* HNO_3 in the presence of 30 μg of $Cu(NO_3)_2$ carrier. The solution is neutralised to pH 4-4·5 with NaOH and 200-300 mg of $NH_2OH.HCl$ are added to reduce the copper to the univalent state. The solution is shaken for 1 min with a 10-ml portion of a 0·02% 2,2′-diquinolyl (cuproïne) solution in isoamyl alcohol. After centrifugation, both phases are separated. 30 μg of $Cu(NO_3)_2$ are again added, and the separation is repeated. The isoamyl alcohol fractions are assembled and counted in a well-type NaI(Tl) crystal scintillator. The radiochemical purity of the organic fractions was checked with a multichannel analyser. The aqueous fraction is γ-spectrometrically controlled for ^{69m}Zn and ^{64}Cu activities. In the presence of high activities of isotopes from Sb, As, Zn, Ag and Cd, it is necessary to wash the isoamyl alcohol fraction thoroughly with water.

RESULTS

The method was tested on a series of synthetic lead samples, on four commercial high-purity lead samples and on a lead alloy.

TABLE IV.—ACTIVATION ANALYSIS OF COPPER IN LEAD

No.	Cu added per g of Pb, *µg*	Weight of lead, *g*	Cu concentration, *ppm*	Cu found, *ppm*	Average
1	6·88	1·0568	10·24*	10·00	10·20 ± 0·24
2	6·88	1·0304	10·24*	10·03	
3	6·88	1·0514	10·24*	10·23	
4	6·88	1·0058	10·24*	10·53	
5	3·44	0·5000	6·80	6·51	6·58 ± 0·14
6	3·44	0·5001	6·80	6·58	
7	3·44	0·5032	6·80	6·47	
8	3·44	0·5030	6·80	6·60	
9	3·44	0·5008	6·80	6·40	
10	3·44	0·5062	6·80	6·55	
11	3·44	0·9792	6·80	6·86	
12	3·44	1·0182	6·80	6·72	
13	0	1·0331	3·36	3·28	3·36 ± 0·16
14	0	1·0007	3·36	3·17	
15	0	1·0074	3·36	3·46	
16	0	1·0171	3·36	3·20	
17	0	0·9792	3·36	3·49	
18	0	1·0002	3·36	3·30	
19	0	1·0198	3·36	3·34	
20	0	0·6671	3·36	3·67	
21	0	1·0001	3·36	3·32	

* Concentration of copper = concentration added + concentration initially present (3·36 ppm).

The synthetic samples were obtained by evaporating different amounts of a standardised copper nitrate solution with gram amounts of lead powder of known copper content. The results of activation analyses of these synthetic samples are shown in Table IV.

The results of the commercial lead samples are given in Table V. Some of the samples contain high concentrations of antimony (JM-4: 0·8%) and silver (VM-1: 11 ppm); no interference, however, was observed from these elements. The copper concentration throughout the ingots appears to be inhomogeneous. The edges of sample VM-3 contain a concentration of copper almost twice as high as in the middle of the ingot.

The lowest quantity of copper analysed was 0·1 μg. Appreciably lower copper concentrations can, however, be determined. One can compute that an irradiation of

TABLE V.—ACTIVATION ANALYSIS OF COPPER

Sample	Weight of lead, *g*	Activity, *c/m*	Cu found, *ppm*	Average
VM-1	0·8265	81,803	3·00	2·83 ± 0·33
	1·2381	130,702	3·20	
	1·2262	104,748	2·59	
	1·1202	88,379	2·39	
	1·0496	103,640	2·99	
VM-2	0·6162	45,637	2·28	2·04 ± 0·23
	0·4987	35,012	2·16	
	0·5588	30,959	1·71	
	0·4352	30,334	2·15	
	0·6747	41,845	1·91	
VM-3	0·1391	61,621	4·11	3·93 ± 0·13
	0·1391	60,500	4·04	
	0·1391	59,551	3·97	
	0·1391	59,985	4·00	
	0·1391	60,187	4·02	
	0·1391	57,804	3·86	
	0·1391	56,764	3·79	
	0·1391	56,789	3·79	
	0·1391	56,379	3·76	
VM-4	0·0585	50,010	2·27	2·23 ± 0·11
	0·0585	51,489	2·34	
	0·0585	51,955	2·36	
	0·0585	45,075	2·05	
	0·0585	47,766	2·17	
	0·0585	48,964	2·22	
JM-4	0·1031	20,580	45·0	43·9 ± 2·9
	0·1002	19,699	44·3	
	0·1077	19,669	41·1	
	0·1032	18,773	41·0	
	0·1066	18,513	47·8	
	0·1063	18,953	49·1	
	0·1116	17,385	43·8	
	0·1030	16,563	45·3	
	0·1033	13,259	38·8	
	0·2011	14,353	43·2	
VM-3	0·1105	125,055	6·62	6·51 ± 0·22
	0·1105	124,639	6·60	
	0·1105	122,161	6·47	
	0·1105	128,453	6·80	
	0·1105	115,881	6·14	
	0·1105	121,309	6·42	

10 hr at 8×10^{11} neutrons . cm^{-2} . sec^{-1} should permit the determination of 0·005 μg of copper.

The copper determination can be completed within 0·5–1 hr after the end of the irradiation. The reproductibility is generally better than 10%; the higher standard deviations of the results of the analysis in Table V are rather produced by inhomogenities of the copper in the lead-metal samples.

The proposed method can be associated with a γ-spectrometric determination of arsenic and antimony in the aqueous layer, using a technique previously presented.[13]

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Zusammenfassung—Submikrogrammengen Kupfer in Bleiproben wurden durch Neutronenaktivierungsanalyse bestimmt. Kupfer wurde durch Extraktion mit 2,2′-Dichinolyl (Cuproin) in Isoamylalkohol abgetrennt. Keine Neben- und Spurenbestandteile der Bleiproben stören bei den Kupferbestimmungen.

Résumé—On dose, dans des échantillons de plomb, des quantitiés de cuivre inférieures au microgramme au moyen de l'analyse par activation de neutrons. La séparation du cuivre a été réalisée par extraction au 2,2′-diquinolyle (cuproïne) en alcool isoamylique. Les constituants secondaires que peuvent renfermer les échantillons de plomb n'interfèrent pas dans les dosages du cuivre.

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STUDIES IN THE POLAROGRAPHY AND COULOMETRY OF THE AQUO AND CHLORIDE COMPLEXES OF RHODIUM(III)

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Summary—The polarography of the aquo and chloride species of rhodium(III) has been investigated. The aquo complex was prepared by fuming in perchloric acid, and the various chloride complexes were prepared by heating in the presence of chloride ion. In all cases, polarography gave irreversible diffusion controlled waves. It is essential that the solution constituents be carefully reproduced for analytical polarography, and that the solutions be stabilised by heating, because equilibrium is established very slowly at room temperature. Mercury cathode electrolysis at a controlled potential showed that the polarographic reduction step involved 3 electrons. This is used as the basis of a coulometric determination of 1·5- to 15-mg amounts of rhodium in 0·2–0·4*M* chloride electrolyte at a potential of −0·2 V *vs.* SCE.

INTRODUCTION

THERE have been various papers concerned with the direct current polarography of rhodium(III) in aqueous media. The behaviours of Na_3RhCl_6,[1] $RhCl_3$[2–4] and $[Rh(NH_3)_3Cl)]Cl_2$[5] have been studied in a variety of non-complexing electrolytes and, in addition, ammonia,[5] bromide,[6] chloride,[1] cyanide,[5,7] EDTA,[8] fluoride,[7,9] oxalate,[2] γ-picoline,[10] pyridine,[5,7,10,11] thiocyanate[5,7,12] and thiourea[13] have been employed as complexing electrolytes. In these latter cases the complex was generally formed by warming a stock solution of Na_3RhCl_6 or $RhCl_3$ with the electrolyte, but in some cases the solution was not warmed and it is difficult to judge the nature of the species actually present on polarography.

It was found possible to have a number of different rhodium(III) species simultaneously present. For example, two waves could be obtained with γ-picoline and pyridine electrolytes[10] if the reaction was incomplete. The first wave was characteristic of Na_3RhCl_6 itself, while the second, more negative wave resulted from the reduction of a new complex species. With these complexing agents acid solutions could not be employed, because under such conditions the chloride complex decomposed with difficulty. With oxalate[2] two different species could also be obtained. It was postulated that Na_3RhCl_6 was first converted to a $Rh(C_2O_4)_2^-$ complex, but prolonged heating gave a $Rh(C_2O_4)_3^{3-}$ complex with a more negative half-wave potential.

Of the species investigated, the chloride complex is reduced at the most positive potentials. Cozzi and Pantani[1] observed that the polarographic wave was complex, and distinguished two composite parts in this case, and also with the bromide[6] and thiocyanate[12] complexes. The first part of the composite wave with bromide was found to be markedly affected by the presence of surface active agents in the solution. This suggests that it is probably an adsorption pre-wave.

The number of electrons involved in the reduction steps has been determined, generally by coulometry, but sometimes by analogy with the polarographic waves obtained with other complexes, usually those of cobalt(III). In general, the reduction proceeds to the metal but there are conflicting claims. In some cases intermediate rhodium(I) and rhodium(II) oxidation states are indicated as products of the electrode reaction, and in the case of fluoride[9] a two-step reduction has been reported. In the cases of γ-picoline and pyridine, a partial controlled potential reduction at a large mercury cathode gave a solution with a composite anodic-cathodic polarographic wave, confirming the existence of a stable intermediate oxidation state.[10] Plots of log $(i/i_d - i))$ *vs.* E_{dme} indicated that the electrode reaction was irreversible in the case of the chloride,[1] γ-picoline,[10] pyridine,[10] thiocyanate[12] and thiourea[13] complexes, but reversible in the case of the bromide[6] complex. In spite of this irreversibility, Cozzi and Pantani[1] calculated a set of successive formation constants for the chloride complexes employing the method of De Ford and Hume.[14]

Most of these electrolytes gave waves that are analytically useful with the emphasis on the polarography of "pure" solutions. Of the electrolytes, EDTA[8] and thiourea[13] have been recommended for the determination of rhodium in the presence of iridium. Douglas and Magee[15] used oscillographic techniques to study the behaviour of a number of rhodium(III) complexes and developed a procedure for the determination of rhodium in rhodium-palladium alloys using a thiocyanate electrolyte. Beran and Doležal[16] have also studied the oscillographic polarography of rhodium(III) in a hydrochloric acid electrolyte, and they detected a stepwise rhodium reduction accompanied by a catalytic hydrogen ion reduction.

Although the polarographic behaviour of a number of complexes has been reported, no investigation has been carried out into the behaviour of the aquo species of rhodium(III). In addition, there has been no attempt to devise accurate coulometric procedures for the determination of rhodium(III). Such coulometric results as have been reported have been single approximate experiments designed to determine the value of *n* in the polarographic step. The present investigation is concerned with the polarographic and coulometric behaviour of the aquo and chloride species of rhodium(III).

EXPERIMENTAL AND RESULTS

Polarograms were recorded on a Leeds and Northrup Type E Electrochemograph with the damping set in the No. 1 position. The cell was a conventional H-type with a saturated calomel electrode. The polarographic currents reported have been corrected for residual effects by subtraction of the current found in blank solutions at the same potential. The polarography was carried out at 25·0° unless otherwise noted.

The controlled potential coulometric titrations were carried out using an apparatus patterned after that of Booman.[17] The conventional H-type cell had a capacity, *V*, of 100 cm^3 and a mercury surface area, *A*, of 16 cm^2. The mercury was introduced into the cell by a bottom stopcock and levelling bulb. The reference electrode was a Beckman saturated potassium chloride-calomel type (39170).

For the usual analysis, approximately 80 ml of the appropriate base electrolyte were taken, de-aerated for 15 min and pre-electrolysed. The mercury was withdrawn from the cell, the rhodium solution was added and the entire electrolyte was de-aerated for an additional 10 min. The mercury was returned to the cell and the electrolysis was carried out. To keep the residual current as low as possible, the potential selected for electrolysis was the lowest value safely on the polarographic limiting current plateau. In calculating the quantity of electricity, *Q*, required for the rhodium reduction, a background correction equivalent to the product of the final constant residual current and time was made.

For a diffusion-controlled electrolysis, the concentration of the reacting substance, C_t at any time *t*, is given by

$$C_t = C_0 e^{-kt} \qquad (18)$$

where C_0 is the concentration of the reacting substance at $t = 0$. If the reduction is diffusion-controlled, a plot of $-2{\cdot}303 \log_{10}(1 - Q_t/Q)$ against t is a straight line with slope of k sec^{-1}.[19] All electrolyses reported in this paper gave such straight line plots, and k values are given.

pH measurements were made using a Cambridge Bench Model pH Meter. The glass electrode was a Cambridge wide range type (42558) and the reference electrode a Leeds and Northrup saturated potassium chloride-calomel type (1191-31). The meter was standardised against a saturated potassium hydrogen tartrate solution prepared according to the directions of the National Bureau of Standards from their sample 188 (pH 3·56 at 25·0°).

For controlled potential electrolytes and pH measurements in chloride solutions the reference electrode was used directly, whereas an intermediate bridge containing a 1*M* sodium nitrate solution was used with perchlorate-containing electrolytes. For coulometry and polarography involving chloride solutions, the agar bridge separating the cell compartments was prepared as a gel saturated in potassium chloride. With perchlorate-containing solutions, a gel 1*M* in sodium nitrate was employed. All potentials (V) reported in this paper are relative to the saturated calomel reference electrode.

Spectra in the visible and ultraviolet regions were recorded using a Bausch and Lomb Spectronic 505 with matched quartz cells of 1- or 10-cm path length. For the mixed aquo-chloride complexes, the estimates of average composition were taken from the results of Wolsey, Reynolds and Kleinberg.[20] The red $RhCl_6^{3-}$ species gives spectrophotometric peaks at 519 and 410 mμ, the yellow $Rh(H_2O)_6^{3+}$ species at 393 and 306 mμ. Between these are a series of mixed complexes of intermediate orange colours and with intermediate peak positions.

All chemicals used were reagent-grade. Prepurified nitrogen (less than 20 ppm of oxygen) was used to displace and exclude oxygen from the solutions for polarography and coulometry.

The standard rhodium solution was prepared from sodium hexachlorhodite, Na_3RhCl_6, supplied by Englehard Industries Inc. (Lot XXV-1); 10·0 g of the salt were dissolved in 5 ml of concentrated hydrochloric acid diluted with double distilled water. The solution was filtered and diluted to a final volume of 2 litres. The rhodium content was determined by thiobarbituric acid precipitation according to the method of Currah, McBryde, Cruikshank and Beamish.[21] Three 10-ml aliquot portions of the solution gave, after ignition in hydrogen, 12·12, 12·14 and 12·09 mg of rhodium. Over the six-month experimentation period, no significant variation of coulometric results was noted, indicating that the rhodium(III) was stable. As a working solution, the stock solution was diluted four-fold with double distilled water.

Studies in Perchlorate Media

The existence of the hexa-aquo complex of rhodium(III) has been postulated by several authors.[22-24] This complex has been prepared from a Na_3RhCl_6 solution by repeated precipitations with sodium hydroxide and dissolution in perchloric acid,[22] by dissolving $Rh(ClO_4)_3{\cdot}6H_2O$ in water[23] and by boiling $Na_3RhCl_6{\cdot}12H_2O$ with 5*M* perchloric acid.[24] In each case the solutions were yellow, and a $Rh(H_2O)_6^{3+}$ species was postulated. Some controversy exists[25] over the nature of the species prepared by boiling $Na_3RhCl_6{\cdot}12H_2O$ with 5*M* perchloric acid, but the interpretation of the spectrophotometric results reported by these authors can be questioned.

Polarography

Solutions to be polarographed were prepared by fuming aliquot portions of the rhodium solution with equal volumes of 72% perchloric acid. The samples were fumed to a volume of about 2 ml, washed down with water and again fumed to the same volume. The resultant solutions were diluted, and sodium perchlorate was added to the extent of 0·1 mole per litre of final volume. The acidity of the solutions was adjusted, when necessary, by the addition of a 1*M* sodium hydroxide solution and they were then heated on a steam bath for at least 1 hr before cooling and making up to the final volume of 100 ml. The ionic strength was approximately 0·13*M*. Spectra of the solutions gave 2 peaks, at 303 mμ and 392 mμ, confirming the existence of the $Rh(H_2O)_6^{3+}$ species.

Polarography gave 2 reduction waves.

Over the pH range 1·5 to 2·7, the first wave had $E_{1/2} = -0{\cdot}38$ V and a limiting current (i_d) independent of pH. The electrode process appeared to be diffusion controlled; i_d was proportional to the concentration of rhodium(III) and to the square root of the height, h, of the mercury column (Table I). The temperature coefficient of i_d was +1·6% per degree (0–32°). The wave was irreversible; a plot of E_{dme} *vs.* $-\log[i/(i_d - i)]$ gave a straight line of slope 112 mV and $E_{1/2}$ had a temperature coefficient of +3·7 mV per degree (0–32°). Above pH 2·9, $E_{1/2}$ became more negative and i_d decreased. This effect can be attributed to hydrolysis.[26]

At a more negative potential, the second wave occurred with a pronounced maximum. The usual suppressors—Methyl Red, gelatin and Triton X-100—had little effect. With a 0·147 m*M* rhodium(III) solution, $E_{1/2}$ was approximately −0·72 V; it became more positive with increasing temperature,

TABLE I

C_{Rh}(III), *mM*	i_d, *μamp*	i_d/C	i_d, *μamp*	i_d/C	
0·13*M Perchlorate* (i_d and *t* measured at −0·6 V)					
	at h_1	at h_1	at h_2	at h_2	
0·0263	0·26	$9{\cdot}8_8$	0·23	$8{\cdot}7_4$	mean $\frac{i_d}{Ch_1 1/2} = 0{\cdot}38$
0·0525	0·51	$9{\cdot}7_3$	0·45	$8{\cdot}5_3$	
0·105	1·00	$9{\cdot}5_2$	0·89	$8{\cdot}4_5$	
0·300	2·80	$9{\cdot}3_3$	2·52	$8{\cdot}4_0$	mean $\frac{i_d}{Ch_2 1/2} = 0{\cdot}38$
0·420	3·85	$9{\cdot}1_7$	3·53	$8{\cdot}4_0$	
0·588	5·39	$9{\cdot}1_7$	4·77	$8{\cdot}1_1$	
0·1*M Chloride* (i_d and *t* measured at −0·3 V)					
	at h_1	at h_1	at h_2	at h_2	
0·0188	0·19	10·3	0·17	$9{\cdot}2_6$	
0·0376	0·38	10·3	0·35	$9{\cdot}1_8$	mean $\frac{i_d}{Ch_1 1/2} = 0{\cdot}42$
0·105	1·10	10·4	1·03	$9{\cdot}8_0$	
0·300	3·16	10·5	2·82	$9{\cdot}4_0$	
0·420	4·35	10·3	3·86	$9{\cdot}1_9$	mean $\frac{i_d}{Ch_2 1/2} = 0{\cdot}42$
0·588	6·06	10·3	5·38	$9{\cdot}1_5$	
0·4*M Chloride* (i_d and *t* measured at −0·3 V)					
	at h_3	at h_3			
0·0294	0·34	11·5	15 min after dilution		
0·117	1·33	11·4			
0·294	3·50	11·9			
0·0294	0·32	11·1	24 hr after dilution		
0·117	1·27	10·9			
0·294	3·35	11·4			
0·294	3·25	11·0	diluted and heated for 1 hr		
6*M Chloride* (i_d and *t* measured at −0·4 V)					
	at h_3	at h_3			
0·0294	0·29	$9{\cdot}9_3$			
0·117	1·13	$9{\cdot}6_5$			
0·294	2·93	$9{\cdot}9_6$			

Capillary Characteristics

Capillary (*1*)	h_1 eff = 62·1 cm	m_1 = 2·021 mg/sec	
	h_2 eff = 50·3 cm	m_2 = 1·623 mg/sec	
	0·13*M* perchlorate	$t_1 = 4{\cdot}4_0$ sec	$t_2 = 5{\cdot}4_5$ sec
	0·1*M* chloride	$t_1 = 4{\cdot}2_9$ sec	$t_2 = 5{\cdot}2_9$ sec
Capillary (*2*)	h_3 eff = 62·0 cm		
	0·4*M* chloride	$t_3 = 3{\cdot}5_8$ sec	
	6*M* chloride	$t_3 = 3{\cdot}3_8$ sec	

but also more negative with increasing rhodium(III) concentration. The electrode process was not diffusion controlled; the limiting current could only be approximately measured as the minimum before the discharge of the supporting electrolyte but it showed little variation with *h* and it had a temperature coefficient of −2·7% per degree (0–32°). The wave height was dependent on both the concentration of rhodium and the acidity of the solution (Fig. 1).

Additional experiments were performed using $Rh(H_2O)_6^{3+}$ prepared by a second method. A portion of the working solution was taken and the rhodium(III) was precipitated using a sodium hydroxide solution. The precipitate was washed once with water and taken up in 50 ml of perchloric acid solution of pH 1·3. The resulting polarogram was similar to those from fumed samples, except that a prewave representing about 5% of the total wave height occurred with $E_{1/2}$ near 0 V. This may be attributed to a chloride complex (ref. 22, *vide infra*) which was not completely destroyed by the single precipitation.

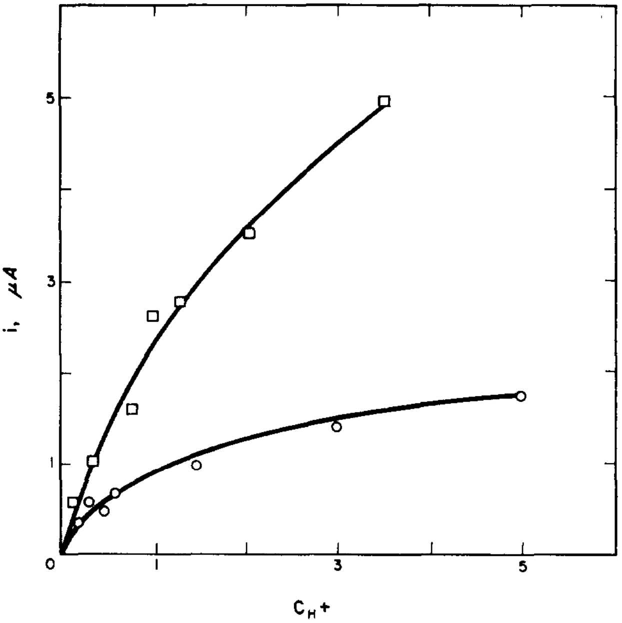

FIG. 1(*a*).—"Second" wave at rhodium(III) concentration of 0·147m*M*:
○ Perchlorate media, values of C_{H}^{+} are in $M \times 10^3$.
□ Chloride media, values of C_{H}^{+} are in $M \times 10^2$.

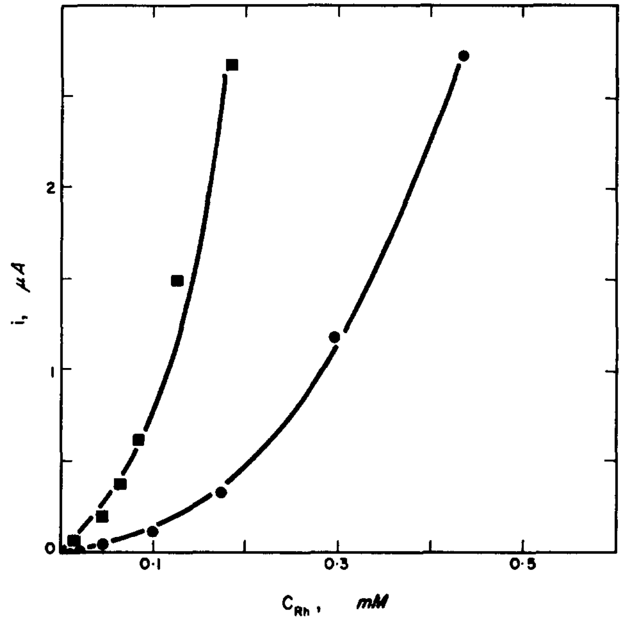

FIG. 1(*b*).—"Second" wave at fixed pH:
● Perchlorate media, pH 2·33 ± 0·07.
■ Chloride media, pH 3·04 ± 0·04.

Controlled potential electrolysis

Samples of working solution were fumed with 10 ml of 72% perchloric acid to a volume of 5 ml, washed down and fumed again to the same volume. This solution was added to a pre-electrolysed 0·1*M* sodium perchlorate base electrolyte for coulometry at −0·55 V. For two samples the pH of the fumed solution and of the base electrolyte was adjusted to a value of 2·1 ± 0·1 before electrolysis ($k = 0{\cdot}05\ sec^{-1}$). For two other samples the fumed solution was used with no prior reduction of acidity ($k = 0{\cdot}14\ sec^{-1}$). Assuming a 3-electron reduction, the results are in fair agreement with the rhodium taken (Table II).

TABLE II

Reduction	Background, *mamp*	Rh taken, *mg*	Rh found, *mg*		
Perchlorate medium, pH 1	0·6–0·8	7·56	7·52	7·46	
Perchlorate medium, pH 2·1	0·3–0·4	6·07	6·00	6·06	
Chloride medium, 0·2–0·4*M*	0·01–0·04	15·09	15·05		
		10·59	10·60	10·55	
		7·56	7·56	7·54	7·50
			7·53	7·53	7·51
		6·07	6·06	6·02	6·06
			6·06	6·08	
		4·55	4·57		
		3·04	3·04		
		1·52	1·55	1·55	
		7·39[a]	7·40	7·38	
Chloride medium, 6*M*	0·08–0·16	9·08	9·04		
		7·56	7·53	7·55	
		6·07	6·05		
		3·04	3·03		
		1·52	1·52		
Chloride medium (after perchlorate fuming)	0·05	7·56	7·56		
		6·07	6·04		

[a] Na_3RhCl_6 solution provided and standardised by Mrs. A. Lee

Studies in Chloride Media

In aqueous solutions containing chloride ions, rhodium(III) exists in a series of complexes with a general formula of $RhCl_n(H_2O)_{6-n}^{3-n}$ where *n* is 0–6. The distribution of rhodium among the various species depends on the concentration of chloride ion,[1,20,24] temperature [20,24] and time.[20,24] At room temperature, equilibrium among the different species is established slowly.

Polarography

6M Hydrochloric acid. In this electrolyte $RhCl_6^{3-}$ is the predominant solution constituent.[24] Solutions were prepared by heating aliquot portions of rhodium solution with equal volumes of 12*M* hydrochloric acid on the steam-bath for about 2 hr, followed by cooling and dilution with 6*M* hydrochloric acid. The resulting solutions were red in colour, and gave spectrophotometric peaks at 519 and 410 mμ confirming the existence of the $RhCl_6^{3-}$ species.[20,24] The positions of the peaks did not shift over a period of at least 4 weeks.

Polarography of these solutions gave one composite wave as reported by Cozzi and Pantani.[1] The behaviour did not correspond to the existence of an intermediate oxidation state, because the ratio of component heights was variable; neither does it result from the existence of two species, for $RhCl_6^{3-}$ is the only significant contribution. Plots of E_{dme} *vs.* $-\log [i/(i_d - i)]$ gave two intersecting straight lines, the first of slope 170 mV, the second of slope 57 mV. Assuming $n = 3$ for the over-all reduction, both parts of the wave are thus irreversible. The second line extrapolated to $-\log [i/(i_d - i)] = 0$ gave an arbitrary $E_{1/2} = -0{\cdot}26$ V. The limiting currents (Table I) were proportional to the concentration of rhodium(III).

0·4M Chloride. At chloride ion concentrations less than 6*M*, there is a replacement of chloride ion by water, and the rhodium exists in a series of mixed complexes.[1,20,24] Aliquot portions of rhodium solution were evaporated with hydrochloric acid as before to a volume of 5 ml, and were then diluted to 100 ml with 0·1*M* sodium chloride to give a final chloride ion concentration of 0·4*M*. (These conditions were similar to those used for much of the coulometry, *vide infra*.) Within 2 min after dilution, a spectrum was recorded which showed peaks at 509 and 406 mμ, indicating that some exchange of water for chloride had already occurred. The peaks continued to shift at a decreasing rate over a period of 2 weeks. After this time the peaks were at 481 mμ and 379 mμ, indicating an average constituent composition of approximately $RhCl_{3\cdot5}(H_2O)_{2\cdot5}{}^{0\cdot5-}$. Polarography of these solutions was done 15 min after dilution, and repeated 24 hr later (Table I). In each case, the limiting current was proportional to the concentration of rhodium. During the 24-hr time interval i_d/C decreased and $E_{1/2}$ shifted by about 30 mV to a more negative value. These shifts suggest that replacement of chloride by water gives a species more difficult to reduce and with a lower diffusion coefficient. This is in contrast to the long term behaviour reported by Simpson, Evans and Saroff.[3]

It was found that the final spectrophotometric equilibrium behaviour could be achieved by heating the freshly diluted rhodium solution for 1 hr at 100° and cooling. These solutions were then polarographed (Table I).

0·1*M Chloride*. The polarography was also investigated under conditions comparable to the acidities and ionic strengths used in the investigation of the aquo species. Aliquot portions of the rhodium working solution were diluted with suitable volumes of 0·1*M* sodium chloride solution. The acidity was then adjusted using 1*M* hydrochloric acid or 1*M* sodium hydroxide reagent. The solutions were heated on a steam-bath for at least 1 hr, cooled and adjusted to volume. The pH was measured before polarography. Spectra showed peaks at 473 and 373 mμ, indicating an over-all constituent composition of approximately $RhCl_3(H_2O)_3$. This spectrum did not change over a 2-week period.

Polarography gave 2 reduction waves.

The first wave was a composite of two waves. When $-\log [i/(i_d - i)]$ was plotted against E_{dme}, two intersecting straight lines were again obtained with slopes of 187 mV and 87 mV respectively. An arbitrary $E_{1/2} = -0{\cdot}07$ V was found as before. A temperature coefficient of +3·5 mV per degree (0–32°) indicated an irreversible reaction.

Over the pH range 1·3–3·8 the limiting current was independent of pH. The electrode process appeared to be diffusion controlled; i_d was again proportional to the concentration of rhodium(III) and to the square root of the height of the mercury column (Table I). The temperature coefficient of i_d was +1·6% per degree (0–32°). Above pH 3·9, i_d decreased with time, indicating hydrolysis. For rhodium concentrations greater than 0·214m*M*, it was necessary to add 0·001% Triton X-100 to suppress a maximum.

As was found in perchlorate media, a second wave occurred, with a maximum which was unaffected by the usual suppressors (Fig. 1). $E_{1/2}$ was approximately −1·00 V.

Controlled potential electrolysis

Controlled potential reductions were carried out in 0·2–0·4*M* chloride and 6*M* hydrochloric acid media. For coulometry in both media, aliquot portions of rhodium working solution were heated on a steam-bath together, with 2–5 ml of concentrated hydrochloric acid, to a red solution of final volume 2–5 ml.

6*M Hydrochloric acid*. In this base electrolyte $RhCl_6{}^{3-}$ is the predominant species throughout the electrolysis. The rhodium solution was added to a pre-electrolysed 6*M* hydrochloric acid base electrolyte for electrolysis at −0·37 V ($k = 0{\cdot}12$ sec^{-1}). The results are consistent with a 3-electron process and are calculated on that basis (Table II).

0·2–0·4*M Chloride*. Spectra showed that in this medium the average solution constituent varied over the time of electrolysis from $RhCl_6{}^{3-}$ at the beginning to approximately $RhCl_4(H_2O)_2{}^{1-}$ 90 min later. A base electrolyte of 0·1*M* sodium chloride solution was used, giving a total chloride ion concentration of 0·22–0·40*M*, depending on the volume of the added rhodium-hydrochloric acid solution. The potential for electrolysis was −0·2 V ($k = 0{\cdot}05$ sec^{-1}). The background current was significantly less than that in 6*M* hydrochloric acid, and the results are again consistent with a 3-electron process (Table II).

Conversion of the aquo complex to a chloride complex. Aliquot portions of rhodium solution were fumed in perchloric acid as previously described, diluted to 75 ml and heated on a steam-bath for several hours with a large excess of sodium chloride. Coulometry at −0·2 V showed about 75% of the rhodium(III) in the easily reduced chloride form.

On the other hand, fumed samples were similarly diluted but their acidity was adjusted to approximately 2·5 with 1*M* sodium hydroxide solution before the excess of chloride was added. After 2–3 hr heating, the yellow solution had become pink. Coulometry of these solutions was quantitative (Table II).

CONCLUSIONS

For both the aquo and chloride complexes, polarographic waves were found corresponding to the irreversible reduction of rhodium(III) to the metal. In addition, in solutions of low acidity, a second reduction wave was observable. This second wave was not observable in more acid solutions because of the prior discharge of the supporting electrolyte. It was found that the reduction of the various rhodium(III) chloride species occurred at more positive potentials than that of the rhodium(III) aquo species. A similar behaviour has been noted by Kolthoff and Lingane[27] in the polarographic reduction of the chloro and aquo complexes of cobalt (II) and nickel(II).

With the rhodium(III), exchanges of chloride ions and water molecules occurred only slowly at room temperature in acid solutions. The chloride complexes are inert, yet only one polarographic wave resulted in systems where the rhodium(III) must have been distributed amongst a number of complexes. A possible explanation is that values of $E_{1/2}$ characteristic of the various inert complexes are so close together that only one polarographic wave is apparent. There is a claim[1] that increased chloride concentration shifts $E_{1/2}$ to more negative values, as would be expected for a reversible reduction in a labile system. However, our polarography in 0·4*M* hydrochloric acid suggests that the opposite is true, because replacement of chloride ion by water on standing gave the opposite effect, *i.e.*, the $E_{1/2}$ of the rhodium(III) became more negative. (The $E_{1/2}$ of the wave in 6*M* hydrochloric acid cannot be directly compared with that in less concentrated chloride media because of the greatly differing ionic strengths.) Effects similar to ours have been noted in thiocyanate media.[6] In any case, because of the wide variation in behaviour of the different rhodium(III) species, analytical polarography can only be done when strict attention is paid to reproducing the solution constituents and to stabilising the system by heating.

The number of electrons involved in the reduction of both the chloro and aquo species is 3. It was found that quantitative reduction of the rhodium(III) could be carried out with 100% current efficiency on a mercury cathode. McBryde, Graham and Ott[28] also studied the deposition of rhodium at a controlled potential, but using a platinum cathode and procedures based on the work of McNevin and Tuthill.[29] In acid solutions they found that hydrogen was evolved simultaneously with the deposition of rhodium. This was eliminated in solutions buffered at pH 4, but in all cases the rhodium deposit was contaminated with oxide and it was necessary to reduce it in hydrogen for weighing. The coulometry reported here was done in acid solutions using a mercury cathode with its accompanying high hydrogen overpotential.

The coulometry in perchlorate media is not suitable for quantitative work because of the large background corrections. Of the two methods in chloride media, coulometry in 0·2–0·4*M* chloride gives the smaller background corrections. In contrast to polarography, it is not essential to have a reproducible distribution of rhodium among the chloride complexes. The method is only applicable in the absence of interfering elements; the analysis would not be directly applicable to rhodium in the presence of the other platinum metals.

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Zusammenfassung—Die Polarographie der Aquo- und Chloridkomplexe von Rhodium(III) wurde untersucht. Der Aquokomplex wurde durch Abrauchen mit Überchlorsäure hergestellt, die Chloridkomplexe durch Erhitzen in Gegenwart von Chlorid. In allen Fällen ergaben sich irreversible diffusionskontrollierte polarographische Stufen. Wesentlich ist, daß zur analytischen Polarographie die Bestandteile der Lösung sorgfältig reproduziert werden und daß die Lösungen durch Erhitzen stabilisiert werden, da sich bei Zimmertemperatur das Gleichgewicht nur sehr langsam einstellt. Elektrolyse bei kontrollierter Spannung an einer Quecksilberkathode zeigte, daß der polarographische Reduktionsschritt 3 Elektronen einschließt. Dies wurde zur Grundlage einer coulometrischen Bestimmung von 1,5–15 mg Rhodium in einer 0,2–0,4 m Chloridlösung bei −0,2 V gegen die gesättigte Kalomeellektrode gemacht.

Résumé—On a étudié la polarographie des espèces aquo et chlorure du rhodium (III). Le complexe aquo a été préparé au moyen d'acide perchlorique et les divers complexes chlorés ont été préparés par chauffage en présence d'ion chlore. Dans tous les cas, la polarographie donne des vagues de diffusion contrôlées irréversibles. Il est essentiel de reproduire soigneusement les constituants de la solution pour la polarographie analytique et de stabiliser les solutions par chauffage, car l'équilibre s'établit très lentement à la température ambiante. L'électrolyse avec cathode de mercure à potentiel contrôlé montre que le degré de réduction polarographique met en jeu 3 électrons. On utilise ce fait comme base d'un dosage coulométrique de 1,5 à 15 mg de rhodium dans un électrolyte 0,2 à 0,4 M en chlorure, à un potentiel de −0,2 V par rapport à l'électrode étalon.

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DETERMINATION OF COBALT IN COBALT-DOPED SODIUM CHLORIDE CRYSTALS

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Summary—Cobalt in low concentrations in single crystals, grown from sodium chloride melts containing cobalt chloride, is rapidly determined, without destroying the crystals, by measuring the absorbance of the 215-mμ band. The lower limit for measurement of cobalt by this method is about 10^{16} cobalt ions/cc for a crystal piece 1 cm thick. The molar extinction coefficient of the 215-mμ absorption band in the crystals is about 7000. Single-sweep polarography is used to calibrate the absorbance by determining the concentration of cobalt in solutions prepared from the cobalt-doped sodium chloric crystals. Cobalt can be determined in sodium chloride solution (0·05 g of NaCl/ml) in concentrations as low as 5×10^{-9} g/ml by single-sweep polarography. This corresponds to 2×10^{15} cobalt ions/cc of crystal.

INTRODUCTION

BECAUSE of the interest in the formation of colour centres in alkali-halide crystals containing bivalent cations of the first transition series, a method for the non-destructive determination of the cobalt content of cobalt-doped sodium chloride single crystals has been developed. The determination is made by relating the optical absorbance of cobalt to the concentration of cobalt in the crystals. The strong absorption band at 215 mμ in these crystals[1] was used, because the absorption bands which have been reported[2] in the visible region are extremely weak (only heavily doped, turbid crystals exhibit them). Because of its extreme sensitivity, single-sweep polarography was used for the determination of cobalt in solutions prepared from the crystals and the absorption method was calibrated with this polarographic method.

EXPERIMENTAL

Crystals

Cobalt-doped sodium chloride single crystals were grown in a helium atmosphere by the Kyropoulos technique. In general, reagent-grade materials were used, although in some cases the cobalt(II) chloride was prepared from recrystallised hexa-aquocobalt(II) chloride. The melts, which initially contained mole fraction of cobalt ions between 5×10^{-5} and 1×10^{-3}, were stirred for 1 hr, then the crystals were pulled from the melt at 10 mm/hr. When the growth was complete, the crystals were cooled to room temperature in a helium atmosphere.

Absorbance measurements

The absorption spectra of pieces cleaved perpendicular to the axis of the boule were measured at room temperature with a Cary Model 11 spectrophotometer. A few measurements were made at liquid nitrogen temperature using a Beckman DK-2 spectrophotometer equipped with a special stainless-steel Dewar vessel having quartz windows. All crystals used in this work were free from turbidity.

Polarographic measurements

The concentration of cobalt in the crystals was determined polarographically using solutions prepared from the crystals. The polarograms were obtained with a Davis Differential Cathode-Ray

Polarotrace in conjunction with a Moseley x-y recorder. The start potential of the Polarotrace was set at −1·20 V and the cobalt peak was measured at about −1·45 V *vs.* a mercury pool. The solutions used to obtain a working curve were prepared from single-crystalline sodium chloride and a 10 ppm solution of cobalt(II) ions. The cobalt solution was prepared by diluting a standard cobalt(II) sulphate solution obtained from Southwestern Analytical Chemicals, Austin, Texas, U.S.A. 0·5-g samples were cleaved from crystal pieces whose absorption spectra had been measured and dissolved in enough water to yield 10 ml of solution. Distilled water which had been passed through an ion-exchange column was used in the preparation of all solutions.

RESULTS AND DISCUSSION

In cathode-ray polarography the reduction of cobalt is not completely reversible[3] and hence at low concentrations the wave is not normally well defined. The use of the slope compensating circuit of the Davis polarograph resulted in much better resolution and more accurate measurement of the cobalt peak (Fig. 1). The relationship between the peak height of the polarograms and the cobalt concentration is linear throughout the range of the study ($5{\cdot}0 \times 10^{-7}$ to $5{\cdot}0 \times 10^{-9}$ g/ml); typical values are shown in Table I. A plot of peak height *vs.* concentration gives a straight line passing through the origin, which shows that the sodium chloride used to make up the standard solutions contained no measurable amount of cobalt. The effect of the sodium chloride concentration on the height of the cobalt peak was investigated using solutions containing approximately 0·045 and 0·055 g of sodium chloride/ml. This variation in sodium chloride concentration had no effect on the peak heights. The reproducibility of the polarographic analysis of duplicate samples of known cobalt concentration indicated that the method is precise to ±10% of the amount of cobalt present. It is estimated that cobalt can be determined at concentrations as low as 5×10^{-9} g/ml, which corresponds to 2×10^{15} cobalt-ions/cc of crystal in this work.

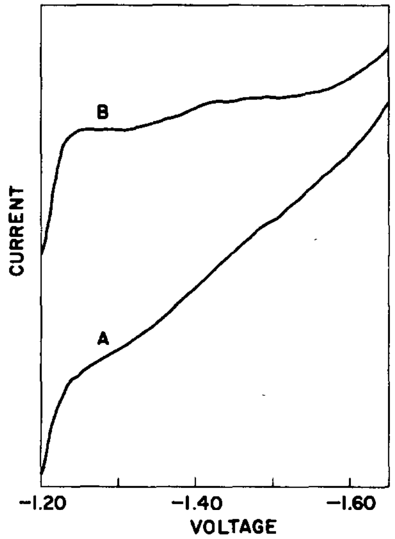

FIG. 1—Single-sweep polarograms of a 0·05 ppm solution of cobalt(II) ions (0·05 g of NaCl/ml supporting electrolyte):—

Curve A: without slope compensation.
Curve B: with slope compensation.

A typical absorption spectrum of a cobalt-doped sodium chloride crystal is shown

TABLE I—COBALT CONCENTRATION *vs.* PEAK HEIGHT IN 0·5*M* NaCl SOLUTION

Cobalt ($Co^{2+} \times 10^{-8}$ g/ml)	Peak Height (i_h, divisions[a])
5·0	6·5
10·0	13·0
20·0	27·0
30·0	39·0
40·0	51·0

[a] Measured on 10 × 10 to the 0·5-in. graph paper. Instrument settings are SSF = X10-1, ASF = X1, slope comp. = 3·0 and cond. comp. = 1/4.

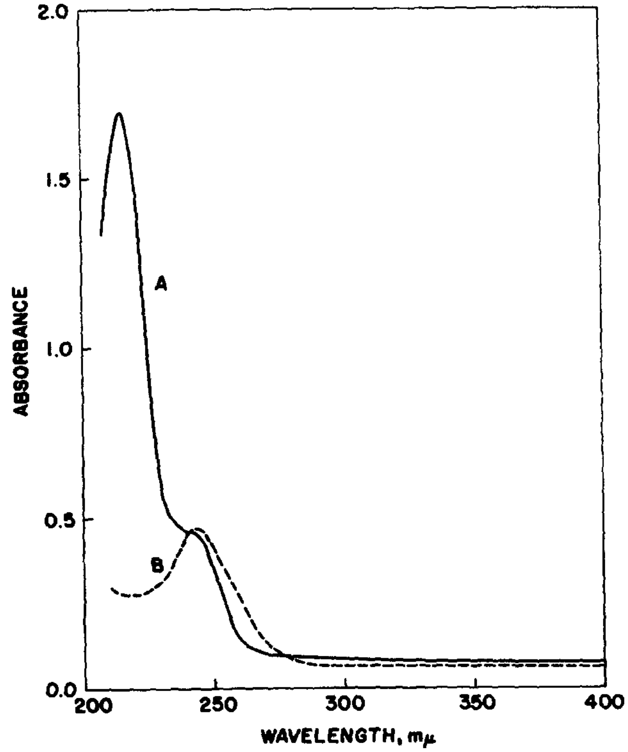

FIG. 2—Absorption spectra measured at room temperature:—
Curve A: cobalt-doped sodium chloride, sample thickness 3·40 mm.
Curve B: nickel-doped sodium chloride, sample thickness 6·66 mm.

in Fig. 2, Curve A. The crystal has a strong absorption band at 215 mμ with a shoulder at about 245 mμ. Measurement of the spectrum at liquid nitrogen temperature resulted in the resolution of the shoulder into a separate band at about 240 mμ with no appreciable shift in the position of the 215-mμ band. The incorporation of nickel into sodium chloride crystals gives rise to a band at about 242 mμ,* whose absorption does not fall off to zero at 215 mμ. It was, therefore, necessary to determine, before using the 215-mμ band for analytical purposes, whether the shoulder in the spectrum of cobalt-doped sodium chloride was caused by a nickel impurity. The shape of the band in nickel-doped sodium chloride is shown in Fig. 2, Curve B. A polarographic

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* Kats[4] reported the value 246 mμ.

determination of nickel showed that the nickel content of the cobalt-doped crystals is about the same as that of undoped crystals. Further, the nickel content of the cobalt-doped sodium chloride crystal, whose spectrum is shown by Curve A of Fig. 2, is only about one-tenth that of the nickel-doped crystal whose spectrum is shown by Curve B, although the absorption coefficient of the shoulder in Curve A is greater than that of the band in Curve B. The concentration of nickel in the cobalt-doped sodium chloride crystals is insufficient, therefore, to produce the 245-mμ shoulder.

Jain and Parashar[1] noted a marked dependence of the shape and perhaps height of the 215-mμ band upon the thermal treatment of the crystals. We found only a slight dependence, if any, upon thermal history. Because the visible spectrum of some of the doped crystals reported on by Jain and Parashar shows absorption bands, at least some of their crystals contained more cobalt than the ones investigated in this study. Possibly the difference in behaviour upon thermal treatment is a result of a difference in cobalt concentration. It is also interesting that no 245-mμ shoulder is discernible in their spectra. We found that in heavily doped, turbid crystals the 245-mμ shoulder has a tendency to merge with the 215-mμ peak as the cobalt concentration rises.

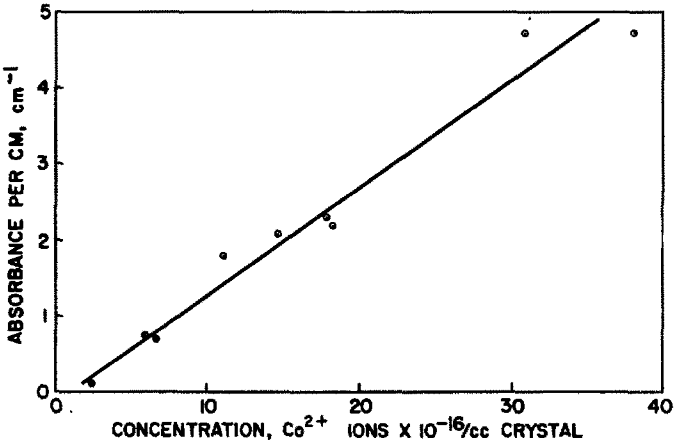

FIG. 3—Proportionality between 215-mμ band intensity and cobalt concentration in cobalt-doped sodium chloride.

The absorbance per centimeter of the 215-mμ band as a function of the polarographically determined cobalt concentration is shown in Fig. 3. The absorbance of the band was taken as the difference between the absorbance measured at 215 mμ and at 400 mμ for a given crystal piece. The molar extinction coefficient of the 215-mμ band as calculated from the straight line of Fig. 3 is about 7000. The lower limit for the detection of cobalt in cobalt-doped sodium chloride crystals by optical means is about 10^{16} cobalt ions/cc for a crystal piece 1 cm thick.

Acknowledgment—We wish to thank Mr. E. J. Dibble for assistance in growing the crystals.

Zusammenfassung—Die starke Absorptionsbande bei 215 mμ in Einkristallen aus Kobaltchlorid enthaltenden Natriumchloridschmelzen gestattet, schnell geringe Kobaltkonzentrationen in den Kristallen zu bestimmen, ohne sie zu zerstören. Die untere Grenze für diese Kobaltbestimmungsmethode ist etwa 10^{16} Kobaltionen pro

cm^3 für 1 cm dicke Kristalle. Der molare Extinktionskoeffizient der 215 mμ-Bande in NaCl:Co-Kristallen ist etwa 7000. Durch "single sweep"-Polarographie wurde Kobalt in den Lösungen aus NaCl:Co-Kristallen bestimmt. Kobalt kann in Natriumchloridlösungen (0,05 g NaCl/ml) in Mengen bis herunter zu 5×10^{-9} g/ml bestimmt werden. Das entspricht $2 \cdot 10^{15}$ Kobaltionen pro cm^3 Kristall.

Résumé—La forte bande d'absorption apparaissant à 215 mμ dans les cristaux uniques développés à partir d'une masse fondue de chlorure de sodium contenant du chlorure de cobalt offre un moyen de dosage rapide de faibles concentrations de cobalt dans les cristaux, sans destruction de ceux-ci. La limite inférieure de dosage du cobalt par cette méthode est d'environ 10^{16} ions cobalt/cc pour un cristal d'un cm d'épaisseur. Dans les cristaux NaCl:Co, le coefficient d'absorption molaire de la bande 215 mμ est d'environ 7000. On a utilisé la polarographie pour déterminer la concentration du cobalt dans des solutions préparées à partir de cristaux NaCl:Co. On peut doser le cobalt dans des solutions de chlorure de sodium (0,05 g NaCl/ml) à des concentrations aussi faibles que 5×10^{-9} g/ml. Ceci correspond à 2×10^{15} ions cobalt/cc de cristal.

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ANALYTICAL APPLICATIONS OF CACOTHELINE—II*

DETERMINATION OF THE FORMAL REDOX POTENTIAL OF THE CACOTHELINE-REDUCED CACOTHELINE COUPLE

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Summary—An improved method is described for the preparation of cacotheline in a high degree of purity. Using this material, the formal redox potential of the cacotheline-reduced cacotheline couple in 1–6*F* hydrochloric acid media has been determined by three different methods.

CACOTHELINE appears to have been used as a redox indicator as early as 1894 by Borgmann[1] in the titrimetric determination of tin(II) with an alcoholic solution of iodine. Kuchment and Gengrinovich[2] employed cacotheline as an internal indicator in the titration of iron(III) chloride in boiling 2*M* hydrochloric acid solution with tin(II) chloride solution. Cacotheline has been used as a redox indicator by various workers and some of the uses have been summarised by Lang.[3] Syrokomskii and Silaeva[4] titrated titanium(III) in acid solution with cerium(IV) sulphate solution, adding cacotheline towards the close of the titration to serve as indicator. Sierra and Monllor[5] employed cacotheline as an indicator in the titration of iron(III) with a standard solution of thiosulphate at the boiling temperature using copper sulphate as catalyst. The same investigators[6] employed cacotheline and thiosulphate in the titration of copper(II) at the boiling temperature using zinc sulphate as catalyst and a mixture of thiocyanate-oxalate to prevent the formation of a precipitate. Also, they extended the use of the indicator to the titrimetric determination with sodium thiosulphate of iron(III) and copper(II) when present in mixtures. Wehber[8] suggested the use of cacotheline as an indicator to detect the excess of tin(II) chloride added for the reduction of iron(III). Dichromate solution is then added carefully until the colour changes to yellow or greenish-yellow. The iron(II) formed by reduction is finally titrated with dichromate solution using sodium diphenylamine sulphonate as indicator. Hume and Kolthoff[9] made a similar use of cacotheline in the reduction of iron(III) with tin(II) chloride before titration with cerium(IV) sulphate. Wehber, Johannsen and Heydecke[10] proposed the use of cacotheline and *N*-methyldiphenylamine sulphonic acid in the differential titration of titanium(III) and iron(II), respectively, in mixtures. Szarvas and Lantos[11] employed cacotheline as a redox indicator in the titration of iron(III), chromium(VI), cerium(IV) or vanadium(V) with tin(II) chloride solution. They have used cacotheline and diphenylamine as redox indicators in the stannometric differential determination of iron(III) and

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* Part I: *Talanta*, 1958, **1**, 169.

chromium(VI) or iron(III) and vanadium(V) in mixtures. Recently, Mitsuokiboku[12] titrated tin(II) chloride with hexacyanoferrate(III) in the presence of $Na_4P_2O_7$ or $Na_5P_3O_{10}$ at pH 11–12·5, using cacotheline as indicator.

In view of the importance of cacotheline as a redox indicator, systematic work on its analytical applications was started in this laboratory in 1955. During 1955–57 the formal redox potential of cacotheline was determined under varying acid conditions.[13] Cacotheline was used as a redox indicator in the titration of (a) iron(III), hexacyanoferrate(III) and chromium(VI) with titanium(III) chloride, (b) vanadium(V), chromium (VI), hexacyanoferrate(III) and iodine by tin(II) chloride.[13] Since this work was completed, Szarvas and Lantos[14] have published some data concerning the redox potential of the cacotheline system. However, neither the earlier Indian work[13] nor the recent work of the Hungarian investigators[13] specified the purity of the cacotheline employed. During the last two years the present authors have succeeded in obtaining cacotheline in a high degree of purity (99–99·5%). Therefore, it was considered worthwhile to present the data on the formal redox potential of cacotheline obtained by us using a pure sample of the indicator. Moreover, the methods used for determination of the formal redox potential in the present work are different from that of the Hungarian workers, who employed spectrophotometric measurements.

EXPERIMENTAL

Improved Method for Preparation of High Purity Cacotheline

A typical method of preparation of cacotheline is as described by Leuchs, Osterburg and Kaehrn.[15] The red solution obtained by dissolving 39 g of dry brucine in 200 ml of 5*M* nitric acid is heated for 15 min at 50–60°, during which time crystals separate. The flask is then kept in ice for 1 hr, after which the crystals are filtered off by suction and washed with 1*M* nitric acid, acetone and ether in succession. The yield of cacotheline is reported as 43–45 g, *i.e.*, 86–89% of the theoretical yield. Four samples prepared by the present authors according to the above instructions assayed* 83·8, 84·1, 84·3 and 84·6% pure, respectively. The decomposition temperature of the samples averaged 235°. The last three samples, when dried on an air-oven at 110° for 6 hr, assayed 94·7, 95·2 and 95·5% pure, respectively.

Attempts have been made by us to obtain a sample of cacotheline of higher purity by varying the conditions of treatment of brucine with nitric acid, such as concentration of nitric acid, time and temperature of heating, *etc.* Ultimately, it was found that the following procedure yields cacotheline of 99–99·5% purity. Ten g of dry brucine are dissolved at room temperature in 75 ml of 3·5*M* nitric acid, prepared from analytical reagent grade nitric acid at room temperature, and the mixture heated on a water-bath for 2 hr, with occasional stirring. It is then cooled to room temperature and kept in an ice-bath for 3 hr. The crystals of cacotheline are filtered off on a Buchner funnel under suction, washed with 100 ml of water, then with 15 ml of acetone and finally with 30 ml of ether. The product is dried in air for 3 hr and for 6 hr in an air-oven at 110°. The yield is 9 g of cacotheline (decomposition temperature of 259°).

Determination of Formal Redox Potentials of the Cacotheline-Reduced Cacotheline Couple in 1–6F† Hydrochloric Acid Media‡

Reagents

0·005*M* *Cacotheline solution.* Prepared by weighing out the pure solid and dissolving in water. The solution was standardised by electrometric titration with tin (II) chloride solution in an inert atmosphere.

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* By potentiometric titration with tin(II) chloride in a medium of 4*M* hydrochloric acid and under an atmosphere of carbon dioxide.

† If the concentration of hydrochloric acid exceeds 6*F*, then the tin(II) chloride used in all three methods reduces the cacotheline irreversibly.

‡ Potential measurements in sulphuric acid media are in progress and will be reported in due course.

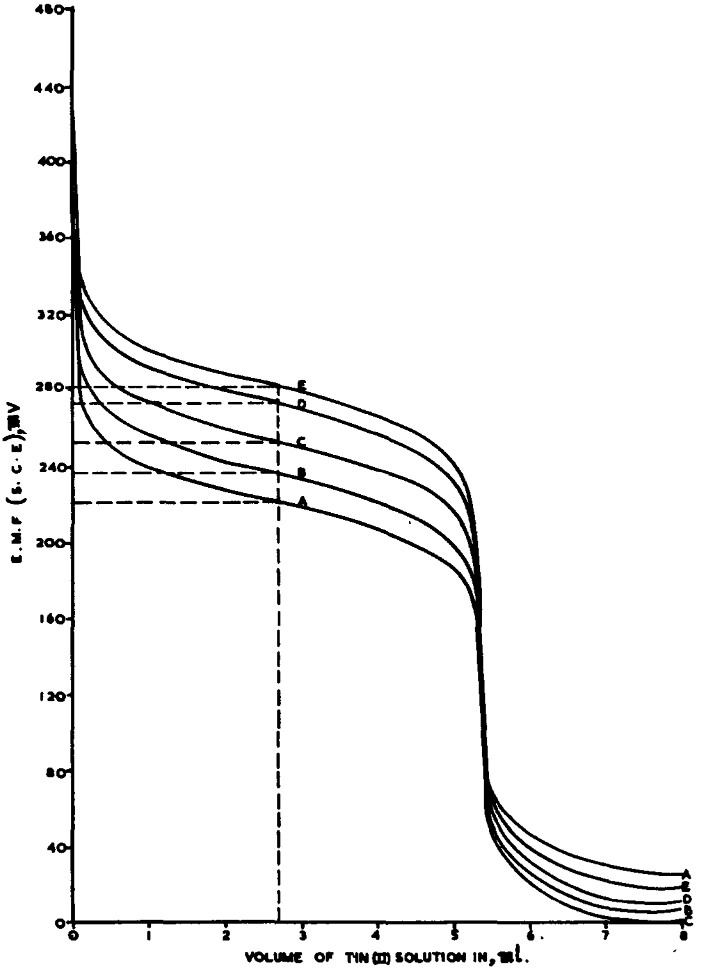

FIG. 1.—Potentiometric titration of cacotheline with tin(II) at different hydrochloric acid concentrations:

A–A	0·5F,
B–B	1·0F,
C–C	2·0F,
D–D	3·0F,
E–E	4·0F.

0·1N *Tin*(II) *chloride solution.* Prepared by dissolving analytically pure tin in analytical reagent grade hydrochloric acid in the hot and suitably diluting with boiled water. The solution was preserved in an inert atmosphere and delivered through an automatic burette. It was standardised by titration with a standard solution of potassium iodate using starch as indicator.[18]

0·1N *Cerium*(IV) *sulphate solution.* Prepared from B.D.H. analytical reagent grade cerium(IV) sulphate and standardised against sodium oxalate potentiometrically.

Procedure

Three different methods were employed for determination of the formal redox potentials.

Method A. This method is similar to that used by Conant and Fieser[16] for determination of the redox potentials of several quinones, except that tin(II) chloride was employed as the titrant in place of titanium(III) chloride because the latter reduces cacotheline irreversibly. From the potentiometric titration curves of cacotheline with tin(II) chloride at various acidities the formal redox potentials are evaluated. Typical potentiometric titration curves at five different acidities are given in Fig. 1.

Method B. Fifty ml of cacotheline solution are reduced at a given acidity with a calculated volume of tin(II) chloride solution which is just enough to reduce the cacotheline and the mixture diluted with hydrochloric acid or water as desired to 100 ml. The concentration of reduced cacotheline solution was 0·002449*M*. Fifty ml of this solution were mixed with 50 ml of 0·002449*M* cacotheline solution. Using this mixture with an immersed platinum rod electrode as a half cell and a saturated calomel electrode as reference half cell, the e.m.f. of the resulting cell is measured in the usual way. From this value the formal redox potential of the cacotheline system is obtained. Precautions are taken to exclude air throughout the operations.

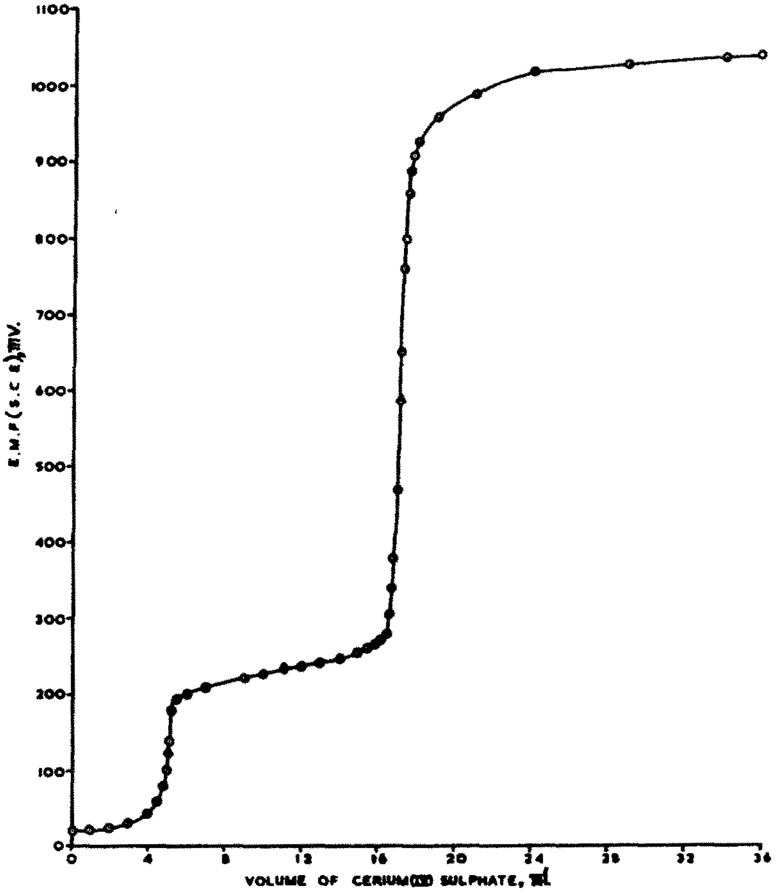

FIG. 2.—Potentiometric titration of a mixture of tin(II) and reduced cacotheline with cerium(IV) sulphate.

Method C. This method is similar to that used by Walden, Hammett and Chapman[17] for determination of the redox potential of the ferroin-ferriin system. A differential potentiometric titration of a mixture of tin(II) chloride and reduced cacotheline is carried out with a standard solution of cerium(IV) sulphate or potassium dichromate in 1*F* hydrochloric acid. A typical differential potentiometric titration curve is given in Fig. 2.

The formal redox potentials of the cacotheline-reduced cacotheline couple obtained by the three methods (uncorrected for liquid junction potential) are given in Table I.

TABLE I.—FORMAL REDOX POTENTIALS OF THE CACOTHELINE-REDUCED CACOTHELINE COUPLE
(TEMPERATURE: 28°)

Hydrochloric acid, F	Formal redox potential (N.H.E.), V		
	Method A[a]	Method B[b]	Method C[c]
0·499	—	0·463[d]	—
0·548	0·464	—	—
0·996	—	—	0·483
0·996	—	0·482	—
1·030	0·480	—	—
1·045	—	—	0·480
1·990	—	0·495[e]	—
1·990	0·495[e]	—	—
2·960	0·516	—	—
2·990	—	0·513	—
3·926	0·525	—	—
3·990	—	0·525	—
5·000	—	0·534	—

[a] 50 ml of 0·004898M cacotheline solution titrated with tin(II) chloride in an inert atmosphere. This concentration is used to get good potential breaks at the equivalence point. The hydrochloric acid concentration given is that which obtains at the mid-point of the titration curve, taking into consideration the acid added along with the tin(II) chloride and the acid used up during chemical reaction.

[b] Concentration of cacotheline and reduced cacotheline both equal to 0·001225M.

[c] In the differential titration of tin(II) and reduced cacotheline with cerium(IV) sulphate or potassium dichromate, concentration of reduced cacotheline was 0·004082M.

[d] Szarvas and Lantos[14] reported a potential of 0·515 V for a system of hydrogen activity 0·501.

[e] Szarvas and Lantos[14] reported a potential of 0·549 V for a system of hydrogen activity 2·00.

Zusammenfassung—Eine verbesserte Methode zur Darstellung hochreinen Kakothelins wird beschrieben. Mit diesem Material wurde das formale Redoxpotential des Redoxpaars Kakothelin—reduziertes Kakothelin in 1–6F salzsauren Medien mit drei verschiedenen Methoden bestimmt.

Résumé—On décrit une méthode améliorée de préparation de la cacothéline à haut degré de pureté. En utilisant ce produit, on déterminé, par trois méthodes différentes, le potentiel redox défini du couple cacothéline-cacothéline réduite en milieu 1–6 F en acide chlorhydrique.

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LE TITRAGE ENTHALPIMÉTRIQUE DE QUELQUES DIAMINES

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Résumé—Dans ce travail on a procédé au titrage enthalpimétrique des o,m,p-phénylène-diamines, par du l'acide clorhydrique, en représentant graphiquement les courbes de neutralisation, par des coordonnées droites et aussi par des coordonnées obliques, afin d'éliminer les effets thermiques secondaires. Par cette méthode, on a pu mettre en evidence les deux degrés de dissociation dans tous les trois cas, et on a calculé les chaleurs de neutralisation correspondantes. Il résulte des valeurs des chaleurs de neutralisation que l'ortho et la para-phénylène-diamine, ont un caractère basique plus prononcé que l'aniline et que la méta-phénylène-diamine, comme consequence d'un effet de conjugaison dont l'influence s'exerce par l'accroissement de la densité électronique chez les atomes d'azote dans les positions ortho et para. On constate aussi que la règle de Bredig ne s'applique pas à la série aromatique, justement en raison de l'effet de conjugaison signalé.

La méthode enthalpimétrique consiste, comme l'indique la littérature, dans la détermination de la variation de température ΔT au cours d'une réaction chimique, en fonction du volume de réactif ajouté Δn.[1]

Nous avons appliqué cette méthode à l'étude de la réaction de neutralisation de quelques réactifs organiques contenant du soufre, introduits par nous en chimie analytique, sans que, jusqu'ici, nous ayons pu appliquer cette méthode aux réactions de précipitation de ces réactifs avec différents cations lourds (Ag^+, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, *etc.*).

Les résultats satisfaisants obtenus au titrage de quelques réactifs à deux fonctions thioliques (amides de l'acide hydrazin N-N'-bisthiocarbonique)[2] nous ont incités à étudier d'autres dérivés bifonctionnels, tels que les diamines. Notre but est de tirer au clair certaines réactions de ces diamines, pour étudier ensuite une série de combinaisons que forment celles-ci, utiles en chimie analytique.

Dans le travail présent nous abordons une étude parallèle sur des diamines aliphatiques et aromatiques, mais ne présentons que les données relatives aux trois isomères du diamino-benzène (o, m, p-phénylène-diamine), que l'on emploie à la détermination quantitative de quelques cations.[3]

Dans cette première étape, nous nous sommes arrêtés à la réaction de neutralisation de ces diamines, par du HCl, comparativement à l'aniline, afin de pouvoir étudier leur basicité en fonction de la position des deux groupes amino.

DONNÉES EXPÉRIMENTALES ET DISCUSSIONS

1. *Détermination de la constante enthalpimétrique de la cellule de titrage*

Avant de procéder à un titrage enthalpimétrique, il importe de déterminer la constante enthalpimétrique de la cellule, par titrage d'une solution de HCl 10^{-2} m par une solution de NaOH 10^{-1} m, en employant la relation:

$$Q = N_m \frac{\Delta H}{\Delta T_Q} \tag{1}$$

où: Q est la constante enthalpimétrique de la cellule.

N_m = nombre de moles du produit formé

$\Delta H = \Delta H^\circ = 13{,}4$ Kcal/mole

ΔT_Q = variation totale de température, à la neutralisation de 250 ml de HCl 10^{-2} m par du NaOH 10^{-1} m.

La courbe de titrage enthalpimétrique correspondante est donnée dans la fig. 1, et la valeur de la constante enthalpimétrique est:

$$Q = N_m \frac{\Delta H}{\Delta T_Q} = 0{,}003063 \cdot \frac{13{,}4}{0{,}12} = 0{,}34205 \text{ Kcal/mole.}$$

2. *Le titrage enthalpimétrique de l'aniline*

Afin de disposer d'un point de référence à l'interprétation des résultats, nous avons jugé utile de titrer enthalpimétriquement l'aniline. La courbe de titrage est représentée à la fig. 2, et la chaleur de neutralisation calculée a la valeur:

$$\Delta H = -\frac{Q}{N_m} \,.\, \Delta T = \frac{0{,}34205}{0{,}03716} \,.\, 0{,}86 = -7{,}916 \text{ Kcal/mole.}$$

Cette valeur nous servira de référence pour les données qui suivent ($K = 5{,}4.\ 10^{-10}$).[4]

3. *Le titrage enthalpimétrique de la o-phénylène-diamine*

Dans ce cas le titrage a été effectué sur une solution n/5 o-phénylène-diamine, par HCl n, la courbe de titrage enthalpimétrique étant représentée à la fig. 3.

Les points B et C correspondent à la neutralisation des deux groupes amino. Afin d'écarter l'influence des effets thermiques secondaires, nous avons appliqué une transformation, en passant des coordonnées droites aux coordonnées obliques, en a l'aide des équations de transformation:

$$X = x\sqrt{1 + p^2} \tag{2}$$

$$Y = y - px \tag{3}$$

où X et Y sont les coordonnées obliques, x et y les coordonnées droites et $p = \Delta T/\Delta n$ la pente de la dernière portion de la courbe (CD), fig. 4.

On remarque que par cette transformation on obtient des valeurs moindres de la variation de température ΔT (les points E′ et F′) qui représentent cependant seulement l'effet thermique de la réaction de neutralisation. La chaleur de neutralisation, correspondant aux deux paliers, a les valeurs suivantes:

$$\Delta H_1 = \frac{Q}{N_{m1}} \,.\, \Delta T_1 = -8{,}770 \text{ Kcal/mole}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} \,.\, \Delta T_2 = -3{,}871 \text{ Kcal/mole}$$

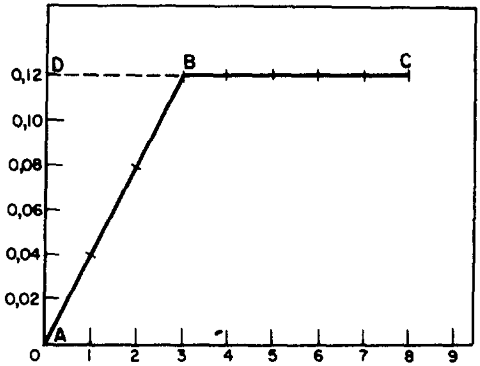


FIG. 1.

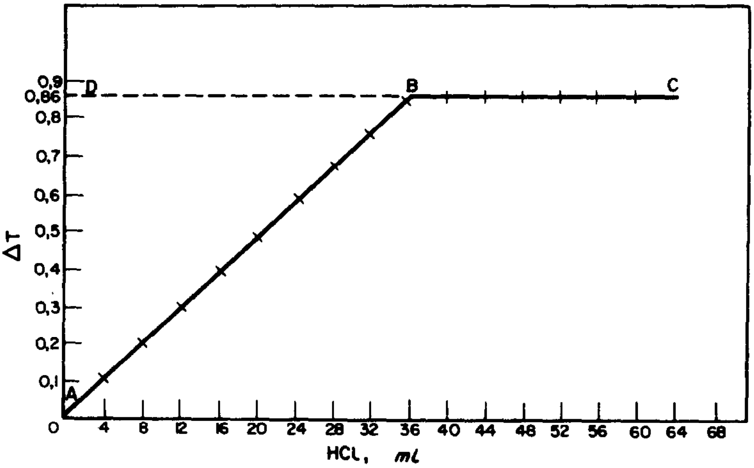


FIG. 2.

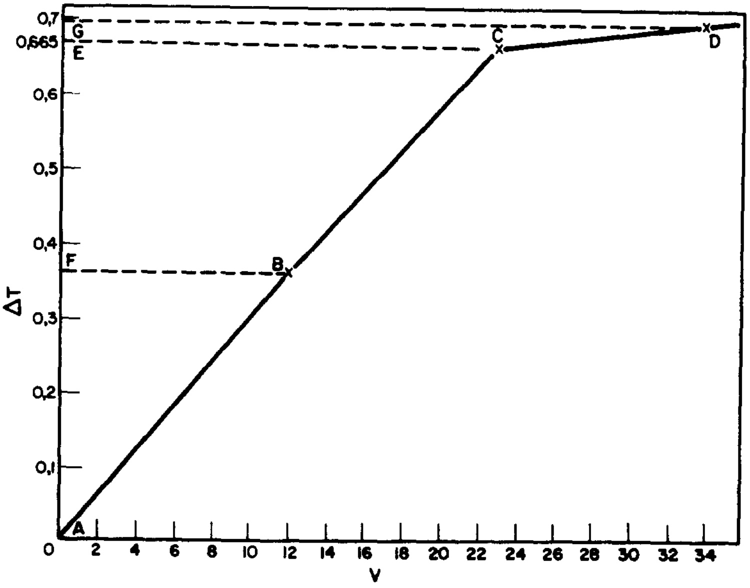


FIG. 3.

Comparativement à l'aniline, on observe que dans le premier palier l'o-phénylène-diamine est une base plus forte (chaleur de neutralisation plus grande); ce fait peut être expliqué par un effet de conjugaison de l'un des groupements aminé avec le noyau benzénique, ce qui provoque une augmentation de la densité électronique à l'azote du deuxième groupement amino et, par conséquent, de la basicité de celui-ci. Cette explication nous paraît plausible, parce que le groupement aminé est un substituant du I^{er} ordre et que l'influence de l'effet de conjugaison des substituants du I^{er} ordre se manifeste dans les positions ortho et para (voir ci-après).

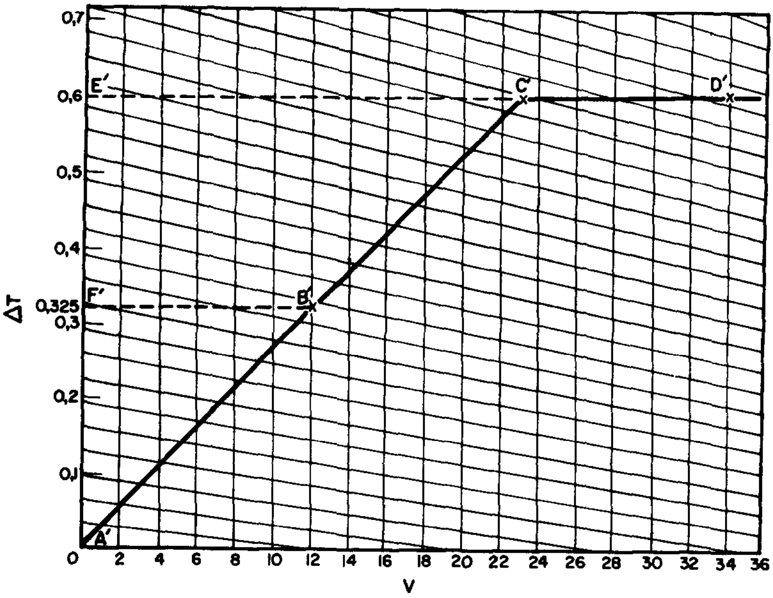


Fig. 4.

La basicité de la deuxième fonction diminue sensiblement par rapport à celle de l'aniline (la chaleur de neutralisation est plus faible).

Nous soulignons le fait que la littérature chimique ne consigne qu'une seule constante de dissociation pour l'o-phénylène-diamine, qui est plus petite que la constante de dissociation de l'aniline ($K_1 = 2{,}35 \cdot 10^{-10}$).[4] Or le titrage enthalpimétrique met en évidence aussi le deuxième palier de dissociation de l'o-phénylène-diamine, et de la chaleur de neutralisation plus grande pour le premier palier de dissociation, il résulte que l'o-phénylène-diamine est une base plus forte que l'aniline. Il va sans dire que des recherches complémentaires s'imposent pour venir étayer ce point de vue.

4. *Le titrage enthalpimétrique de la m-phénylène-diamine*

Dans ce cas aussi le titrage a été fait sur une solution d'environ n/5 m-phénylène-diamine, par HCl n; les courbes de titrage enthalpimétrique en coordonnées droites et obliques sont représentées aux fig. 5 et 6.

Les deux paliers de dissociation sont très nets, de même que le fait que la variation

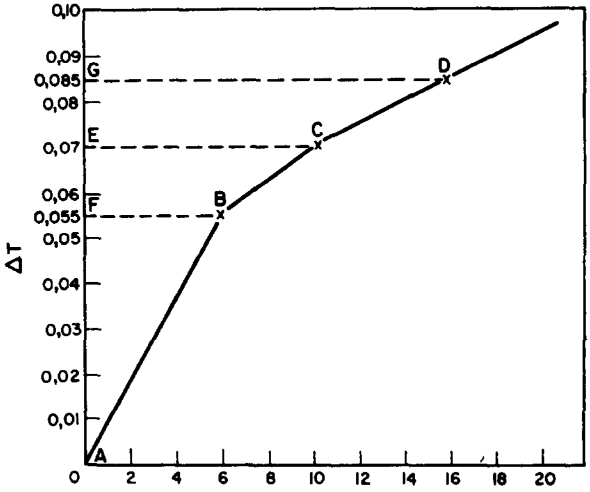


FIG. 5.

de température est beaucoup plus petite dans ce cas que dans celui de l'o-phénylène-diamine. La chaleur de neutralisation, pour les deux paliers, a les valeurs suivantes:

$$\Delta H_1 = \frac{Q}{N_{m1}} \cdot \Delta T_1 = -2{,}158 \text{ Kcal/mole}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} \cdot \Delta T_2 = -0{,}1619 \text{ Kcal/mole.}$$

Il ressort des valeurs des chaleurs de neutralisation de la m-phénylène-diamine dans les deux paliers que celle-ci a un caractère basique beaucoup plus atténué que l'aniline et que l'o-phénylène-diamine. L'explication en serait que, dans ce cas, l'effet de conjugaison ne se fait plus sentir. Il nous semble de ce fait anormal que

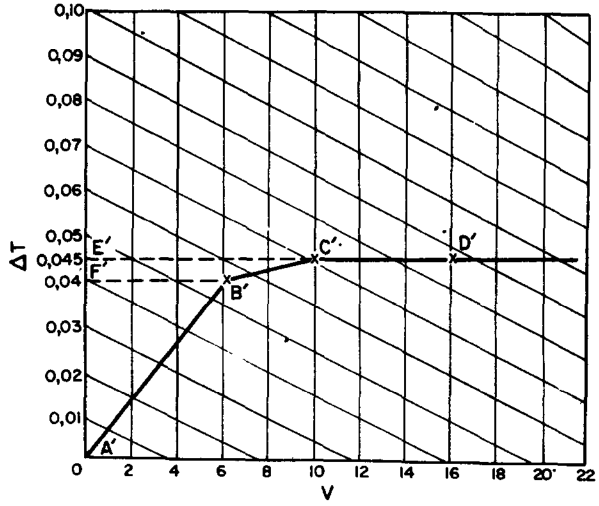
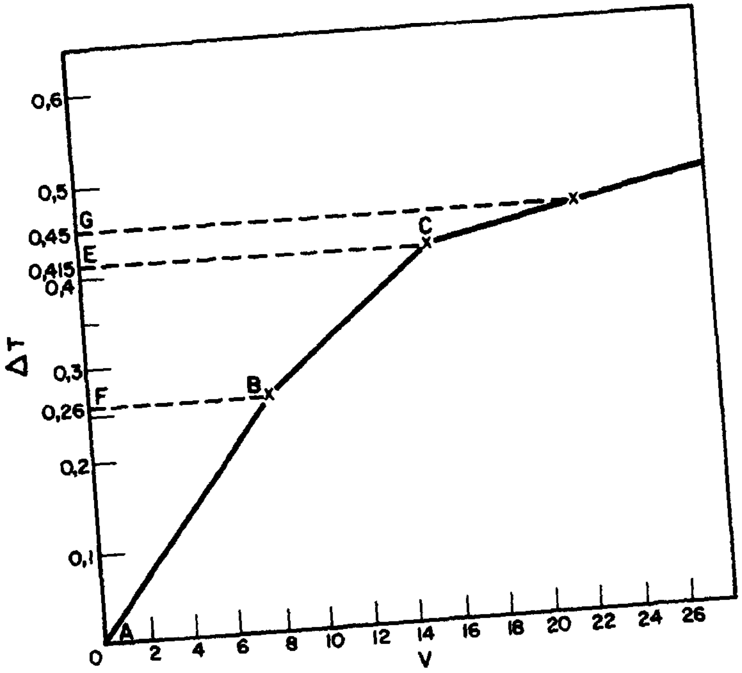


FIG. 6.


0,6
0,5
0,45
0,415
0,4
0,3
0,26
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0,1
ΔT
G
E
F
A
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C
0
2
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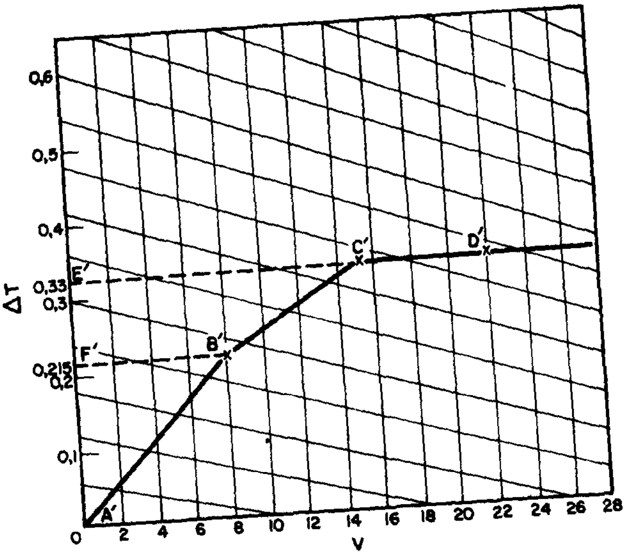
8
10
12
14
16
18
20
22
24
26
V

Fig. 7.


0,6
0,5
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0,215
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A′
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D′
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
V

Fig. 8.

la littérature indique pour une constante de dissociation de la m-phénylène-diamine une valeur plus grande que pour l'aniline, valeur même plus grande que pour l'o-phénylène-diamine ($K_1 = 6,0 . 10^{-10}$),[4] ce qui ne nous semble ni possible ni exact. Nous exprimons notre opinion avec toute les réserve d'usage car d'autres vérifications s'imposent.

5. *Le titrage enthalpimétrique de la p-phénylène-diamine*

Titrage enthalpimétrique de la p-phénylène-diamine sur une solution 10^{-1} m, par du HCl m. Les deux courbes de titrage en coordonnées droites et obliques sont représentées aux figures 7 et 8.

Dans ce cas aussi les deux droites de dissociation sont visibles, et la variation de la température au cours du titrage est plus grande que dans le cas de la m-phénylène-diamine, mais inférieure à celle que l'on enregistre avec la o-phénylène-diamine. Les chaleurs de neutralisation, correspondant aux deux droites, sont:

$$\Delta H_1 = \frac{Q}{N_{m1}} . \Delta T_1 = -8,703 \text{ Kcal/mol.}$$

et

$$\Delta H_2 = \frac{Q}{N_{m2}} . \Delta T_2 = -2,482 \text{ Kcal/mol.}$$

Il ressort de ces valeurs de la chaleur de neutralisation que sur le premier palier la p-phénylène-diamine est une base plus forte que l'aniline, quoique certaines sources bibliographiques indiquent une valeur de la constante de dissociation plus petite que pour l'aniline ($K = 1,23 . 10^{-10}$).[5] Il n'en est pas moins vrai que certains manuels donnent, pour le premier palier de dissociation de la p-phénylène-diamine une valeur plus grande que pour l'aniline ($K_1 = 1,3 . 10^{-8}$).[4,6]

La basicité plus grande que manifeste la p-phénylène-diamine s'expliquerait également par un effet de conjugaison, tout comme dans le cas de l'o-phénylène-diamine. Sur le second palier, la p-phénylène-diamine est une base plus faible même que l'aniline.

En outre on constate que la règle de Bredig,[7] suivant laquelle la dissociation des polyamines augmente avec l'éloignement réciproque des deux groupes amino, ne s'applique pas dans ce cas, de même que, en général, dans la série aromatique. Selon cette règle, la m-phénylène-diamine devrait être une base plus forte que l'o-phénylène-diamine. Or, il résulte des valeurs des chaleurs de neutralisation, correspondantes aux premiers paliers de dissociation des trois diamines que l'o-phénylène-diamine a le caractère basique le plus prononcé; vient ensuite la p-phénylène-diamine, tandis que la m-phénylène-diamine est une base plus faible même que l'aniline.

CONCLUSIONS

1. On a procédé au titrage enthalpimétrique des o, m, p-phénylène-diamines par HCl, en représentant graphiquement les courbes de neutralisation par des coordonnées droites et aussi par des coordonnées obliques, afin d'éliminer les effets thermiques secondaires.

2. Grâce à cette méthode, on a pu mettre en évidence les deux droites de dissociation dans tous les trois cas, et on a calculé les chaleurs de neutralisation correspondantes.

3. Il résulte des valeurs des chaleurs de neutralisation que l'ortho et la para-phénylène-diamine ont un caractère basique plus prononcé que l'aniline et que la méta-phénylène-diamine, comme conséquence d'un effet de conjugaison dont l'influence s'exerce par l'accroissement de la densité électronique au niveau des atomes d'azote en positions ortho et para.

4. On constate que la règle de Bredig ne s'applique pas à la série aromatique, en raison de l'effet de conjugaison signalé.

Summary—Neutralisation curves for the enthalpimetric titration of *o*-, *m*- and *p*-phenylenediamines with hydrochloric acid have been presented on rectangular Cartesian co-ordinates, and also on oblique co-ordinates to eliminate secondary thermal effects. It has thus been possible to demonstrate the two degrees of dissociation in all three cases, and to calculate the corresponding heats of neutralisation. These values show that *o*- and *p*-phenylenediamine are both more basic in character than aniline and than *m*-phenylenediamine, because of conjugation resulting in an increase of electron density at the nitrogen atoms in the *o*- and *p*- positions. It may be concluded that Bredig's rule does not apply to the aromatic series because of this conjugation.

Zusammenfassung—Die Neutralisationskurven enthalpimetrischer Titrationen von *o*-, *m*- und *p*-Phenylendiamin mit Salzsäure wurden in cartesischen Koordinaten angegeben, sowie in schiefen Koordinaten, um sekundäre thermische Effekte auszuschalten. Es war so in allen drei Fällen möglich, die beiden Dissoziationsstufen zu zeigen und die entsprechenden Neutralisationswärmen zu berechnen. Die Werte zeigen, daß *o*- und *p*-Phenylendiamin beide stärker basisch sind als Anilin und *m*-Phenylendiamin, da die Konjugation ein Anwachsen der Elektronendichte bei den Stickstoffatomen in *o*- und *p*-Stellung bewirkt. Man kann daraus schließen, daß wegen dieser Konjugation die Bredigsche Regel für die aromatische Reihe nicht gilt.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL-GRADE REAGENTS—II*

CAESIUM SALTS

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Summary—The ten commonest caesium salts have been investigated by the method of derivatography, their weight change, rate of weight change and enthalpy change being measured as a function of temperature. On the basis of these experiments, those temperatures at which the salts can be dried without danger of decomposition are deduced. The results can be interpreted by the acid-base theory of high temperatures.

In a previous communication[1] we reported on our thermoanalytical investigations of analytical-grade ammonium salts. In the present paper our results gained with caesium salts are discussed.

EXPERIMENTAL

The derivatograph was as described previously.[1] The samples were again weighed into a platinum crucible, but 400–500 mg were taken and the rate of heating was 10°/min. Samples were pulverised in a porcelain mortar, then passed through a 0·045-mm sieve before being weighed.

Most of the salts used in the experiments were either analytically pure or so-called purissimum reagents (E. Merck, Darmstadt, Germany).

Table I

Figure	Caesium salt	Formula	DTA peaks,[a] *°C*	M.p., *°C*	DTG peaks,[a] *°C*	Temperature of drying,*°C*
1	Fluoride	CsF	Endothermic: (142, 180, 260)	680	(190, 260)	<620
2	Chloride	CsCl	Endothermic, reversible: 450	640		<600
3	Bromide	CsBr		630		<600
4	Iodide	CsI		620		<580
5	Sulphate	Cs_2SO_4	Endothermic, reversible: 710	1040		<1000
6	Aluminium sulphate	$CsAl(SO_4)_2\cdot 12H_2O$	Endothermic: 90, 110, 220, 820		90, 110, 220, 820	Room temperature[b]
7	Carbonate	$3Cs_2CO_3\cdot 10H_2O$	Endothermic: 180, 220, 250	80, 800	180, 220 250	<50[c]
8	Chromate	Cs_2CrO_4	Endothermic, reversible: 800	1020		<1000
9	Dichromate	$Cs_2Cr_2O_7$	(320)	400	(320)	<360
10	Nitrate	$CsNO_3$	Endothermic, reversible: 150	410		<370

[a] Peaks indicated in brackets are from the presence of small concentrations of impurities.

[b] Anhydrous caesium aluminium sulphate can be heated between 250 and 650° without decomposition.

[c] Anhydrous caesium carbonate can be heated between 300 and 700° without decomposition.

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* Part I: see reference 1.

RESULTS AND DISCUSSION

Caesium fluoride

The derivatogram of caesium fluoride (Fig. 1) shows that the substance contained 3% of volatile material, which was removed up to 350°. Two peaks can be observed on the DTG curve and three peaks on the DTA curve. The first, endothermic peak of the DTA curve, which was not accompanied by any weight change, indicates that the substance also contained $CsHF_2$, the melting of which was the cause of this peak at 142° (in good agreement with the literature value of 142°[12]). The first process accompanied by weight change (180°) is probably the departure of hydrogen fluoride, the amount of which is about 0·6%. The second process (peak at 260°) corresponds to the departure of water which is sufficiently strongly bound that it is not removed on desiccation over phosphorus pentoxide under vacuum. That the peak corresponded to water was proved by the following experiment: the sample was left in contact with the air for some minutes, then the derivatographic measurement repeated. Because the sample had taken up water, the height of this step increased (see dotted line in Fig. 1).

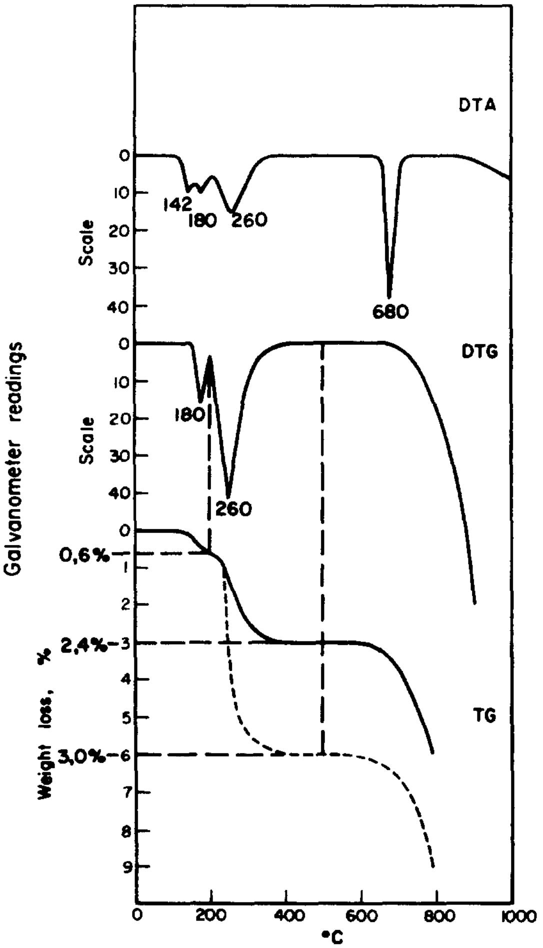

FIG. 1.—Caesium fluoride.

When the temperature is raised even higher, no further changes took place up to the melting point at 680°. From the TG and DTG curves, however, it can be seen quite clearly that volatilisation of the substance began immediately above the melting point, in contrast with the previously recorded observation that it began only at about 990°.[4]

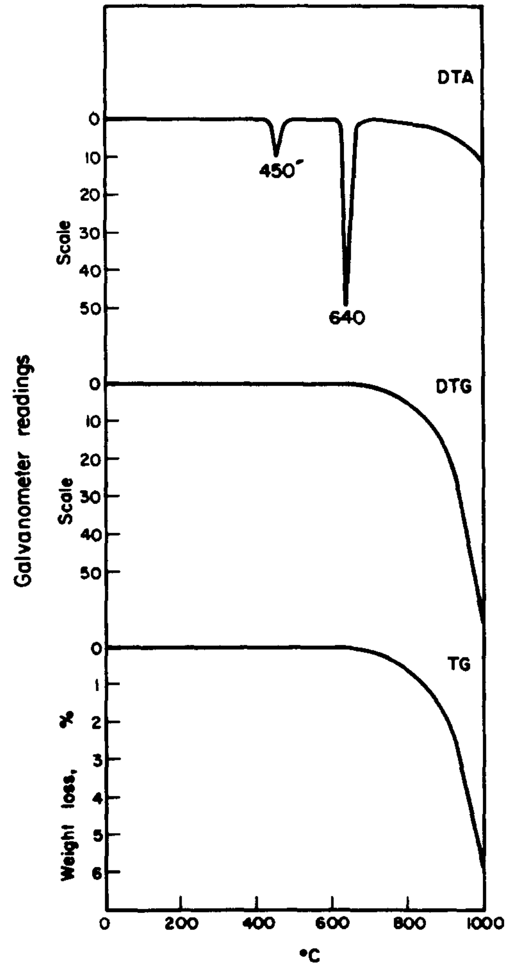

FIG. 2.—Caesium chloride.

Caesium chloride

Caesium chloride crystals are completely stable up to their melting point. The DTA peak (Fig. 2), indicating an endothermic change at 640°, is from the melting point. If the temperature is raised further, volatilisation of the caesium chloride becomes more and more intensive, and up to 1000°, under the given experimental conditions, a weight loss of 6% was observed. Duval and coworkers[5] found that caesium chloride is weight-stable up to 877°.

On the DTA curve there is an endothermic peak at 450°, which is not accompanied by any weight change. This corresponds to recrystallisation of the caesium chloride, the original "caesium chloride" lattice being transformed to a "sodium chloride" lattice structure. The process is reversible, as proved by the cooling curve of the substance obtained experimentally.

Caesium bromide

The caesium bromide sample contained neither mechanically nor chemically bound water. On the DTA curve, indicating the enthalphy changes, only the peak from the melting point at 630° is to be observed (Fig. 3). In the region of this temperature a slight loss of weight is indicated, arising from volatilisation of the sample.

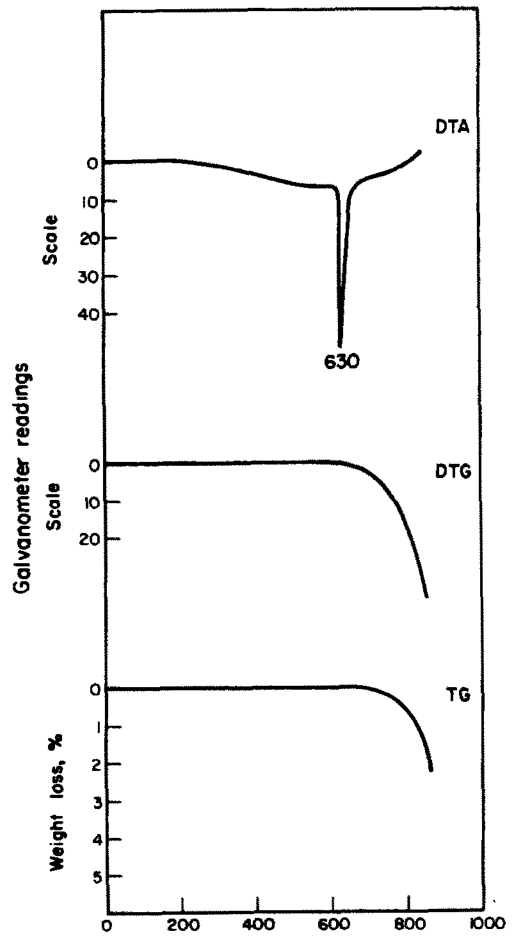

Fig. 3.—Caesium bromide.

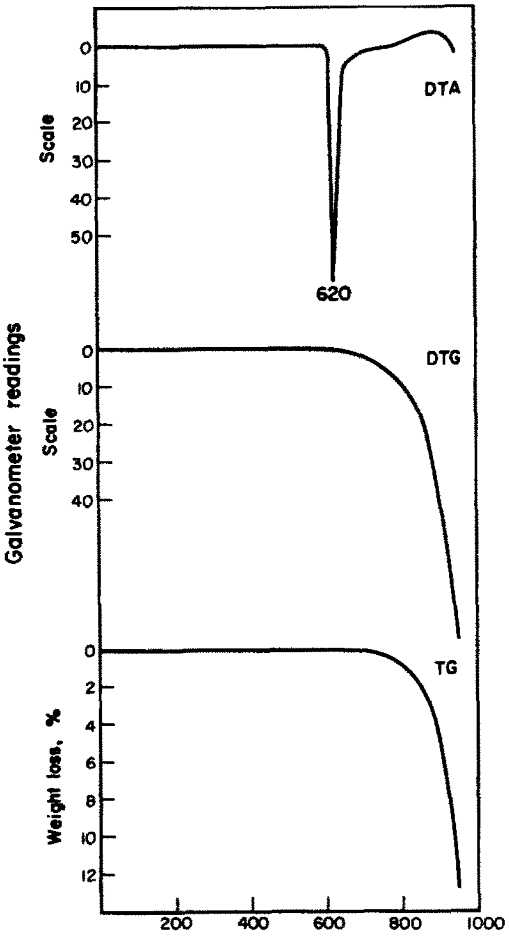

Fig. 4.—Caesium iodide.

Caesium iodide

The thermal properties of caesium iodide are similar to those of caesium bromide. Up to 620° there is no weight nor enthalphy change observable (Fig. 4). Above the melting point at 620°, the substance is slightly volatilised, as indicated on the TG curve.

Caesium sulphate

According to the thermoanalytical curves (Fig. 5), caesium sulphate is weight-stable up to 1040°. There is a reversible change of modification observable at about 710°, where the orthorhombic crystals are transformed to hexagonal ones. The heat effect—in agreement with the literature[6]—is very small. Our investigations, however, by measuring the temperature in the sample itself, proved that this temperature is higher by 50° than that recorded in the literature.

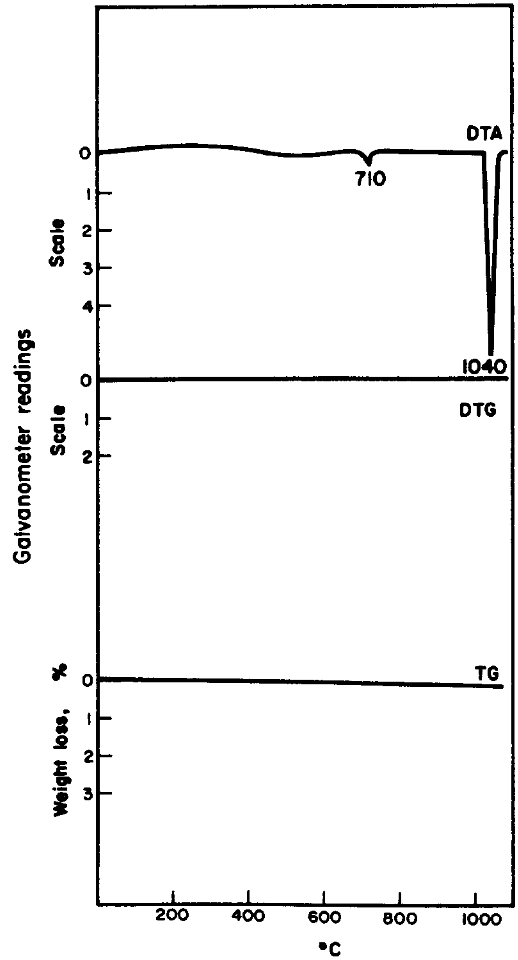

Fig. 5.—Caesium sulphate.

Caesium aluminium sulphate dodecahydrate

Caesium aluminium dodecahydrate has a stable stoichiometric composition up to 40°. On being heated above 40°, water is lost in three steps (Fig. 6). These indicate that the water is bound by different strengths, which can be seen especially well on the DTG curve. From the latter it can be established that in the first step 4, in the second 6 and in the third 2 molecules of water of crystallisation are removed from the substance, similarly to the decomposition of potassium aluminium sulphate

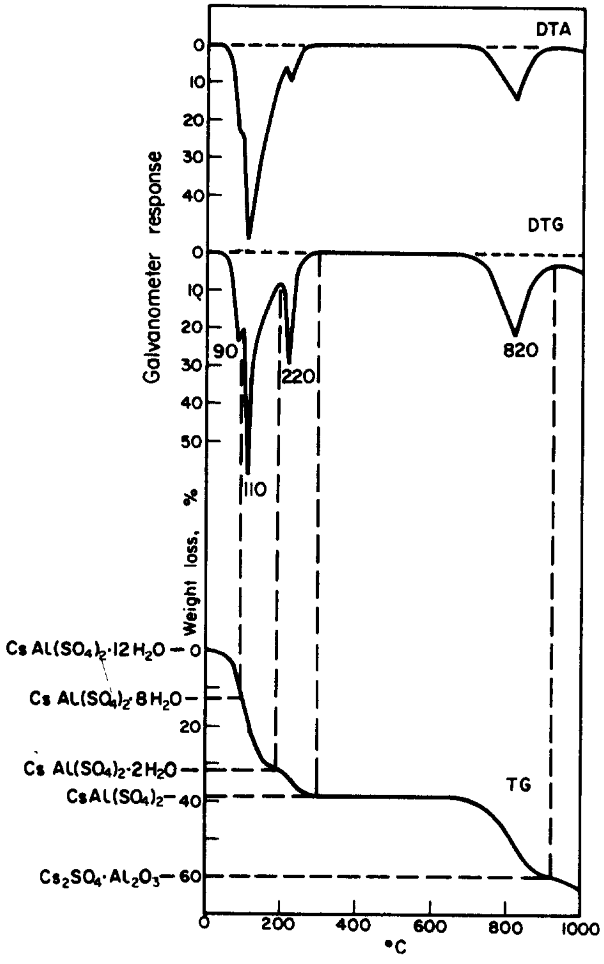

FIG. 6.—Caesium aluminium sulphate dodecahydrate.

dodecahydrate.[7] On the DTA curve the first and second processes overlap considerably and as a result only an inflection point is observable on the DTA curve. After the departure of all water of crystallisation the anhydride is stable between 250 and 680°. Above this temperature the sulphur trioxide bound to the aluminium oxide is lost (up to 920°), while the sulphur trioxide bound to the caesium oxide is lost only at a higher temperature.

Caesium carbonate

The thermoanalytical curves of caesium carbonate (Fig. 7) show that the sample contained a considerable amount of water of crystallisation. This corresponded very closely to the composition 3 $CsCO_3 \cdot 10H_2O$ reported in the literature.[8] According to the DTG curve, however, the water of crystallisation is somewhat surprisingly lost in four steps. In the first step about 0·5 mole, in the second about 1 mole, in the third also about 1 mole and in the fourth 0·8 mole of water is lost. Experiments were also made under different circumstances, using a slower rate of heating, but in all cases the water was found to depart in these four steps; the amounts of water corresponding to the individual steps did, however, change. The departure of water of crystallisation is also indicated on the DTA curves by four individual peaks, which contrasts with Reisman's observations,[9] but the processes, because of their strong overlapping, could be discerned only by points of inflection. There is also an endothermal peak at 80° on the DTA curve, which is presumably caused by the melting of the substance in its own water of crystallisation. Although caesium carbonate melts at 800°, a weight loss was observed even at lower temperatures (from about 700°), this increasing with increase of temperature.

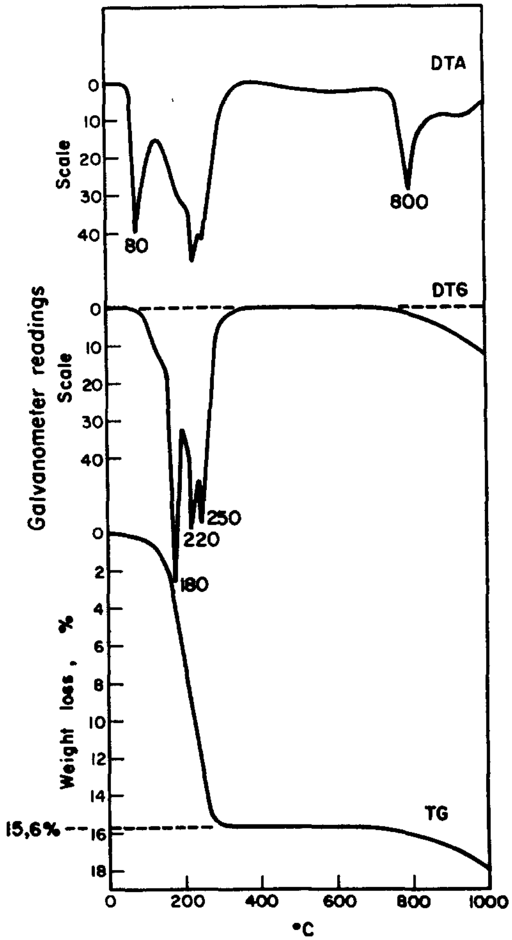

FIG. 7.—Caesium carbonate.

Caesium chromate

The derivatogram of caesium chromate (Fig. 8) shows that the substance has practically a constant weight. There is a reversible process with a slight enthalpy change at 800°, indicated by the DTA curve; this is caused by the change of the yellow, prismatic α modification to the yellow, orthorhombic β one. The temperature of this transformation is not, however, to be found in the literature. The reversibility of the process was proved by obtaining the cooling curve. The melting point of caesium chromate was found to be at 1020°.

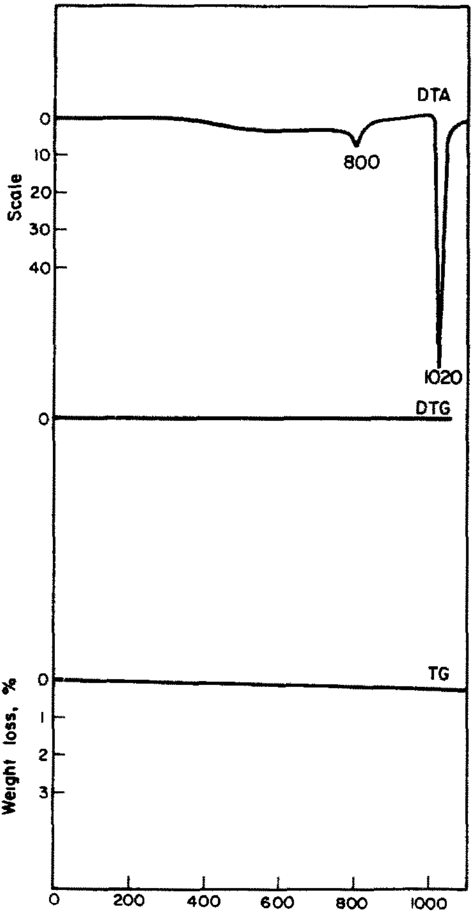

Fig. 8.—Caesium chromate.

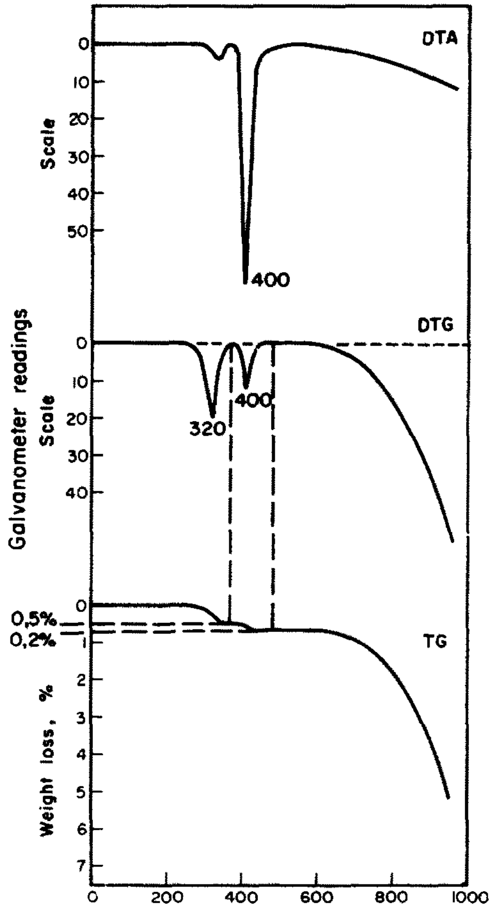

Fig. 9.—Caesium dichromate.

Caesium dichromate

Fig. 9 shows the derivatogram of a sample of caesium dichromate produced by Chemapol (Czechoslovakia). According to this, the substance is stable up to 300°, while at 320° (DTA maximum) a 0·5% weight loss occurred, probably because of some impurities. There is a reversible DTA peak at 400°, which, as far as we could establish, corresponds to the melting of caesium dichromate. At higher temperatures the substance volatilises. During the melting itself there is a small (*ca.* 0·1%) loss of weight indicated, which can be seen on both the TG and DTG curves. Similar effects have previously been encountered in connection with the melting of numerous organic and inorganic substances.

Caesium nitrate

Caesium nitrate was prepared in our laboratory from silver nitrate and caesium chloride. The derivatogram (Fig. 10) indicates that the salt has a constant weight up to 550° and decomposition takes place only above this temperature. There are two endothermic peaks to be seen on the DTA curve. The first, at 150°, indicates the reversible transformation of the hexagonal crystal form to a cubic one, while the second, at 410°, shows the melting point. After melting, and above 600°, decomposition of the caesium nitrate begins, first to caesium nitrite, finally to caesium oxide.

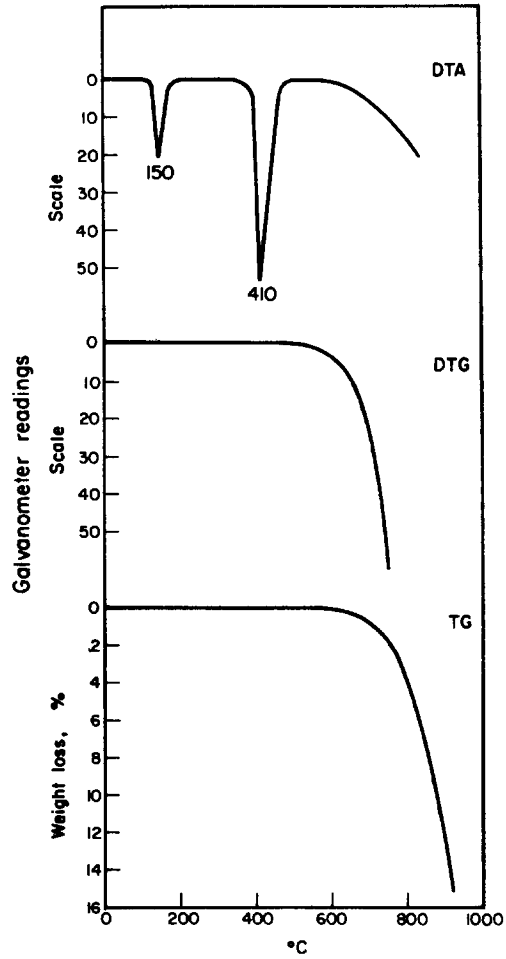

Fig. 10.—Caesium nitrate.

CONCLUSIONS

The results gained by derivatographic measurements can be interpreted very satisfactorily by the theory of high temperature systems worked out by Erdey and his coworkers[10,11]. Because the acidic cation was the same in all cases, the influence of the basic anions on the thermal properties of the substances was examined.

From the investigations of the halides the melting point decreases with decrease in electronegativity (*i.e.*, with increase of polarisability and diameter): CsF > CsCl > CsBr > CsI. There is a relatively greater difference between fluoride and chloride, which can be interpreted in terms of the especially strong basicity of the fluoride anion.

On the right-hand side of the Periodic Table occur the acidic cations (C^{4+}, N^{5+}, S^{6+}, Cr^{6+}), which are unstable alone. They always occur in neutralised forms together with oxygen (CO_3^{2-}, NO_3^-, SO_4^{2-}, CrO_4^{2-}) in the form of stable ions.

By comparing the melting points of caesium sulphate, chromate and dichromate, it can be established that these are in good agreement with Erdey's theory of high temperature reactions. Both the central acidic cations of sulphate and chromate have their oxidation number of +6, from which the basic anions SO_4^{2-} and CrO_4^{2-} are derived by neutralisation with the O^{2-} ion. The melting point of sulphate is higher (1040°), because it has been derived from the S^{6+} acidic cation with a smaller diameter, than the melting point of chromate (1020°), which is derived from the Cr^{6+} acidic cation with a larger diameter. However, if one O^{2-} ion of the chromate ion is replaced by another CrO_4^{2-} ion *i.e.*, by a less strongly basic part, the strength of the bond formed in this case decreases further, and the melting point is, therefore, even lower (400°).

In the decomposition of caesium aluminium sulphate dodecahydrate one can discern three types of water bound to the molecule by different strengths. This is also caused by differences in the strengths of acidic and basic ions. Four moles of water, which are removed in the first heating step, are bound to the acidic K^+ cation, while the second 6 moles are bound to the acidic Al^{3+} cation. The remaining 2 moles are co-ordinated to SO_4^{2-} ions, as in the case of potassium aluminium sulphate dodecahydrate.[7] The difference in acid strength is also the cause of the fact that in caesium aluminium sulphate, first aluminium and only later caesium sulphate decomposes, because Al^{3+} is a more strongly acidic cation than Cs^+.

The curious phenomenon that in the case of caesium carbonate, water molecules are lost in several well defined steps, can also be interpreted in terms of water molecules co-ordinated to various lattice points and bound by various strengths. A more thorough study of the phenomenon will be described later.

From the derivatogram of caesium nitrate it is interesting to point out that the substance remains completely unchanged even 150° above its melting point. Decomposition of the molten substance only takes place higher than this temperature.

Acknowledgement—Several of the caesium salts were made available by the courtesy of E. Merck, Darmstadt, Germany, for which the authors wish to express their sincere thanks.

Zusammenfassung—Zehn der am häufigsten vorkommenden Caesiumsalze wurden derivatographisch untersucht. Gewicht, Geschwindigkeit der Gewichtsänderung und Enthalpieänderung wurden als Temperaturfunktionen gemessen. Auf Grund dieser Versuche konnten die Temperaturen herausgefunden werden, bei denen die Substanzen ohne Zersetzungsgefahr getrocknet werden können. Die Ergebnisse lassen sich mit der Säure-Basen-Theorie hoher Temperature interpretieren.

Résumé—On a étudié les dix sels plus communs du césium par dérivatographie. On a mesuré le poids, la vitesse de variation de poids, et les variations d'enthalpie en fonction de la température. Sur la base de ces expériences, on peut fixer les températures auxquelles les substances peuvent être séchées sans danger de décomposition. On peut interpréter les résultats par la théorie acide-base aux hautes températures.

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POLAROGRAPHIC STUDY OF URANYL—PYROPHOSPHATE COMPLEX IN THE PRESENCE OF VARIOUS SURFACE-ACTIVE SUBSTANCES

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Summary—The effect of various surface-active substances on the characteristics of the polarograms of uranyl-pyrophosphate complexes is studied in detail. In the absence of surface-active substances, reversible and diffusion-controlled reduction waves are obtained when the ligand concentration is 0·05–0·30*M* and the pH 1·05–4·0. Beyond pH 4·0, the irreversible waves are rendered reversible by the addition of 0·04% α-naphthol, 0·02% β-naphthol, and 0·002% Triton X-100 and 0·18% camphor, shifting the waves to a more negative potential. The formation of a 1:1 complex is confirmed by conductometry.

POLAROGRAPHIC studies of pyrophosphate complexes of various metals have been reported by Rogers and Reynolds,[1] Laitinen and Onstott,[2] Subrabmanya[3] and Ram, Kumar and Shinha.[4] Vaid and Ramachar[5,6] have also investigated the complex formation between $P_2O_7^{4-}$ and bivalent metal ions and have proved the formation of a complex of the type $[M(II)P_2O_7]^{2-}$ by potentiometric, conductometric and spectrophotometric methods. In these investigations, no mention is made of the uranyl-pyrophosphate system.

The effect of surface-active substances on polarographic waves has been described by several authors.[7–10] They pointed out that such substances shift the half-wave potential, particularly of irreversible waves, to a more negative potential.

In the present paper the influence of surface-active substances on the polarographic behaviour of uranyl-pyrophosphate complexes has been studied in detail.

EXPERIMENTAL

Apparatus

All polarograms were manually recorded using a Sargent Model XII Polarograph, equipped with a Leeds and Northrup Students Kohlrausch slide wire. A modified H-cell, containing an external saturated calomel reference electrode (S.C.E.) and a potassium chloride-agar plug, was used. The cell was thermostated at 30° ± 0·01°.

The dropping mercury electrode used had the following characteristics in 0·2*M* sodium perchlorate at an applied potential of −0·5 V *vs.* S.C.E.: m = 1·705 mg/sec, t = 4·30 sec at mercury column height h = 69·5 cm.

Reagents

All the reagents used were polarographically pure.

Uranyl perchlorate solution. Prepared and analysed as described previously.[11]

0·5*M Stock solution of sodium pyrophosphate.* Prepared by dissolving 22·304 g of $Na_4P_2O_7 \cdot 10H_2O$ (Wako Pure Chemical Industries Co., special grade) in water and diluting the solution to 100 ml with water.

In order to obtain a higher concentration of camphor solution, a 10% alcoholic stock solution was used.

RESULTS AND DISCUSSION

The polarographic characteristics of the uranyl-pyrophosphate complexes were studied systematically over the pH range 1·05–11·6 to establish the nature of the complexes and electrode reactions. In the pH range 1·05–4·0 and a concentration of sodium pyrophosphate varying from 0·05 to 0·30*M*, both the mean value of $E_{3/4} - E_{1/4}$ and the mean slope of the conventional logarithmic plots were −0·060 V *vs.* S.C.E. These are in excellent agreement with the theoretical value for a reversible one-electron reduction.

The temperature coefficient of half-wave potential was −0·35 mV/°C in the temperature range 26–46°, providing further evidence of the reversible character of this process. The temperature coefficient of the diffusion current is 1·57%/°C, and the value of $i_d/h^{1/2}$ is 0·389 ± 0·006 for the height of mercury column from 44 to 89 cm at pH 2·50. Therefore, it is inferred that the electrode reactions were entirely diffusion-controlled.

TABLE I.—EFFECT OF pH ON URANYL-PYROPHOSPHATE WAVE
[1·0*mM* $UO_2(ClO_4)_2$, 0·05*M* $Na_4P_2O_7$ AND 0·2*M* $NaClO_4$]

pH	$-E_{1/2}$ (*vs.* S.C.E.), *V*	$E_{3/4} - E_{1/4}$, *V*	Slope of log plot	i_d, *μA*
1·05	0·174	−0·059	−0·059	4·12
1·45	0·231	−0·060	−0·060	4·10
1·75	0·255	−0·060	−0·060	3·85
2·08	0·280	−0·060	−0·059	3·58
2·60	0·325	−0·060	−0·060	3·21
3·10	0·356	−0·059	−0·060	2·91
3·35	0·377	−0·061	−0·058	2·30
3·60	0·382	−0·059	−0·060	1·75
4·00	0·398	−0·064	−0·061	1·44
4·80	0·950	−0·095	−0·091	3·10
5·70	0·994	−0·120	−0·114	4·05
6·00	1·038	−0·106	−0·110	3·90
7·50	1·024	−0·098	−0·096	3·81
9·20	1·009	−0·100	−0·114	2·81
10·60	0·997	−0·098	−0·110	2·18
11·60	0·975	−0·094	−0·099	2·05

Above pH 4·0, the reversible wave gradually turned into an irreversible wave; the value of $E_{3/4} - E_{1/4}$ was in the range −0·094 to −0·120 V for the pH range 4·8–11·6 and constant sodium pyrophosphate concentration (0·05*M*)(Table I). In the pH range 4·0–4·8, the polarograms were badly deformed in shape and the diffusion plateau gradually disappeared.

Influence of pH *and ligand concentration*

The half-wave potentials for solutions of 1·0*mM* uranyl perchlorate in 0·2*M* sodium perchlorate at varying concentrations of pyrophosphate (0·05–0·30*M*), and over the pH range 1·05–4·0 are given in Fig. 1. At pH lower than 1·05, the half-wave potentials kept a constant value at −0·174 V *vs.* S.C.E., which is identical with the half-wave potential of the simple uranyl ion, showing that no chelate was formed. In the pH range 1·05–4·0, the half-wave potentials were shifted to the negative side as the pH value was increased; the slope of the straight lines, −0·070, indicated that approximately one hydrogen ion participated in the electrode reduction.

The diffusion currents gradually decreased as the pH was increased up to 4·0 (Table I). This is probably caused by the progressive ionisation of pyrophosphoric acid and pyrophosphate ions and the resulting changes in the nature of the uranyl-pyrophosphate complexes.

The slope of the straight line for the plot of $-E_{1/2}$ against the logarithm of the concentration of pyrophosphate should be $-(p - q)0{\cdot}060$, where $(p - q)$ is the difference in number of ligands attached to the uranium(VI) and uranium(V) chelates. As shown in Fig. 2, the slopes of the straight lines are $+0{\cdot}061$ and $0{\cdot}000$, corresponding to values for $(q - p)$ of 1 and 0, respectively, at a ligand concentration higher than 0·095*M* and lower than 0·095*M* at pH 2·50. This indicates that two kinds of reduced complex species exist at ligand concentration 0·05–0·30*M*. Fig. 2 also shows the variation of the diffusion current with the logarithm of the ligand concentration. The point of greatest change comes approximately at the log C_M where the slope of the log C_M *vs.* $-E_{1/2}$ line also changes, indicating the possibility of the existence of different uranyl-pyrophosphate complexes at different ligand concentrations.

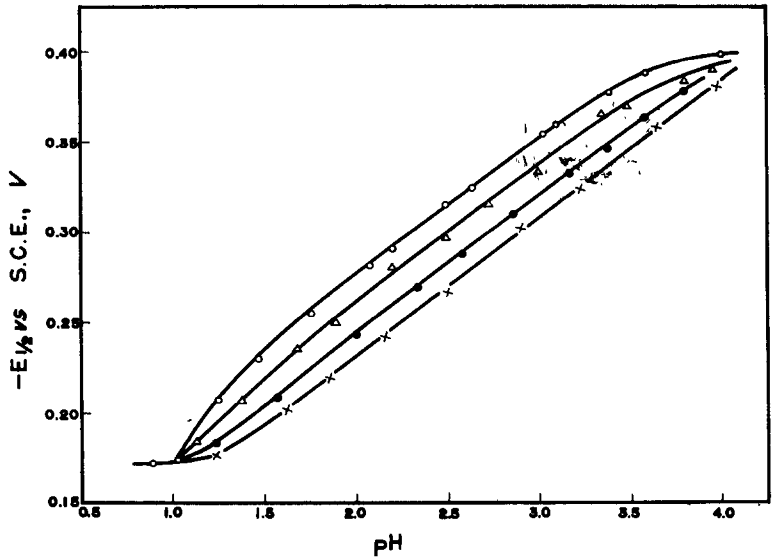

FIG. 1.—Plot of $-E_{1/2}$ as a function of pH:

○—0·05*M*,
△—0·10*M*,
●—0·20*M*,
×—0·30*M*.

Effect of surface-active substances

As shown in Table I, the reversible waves turned to irreversible ones by shifting the $E_{1/2}$ to a more negative potential at pH beyond 4·0. In an attempt to establish the reversibility of the electrode reaction, which is essential to obtain quantitative information about the complexes, various surface-active substances were used.

The effects of Triton X-100, thymol, gelatin, α-naphthol, β-naphthol and camphor upon the half-wave potential, the slope of current-voltage curve and the diffusion current are shown in Table II. Fig. 3, which illustrates the polarograms in the presence of various surface-active substances, indicates that all the surface-active substances used, except gelatin, shifted the $E_{1/2}$ to more negative potentials, besides rendering the waves more reversible in nature. These effects may be attributed to the hindrance of electro-reduction by adsorption of the surface-active substances on the electrode-electrolyte interface. The wave-heights observed in the presence of surface-active substances were not appreciably changed. This may be because of the absence of visible maxima in the reduction waves of the uranyl-pyrophosphate.

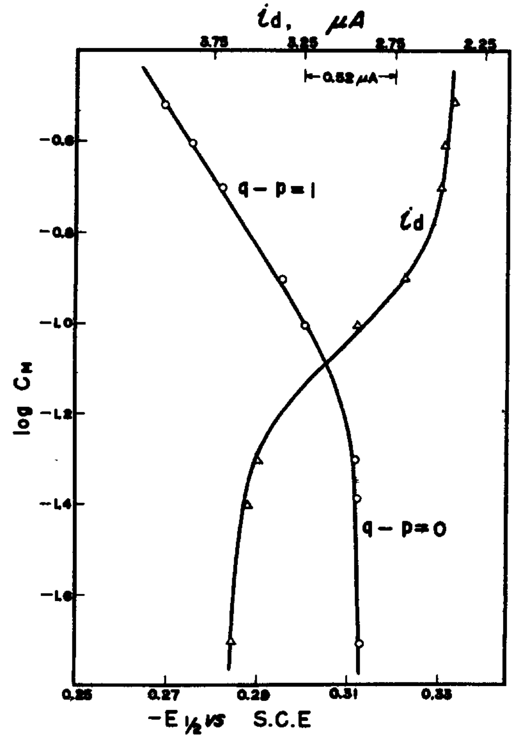

FIG. 2.—Effect of log C_M on $-E_{1/2}$ and i_d at pH 2·50.

Thymol and gelatin were found to be the least effective agents to remedy the irreversible polarograms of uranyl-pyrophosphate complexes, even at the high concentration of 0·01 %. Although Triton X-100 shifted the reduction wave to a more negative potential and the wave also became steeper, the effects were not so pronounced as with α-naphthol and β-naphthol. Camphor exerts the most remarkable effect on the polarograms. The higher the concentration of camphor, the steeper is the slope of the wave. α-Naphthol, β-naphthol and a mixture of Triton X-100 and camphor were found to be the best agents for rendering the irreversible wave reversible and symmetrical. The optimum amounts of these surface-active substances were found to be 0·04 % α-naphthol, 0·02 % β-naphthol, and 0·002 % Triton X-100 and 0·18 % camphor. Under these conditions, both values of $E_{3/4} - E_{1/4}$ and the conventional log plots averaged —0·060 V *vs.* S.C.E. These results provide an excellent

TABLE II.—EFFECT OF SURFACE-ACTIVE SUBSTANCES ON URANYL-PYROPHOSPHATE WAVE [1*mM* $UO_2(ClO_4)_2$, 0·05*M* $Na_4P_2O_7$, 0·2*M* $NaClO_4$ AND VARIOUS SURFACE-ACTIVE SUBSTANCES AT pH 6·0]

Surface-active substance	Concn., %	$E_{3/4} - E_{1/4}$, *V*	$-E_{1/2}$ (*vs.* S.C.E.), *V*	i_d, μA
—	—	−0·106	1·038	3·70
Triton X-100	0·0004	−0·100	1·071	3·70
	0·0012	−0·100	1·140	3·75
	0·0060	−0·080	1·450	4·00
Thymol	0·002	−0·101	1·005	3·90
	0·01	−0·091	1·014	4·10
Gelatin	0·002	−0·126	0·997	3·90
	0·01[a]	—	—	—
α-Naphthol	0·002	−0·095	1·024	3·48
	0·01	−0·080	1·072	3·90
	0·03	−0·068	1·090	3·98
	0·04[b]	−0·059	1·104	3·98
	0·05[b]	−0·059	1·124	4·10
β-Naphthol	0·002	−0·090	1·020	3·80
	0·01	−0·071	1·055	3·70
	0·02[b]	−0·060	1·067	3·80
	0·03	−0·046	1·075	3·75
Triton X-100 and β-naphthol	0·002 0·01	−0·140	1·215	4·50
Camphor	0·005	−0·096	1·020	3·60
	0·02	−0·031	1·050	3·60
	0·06	−0·020	1·218	4·70
	0·10	−0·018	1·241	4·60
Triton X-100 and camphor	0·002 0·09	−0·074	1·308	3·75
	0·002 0·18 b	−0·060	1·311	3·55

[a] Wave badly deformed

[b] Reversible wave

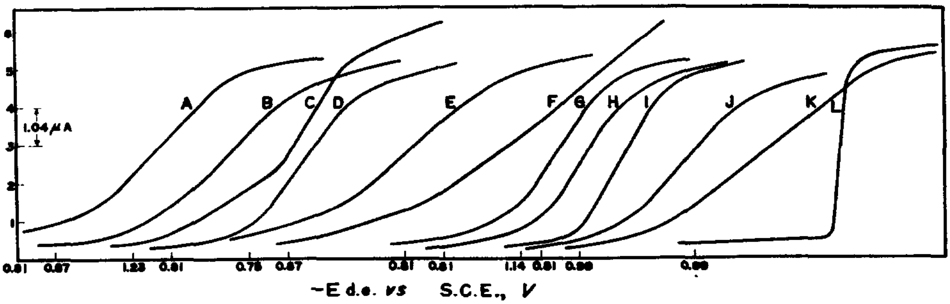

FIG. 3.—Polarograms of solutions containing 1·0*mM* $UO_2(ClO_4)_2$, 0·05*M* $Na_4P_2O_7$, 0·2*M* $NaClO_4$, at pH 6·0 with various surface-active substances:

(A) no surface-active substance; (B) 0·0004% Triton X-100; (C) 0·006% Triton X-100; (D) 0·01% thymol; (E) 0·002% gelatin; (F) 0·01% gelatin; (G) 0·01% α-naphthol; (H) 0·01% β-naphthol; (I) 0·002% Triton X-100 and 0·09% camphor; (J) 0·005% camphor; (K) 0·002% Triton X-100 and 0·01% β-naphthol; (L) 0·06% camphor.

method for making a quantitative investigation of the uranyl-pyrophosphate complexes at a pH beyond 4·0. However, the addition of a mixture of 0·002% Triton X-100 and 0·18% camphor is inferior to the addition of 0·04% α-naphthol or 0·02% β-naphthol because of the sublimation of camphor at higher concentration, thus influencing the reproducibility of the wave.

Effect of pH *and ligand concentration on polarograms in presence of surface-active substances*

The dependence of the polarographic characteristics on the pH was determined by polarographing a solution of 1*mM* uranyl perchlorate in the presence of various surface-active substances (Table III). The values of $E_{3/4} - E_{1/4}$ and the slopes of the conventional logarithmic plots averaged −0·060 V at pH around 5·1–9·0, indicating a reversible one-electron reduction. At pH lower than 5·1 or higher than 9·0, the electrode reduction became irreversible. The half-wave potentials are practically independent of pH, showing that no hydrogen ion is involved in the reduction.

TABLE III.—EFFECT OF pH ON THE CHARACTERISTICS OF POLAROGRAMS IN THE PRESENCE OF SURFACE-ACTIVE AGENTS [1·0 × $10^{-3}M$ $UO_2(ClO_4)_2$, 0·2*M* $NaClO_4$, 0·05*M* $Na_4P_2O_7$ AND VARIOUS SURFACE-ACTIVE SUBSTANCES]

Surface-active substance	pH	$-E_{1/2}$ (*vs.* S.C.E.), *V*	$E_{3/4} - E_{1/4}$, *V*	Slope of log plot	i_d, *μA*
Triton X-100 (0·002%) and camphor (0·18%)	5·85	1·300	−0·060	−0·059	3·60
	6·00	1·314	−0·060	−0·059	3·61
	6·80	1·296	−0·065	−0·064	3·30
	8·10	1·233	−0·063	−0·061	2·95
	9·50	1·265	−0·057	−0·059	2·40
	10·40	1·230	−0·076	−0·079	2·10
β-Naphthol (0·02%)	5·10	1·050	−0·065	−0·064	4·00
	5·67	1·066	−0·064	−0·062	3·91
	6·00	1·067	−0·060	−0·059	3·91
	6·50	1·082	−0·060	−0·059	3·70
	6·96	1·088	−0·060	−0·059	3·51
	7·31	1·093	−0·060	−0·060	3·47
	7·75	1·093	−0·059	−0·058	3·50
	8·10	1·091	−0·060	−0·059	3·40
	8·50	1·092	−0·059	−0·059	3·30
	9·00	1·081	−0·062	−0·060	2·85
	9·20	1·059	−0·066	−0·070	2·60
	9·50	1·043	−0·086	−0·087	2·60
α-Naphthol (0·04%)	5·10	1·085	−0·057	−0·058	4·05
	5·45	1·092	−0·059	−0·059	4·15
	5·80	1·097	−0·060	−0·059	4·20
	6·30	1·108	−0·059	−0·059	4·20
	6·75	1·112	−0·056	−0·057	3·70
	7·30	1·113	−0·057	−0·057	3·65
	7·80	1·114	−0·060	−0·060	3·30
	8·41	1·115	−0·058	−0·059	3·20
	9·00	1·110	−0·060	−0·059	3·00
	9·30	1·089	−0·083	−0·085	3·00

The half-wave potentials for a solution at pH 6·5 were plotted against the logarithm of the ligand concentration. As shown in Fig. 4, there is one breaking point at 0·2*M* sodium pyrophosphate in the β-naphthol system, indicating the possible existence of two different reduced complex species. The slopes are 0·000 and 0·060, corresponding to (q − p) values of 0 and 1 for a ligand concentration higher and lower than 0·2*M*, respectively. On the other hand, in the α-naphthol system, the slope of the log C_M *vs.* $-E_{1/2}$ plot is zero, showing that uranium(VI) and uranium(V) have the same number of ligands.

Mole ratio of complex

The metal-ligand ratio of the uranyl-pyrophosphate complex was determined to be 1 : 1 by the conductometric titration method (Fig. 5). The result was in good accordance with that of Vaid and Ramachar[6] and of Rogers and Reynolds[1] obtained by potentiometric, conductometric and spectrophotometric methods for bivalent metal ion–pyrophosphate complexes.

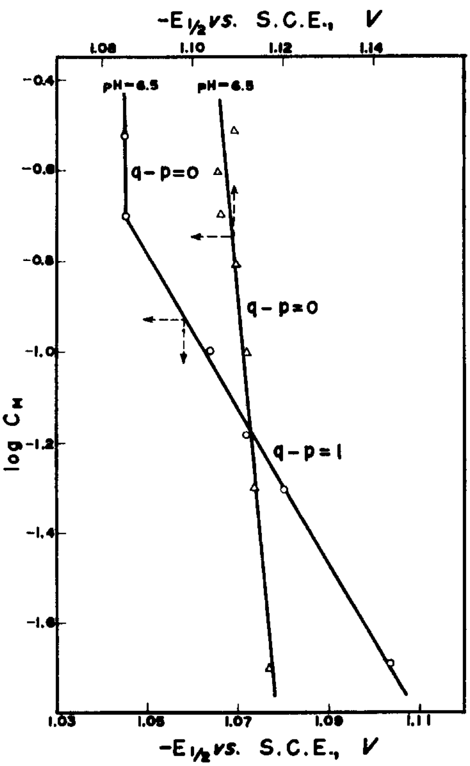

FIG. 4.—Plot of $-E_{1/2}$ *vs.* log C_M:
△—0·04% α-naphthol,
○—0·02% β-naphthol.

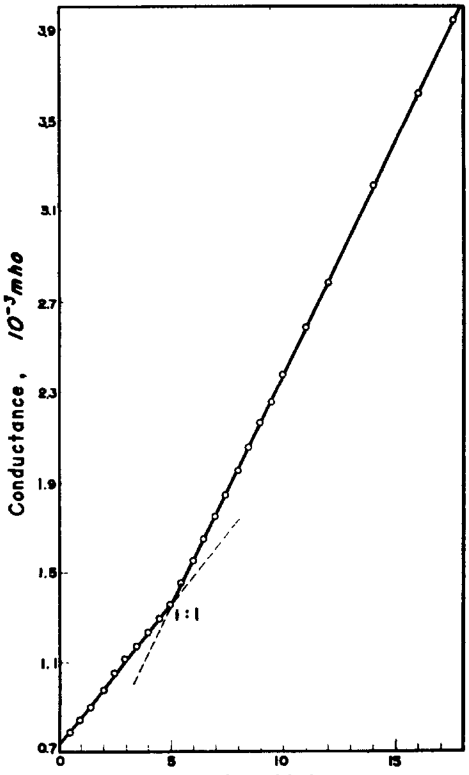

FIG. 5—Conductometric titration [5·0 ml of 10*mM* $UO_2(ClO_4)_2$ + 160 ml of H_2O + x ml of 10*mM* $Na_4P_2O_7$].

Acknowledgement—The authors thank the National Council of Science Development which supported the work described.

Zusammenfassung—Der Einfluß verschiedener oberflächenaktiver Substanzen auf die Eigenschaften der Polarogramme von Uranyl-Pyrophosphat-Komplexen wurde im Einzelnen untersucht. Ohne oberflächenaktive Stoffe wurden reversible und diffusionskontrollierte Reduktionswellen erhalten, wenn die Ligandenkonzentration zwischen 0,05 und 0,30m und der pH zwischen 1,05 und 4,0 lagen. Bei pH-Werten über 4,0 ließen sich die irreversiblen Wellen durch Zugabe von 0,04% α-Naphthol, 0,02% β-Naphthol, und 0,002% Triton X-100 und 0,18% Camphor reversibel gestalten, wobei sich die Wellen zu negativerem Potential verschieben. Konduktometrisch wurde Bildung eines 1:1-Komplexes bestätigt.

Résumé—On a étudié en détail l'effet de diverses substances tensio-actives sur les caractéristiques des polarogrammes des complexes uranyl-pyrophosphate. En l'absence de substances tensio-actives, des vagues de réduction réversibles et à diffusion contrôlée ont été obtenues lorsque la concentration en complexe est comprise entre 0,05*M* et 0,30*M*, et le pH entre 1,05 et 4,0. Au-delà de pH 4,0, les vagues irréversibles sont converties en vagues réversibles par l'addition de 0,04% d'α naphtol, 0,02% de β naphtol, 0,002% de Triton X-100 et 0,18% de camphre, déplaçant les vagues vers les potentiels plus négatifs. On a confirmé par conductimétrie la formation d'un complexe 1:1.

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A COMPARISON OF THE SPECTROGRAPHIC AND SPECTROPHOTOMETRIC METHODS OF DETERMINING GOLD IN FIRE ASSAY BEADS

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Summary—A comparison is provided of the accuracy of two established spectrographic methods and a spectrophotometric method for the determination of gold in silver assay beads. The results indicate that the determination for gold in beads can be accomplished with equal precision and accuracy by the three methods.

Various wet and dry methods have been proposed for the determination of gold in ores, concentrates, *etc.* From the practical point of view, the most useful of these is the classical fire assay in which lead and silver serve as the collector. The resulting lead alloy or button is cupelled to form finally a silver-gold alloy, which may be parted by acids to give gold which is weighed directly.

For microgram amounts of gold particularly, the classical method has sometimes been modified to allow the application of spectrographic or spectrophotometric adaptations. The latter techniques required dissolution of the parted residue in *aqua regia* and, subsequently, the removal of nitric acid by evaporations with intermittent additions of hydrochloric acid. This process is time-consuming, and, therefore, spectrographic methods are frequently used in those laboratories where suitable equipment is available. By this process a great many determinations can be completed during a single day. While various opinions have been entertained concerning the relative accuracy of the two methods as applied to silver-gold beads, no information has been recorded to allow a reasonable comparison. The present work was undertaken to provide such results and, in order to ensure an acceptable conclusion, the spectrographic results were obtained from two laboratories, each employing a distinct technique, and each having extensive experience in the application of their methods. These were the research laboratories of Falconbridge Nickel Mines Limited at Thornhill, Ontario and the Laboratory Branch of the Ontario Department of Mines at Toronto. The spectrophotometric analyses were made in the chemical laboratories of the University of Toronto, from which the gold solutions were distributed without revealing the standardised values. The following report includes a description of the three procedures used together with the results obtained.

EXPERIMENTAL

Apparatus and reagents

Cupels. Obtained from A. P. Green Fire Brick Co. Ltd., Toronto, Canada.

Beckman Model B spectrophotometer with 5-cm Corex cells.

"Hevi-duty" muffle furnace

Applied Research Laboratories two-metre grating spectrograph

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Standard gold solution. Prepared by dissolving spectrographically standardised gold in *aqua regia*, removing nitrous acid by evaporating 3 times in the presence of a few drops of HCl and a few mg of NaCl. The solution was standardised by hydroquinone.[1] Dilute gold solutions were prepared by a suitable dilution with 0·1*M* HCl. All other chemicals were reagent-grade.

Lead-gold alloys. Prepared by constructing lead boats from sheet lead and adding the desired volume of standard gold solution. This procedure avoided any possibility of loss of gold through faulty collection by the complete assay fusion procedure.

A 4″ × 6″ sheet of lead foil was folded into a boat with a base area of 2″ × 4″. Five ml of a standard gold solution were added by a calibrated pipette to the boat, and the solution was then evaporated overnight in a steam cabinet. Ten mg of silver powder were added to the boat, which was then folded carefully to a roll approximately 1·5″ × 0·75″ diameter, weighing 20–23 g.

Procedures

The lead buttons were cupelled on S. A. No. 8 cupels to isolate the gold-silver alloy. The opening temperature was 980°, the 20–30 min drive occurred at 950° and the finishing temperature was 980°.

The silver beads were parted in a small beaker by adding 5 ml of 1:2 nitric acid and heating to incipient boiling. Heating was continued for 5–10 min until all of the silver was dissolved. The contents of the beaker were filtered through a 7-cm No. 42 Whatman paper, and the paper and beaker were washed thoroughly with water. Any silver chloride was removed by washing with 1:1 aqueous ammonia and then with water. The paper and the gold residue were transferred to the parting beaker, which was heated overnight at 450° to burn the paper. Two to three ml of *aqua regia* were added, and the solution was then evaporated to dryness three times in the presence of 1 ml of 2% aqueous NaCl and a few drops of HCl. The residue was dissolved in an aqueous solution containing 10% hydrobromic acid and 0·2% hydrochloric acid, and made up to a volume of 25·0 ml. The absorbance of the bromaurate was measured at 380 mμ in 5-cm cells against a water blank. A standard curve was prepared by adding hydrobromic acid to dilute gold solutions. The results are recorded in Table I. Blank lead buttons and lead buttons containing aliquots of standard gold

Table I.—Recovery of gold by the colorimetric method

Gold added, μg	Gold found, μg					Average, μg
Blank	1·7	1·3	1·7	1·5		1·6
	1·5	1·5	1·5			±0·1
	1·7	1·9	1·5			
	19·1	20·1	19·7	19·3	18·7	
20·5	19·1	20·3	19·7	19·8	18·7	
±0·2	(24·2)	19·4	19·7	19·3	—	
	19·5	20·3	19·9	20·5	20·3	
	19·5	20·5	19·9	21·4	19·9	
	19·5	21·0	20·1	21·2	19·7	19·9
						±0·5
	39·8	38·0	39·4	38·8	39·0	
	39·0	40·0	39·4	39·0	39·0	
40·6	(63·9)	39·0	37·2	39·2	37·8	
±0·1						
	39·4	39·4	40·8	39·8	39·4	
	39·6	39·6	37·6	39·6	40·2	
	39·6	—	39·8	40·0	39·6	39·3
						±0·6
	57·0	56·8	60·0	54·1	60·0	
	57·2	59·5	59·5	57·8	60·4	
	56·8	56·6	55·8	58·5	58·7	
60·8						
+0·3	58·5	56·5	55·0	58·3	59·1	
	59·5	57·6	57·0	58·3	58·9	
	58·3	—	59·1	56·6	58·3	58·0
						+1·2

solutions were cupelled and treated as described. Results for blanks and standards are recorded in Table I. These results provide sufficient evidence that the spectrophotometric method, applied to the determination of gold in beads, may be used to determine the relative efficiencies of the spectrographic method.

The following modification of the spectrographic method, developed by Scobie,[2] was used by the Ontario Department of Mines for the spectrographic analysis of silver beads.

Silver beads weighing approximately 100 mg were formed in a small steel die and mounted on pointed copper rods. The mounted silver bead as the lower electrode was arced against a conical-tipped graphite electrode using a high-voltage (5 KV) a.c. arc at 2·2 amp. An applied Research Laboratories 2-metre grating spectrograph was used. The film was calibrated by the iron line-group method of Dieke and Crosswhite.[3,4] The silver background adjacent to the copper line at 3274 Å was used for internal standardisation. The gold line used was 2675·95 Å. A calibration curve was established from standard beads prepared by evaporating aliquots of standard gold solutions in lead boats, adding 100 mg of silver and cupelling. The weight of gold was calculated from the percentage of gold in the silver, and the accurate weight of the silver bead.

TABLE II.—COMPARISON OF AMOUNTS OF GOLD RECOVERED FOR THE THREE METHODS FOUND

Gold added,* μg		Gold found, μg Colorimetric			Spectrographic†			Spectrographic‡		
0		0	0·6		8	8	8	5	5	5
		Ave.	0·15		8	8	8			
					8			5		
20·8	20·8	20·8	20·8	20·8	21	20	21	21	22	20
20·8	20·8	21·0	20·8	21·0	22	20	21			
20·8	21·2	20·1	20·1	19·3						
		20·1	20·1	19·7						
Ave.	20·9	Ave.	20·4		Ave.	21		Ave.	21	
	±0·1		±0·5			±0·5			±1	
41·5	41·5	41·1	41·6	41·9	38	42	40	39	42	42
41·3	41·9	41·3	43·5	—	39	38	39			
42·1	41·9	39·8	39·4	40·9						
		42·1	39·8	40·6						
Ave.	41·7	Ave.	41·1		Ave.	39		Ave.	41	
	±0·3		±0·9			±1			±1	
61·2	61·4	61·6	61·6	61·2	59	60	61	62	60	62
61·2	62·3	61·8	63·2	61·4	57	53	54	64		
62·3	62·3	59·7	60·1	(30·7)						
		60·0	61·2	60·8						
Ave.	61·8	Ave.	61·1		Ave.	57		Ave.	62	
	±0·5		±0·7			±3			±1	

* These values were obtained for the standard curve and therefore represent the precision of the measurement.

† Falconbridge Nickel Mines Limited

‡ Ontario Department of Mines, Laboratory Branch

The Falconbridge spectrographic method involved an arrested cupellation of the lead buttons. The procedure has been used for the determination of silver, gold, platinum, palladium and rhodium.[5]

Lead buttons were cupelled to a weight of approximately 50 mg. The cupel was removed from the furnace and placed in a stream of nitrogen so that the bead was instantly frozen without oxidation. With experience, the bead weight could be judged accurately before freezing.

Four holes, approximately 1/32″ deep, were pricked in the top of a clean, copper electrode with a center punch. The lead bead was attached firmly to the top of the copper rod by covering the bead with aluminium foil and tapping it with a hammer until flattened. The copper rod served as the lower electrode and was made the cathode. The samples were sparked against a graphite anode with a peak voltage of 20 KV and a radio frequency current of 5 A. Lead was used as an internal standard employing the line at 3118·92 Å. The gold lines used were at 2675·95 Å, 2427·95 Å and 3122·78 Å.

Standards used for calibration were prepared by melting pure lead in a graphite crucible, and dissolving various amounts of gold, silver and several platinum metals. The weight of gold in the sample was calculated from the percentage of gold in the lead and the accurate weight of the lead bead.

In preparation for the comparison of the accuracy and precision of the described methods a set of artificial lead buttons was prepared as described above. These buttons were made up of samples of four different concentrations: 0 (blank), 20, 41 and 62 μg of gold. Each of these weights was contained in 5 ml of standard solution. Each lead button contained 10 ± 1 mg of silver and weighed approximately 20 g. Simultaneously with the preparation of these buttons, the above three weights of gold, each in 5-ml aliquots, were treated with hydrobromic acid, as described in the procedure, and the absorbances were determined from the standard curve. This procedure was followed to allow a direct comparison of the absorbance values with those obtained for the button. This precaution avoided the usual error of dilution, and was preferred to a calculation of the gold content from the gravimetric values. In this way an estimate of precision is also achieved.

Several sets of the four different gold concentrations were determined by the colorimetric procedure described after cupellation. Other sets of samples were analysed spectrographically, after an arrested cupellation of the button, by the Falconbridge Nickel Company. Buttons for the Provincial Assay Laboratory were adjusted to contain 100 mg of silver by addition of silver powder, and were subsequently cupelled. The results for samples analysed by the three methods are recorded in Table II.

DISCUSSION

The results recorded in Table I prove that the colorimetric procedure described may be used for the determination of the gold content of lead buttons. Table II indicates that the determination of gold in beads can be accomplished with equal accuracy by the spectrographic determination in silver-gold beads or in lead-silver-gold beads, and by a colorimetric determination as bromaurate.

Acknowledgment—The authors are grateful to W. L. Ott of Falconbridge Nickel Mines Limited and W. D. Taylor of the Ontario Department of Mines for the spectrographic results.

Zusammenfassung—Dieser Bericht vergleicht die Genauigkeit zweier bekannter spektrographischer und einer spektrophotometrischen Bestimmungsmethode für Gold in Perlen von der Silberprobe. Die Ergebnisse zeigen, daß die Goldbestimmung in den Perlen mit gleicher Genauigkeit und Richtigkeit nach allen drei Methoden durchgeführt werden kann.

Résumé—Dans ce mémoire, on compare les précisions de deux méthodes spectrographiques et d'une méthode spectrophotométrique établies pour le dosage de l'or dans les perles d'essai en argent. Les résultats montrent que le dosage de l'or dans les perles peut être effectué avec une même précision et une même justesse par trois méthodes.

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CHELATING RESINS—THEIR ANALYTICAL PROPERTIES AND APPLICATIONS

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Summary—This review provides some factual information on the knowledge which has been assembled on chelating resins, particular emphasis being placed on their contribution to basic research into complexation reactions and on the fact that they add another unit operation to the analytical separations available.

CHELATING resins are ion exchangers in which various chelating agents have been incorporated. Examples are dimethyglyoxime or iminodiacetic acid introduced into the matrix of a styrene-divinylbenzene polymer. These substances—invented some ten years ago—combine two well-known analytical processes: ion exchange and complexation reactions. The combination of the two processes in one single system is an innovation which greatly enlarges the scope of fundamental knowledge about ion exchangers and their applications.

Chelating ion exchangers are distinguished from the ordinary type of ion exchanger by three main properties:

(a) *High selectivity.* The affinity of particular metal ions to a certain chelating ion exchanger depends mainly on the chelating group and not on the size of the ion, its charge, or other physical properties which determine the order of preference in the case of the ordinary ion exchanger.

(b) *Bond strength.* In ordinary ion exchangers the binding is electrostatic with a strength of the order of 2-3 kcal/mole, while in the resins dealt with here the binding energy is of the order of 15-25 kcal/mole.

(c) *Kinetics.* While in the ordinary type of exchanger, exchange processes are more rapid and controlled by diffusion only, which is itself a function of the mobility and the concentration gradient of the ions entering and leaving, the exchange process in a chelating exchanger is slower and controlled either by a particle diffusion mechanism or by a second order chemical reaction.

These three differences point the way to a further extension of the separation possibilities of cations and anions in different media on a chelating ion exchanger. The interesting property of this material to act as a solid complexing agent combined with the ability to carry out complexing processes in two-phased systems—solid-liquid—further widens the scope for fundamental research into complexation mechanisms.

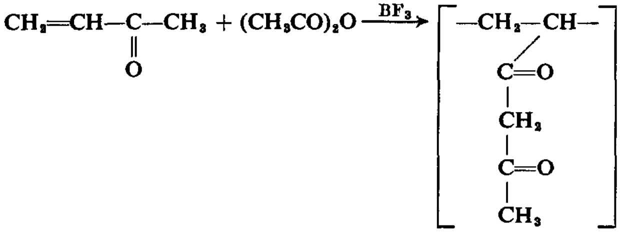
It is the aim of this review to provide some factual information on the knowledge which has been assembled on chelating resins, particular emphasis being placed on their contribution to basic research into complexation reactions and on the fact that they add another unit operation to the analytical separations available.

TYPES OF RESIN AND THEIR PREPARATION

Information on chelating groups introduced into a polymer matrix has already been partly summarised in previous reviews[1,2] and by Rieman and Breyer.[3] In the present review, therefore, only the important new types that have been added in the meantime are covered.

Polyvinylacetonyl ketone[4]

This resin is prepared by ionic polymerisation of vinyl methyl ketone and its simultaneous condensation with acetic anhydride. The relevant reaction may be described in the following general form:



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + (CH_3CO)_2O \xrightarrow{BF_3} [-CH_2-CH(-CO-CH_2-CO-CH_3)-]$$

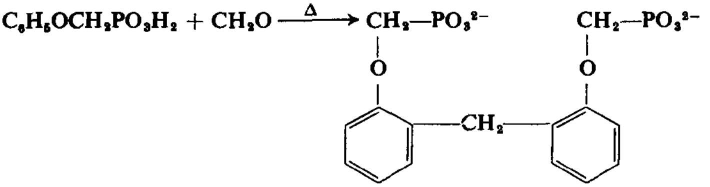
The monomer analogue of this polymer is acetylacetone, the chelating properties of which are well known. So far only the stability constants of the polymer with copper(II) and uranyl ions have been determined ($\log K_{UO_2^{2+}} = 8{\cdot}8$; $\log K_{Cu^{2+}} = 7{\cdot}0$).

Phosphonic acid groups incorporated into a phenol-formaldehyde matrix[5,6]

The reaction takes place in stages:

$$PCl_3 \xrightarrow[205°C]{H_2CO} ClCH_2POCl_2 \xrightarrow{NaOH} ClCH_2PO_3Na_2$$

$$C_6H_5ONa + ClCH_2PO_3Na_2 \xrightarrow{HCl} C_6H_5OCH_2PO_3H_2 + 3NaCl + H_2O$$

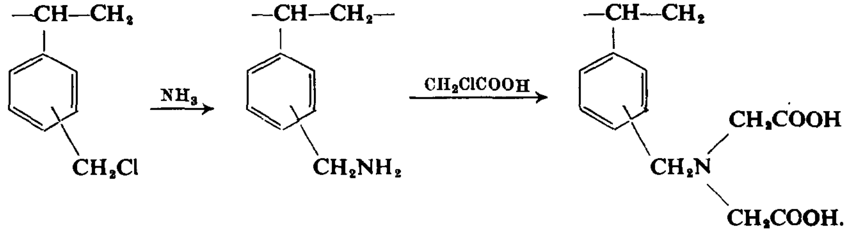


This resin shows special chelating properties with respect to the $Cu(NH_3)_4^{2+}$ ion, and it may be expected to show a strong affinity to other metal ions producing phosphate complexes, which have, however, not yet been investigated. The chelating property of this resin is proved by the fact that the elution of metals with a salt extracts only 5% of the metals, while with an acid above 90% are eluted.

Iminodiacetic acid in a styrene–divinylbenzene matrix

This resin is known under the trade names of Dowex Chelating Resin A-1 and Chelex 100, and it is the only one available commercially and of which the physical and chemical properties have been explored to any extent.

For the synthesis of this substance chloromethylated styrene-divinylbenzene is used as the starting material, which undergoes a process of amination and is then treated with monochloracetic acid:



Details of this synthesis are given in the patent published by the Dow Chemical Company.[7]

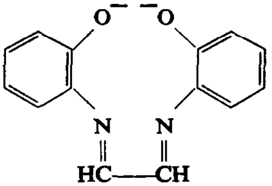
Polymers of the same type, but with other amino acid functional groups—glycine, nitrilotriacetic acid and the like—have been synthesised and characterised by Morris *et al.*,[8] Hering[9,10] and Blasius and Bock.[41]

Copolymers of the phenol-formaldehyde type

Pennington and Williams[25] polymerised formaldehyde with various derivatives of phenol, such as *o*-aminophenol, resorcinol, *β*-resorcylic acid, *etc.*, and obtained ion exchangers possessing superior selectivities for transition and alkaline earth metal ions.

Glyoxal-phenol derivatives

Considerable publicity was given recently to the work of Bayer,[39] who succeeded in constructing very specific chelating agents and incorporating them into macromolecules. He condensed *o*-aminophenol with glyoxal and obtained glyoxal-bis-2-hydroxyanil in a polymer matrix as a result. This substance shows a high affinity for copper, uranyl and nickel ions. The structure of the ligands taking part in the co-ordination process is as follows



The ions of the metals referred to are bound to the ligands at four locations (2 oxygens and 2 nitrogens) and in addition to 2 water molecules.

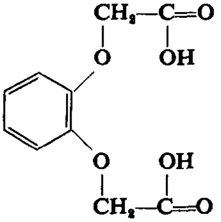
In a similar fashion Bayer synthesised another reagent, which instead of the hydroxylic groups contained mercapto groups, and he obtained a polymer specific for gold, silver and mercury ions. With this reagent Bayer extracted 1·4 μg of gold from 100 l. of sea water.

A polymer containing the ligand dimethylaminobenzylidenerhodanine

This reagent, which commonly serves for the photometric determination of the copper group and the noble metal ions OsO_4^{2-}, Pt^{4+} and Pd^{2+}, was introduced into a polymer matrix by Lewandowski and Zczepaniak.[40] The chelating ion exchanger obtained showed selective absorption properties for these metals.

Oxygen donor ligands incorporated in a resin

Blasius and Kynast[42] introduced the following ligand into a resin matrix



The resulting resin showed a strong affinity for zirconium(IV), the structure of the complex obtained being octahedral.

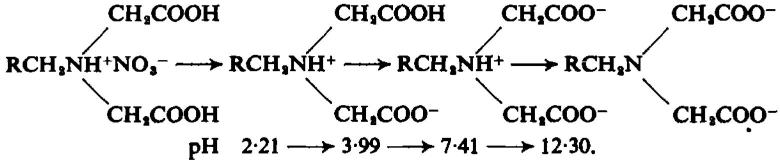
FUNDAMENTAL PROPERTIES

Structure of the resins

The relationship between the number of rings substituted by chelating ligands and the total number of rings, is found by elemental analysis of the resin. Work of this kind has been undertaken by Schwartz[11] as well as by Loewenschuss and Schmuckler,[12] who investigated the number of substituted rings in Dowex A-1 and found that of every 8 rings in the resin 5 are substituted with iminodiacetic acid.

Information on the location of the charges in the functional groups may be obtained by means of the infrared spectrum of the resin at various pH. A qualitative analysis of the Dowex A-1 resin was made by Schwartz[11] at various pH, with the resin immersed in a buffer solution of acetic acid-sodium acetate and at constant ionic strength.

The locations of the various groups as a function of pH, as obtained by Schwartz, are as follows:



$$\mathrm{RCH_2NH^+NO_3^-}\begin{smallmatrix}\nearrow\mathrm{CH_2COOH}\\ \searrow\mathrm{CH_2COOH}\end{smallmatrix} \longrightarrow \mathrm{RCH_2NH^+}\begin{smallmatrix}\nearrow\mathrm{CH_2COOH}\\ \searrow\mathrm{CH_2COO^-}\end{smallmatrix} \longrightarrow \mathrm{RCH_2NH^+}\begin{smallmatrix}\nearrow\mathrm{CH_2COO^-}\\ \searrow\mathrm{CH_2COO^-}\end{smallmatrix} \longrightarrow \mathrm{RCH_2N}\begin{smallmatrix}\nearrow\mathrm{CH_2COO^-}\\ \searrow\mathrm{CH_2COO^-}\end{smallmatrix}$$

$$\mathrm{pH}\ \ 2{\cdot}21 \longrightarrow 3{\cdot}99 \longrightarrow 7{\cdot}41 \longrightarrow 12{\cdot}30.$$

He arrived at these conclusions through the following experimental observations. At low pH in a sodium nitrate medium a characteristic absorbance of the nitrate ion was found at 7·21 μ, which means that in an acidic medium Dowex A-1 acts as an anion exchanger, assuming the form of a quaternary ammonium salt of the type $R_3NH^+NO_3^-$. A further characteristic absorbance at low pH was found at 5·70–5·75 μ, which proves that the carboxylic groups present are non-ionised. With rising pH this absorbance disappears. At high pH (12·3) an absorbance appears at 9·0 μ, proving the presence of a tertiary amine.

Swelling

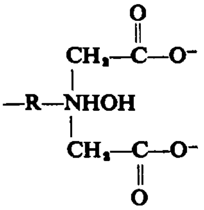
This is a measure of the elastic properties of a resin and a very important source of information for thermodynamic and kinetic data. The water uptake (or swelling) of chelating resins is especially pronounced because of their low cross-linking. In the case of Dowex A-1[13] the volume of the resin in the hydrogen form is 0·45 and in the sodium form 1·00. These large differences in volume are a great disadvantage in column operation.

Schwartz[11] investigated the changes in the swelling of Dowex A-1 as a function of pH, in the presence of sodium and zinc ions, respectively. In the sodium form there is an appreciable rise in swelling as the pH increases, whilst in the zinc form the rise is slight. This is because the co-ordination sites in the case of zinc are occupied by iminodiacetic acid, so that water cannot penetrate into the resin.

Krasner and Marinsky[14] measured the water uptake of Dowex A-1 at various pH in order to get osmotic coefficient values, which are necessary for determining the dissociation of the iminodiacetic acid groups in this resin.

Acidity constants

The functional groups incorporated in macromolecules must have pK_a values approaching those of the monomeric complexants. Taking Dowex A-1 as an example, three acidity constants may be expected. In iminodiacetic acid, the analogous monomer, Chaberek and Martell[15] determined only two such constants, the third being difficult to establish experimentally. Marinsky and Krasner[16] showed that in the resin Dowex A-1 the functional groups exist in three forms in different pH ranges. He determined the first acidity constant by means of potentiometric titration with sodium hydroxide, the value obtained being 1·2 × 10^{-3}, which is close to the first constant of the monomer iminodiacetic acid[15] (2·9 × 10^{-3}). He then proceeded to determine the third constant of the resin, which has a mildly alkaline form and of which the structure is



$$\begin{array}{l} \qquad\qquad\quad O \\ \qquad\qquad\quad \| \\ \qquad\quad CH_2—C—O^- \\ \qquad\quad | \\ —R—NHOH \\ \qquad\quad | \\ \qquad\quad CH_2—C—O^- \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad O \end{array}$$

This was achieved experimentally by potentiometric titration with sodium hydroxide labelled with ^{22}Na and by controlling the activity of the sodium and hydrogen ions in both the aqueous and the solid phases. The value obtained was 10^{-14}.

Recently, Krasner and Marinsky[14] redetermined the first acidity constant with the aid of a different, more accurate approach, namely, taking potentiometric neutralisation titration data and water absorption measurements as a function of pH and using an equation which is a combination of the Gibbs-Donnan equation and that of Katchalsky, in order to introduce the corrections necessary for obtaining the thermodynamic values. The second acidity constant is difficult to obtain experimentally, because the second end-point in the potentiometric titration with sodium hydroxide is not sharp. Leyden and Underwood[17] showed that if this titration is carried out in a medium of isopropyl alchol with tetra-n-butylammonium hydroxide as titrant, equilibrium is reached much more rapidly and two sharp end-points are obtained. No attempt was, however, made to pass from the apparent values resulting from that titration to thermodynamic values.

Acidity values have also been determined for other polymers, such as PAK (polyvinylacetonyl ketone) and PAA (polyacrylic acid). This work was done by Gregor, Luttinger and Lobel,[18] who carried out potentiometric titrations with sodium hydroxide in order to correlate pH with α (the degree of neutralisation.) The acidity constants were then obtained through the Henderson-Hasselbach equation.

Trostyanskaya and Nefedova[19] synthesised a resin containing the ligand diethanolamine as the functional group and studied its properties. They, too, titrated the resin with sodium hydroxide and found two end-points, one at pH 5·0, the other at pH 10·5.

Stability constants with metal ions

For determining the stability constants of the various metal ions with the chelating resins the stoichiometry of the reaction between the two must first be established, *i.e.*, the amount (mmoles) of functional groups in the resin needed for each mmole of metal ion. It was found that two stoichiometric ratios are possible, depending on the experimental conditions.

In the case of Dowex A-1, in contact with trace quantities of metal ions, complexes of the ratio 1 : 2 (of the form MR_2) are formed, as between the metals and iminodiacetic acid in solution. Marinsky[20] and Hering[21] independently determined the first constant of such complexes by potentiometric titrations for nickel and copper ions, obtaining numerical results that were very close to the first constant between iminodiacetic acid and these metals in solution.

If the process takes place in the presence of an excess of metal ions, complexes of the ratio 1 : 1 (of the form MR) are formed. Loewenschuss and Schmuckler[12] showed that the resin had the same maximum capacity for Cu^{2+}, Fe^{3+} and Th^{4+}, and that for each mmole of nitrogen in the resin 1 mmole of metal ion is adsorbed irrespective of the charge (which is analogous to complexation with EDTA). They also determined the apparent stability constants of copper and nickel with the resin through competing equilibria of the metal ions between the ligand *N*-hydroxyethylenediaminetriacetic acid and Dowex A-1. Gregor, Luttinger and Loebl[18] determined the stability constants of metal ions with the resins PAA and PAK by potentiometric titrations of the resin with sodium hydroxide both in the presence and in the absence of complexing metal ions. In order to calculate the constant from the experimental data they used a modification of Bjerrum's method.

Kinetics

Three investigators carried out experiments with a view to finding the rate determining step in the chelating exchange process on Dowex A-1. Turse and Rieman[34] used a modified limited-bath technique in order to study the exchange kinetics of several pairs of metals: calcium–magnesium, sodium–calcium, *etc.*, and concluded that the rate-determining step is controlled by a second-order chemical reaction, the size of the particles having no effect.

Other workers, however, reached the conclusion that the rate determining step is controlled by particle diffusion. Heitner-Wirguin and Markovitz[35] also used the limited-bath technique in order to examine the exchange rate between the sodium form of Dowex A-1 and the metals strontium, calcium and magnesium. They showed that the graphic correlation of Bt *versus* t (where B = a constant dependent on the radius of the particles and the diffusion co-efficient, and t = time) gives straight lines crossing the origin irrespective of either the temperatures at which the experiments are carried out or of the radii of the particles. Measurements at different temperatures enabled them to calculate the activation energies and to show that these energies are higher in the case of a chelating exchange than in that of an ordinary exchange. Schwartz, Marinsky, and Spiegler[36] came to a similar conclusion through a different experimental approach. They carried out self-exchange measurements using ^{60}Co, ^{22}Na and ^{65}Zn isotopes in a manner similar to the experiments conducted by Boyd and Soldano[37] with ordinary ion exchangers. Their approach has the advantage that there are no swelling changes of the resin during the exchange process and no changes in the mobility and the charge of the exchanging ions, so that the system contains fewer variables and is less complicated. The divergence over the two proposed mechanisms now seems to have been settled in favour of the diffusion-controlled rate-determining step. Thus, the recent work of Varon and Rieman[43] has shown that Turse and Rieman's earlier conclusion, that the rate-determining step is controlled by a second-order chemical reaction, was based on an experimental error in establishing the capacity of the resin. The error was due to the fact that when the sodium form of the resin is washed with water, partial hydrolysis takes place, which reduces the sodium capacity of the resin. To overcome this difficulty, a new series of experiments was carried out by the shallow-bed method, and this led to the conclusion reached by the other workers.

Similar work was carried out by Hojo,[38] who used a different resin for silver, mercury and copper ions. He, too, reached the conclusion that the process is controlled by particle diffusion.

PRACTICAL APPLICATIONS

Uses in nuclear chemistry

It seems that chelating resins could serve as valuable tools for the production of radioactive tracers of high specific activity using the Szilard-Chalmers method (an n,γ reaction). Neutron activation of a chelating resin to which metal ions are bound leads to a reaction which may be schematically described as follows:

$$\text{R-chelating ligand-M}^{x} + \text{n} \rightarrow \text{R-chelating ligand} \ldots \text{M}^{x+1} + \gamma$$

where x is the atomic weight of the metal ion.

The bond of that portion of the metal ions bound to the resin which undergoes an n,γ reaction will be weakened, so that the labelled ions may be liberated from the resin by shaking the solid with a solution containing the metal ion M as carrier. In this manner a solution of high specific activity may be obtained, but the method has so far not been tried in practice.

Other applications in this field were made by Forberg and Lundgren,[22] who separated transition metal ions (Ni^{2+}, Cu^{2+}) on Dowex A-1 from irradiated Na_3PO_4. Christell, Forberg and Westermark[23] measured the exchange between lanthanum and copper in a copper-saturated Dowex A-1 resin, by measuring the activity of ^{140}La in both the resin and the solution phases. The same workers also tried to separate two lanthanides (La^{3+} and Lu^{3+}) on a column of calcium-saturated Dowex A-1, but it seems that this separation has, as yet, no practical advantage over more conventional separation techniques for the lanthanides using ordinary ion exchangers.

Separation possibilities

Hering[26,27] absorbed a number of transition and alkaline earth metals on columns containing resins with aminocarboxylic groups, then eluted the metals with dilute acids, and showed the relationship between elution curves and pH. He defined a new concept, the *decomplexation pH* (*DpH*): during the acidic elution process of a mixture of metals, each of the latter will appear in the eluent with a certain, characteristic pH, which is dependent on the stability constants of the various metals with the chelating resin. Correlation of the metal ion concentration leaving the column *versus* the pH produces the desired DpH values, which may also serve to calculate the stability constants of the metals with the chelating resin. Schmuckler and Friedman[28] showed that the separation possibilities of metal ions on Dowex A-1 could be extended by the use of selective complexing agents in the feed and elution stages.

Helfferich[29,30] widened the scope for utilising ion exchangers by establishing that besides metals, ligands, too, could be separated on these resins. He called this process *ligand exchange*, which means, in effect, that if the resins contain complexing metal ions, *e.g.*, Cu^{2+}, Ni^{2+} or Ag^{+}, the solid sorbent may be used for selective exchange of the ligands bound to these metals, *e.g.*, amines. With this idea he made an important contribution to the chromatography of ligands extant in nature–proteins, *etc.*

Recovery of traces of metal ions

Turse and Rieman[24] succeeded in absorbing 1·00 ppm of Cu^{2+} from a medium of $1M$ ammonium chloride on Dowex A-1 with a 99% recovery or better. A concentration of 0·32 ppm of Cu^{2+} from $0{\cdot}5M$ sodium chloride (ratio of electrolyte to copper of *ca.* 100 : 1) was achieved on other chelating resins by Pennington and Williams.[25] These examples prove that the strong bond of the metals to the chelating resins enables them to be extracted from very dilute solutions of high ionic strength, a process impossible with ordinary exchangers.

Miscellaneous analytical determinations

The most important use in this field is the determination of calcium in sodium hydroxide[31] and in lithium salts.[32] The small quantities of calcium (2-10 ppm) present in these salts were absorbed on Dowex A-1 resin; the calcium was then eluted from the resin with $2M$ hydrochloric acid and titrated complexometrically.

This use may be extended to the analytical determination of traces of complexing metal ions in pure salts and other compounds, where the metal ions must first be concentrated before they can be determined analytically.

Extraction of metals from complexing media and slightly soluble salts

It has already been shown that complexing metal ions may be extracted from a complexing medium, *e.g.*, copper from a chloride, ammonia or phosphate medium. What has to be clarified is the mechanism of binding, a problem attacked by Loewenschuss and Schmuckler,[12] who made equilibrium measurements of copper ions bound to bi- and tridentate aminocarboxylic ligands brought into contact with measured quantities of Dowex A-1. They showed that with each copper atom entering the resin, 1 molecule of the ligand to which the copper is bound in solution also enters. In other words, Dowex A-1 may serve as a solid chelating agent in which a definite quantitative relation exists between the absorptive capacity and the quantity of competing ligands (in the solution phase and in the resin). Rich[38] showed that even slightly soluble salts of various metals, *e.g.*, lead sulphate or calcium fluoride,[2] may be dissolved with the aid of Dowex A-1, dissolution being fairly rapid (5-60 min), but the mechanism of this process is not yet clearly understood.

CONCLUSION

The process of chelation in the solid phase presents a challenge both for basic research and to the industrial chemist looking for new analytical methods. The field is as yet rather young, and it is developing slowly because of the scarcity of suitable, commercially available substances. The only one of which the properties could be investigated and for which uses could be found is the resin Dowex A-1 (Chelex-100) and it is this that has been mentioned on several occasions throughout the present paper. If any advances are to be made in this field, a great deal of synthetic work must be invested with a view to enlarging the variety of ion exchangers having different ligands. The aim of such syntheses should be to devise substances of high selectivity and rapid exchange. As regards selectivity, Bayer[39] stressed the interesting fact that chelating ligands bound to macromolecules have a higher selectivity for certain metal ions than the same ligands in their monomer form because of their particular steric arrangement. This is not so with the resin Dowex A-1, but for proteinic mercapto groups Bayer could show that while in solution they had affinities to a number of metal ions, on a macromolecule they had an exclusive affinity to copper.

Résumé—Cette revue apporte des renseignements expérimentaux, concernant les connaissances que l'on a rassemblées sur les résines chélatantes. On insiste particulièrement sur leur contribution à la recherche de base dans les réactions de complexation, et sur le fait qu'elles ajoutent une autre technique fondamentale aux séparations analytiques existantes.

Zusammenfassung—Diese Übersicht vermittelt einiges Tatsachenmaterial über chelatbildende Harze. Dabei wird besonderer Nachdruck auf ihren Beitrag zur Grundlagenforschung über Komplebildungsreaktionen gelegt sowie auf die Tatsache, daß ihre Verwendung sich als neue Grundoperation den bisher bekannten analytischen Trennverfahren zugesellt.

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SHORT COMMUNICATIONS

Colorimetric determination of vanadium(V) with 4-(2-pyridylazo)-resorcinol

(*Received* 18 *May* 1964. *Revised* 7 *October* 1964. *Accepted* 9 *October* 1964)

4-(2-PYRIDYLAZO)-RESORCINOL (PAR)[1] has been widely used as a reagent for the colorimetric determination of metal ions, *e.g.*, niobium,[2-5] uranium,[6-9] cobalt,[6,10] lead,[6] thorium,[11] scandium,[12,14] indium,[15,16] gallium[17,18] and palladium.[19]

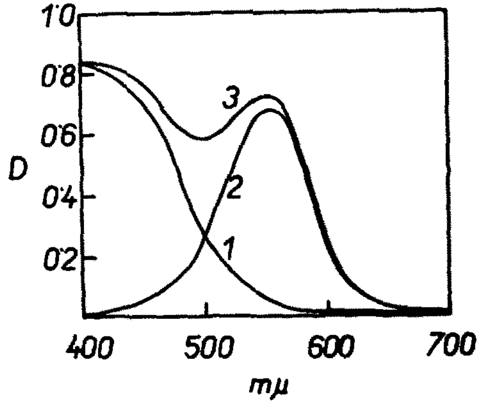

FIG. 1.—Absorption curve of vanadium(V) complex with PAR:
1—PAR *vs.* water; 2—V + PAR *vs.* PAR; 3—V + PAR *vs.* water.
(0·5 μmole of V^{5+}; 5 μmole of PAR; 1 ml of buffer; volume, 25 ml; 1-cm cuvette).

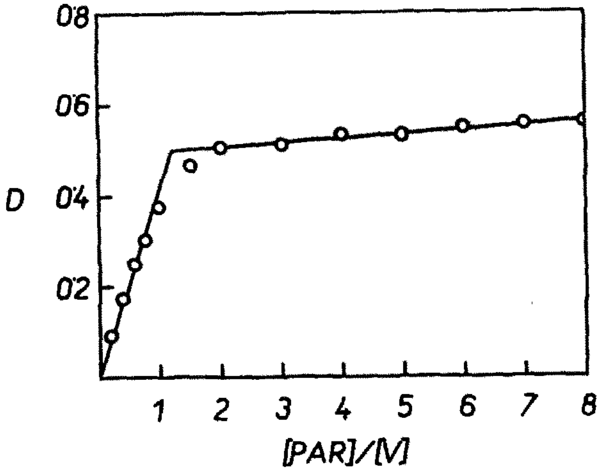

FIG. 2.—Molar ratio method (0·5 μmole of V^{5+}; 1 ml of buffer; 0·1–4 μmole of PAR; volume, 25 ml; 1-cm cuvette; 550 mμ *vs.* water).[11]

We have now found that with PAR vanadium(V) gives a very sensitive violet coloration suitable for colorimetric determination of the latter. The absorption maximum is at 550 mμ (Fig. 1), where the absorption of the reagent itself is only small. The composition of the complex has been investigated by three methods (Figs. 2, 3 and 4), which all show that the V:PAR ratio is 1:1. The Bouguer-Lambert-Beer law is followed over a wide range of concentrations (0·04–1 μg/ml), which permits the determination of 1–5 μg of vanadium(V) in 25 ml of test solution. The sensitivity of the proposed method is one of the highest known for vanadium (Table I). The V-PAR complex is stable over a wide pH-range, so that various buffer solutions can be used (Fig. 5).

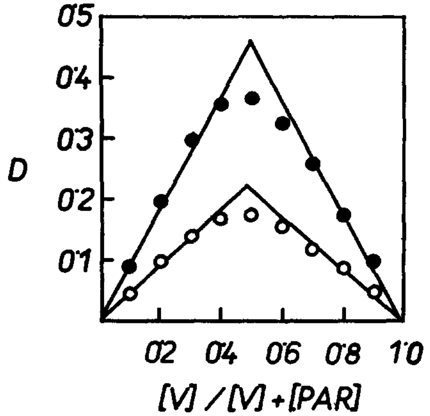

FIG. 3.—Continuous variation method:[20,21]
●—1 μmole of V^{5+} + PAR; 1 ml of buffer; volume, 25 ml; 1-cm cuvette; 550 mμ; with correction for PAR;
○—the same, but with 0·5 μmole of V^{5+} + PAR.

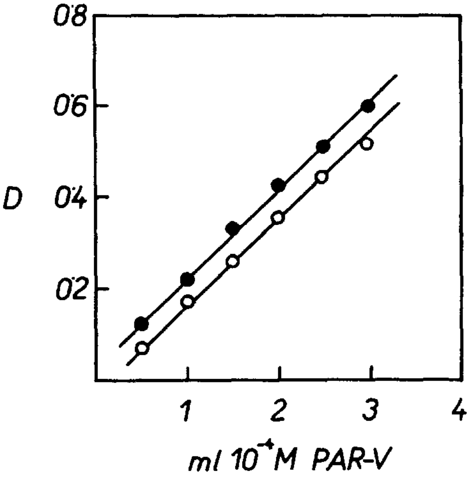

FIG. 4.—Harvey-Manning plot for V-PAR complex:[22]
●—0·05–0·3 μmole of V^{5+}; 1 ml of buffer; sodium chloride medium (μ = 0·5); 5 μmole of PAR; volume, 25 ml; 550 mμ vs. PAR; 2-cm cuvette;
○—the same, but vice versa—with excess of V^{5+} and insufficiency of PAR, vs. water.

In a previous paper[16] it has been established that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) has a specific action towards quinquevalent vanadium ions in that it does not form stable complexes in contrast to most other metal ions. This fact was used for increasing the selectivity of the colorimetric determination of vanadium with Xylenol Orange (XO) and more than 20 ions do not

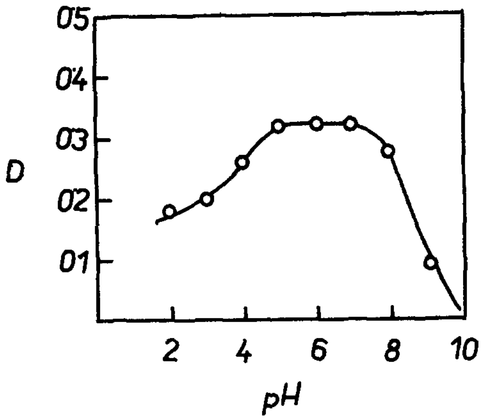

FIG. 5.—pH-Dependence of the optical density of vanadium(V) complex with PAR (0·5 μmole of V^{5+}; 2 ml of buffer; 10 μmole of PAR; volume, 50 ml; 1-cm cuvette; *vs.* water.)

TABLE I.—SENSITIVITY OF VARIOUS COLORIMETRIC METHODS FOR THE DETERMINATION OF VANADIUM

Method	Sensitivity, μg of V/cm^2 (for log I_0/I = 0·001)	Molecular extinction coefficient
Hydrogen peroxide	0·1800 (450 mμ)[24]	300 (450 mμ)[25]
Phosphotungstic acid	0·0200 (375 mμ)[24]	2000 (400 mμ)[25]
8-Hydroxyquinoline ($CHCl_3$ extraction)	0·0160 (550 mμ)[24]	—
PAN ($CHCl_3$ extraction)	0·0030 (615 mμ)[26]	16900 (615 mμ)[27]
Xylenol Orange	0·0026 (530 mμ)[26]	13000 (520 mμ)[28]
PAR (in presence of DCTA)	0·0014 (550 mμ)	36000 (550 mμ)

then interfere with the determination. Hence, the influence of DCTA on the V-PAR complex has been studied and it has been established that the latter acts in a similar manner to the V-XO complex: a 5000-fold molar excess of DCTA decreases the optical density by about 40% in respect to its nominal value (regardless of the pH of the solution in the range 5–8). EDTA breaks down the complex, but tartaric acid, oxalic acid, sodium fluoride, *etc.*, have little influence. The maximum optical density of a V-PAR solution in the presence of DCTA is attained within 30 min, probably because of the equilibrium between the DCTA-V and PAR-V complexes; the optical density then remains constant for 2 hr.

The presence of DCTA prevents the reaction of many metal ions with PAR, making this method one of the most selective for determination of vanadium. The influence of 30 ions has been studied and the maximum ratios below which no interference is observed are given in Table II. Only a few ions have a considerable influence on the proposed method, *e.g.*, niobium, uranium and titanium. Other ions, such as indium, molybdenum, tin and thallium, do not interfere in moderate amounts, while the rest of the tested ions have no influence over a wide concentration range. The calibration curve must be constructed at a constant concentration of DCTA against a blank containing a constant concentration of PAR. In the presence of coloured ions the blank should be prepared with the same concentrations of the relevant ions.

Procedure. Add to 5–15 ml of slightly acidic test solution, containing 1–5 μg of vanadium(V), 5 ml of 0·05*M* DCTA, 1 ml of 2*M* ammonium acetate (adjusted with acetic acid to pH 5·5 using a glass electrode and pH-meter) and 2 ml of 0·001*M* PAR. Dilute to 25 ml. Measure the optical density of the solution after 30 min on a spectrophotometer at 550 mμ or on a Pulfrich photometer (filter S53) in a 5-cm cell against the same concentration of PAR, DCTA and buffer.

The proposed method has many advantages compared with other colorimetric methods for vanadium. It has a high sensitivity and the interference from many elements can be masked with DCTA. Also, PAR undergoes no acid-base change within the pH-range in which the vanadium complex is suitable for colorimetric determination. Finally, the pH-range for development of the V-PAR coloration is fairly wide, the actual development of the coloration is relatively quick and

TABLE II.—DETERMINATION OF 1 μg OF VANADIUM IN THE PRESENCE OF FOREIGN IONS

	Foreign ion, μg	Weight ratio of V^{5+}:Me	Vanadium(V), μg	
			Found	Difference
Fe^{3+}	5000[a]	1:5000	1·00	+0·00
Al^{3+}	10000	1:10000	1·08	+0·08
Pb^{2+}	5000	1:5000	1·04	+0·04
Zn^{2+}	5000	1:5000	1·04	+0·04
Cu^{2+}	5000[a]	1:5000	0·96	−0·04
Mn^{2+}	5000[a]	1:5000	0·91	−0·09
Co^{2+}	5000[a]	1:5000	1·08	+0·08
Ni^{2+}	5000[a]	1:5000	1·08	+0·08
Bi^{3+}	200[b]	1:200	1·06	+0·06
Sn^{4+}	30[b,c]	1:30	1·01	+0·01
Tl^{3+}	50[b]	1:50	1·08	+0·08
Sb^{5+}	100[b,c]	1:100	0·96	−0·04
Ga^{3+}	2000[b]	1:2000	1·05	+0·05
In^{3+}	10[b]	1:10	0·90	−0·10
La^{3+}	2500	1:2500	1·01	+0·01
Y^{3+}	100[b]	1:100	1·00	+0·00
Mg^{2+}	200[b]	1:200	1·08	+0·08
Ca^{2+}	1250[b]	1:1250	1·00	+0·00
Sr^{2+}	5000	1:5000	1·06	+0·06
Ba^{2+}	2500[b]	1:2500	1·05	+0·05
Ti^{4+}	1[b]	1:1	1·00	+0·00
Zr^{4+}	15[d]	1:15	1·09	+0·09
Nb^{5+}	0·5[b,c]	1:0·5	1·15	+0·15
CrO_4^{2-}	5000[b]	1:5000	1·04	+0·04
MoO_4^{2-}	50[b]	1:50	1·00	+0·00
WO_4^{2-}	250[b]	1:250	0·90	−0·10
UO_2^{2+}	0·5[b]	1:0·5	1·05	+0·05
NaF	50 mg		1·00	+0·00
Tartaric acid	50 mg		1·05	+0·05
Sodium phosphate	50 mg		1·00	+0·00

[a] Measured against the same concentration of the coloured ion.

[b] Maximum ratio of V^{5+}:Me.

[c] In the presence of 10 mg of sodium potassium tartarate.

[d] Previously boiled with DCTA.

the reaction occurs in aqueous solution. Compared to the use of XO, PAR has the shortcoming that titanium, zirconium and uranium interfere to a higher degree with the determination of vanadium. On the other hand, PAR is better than XO in the presence of molybdenum and tungsten.

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Summary—4-(2-Pyridylazo)-resorcinol has been found to undergo a very sensitive colour reaction with vanadium(V). In the presence of 1,2-diaminocyclohexanetetra-acetic acid the reaction is highly selective.

Résumé—On a trouvé que le 4-(2-pyridylazo)-résorcinol donne, avec le vanadium(V), une réaction colorée très sensible. En présence d'acide 1,2-diaminocyclohexanetétracétique, la réaction est hautement sélective.

Zusammenfassung—4-(2-Pyridylazo)-resorcin gibt eine sehr empfindliche Farbreaktion mit Vanadium(V). In Gegenwart von 1,2-Diaminocyclohexantetraessigsäure ist die Reaktion hochselektiv.

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Determination of sulphur monochloride by oxidation with chloramine-T

(*Received* 5 *November* 1964. *Accepted* 21 *December* 1964)

INVESTIGATIONS carried out by the present authors showed that a solution of sulphur monochloride in dioxan could be oxidised by an excess of acidified chloramine-T solution. The sulphur present in sulphur chloride is quantitatively converted to sulphuric acid. A rapid and an elegant method for the determination of sulphur chloride has been evolved and it is described in this communication.

Reagents

Chloramine-T. About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodometrically in an acidic medium as described earlier.[1,2]

Sulphur chloride. A sample of sulphur monochloride was treated with 10% of its weight of active charcoal and of pure sulphur; this was refluxed on a water-bath in an all-glass apparatus, then distilled under reduced pressure (28 mm at 41°).[3] The middle fraction of the distillate was collected and preserved in sealed tubes. A solution of such a sample (6%) in carbon tetrachloride was analysed by two methods.

The sulphur content was determined by the mercury decomposition method[4] described by Rao and Rao and the chlorine was determined by the sulphur iodide method described by Rao.[5] The analytical results indicated that the purity of the sulphur chloride was at least 99·9% and that the atomic ratio sulphur:chlorine was 1:1. A solution of sulphur chloride in pure dry dioxan (6%) also gave the same result.

Procedure

An aliquot of the sulphur chloride solution in dioxan (5 ml) was added to a known excess of acidified chloramine-T solution (50 ml of chloramine-T with 25 ml of $2M$ HCl and 10–25 ml of dioxan in a stoppered conical flask). The reactants in the flask were well shaken and set aside for

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Determination of sulphur monochloride by oxidation with chloramine-T

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INVESTIGATIONS carried out by the present authors showed that a solution of sulphur monochloride in dioxan could be oxidised by an excess of acidified chloramine-T solution. The sulphur present in sulphur chloride is quantitatively converted to sulphuric acid. A rapid and an elegant method for the determination of sulphur chloride has been evolved and it is described in this communication.

Reagents

Chloramine-T. About 15 g of a recrystallised sample of pure chloramine-T were dissolved in 1 litre of water and stocked in an amber coloured bottle. The solution was standardised iodometrically in an acidic medium as described earlier.[1,2]

Sulphur chloride. A sample of sulphur monochloride was treated with 10% of its weight of active charcoal and of pure sulphur; this was refluxed on a water-bath in an all-glass apparatus, then distilled under reduced pressure (28 mm at 41°).[3] The middle fraction of the distillate was collected and preserved in sealed tubes. A solution of such a sample (6%) in carbon tetrachloride was analysed by two methods.

The sulphur content was determined by the mercury decomposition method[4] described by Rao and Rao and the chlorine was determined by the sulphur iodide method described by Rao.[5] The analytical results indicated that the purity of the sulphur chloride was at least 99·9% and that the atomic ratio sulphur:chlorine was 1:1. A solution of sulphur chloride in pure dry dioxan (6%) also gave the same result.

Procedure

An aliquot of the sulphur chloride solution in dioxan (5 ml) was added to a known excess of acidified chloramine-T solution (50 ml of chloramine-T with 25 ml of $2M$ HCl and 10–25 ml of dioxan in a stoppered conical flask). The reactants in the flask were well shaken and set aside for about 0·5 hr. At the end of this period 30 ml of 10% potassium iodide solution were added, and the liberated iodine was titrated against standard thiosulphate solution (0·1*N*). The amount of chloramine-T consumed by sulphur chloride was then obtained from the titre, and the number of equivalents of the oxidant required per mole of sulphur chloride was calculated. No blank correction was found to be necessary, the blank being less that 0·05 ml equivalent of thiosulphate.

The analytical values were found to be reproducible and the results of a few representative experiments are given in Table I.

TABLE I.—OXIDATION OF SULPHUR MONOCHLORIDE WITH CHLORAMINE-T

Expt. no.	Sulphur chloride taken, *moles* × 10^5	Chloramine-T consumed, *equivs* × 10^5	Chloramine-T consumed per mole of sulphur monochloride, *equivs*
1.	1·38	13·83	10·02
2.	5·69	56·87	9·99
3.	6·89	68·65	9·96
4.	11·38	113·80	10·00
5.	14·22	142·70	10·03
6.	28·50	284·40	9·98

RESULTS AND DISCUSSIONS

It can be seen from the results in Table I that 10 equivalents of chloramine-T are consumed by 1 mole of sulphur chloride, as would be expected stoichiometrically from the equation

$$S_2Cl_2 + 8\,H_2O + 10\,e \rightarrow 2SO_4^{2-} + 2Cl^- + 16H^+.$$

It was found advantageous to employ a 7 to 8-fold excess of the oxidant over the stoichiometric requirement of the equation.* It is better to add some dioxan to the oxidant before adding the dioxan solution of sulphur chloride. Solutions of sulphur chloride in carbon tetrachloride were found to consume large quantities of chloramine-T even when the solution was homogenised for purposes of oxidation by the addition of dioxan or alcohol. Such solutions in carbon tetrachloride are, therefore, not suitable for this purpose.

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Summary—A rapid method is described for the determination of sulphur monochloride by adding excess of chloramine-T and determining the excess iodometrically.

Zusammenfassung—Eine Schnellmethode zur Bestimmung von Schwefelmonochlorid wird beschrieben. Es wird mit einem Überschuß Chloramin T oxydiert und der Überschuß mit Jodid und Thiosulfat bestimmt.

Résumé—On décrit une méthode de dosage du monochlorure de soufre par addition d'un excès de chloramine T et dosage de l'excès par l'iode et l'hyposulfite.

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* The products of the hydrolysis of sulphur chloride are very varied, including in the present reaction, sulphide, sulphite, thiosulphate, polythionate and elemental sulphur. In the present determination, if the solution of sulphur chloride is concentrated, there is a possibility of the separation of appreciable amounts of elemental sulphur, and this is then difficult to oxidise further by the chloramine-T. Therefore, a large excess of oxidant is recommended. If the sulphur chloride solution is dilute, as little as 30% in excess is sufficient.

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Precipitation of lead sulphate from homogeneous solution by hydrolysis of sulphamic acid

(*Received* 10 *June* 1964. *Accepted* 6 *December* 1964)

THE technique and advantages of precipitation from homogeneous solution have been amply presented by Gordon, Salutsky and Willard.[1] They also reviewed the methods that have been employed to generate sulphate ions for the determination of barium, calcium, strontium and lead. Elving and Zook[2] precipitated lead sulphate by hydrolysis of dimethyl sulphate in 70–80% methanol. Satisfactory accuracy and precision were obtained for amounts of lead in the range of 10 to 100 mg, except in the presence of large amounts of iron(III) and aluminium(III). The conditions under which small quantities of lead are precipitated are somewhat stringent. The concentration of the methanol, amount of dimethyl sulphate added and digestion time required are dependent upon the quantities of lead and foreign ions present. There is also a tendency for the precipitate to "creep." Jarnagin and Kenner[3] precipitated lead sulphate by hydrolysis of sulphamic acid catalysed by the presence of potassium chlorate. A small-sized, uniform precipitate was formed, the volume of which was measured after centrifugation. The successful use of the hydrolysis of sulphamic acid for the precipitation of barium sulphate[4,5] led to the present investigation of the precipitation of lead sulphate by a similar procedure.

EXPERIMENTAL

Reagents

All reagents met American Chemical Society specifications of purity.

Stock solutions of lead nitrate. Prepared by dissolving the reagent in distilled water. Definite volumes of these solutions, measured by means of pipettes, were used in subsequent analyses. The quantity of lead present in the solution delivered by a given pipette was determined by evaporating the solution with an excess of sulphuric acid in a platinum dish. The lead sulphate thus obtained was ignited to constant weight in an electric muffle furnace at 550–600°.

Stock solutions of possible interfering ions were prepared by dissolving the corresponding salts in distilled water.

National Bureau of Standards copper-base alloys were analysed to check the analytical procedure.

Apparatus

Filtering media. Both porcelain filtering crucibles (Coors, fine porosity) and filter paper were used successfully for the filtration. Some difficulty was encountered in bringing the porous porcelain crucibles to constant weight if the excess sulphuric acid solution was not removed by a final wash with ethyl alcohol. With either medium, the precipitate was ignited to constant weight in an electric muffle furnace at 550–600°.

Preliminary experiments

Preliminary tests were made to determine the optimum conditions necessary to effect complete precipitation of the lead sulphate. For these tests, 25 ml of lead nitrate stock solution containing approximately 100 mg of lead ion were pipetted into 250-ml beakers. A weighed portion of reagent grade sulphamic acid and sufficient distilled water to give a solution volume of 100 ml were added to each sample. These solutions were heated to incipient boiling for varying times up to 2 hr. Portions of the supernatant liquid were tested for completeness of precipitation by adding dilute sulphuric acid. Optimum conditions were obtained when 2 g of sulphamic acid were added to the solutions and the period of heating was 1 hr. The use of 0·5- and 1-g portions of sulphamic acid gave results which were slightly low. The heating time and temperature were more critical than the amount of sulphamic acid.

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National Bureau of Standards copper-base alloys were analysed to check the analytical procedure.

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In the analysis of many materials containing lead, such as brass and other alloys, the sample is dissolved in nitric acid. After the removal of tin, frequently the solution is evaporated almost to dryness to remove the excess nitric acid, either before or after the addition of sulphuric acid. In the sulphamic acid procedure, if nitric acid is present, sulphate ions are produced homogeneously by the following reaction in addition to the hydrolysis reaction:

$$NH_2SO_3^- + NO_3^- \rightarrow SO_4^{2-} + N_2O + H_2O.$$

TABLE I.—DETERMINATION OF LEAD IN PRESENCE OF FOREIGN CATIONS

Cation added,	Lead, *mg*		
mg	Taken	Found	Error
None	10·6	10·7	+0·1
		10·5	−0·1
		10·7	+0·1
Av.	10·6	10·6	0·0
None	99·7	99·8	+0·1
		99·9	+0·2
		99·8	+0·1
Av.	99·7	99·8	+0·1
Al(III) 100	99·7	99·8	+0·1
		99·5	−0·2
Av.	99·7	99·6	−0·1
Al(III) 10	99·2	98·7	−0·5
		99·1	−0·1
		99·9	+0·7
Av.	99·2	99·2	0·0
Al(III) 10	11·7	11·5	−0·2
		11·9	+0·2
		11·8	+0.1
Av.	11·7	11·7	0·0
Cu(II) 100	99·7	99·8	+0·1
		99·8	+0·1
		99·7	0·0
Av.	99·7	99·8	+0·1
Cu(II) 10	99·2	99·1	−0·1
		99·0	−0·2
		98·9	−0·3
Av.	99·2	99·0	−0·2
Cu(II) 10	10·6	10·2	−0·4
		10·3	−0·3
Av.	10·6	10·2	−0·4
Fe(III) 100	99·7	99·8	+0·1
		99·8	+0·1
		100·4	+0·7
Av.	99·7	100·0	+0·3
Fe(III) 10	99·2	99·1	−0·1
		99·3	+0·1
		99·0	−0·2
Av.	99·2	99·1	−0·1
Mn(II) 100	99·7	99·0	−0·7
		99·4	−0·3
		99·7	0·0
		99·9	+0·1
		99·7	0·0
Av.	99·7	99·5	−0·2
Mn(II) 10	99·2	99·4	+0·2
		99·4	+0·2
		99·2	0·0
Av.	99·2	99·3	+0·1
Mn(II) 10	10·6	10·4	−0·2
		10·3	−0·3
		10·8	+0·2
Av.	10·6	10·5	−0·1
Ni(II) 100	99·7	99·8	+0·1
		99·5	−0·2
		99·5	−0·2
Av.	99·7	99·6	−0·1
Ni(II) 10	99·2	99·4	+0·2
		99·2	0·0
		99·3	+0·1
Av.	99·2	99·3	+0·1
Ni(II) 10	11·7	11·6	−0·1
		11·6	−0·1
		11·6	−0·1
Av.	11·7	11·6	−0·1
Zn(II) 100	99·7	99·9	+0·2
		99·9	+0·2
		99·9	+0·2
Av.	99·7	99·9	+0·2
Zn(II) 10	99·2	99·4	+0·2
		99·4	+0·2
		99·2	0·0
Av.	99·2	99·3	+0·1
Zn(II) 10	10·6	10·2	−0·4
		10·4	−0·2
		10·6	0·0
Av.	10·6	10·4	−0·2

Mean deviation of all results: 0·18 mg

Thus, in the procedure developed, the sulphamic acid was added before the evaporation to remove the nitric acid.

Procedure

The following procedure is based on the preliminary investigations.

Acidify the solution, containing up to 100 mg of lead ion, with 10 ml of dilute nitric acid, or use the filtrate from the tin determination of a copper-base alloy. Dilute to approximately 50 ml and add 2 g of solid sulphamic acid. Cover the beaker with a raised watch glass and heat on an electric hot plate at incipient boiling until the volume is reduced to 2–5 ml. Add 25 ml of water and digest for 30 min on a hot-plate or steam-bath. Cool to room temperature and filter, using a weighed porcelain filtering crucible or ashless filter paper. Wash the precipitate five times with 1:20 sulphuric acid, then five times with small portions of 50% ethyl alcohol to remove traces of sulphuric acid. Ignite the precipitate to constant weight in an electric muffle furnace at 550–600°.

TABLE II.—DETERMINATION OF LEAD IN NATIONAL BUREAU OF STANDARDS COPPER-BASE ALLOYS

Standard Sample No. 37 Sheet Brass

Composition	%[a]		Lead found, %	Error, %
Lead (as sulphate)	0·964		0·952	−0·012
Lead (as oxide)	0·989		0·941	−0·023
Copper	70·290		0·930	−0·034
Iron	0·290			
Nickel	0·520			
Tin	1·013	Mean	0·941	−0·023
Zinc	26·890	Mean deviation	0·007	

Standard Sample No. 52 Cast Bronze

Composition	%[a]		Lead found, %	Error, %
Lead	1·52		1·50	−0·02
Antimony	0·16		1·49	−0·03
Copper	88·33			
Iron	0·12			
Nickel	0·13	Mean	1·50	−0·02
Tin	7·90	Mean deviation	0·005	
Zinc	1·89			

Standard Sample No. 63 Phosphor Bronze Bearing Metal

Composition	%[a]		Lead found, %	Error, %
Lead	9·74		9·67	−0·07
Aluminium	0·05		9·71	−0·03
Antimony	0·55		9·64	−0·10
Arsenic	0·09			
Copper	78·05			
Iron	0·27			
Nickel	0·008	Mean	9·67	−0·07
Phosphorus	0·62	Mean deviation	0·02	
Sulfur	0·06			
Tin	9·91			
Zinc	0·48			

[a] National Bureau of Standards Analyses.

Interferences

In order to study the effect of foreign cations on the determination of lead by the foregoing method, a series of tests was conducted in which 10 or 100 mg of the cation were added to the lead nitrate solution before the addition of sulphamic acid. The cations employed in this study were those which are most commonly encountered in the analysis of lead alloys.

Table I shows the results of these analyses. The presence of the foreign cations listed in the table does not appear to have any effect on the determination of lead by this method.

Several determinations were made in which the precipitation was accomplished in a 50% ethyl alcohol solvent. Comparable results were obtained, but foreign cations at high concentrations were partially precipitated as the sulphates.

Analysis of standard samples

Results of the analysis of National Bureau of Standards copper-base alloys by the sulphamic acid procedure are given in Table II. A 1-g sample of alloy was dissolved in dilute nitric acid. Insoluble oxides were removed by filtration following the evaporation of the solution almost to dryness and redissolving the soluble nitrates. The filtrate was then analysed for lead by the foregoing procedure.

DISCUSSION

The determination of lead as the sulphate can be accomplished by generation of the sulphate ion homogeneously in solution by the slow hydrolysis and oxidation of sulphamic acid in an aqueous-nitric acid solution. Excellent results were obtained in the analysis of samples containing 10–100 mg of lead. Coarse, well-formed crystals of lead sulphate are produced which are readily transferred from the reaction beaker to the filter. Troublesome "creeping" of the precipitate does not occur and the lead sulphate is easily washed free from adsorbed ions.

Photomicrographs in Figs. 1–3 show that there is little, if any, difference in the size of crystals of lead sulphate produced by the ordinary sulphuric acid method and by the homogeneous precipitation methods in alcohol-water solutions using dimethyl sulphate or sulphamic acid. Fig. 4 shows the remarkable increase in size and regularity of the shape of the crystals of lead sulphate formed by homogeneous precipitation with sulphamic acid in aqueous solution. The crystals produced by the sulphuric acid procedure are more needle-shaped than those formed by homogeneous precipitation. All photographs are at the same magnification. As shown in Table I, the average deviation of all results from the true value was 0·18 mg. This average deviation did not vary significantly with either the amount of lead taken or the amount of foreign cation present. The accuracy and precision of the method for the analysis of three National Bureau of Standards copper-base alloys are given in Table II. The method is believed to be superior to the other methods for the gravimetric determination of lead as the sulphate, in that the conditions for quantitative precipitation are less stringent.

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Summary—The determination of lead as the sulphate is accomplished by generation of the sulphate ion homogeneously from the slow hydrolysis and oxidation of sulphamic acid in an aqueous-nitric acid solution. Samples containing 10–100 mg of lead from copper-base alloys or solutions containing varying amounts of aluminium(III), copper(II), iron(III), manganese(II), nickel(II) and zinc(II) ions have been analysed successfully. Coarse, well-formed crystals are obtained, which filter easily.

Zusammenfassung—Die Bleibestimmung als Bleisulfat wurde so durchgeführt, daß das Sulfat homogen durch langsame Hydrolyse und Oxydation von Amidosulfonsäure in wäßriger, salpetersaurer Lösung erzeugt wurde. Proben mit 10–100 mg Blei aus Legierungen auf Kupfergrundlage oder aus Lösungen mit wechselnden Mengen Al(III), Cu(II), Fe(III), Mn(II), Ni(II) und Zn(II) wurden mit Erfolg analysiert. Grobe, gut ausgebildete Kristalle wurden erhalten, die sich leicht filtrieren ließen.

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* To whom correspondence concerning this work should be sent.

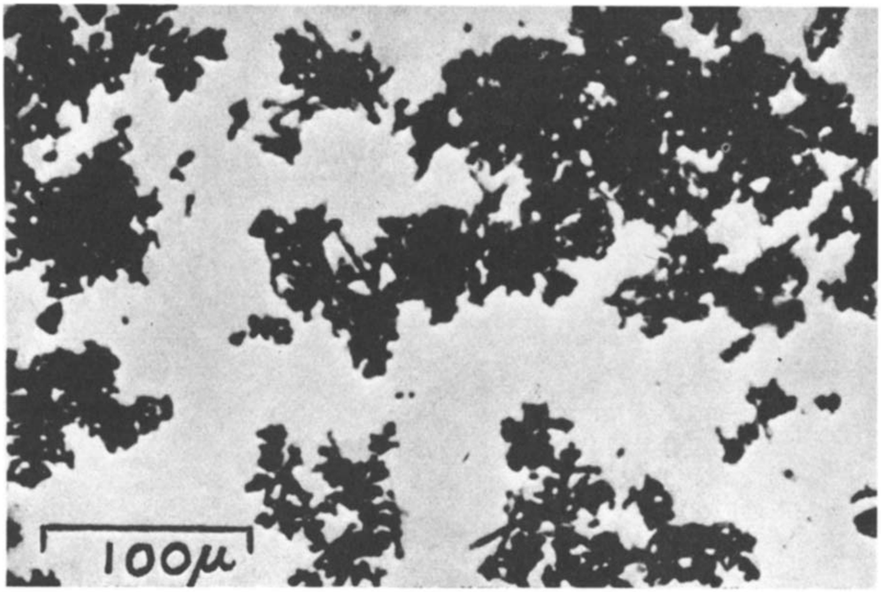

FIG. 1.—Lead sulphate precipitated by conventional sulphuric acid method.

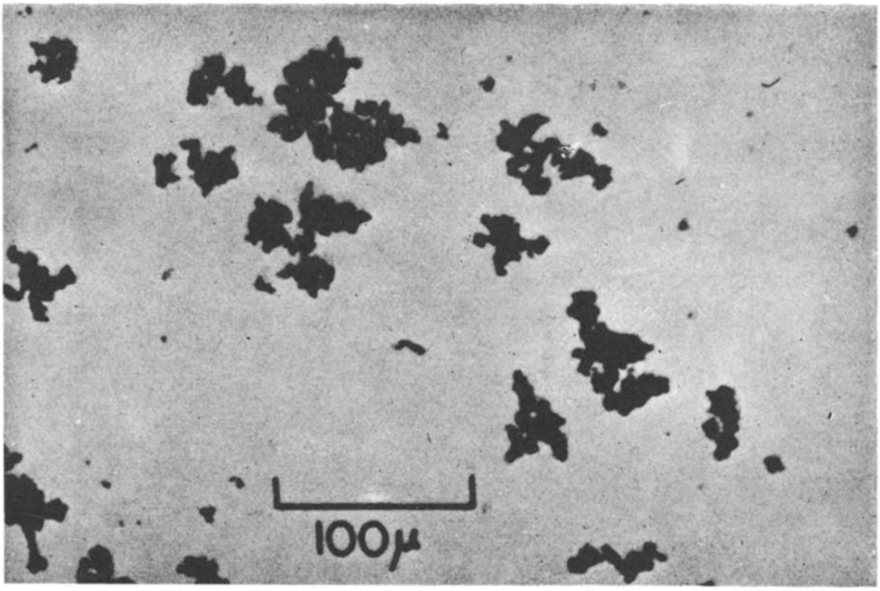

FIG. 2.—Lead sulphate precipitated from homogeneous solution by hydrolysis of dimethyl sulphate.

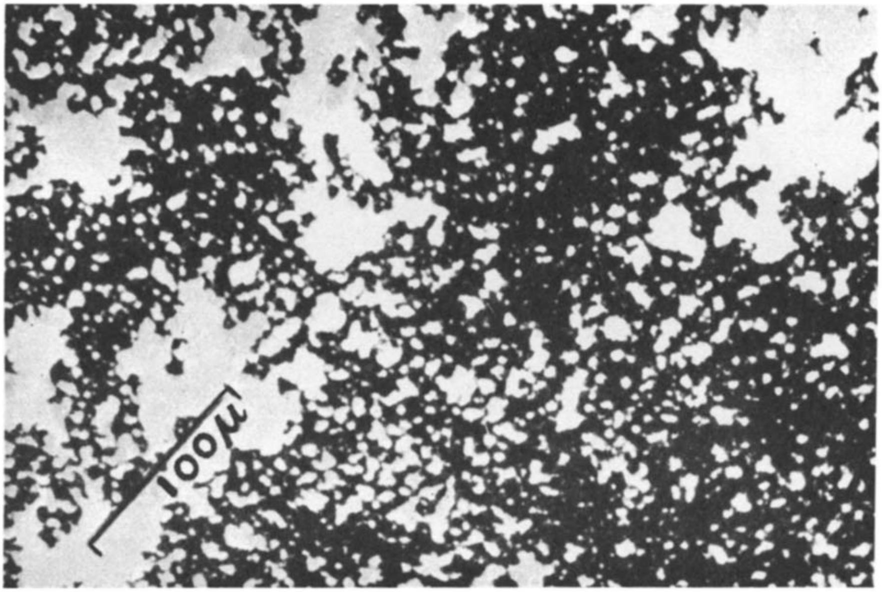

FIG. 3.—Lead sulphate precipitated from homogeneous solution by hydrolysis of sulphamic acid in 50% ethanol.

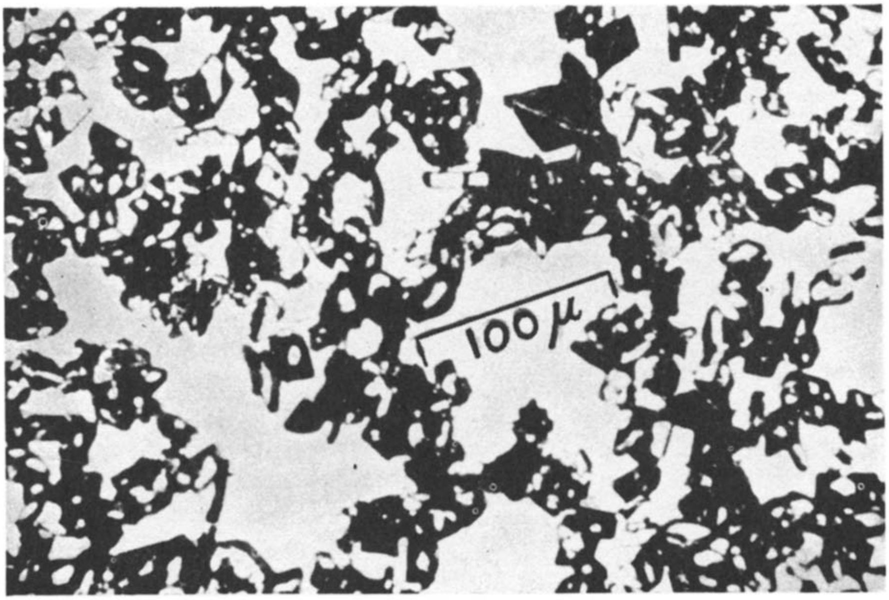

FIG. 4.—Lead sulphate precipitated from homogeneous solution by hydrolysis of sulphamic acid in water.

Résumé—On a dosé le plomb à l'état de sulfate en générant l'ion sulfate en milieu homogène par hydrolyse lente et oxydation de l'acide sulfamique en solution eau-acide nitrique. On a analysé avec succès des échantillons d'alliages base de cuivre contenant 10 à 100 mg de plomb, ou des solutions contenant des quantités variables de Al(III), Cu(II), Fe(III), Mn(II), Ni(II) et Zn(II). On obtient de gros cristaux bien formés, aisément filterables.

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PRELIMINARY COMMUNICATION

Nickel(II) α-benzildioximate: Red or orange?

(*Received* 3 *December* 1964. *Accepted* 30 *December* 1964)

IN 1913 Atack[1] observed that a bright red precipitate, first obtained when nickel is precipitated with α-benzildioxime, becomes yellowish-red on coagulation. Subsequently, many others have described the chelate as being red in colour, although in two instances[2,3] it is characterised as orange. That nickel α-benzildioximate may possibly exist in two differently-coloured structural forms has not been previously reported.

In experiments in this laboratory, Atack's observation has been generally confirmed in that a red precipitate is first obtained, which on heating or standing changes colour to a yellow-orange compound. Further, our experiments indicate the yellow-orange compound to be more stable. In fact, it is difficult to separate the red compound from solution because of its relatively rapid transition to the yellow-orange compound. A brown compound can also be obtained by quenching the transition to yellow-orange.

Preliminary investigations with diffuse reflectance spectrophotometry indicate that the red and yellow-orange precipitates are two different compounds, whereas the brown precipitate appears to be a mixture of the two compounds. The red and yellow-orange compounds also show different crystalline structures when examined under the microscope. However, they both dissolve in chloroform to give yellow solutions with the same absorption spectrum; orange crystals are obtained on evaporation of the solvent. The infrared spectra of the two compounds are very similar with the possible presence of a peak at 3·3 μ in the spectrum of the orange compound.

This phenomenon has not been previously observed for the much-studied nickel(II) dimethylglyoximate; thus, this behaviour of the red and yellow-orange nickel α-benzilglyoximates is of much interest. The investigation of their structures is being continued and will subsequently be reported.

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L. GORDON®

Summary—Preliminary investigations indicate that nickel(II) α-benzildioximate exists in two differently-coloured structural forms. Further work is in progress.

Zusammenfassung—Voruntersuchungen weisen darauf hin, dass Nickel(II)-α-benzyldioximat in zwei unterschieldlich gefärbten Strukturformen existiert. Die Untersuchungen werden fortgesetzt.

Résumé—Des recherches préliminaires montrent que l'α-benzildioximate de nickel(II) existe sous deux formes structurales différemment colorées. D'autres travaux sont en cours.

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A CURRENT-INTEGRATING GAMMA ABSORPTIOMETER AND DATA LOGGER FOR ROUTINE URANIUM ANALYSIS*

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Summary—Uranium concentrations in aqueous and organic solutions are determined by gamma absorptiometry. A ^{241}Am source which emits photons of 60 keV is used with a scintillation detector. The output current from the phototube is integrated for 1 min to give a 2–10 V d.c. signal which is recorded by a data logging system. A unique method requiring aqueous standards only is used to calibrate the system for both aqueous and organic uranium solutions. Detailed statistical analysis of the experimental data is included. A deviation noted from Beer's law is explained by inclusion of scattering effects into the describing model. Solution analyses made using this model result in values accurate to better than ±0·5 g/l. over the range of uranium concentrations from 0 to 120 g/l.

INTRODUCTION

A RECENT study of a solvent extraction process[7] required the analysis of a large number of two-phase samples for uranium concentration in the aqueous and organic phases, aqueous nitric acid concentration and volumetric fraction of organic phase present in a systematic, rapid, relatively foolproof and accurate manner. It is the purpose of this paper to describe the apparatus and procedure used, and the method of calibration.

The techniques involved are standard with the exception of the uranium determinations. Here, gamma absorptiometry is used but the detector current is integrated by an analogue integrator for 1 min rather than making a direct measurement of the steady current. Because the detector current is fluctuating with the source intensity, which has Poisson statistics, the standard deviation of a current measurement varies inversely as the square root of the time over which the measurement is taken. In previously described absorptiometers[3,6] this time would be the time constant of the filtering network for steady currents. When the current is integrated, the measurement time is the integration time. In reference 3 the filter network time constant was 2 sec. Thus, it would be expected that the standard deviation of the current measurements could be reduced by $\sqrt{1/30}$ for this case through a 1-min integration.

EXPERIMENTAL

Apparatus

The uranium concentrations in the aqueous and organic solutions are determined by gamma absorptiometry in a manner similar to that described by Connally[3] and by Whitmer.[6] The solution is placed in a glass cylindrical sample cell which has an inside diameter of 25 mm. Cells of 5-cm (American Instrument Company #5-1000) and 1-cm (American Instrument Company #5-984) path

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lengths are used for organic solutions; a different set of 1-cm and 5-cm cells are used for aqueous solutions, and a 5-cm cell containing distilled water is used exclusively as a reference. The measured path length through the solution along the axis of the cell is 5·0000 ± 0·0001 cm for the 5-cm cells and 1·0000 ± 0·0001 cm for the 1-cm cells. The circular faces of the original cells have been ground such that the over-all path length of glass plus solution is equal for all the 5-cm cells and for all the 1-cm cells as determined by optical measurements.

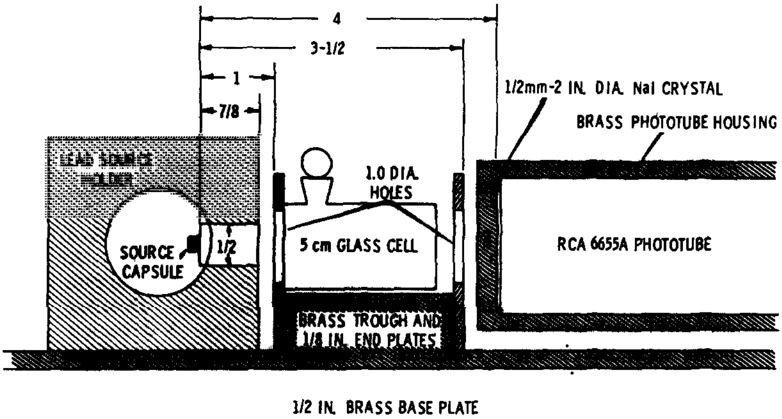

FIG. 1B.—Section drawing of absorptiometer.

The sample cell containing the solution is placed into a trough located between a source housing and a photomultiplier tube-crystal assembly as is pictured in Fig. 1A and shown schematically in Fig. 1B. Ten mg of ^{241}Am (with a half-life of 458 years) is used as a source. The source emits gamma photons of 60-keV energy at a rate of approximately 2·8 × 10^{10} gamma photons/min. A gamma energy scan of the source indicates that no significant number of photons of energy greater than 75 keV are emitted. The source is housed in the same manner as described in reference 5. Although the housing itself affords little collimation, the brass plates at the ends of the trough collimate the low energy photons to a beam 1 inch in diameter.

The photons transmitted by the cell and any others which are scattered around the cell are sensed by a scintillation detector consisting of a 2-inch diameter, 0·5-mm thick sodium iodide crystal attached to an RCA type 6655A multiplier phototube all contained in an assembly which has been described.[3] This phototube utilises caesium-antimony dynodes which results in good gain stability; the drift in gain is steady and about 0·6%/day. The gain of the phototube is temperature dependent (0·3%/°C). Unless the temperature is cycling up and down 4–5° at a frequency corresponding to that of removal and replacement of the sample cells (as is described later), any temperature and long-term drift effects are eliminated by the data treatment.

A Hammer Electric Company N 401, 500–1800 V power supply, quoted as stable to 1 part in 10^5, is used to provide approximately 1000 V negative to the photomultiplier tube dynode resistor chain, which consists of 100-KΩ wire wound resistors. For this voltage and dynode resistor chain the gain sensitivity to fluctuations is 1%/V. The high voltage is adjusted periodically so that a 1-μA current is obtained when the reference cell filled with distilled water is in place. The fatigue rate for the RCA 6655A is not detectable for currents up to 1 μA. The high voltage supply is only disconnected from the phototube for maintenance. After reconnection or voltage adjustment, at least 2 days elapse before the system is again used. In this way the phototube "aging" problem is eliminated.

The output current from the phototube is integrated by a Keithley Model 411C picoammeter wired as an analogue integrator by the connection of high quality capacitors (Southern Electronics PC505G4AE) between the input and output leads and the elimination of the feedback resistor. With the 5-cm and 1-cm cells, 5-μF and 10-μF capacitors are used, respectively. The picoammeter as an amplifier has an open loop gain of 2000 stable to within 1% and the capacitors have temperature coefficients of 0·01%/°C. Here again, unless either the temperature or amplifier gain is changing in a cyclic manner with a frequency approximating to that of the cell removal and replacement, all effects from drifts cancel in the treatment of the data.

Tests have been run to determine the stability of this integration system and to determine the combined magnitude of system transient effects and hysteresis effects characteristic of the phototube.

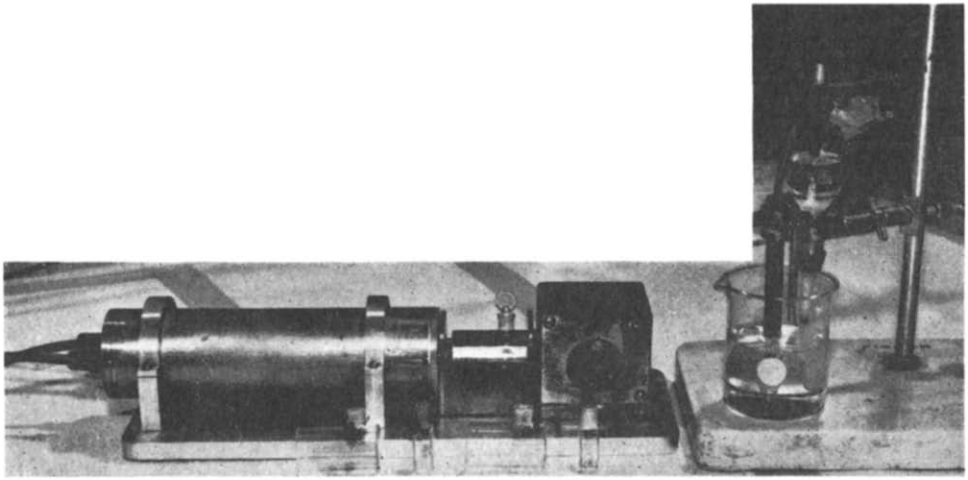

FIG. 1A.—Absorptiometer and pH cell.

These tests, which are described under *Discussion of Errors*, indicate that the integration system is stable to 0·01 % and that any such phototube transient effects are less than 0·02 %.

An integration is carried out whenever the "SEQUENCE TIMER" cycle is initiated (see Fig. 2). A timer cycle begins upon actuation of one of three pushbuttons mnemonically entitled "REF.", "AQUEOUS" and "ORGANIC". The timer motor drives a cam which in turn actuates three microswitches, labelled "INTEGRATE", "ZERO", "READ PRINT AND STEP" in Fig. 2. The timer cycle consists of the following events:

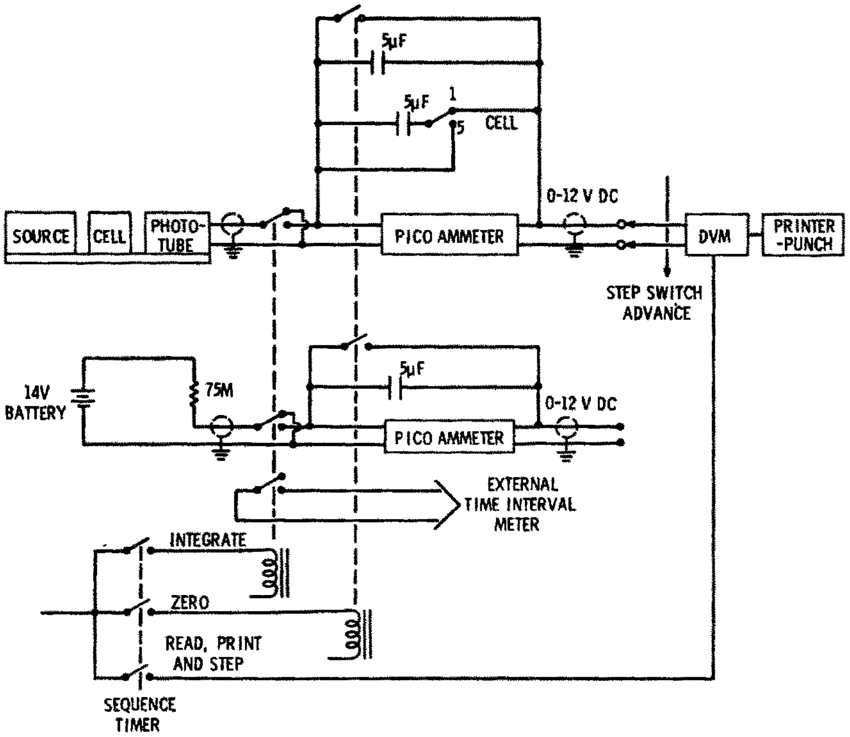

FIG. 2.—Simplified schematic drawing of integrating absorptiometer circuitry.

(1) The "ZERO" switch closes for 1 sec. This causes the integrating capacitors on two parallel integrators to be discharged and hence gives an initial condition of 0 V.

(2) Two sec later the "INTEGRATE" switch closes. This actuates a relay which: (a) connects a relatively constant current source to the lower picoammeter input, (b) connects the phototube anode (which has been grounded until this time) to the upper picoammeter input, and (c) closes a switch which controls an external time interval meter used only during calibrations to give the integration time T. The relative timing errors between these three sets of relay contacts is less than 1 msec.

(3) After approximately 1 min the "INTEGRATE" switch opens, which stops the integrations.

(4) Two sec later the "READ . . ." switch closes, which allows the digital voltmeter (DVM) to balance. The DVM is a 5-digit Kintel Model 502B, which has an accuracy of 0·01 % plus or minus 1 digit and a stability of 0·02 % over a period of 1 week.

The DVM balance causes a printout of the output voltage (V_P) from the upper integrator, then a stepping switch advances, and the voltage of the lower integrator (V_S) is read and printed. The latter voltage is proportional to the time elapsed during the integration period, which varies about 0·5 % because of timer imperfection. Use of the ratio V_p/V_s in the calibrations eliminates timing and stability errors in the circuitry. Drifts in the 14 V battery-75 M resistor current source are eliminated by the data treatment. This method of controlling and measuring the integration time was selected for its simplicity and low cost.

After all the V_p and V_s are logged for a sample, other voltages obtained from a reference voltage supply (V_{R_0}), two precision potentiometers (V_{R_1} and V_{R_2}) and a pH meter (V_{pH}) are logged in turn. Each voltage is logged into punched paper tape and printed on adding machine tape by a Kintel

Model 467-Tally 420-Hewlett Packard 561A data logging system and has recorded with it a 3-digit identification which contains information as to which type of solution is being analysed (organic, aqueous or reference), which size sample cell was used and from which sample port in the test facility the sample was obtained.

Procedure for a typical sample analysis

The mixed aqueous and organic phases from a sample are first transferred from a 100-ml sample bottle into a clean calibrated 100-ml burette. The phases are allowed to separate and the positions of aqueous-organic and organic-air interfaces are read to the nearest 0·1 ml. These readings are dialed into two appropriately labelled, digital indicating, 10-turn precision voltage-dividing potentiometers which are logged at a later time by the DVM (V_{R_1} and V_{R_2}). The reference cell is then analysed as described above by pressing the "ZERO ANALYSIS" button. An aqueous cell (either 1 or 5 cm depending upon the estimated sample concentration) is filled from the tip of the burette, placed in the trough and analysed by pressing the "AQUEOUS ANALYSIS" button. An additional aqueous sample is withdrawn into a small beaker into which pH electrodes are then immersed (Fig. 1A).

TABLE I.—TYPICAL DATA LOGGER OUTPUT TAPE

Printer tape	Data logged	
197 − 09387-3[a]	V_p	for first reference analysis (REF_1)
198 − 11252-3	V_s	for first reference analysis (REF_1)
192 − 09542-3[b]	V_p	for aqueous cell analysis (AQ)
193 − 11263-3	V_s	for aqueous cell analysis (AQ)
194 − 08463-3[c]	V_p	for organic cell analysis (ORG)
196 − 11274-3	V_s	for organic cell analysis (ORG)
197 − 09390-3[d]	V_p	for second reference analysis (REF_2)
198 − 11257-3	V_s	for second reference analysis (REF_2)
199 + 14804-3	V_{R_0}	voltage applied across potentiometer
900 + 02041-3	V_{R_1}	aqueous-organic pot reading
901 + 09684-3	V_{R_2}	organic-air pot reading
902 − 00792-3	V_{pH}	pH of aqueous solution reading
↙ ↓ ↘ Identification Voltage Power of 10 by which voltage is multiplied		

[a] First two digits of identification are sample port number.
[b] Third digit of identification is 1 for 1-cm cell, 2 for 5-cm cell.
[c] Third digit of identification is 4 for 1-cm cell, 5 for 5-cm cell.
[d] Third digit of identification is 7 for reference cell.

The electrodes are connected to the pH meter which has a 0–100 mV output amplified in turn by a 30·00 to 1·00 precision d.c. amplifier to give V_{pH}. The remaining aqueous phase in the burette and some organic phase are drained and discarded.

A 1- or 5-cm organic cell is filled from the burette and analysed as described above by pressing the "ORGANIC ANALYSIS" button. Finally, the reference cell is again analysed to complete the sequence. After the V_s is logged for the reference cell, the data logger steps on and successively reads the other voltages as described above. The resulting printed output appears as shown in Table I.

When all samples from a given run have been processed, the punched tape is identified and submitted for data processing. A data reduction code calculates uranium concentrations, *etc.*, as is described in the next section.

With the data-logging and data processing system described in this section, the analyses of 30 two-phase samples can be obtained within 24 hr after they are taken.

Mathematical model of absorption

In the determination of the uranium concentrations from the data voltages the four ratios $(V_P/V_S)_{REF_1}$, $(V_P,V_S)_{AQ}$, $(V_P/V_S)_{ORG}$ and $(V_P/V_S)_{REF_1}$ are first computed. The four analyses in the sequence, reference-aqueous-organic-reference, are uniformly spaced in time; and it is assumed that the reference ratio applicable at the time of the aqueous and organic analyses may be computed from a linear interpolation between the two reference ratios. Two quantities Q are then computed for the aqueous analysis and the organic analysis which are free from drifts inherent in the apparatus—such as battery voltage or resistance change in the circuit giving V_s. For the aqueous cell

$$Q_{AQ} = \frac{(V_P/V_S)_{AQ}}{\frac{2}{3}(V_P/V_S)_{REF_1} + \frac{1}{3}(V_P/V_S)_{REF_2}} \tag{1}$$

and for the organic cell

$$Q_{ORG} = \frac{(V_P/V_S)_{ORG}}{\frac{1}{3}(V_P/V_S)_{REF_1} + \frac{2}{3}(V_P/V_S)_{REF_2}} \tag{2}$$

A normalised voltage V_P/V_S is proportional to the integrated photon flux at the face of the phototube. This flux consists of two kinds of gamma photons—those which have passed through the cell solution and those which have not. Assuming an average in-solution path length, Beer's Law gives a simple mathematical representation of the flux from the former as a function of the uranium concentration of the solution. Also, assuming that a particular cell is always placed in the same position in the absorptiometer, the flux from the latter is constant. The resulting law is

$$V_P/V_S = A + Be^{-c[U]} \tag{3}$$

where [U] is the uranium concentration of the solution in g/l. The three constants A, B, and c in equation (3) are identified with scattering, solvent, and uranium attenuation, respectively. Here, *scattering* is an omnibus term covering the total geometry of the cell and the experimental apparatus, and the scattering properties of air and apparatus materials. The parameter c depends only on the average in-solution path length and the physics of attenuation of americium-241 gamma photons by uranium atoms. The parameters A and B, on the other hand, fluctuate with instrument shifts. However, A/B should be time invariant, depending only on the cell, solvent and experimental apparatus. The solvent effect should only be present in B. For a reference cell filled with distilled water, equation (3) reduces to

$$(V_P/V_S)_{REF} = A' + B' \tag{4}$$

When a sample cell and the reference cell are analysed alternately the A and B sample cell parameters and the A′ and B′ reference cell parameters will fluctuate as a set, any two remaining in a fixed ratio. Thus, for each sample cell the ratio

$$Q = \frac{(V_P/V_S)_{SAMPLE}}{(V_P/V_S)_{REP}}$$

should satisfy

$$Q = a + be^{-c[U]} \tag{5}$$

where

$$a = A/(A' + B') \text{ and } b = B/(A' + B').$$

Equation (5) will be called the *modified Beer's law*. Assuming good experimental procedure, *a* should depend only on the sample cell and *b* only on the sample cell and the solvent. Hence, for identical cells and a single solvent *a* and *b* should be the same. Following the calibration of a particular sample cell for aqueous uranium solutions, organic uranium solution calibration should entail only replacing "*b*" by

$b' = b\varepsilon$, where *log* ε is the *zero shift* from aqueous to organic solvents. The experiments discussed in the sequel were designed to test these assumptions for two different sample cell sizes and to estimate the aqueous and organic calibration functions.

In the data reduction, the uranium concentrations are found directly from the inverse function of (5), expressing uranium in terms of Q and calibrated parameters. The volumetric fraction of organic phase in the sample is easily found after the burette readings are regenerated from V_{R_0}, V_{R_1} and V_{R_2}. The amount of nitric acid in the aqueous phase is determined, by means of the *HpH* method which has been described,[2] from the pH (which is directly calculated from V_{pH}) and the uranium in the aqueous phase.

Aqueous cell calibration

The purpose of the aqueous cell calibration experiment was to calibrate as precisely as possible the four aqueous and organic sample cells over a uranium concentration range of 0 to 120 g/l. The experiment was designed so that individual calibration functions, expressing uranium concentration in terms of the ratio of the sample cell to reference cell voltage ratios Q, could be determined for each sample cell; further, that a statistical test could be performed to decide whether a single calibration function could be used for sample cells with a common path length; and finally, that the accuracy of the method could be estimated as a function of uranium concentration.

The experimental data were collected in such a manner that a preliminary analysis could be performed to check the stability of the ratio of standard voltage to integration time (V_S/T), to check the stability of the reference cell voltage ratio $(V_D/V_S)_{REF}$ and to allow correction of the data for drift over the entire experimental period.

The fundamental unit in the experimental design for the aqueous calibration (as shown in Table II) was the *loading*. The design consisted of 20 of these loadings. A *loading* specifies both the uranium standard solution used in each of the four sample cells and the order in which these cells are analysed on the absorptiometer. Within a loading, four different uranium standard solutions were used, one to each of the four sample cells. The analysis schedule consisted of 13 independent analyses. Hereafter, the words *sequence position* are used to identify the 13 ordered spots in this schedule. The reference cell was analysed five times for each loading in sequence positions 1, 4, 7, 10 and 13. Between each pair of reference cell analyses, two distinct sample cells were each analysed once. Thus, the complete analysis schedule for a loading always involved five reference cell analyses and two analyses

TABLE II.—AQUEOUS CALIBRATION EXPERIMENTAL DESIGN

Loading number	Analysis sequence within a loading												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	R	A-0	B-1	R	C-2	D-3	R	B-1	D-3	R	A-0	C-2	R
2	R	B-6	D-4	R	A-1	C-0	R	A-1	B-6	R	C-0	D-4	R
3	R	B-7	A-2	R	D-6	C-9	R	D-6	B-7	R	C-9	A-2	R
4	R	D-8	B-0	R	C-6	A-3	R	B-0	A-3	R	D-8	C-6	R
5	R	A-4	C-7	R	B-5	D-9	R	C-7	D-9	R	A-4	B-5	R
6	R	C-1	D-2	R	A-5	B-4	R	A-5	C-1	R	B-4	D-2	R
7	R	C-5	A-6	R	D-1	B-8	R	D-1	C-5	R	B-8	A-6	R
8	R	D-5	C-8	R	B-2	A-7	R	C-8	A-7	R	D-5	B-2	R
9	R	A-8	B-9	R	C-3	D-0	R	B-9	D-0	R	A-8	C-3	R
10	R	A-9	C-4	R	B-3	D-7	R	C-4	D-7	R	A-9	B-3	R
11	R	B-5	D-7	R	A-4	C-6	R	A-4	B-5	R	C-6	D-7	R
12	R	C-5	D-8	R	A-7	B-2	R	A-7	C-5	R	B-2	D-8	R
13	R	C-4	A-5	R	D-0	B-1	R	D-0	C-4	R	B-1	A-5	R
14	R	B-4	A-9	R	D-1	C-2	R	D-1	B-4	R	C-2	A-9	R
15	R	D-3	C-0	R	B-6	A-8	R	C-0	A-8	R	D-3	B-6	R
16	R	D-6	B-8	R	C-9	A-3	R	B-8	A-3	R	D-6	C-9	R
17	R	A-0	B-3	R	C-7	D-9	R	B-3	D-9	R	A-9	C-7	R
18	R	B-9	C-3	R	D-4	A-6	R	D-4	B-9	R	C-3	A-6	R
19	R	C-1	D-5	R	A-2	B-7	R	A-2	C-1	R	B-7	D-5	R
20	R	D-2	A-1	R	B-0	C-8	R	C-8	A-1	R	D-2	B-0	R

TABLE III.—AQUEOUS URANIUM STANDARD SOLUTIONS

Identification	Concentration, *g/l.*
0	Pure distilled water
1	1·018
2	4·990
3	10·044
4	20·046
5	40·324
6	59·903
7	81·364
8	100·544
9	120·642

of each sample cell. Barring drift in the absorptiometer, the two analyses of a sample cell were duplicates because the uranium solutions were not changed within a loading. In the complete schedule of 20 loadings, every sample cell was analysed twice when filled with each of the 10 uranium standards. For each analysis on the absorptiometer, the month, the day and time of the analysis, the loading number, the sequence position number, the cell identification number, the uranium standard solution identification number and the absorptiometer data triplet V_D, V_s and T were recorded.

The complete experimental design is listed in Table II. The letters identify cells—R is the reference, A and B the 1-cm path length cells, and C and D the 5-cm path length cells. The numbers identify standard solutions in order of increasing uranium concentration—Table III gives the specific correspondence. The letter number pairs (A–0, *etc.*) in Table II indicate cell-solution pairings for each loading.

The experimental data were collected on three consecutive days in agreement with the experimental design as depicted in Table II. Loadings 1–5 were done on day 1, 6–13 on day 2 and 14–20 on day 3. The average experimentation time per loading was about 42 min–12 min to clean, dry and fill four sample cells, and 30 min to do the sequence of 13 analyses. Of the 2¼ min/analysis, approximately 1 min (61·7 sec) was actual absorptiometer integration time.

The standard solutions with concentrations given in Table III were made up from crystalline uranyl nitrate hexahydrate (UNH). Enough concentrated nitric acid was added to make each solution 10 g/l. in nitric acid. The standards were analysed according to a method described by Brouns.[1] The method briefly consists of : (1) pipette an aliquot of the standard solution into a weighed crucible, (2) evaporate to dryness, (3) ignite to U_3O_8 and (4) weigh crucible and content. Variation between two similar analyses of the same standard solution by this method was never greater than 0·3%. This analysis procedure was repeated three times for each standard solution. The values quoted in Table III are the averages of the three determinations. At the 95% confidence level, the precision of these averages is about 0·027 g/l.

STATISTICAL ANALYSIS OF AQUEOUS CELL CALIBRATION

In order to estimate the stability and drift characteristics of the absorptiometer, a preliminary statistical analysis (see p. 316 to 317) was done with data from 100 reference cell readings. In summary, the standard deviation of the 100 standard voltage-integration time ratios (V_s/T) was 0·000189, approximately 0·1% of the average reading of —0·18377. From a practical standpoint, variability of this magnitude is minor compared to other errors in the measurement processes. Even so, insight into the standard voltage measurement process is gained from analysis of this variability. In Fig. 3 the plot of the 20 loading averages shows that the (V_s) voltage signal drifts continuously with time. Fig. 4 shows the sequence position (V_s/T) ratios averaged over the 20 readings. The total decay during the reading of five sequence positions is about 0·08% of the average (V_s/T) reading. The short term random fluctuation in the voltage signal has a standard deviation of 0·00003, less than 0·02% of the average signal.

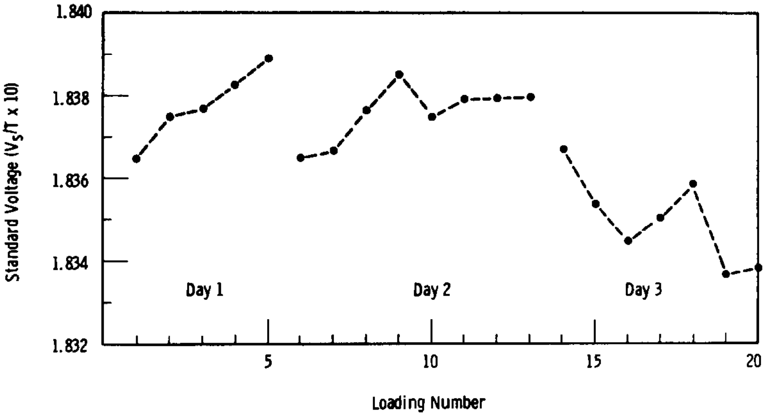

FIG. 3.—Variation of standard voltage with loading.

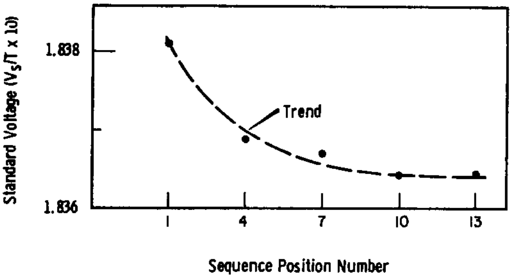

FIG. 4.—Variation of standard voltage with sequence position.

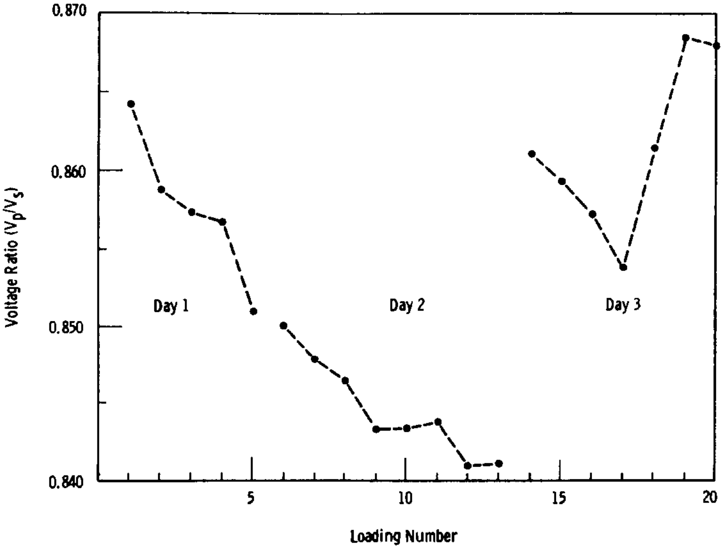

FIG. 5.—Variation of reference cell voltage ratio with loading.

The reference cell voltage ratios (V_P/V_s) were also statistically analysed (see p. 317). The results were similar to that for the (V_s/T) data.. Fig. 5 is a plot of the 20 loading averages and Fig. 6 a plot of the five sequence positions averaged over loadings. The long term drift in the (V_P/V_s) response could presumably arise from the gradual change in phototube sensitivity and source decay. For 2½ of the 3-day experimental period the ratio (V_P/V_s) steadily decreased. Fig. 6 shows a significant within-loading decay similar to that of the (V_s/T) data. The standard deviation of the short term random fluctuation in the (V_P/V_s) signal is 0·00223. The average of the 100 (V_P/V_s) readings is 0·85374; hence, the standard deviation of the residual variability or noise in the (V_P/V_s) signal is about 0·25% of its average. On a relative basis the noise in the (V_P/V_s) signal for the reference cell is about 15 times as great as in the (V_s/T) signal.

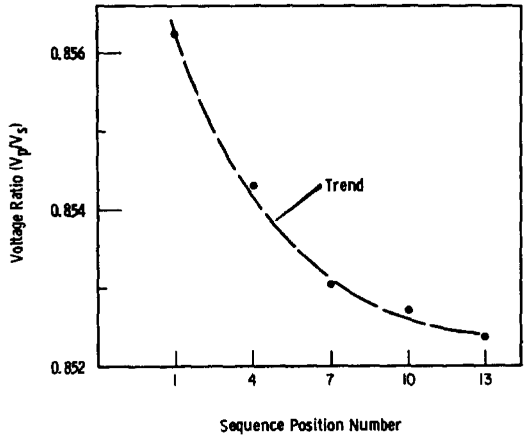

FIG. 6.—Variation of reference cell voltage ratio with sequence position.

There is no evidence that the (V_P/V_s) and (V_s/T) reference cell ratios are correlated. Probably any correlation resulting from the common component (V_s) is masked by the extreme variability in (V_P).

To eliminate as much as possible the time effect in the basic (V_P/V_s) absorptiometer reading, sample cell data were normalised with a linearly interpolated reference cell response from readings taken immediately before and after that of the sample cell pair (see p. 317). For the experimental schedule (see Table II) used for the aqueous calibration, the appropriate weighting factors are either (⅔, ⅓) or (⅓, ⅔) depending upon which reference cell, pre- or post-, is juxtaposed to the sample cell in the analysis schedule. In either case, the normalised sample cell reading has the form

$$Q_{\text{SAMPLE}} = \frac{(V_P/V_s)_{\text{SAMPLE}}}{(\frac{1}{3})(V_P/V_s)_{\text{REF}_1} + (\frac{2}{3})(V_P/V_s)_{\text{REF}_2}} \qquad (6)$$

The normalisation equation (6) is the same as (1) and (2) above. The distinction is in the application because (6) applies to the aqueous calibration data while (1) and (2) apply to routine analysis of aqueous and organic solutions. Assuming that the noise, on a relative basis, in the sample cell ratio $(V_P/V_s)_{\text{SAMPLE}}$ is about the same as that seen in the reference cell ratio and that the time effect in the absorptiometer is removed by the normalisation, the standard deviation of the sample cell normalised reading Q_{SAMPLE} will be approximately 0·31%. This figure of 0·31% considers only the precision with which the *in situ* sample cell uranium concentration is estimated. In general, when the concentration of an aqueous uranium solution is measured with the gamma absorptiometer, additional errors may be involved which are completely independent of the absorptiometer analysis processes, *e.g.*, residual contamination in the sample cell. If such is the case, the standard deviation of the total error could well be much greater than 0·31%. Also, there is no guarantee that the standard deviation will remain 0·31% over the entire uranium range of interest. For trace uranium concentrations the standard deviation certainly will increase.

The 160 sample cell voltage ratios (V_P/V_s), 40 for each of the four cells, A, B, C and D, were normalised with adjacent reference cell data as in equation (6). The normalised data were analysed statistically to determine whether the normalisation process eliminated the time trend seen in the reference cell (V_P/V_s) data, and whether path length was the only characteristic of the four sample cells which affected the absorptiometer reading. The details of the analysis are included on p. 317 to 318. The analysis indicated no significant time effect in the Q_{SAMPLE} values, so that the normalisation process proved successful. Data from the two 1-cm path length cells A and B appeared to be replicates using a single cell, as did the data from the two 5-cm path length cells C and D.

As a result, the entire set of normalised ratios were expressed as 20 averages, each involving all readings using cells of the same path length and filled with the same uranium solution. The remaining degrees of freedom estimated the replication error about these averages. The replication standard error was approximately 0·0012 in absolute units. It did not depend on sample cells or on uranium concentration. In relative units it increased from 0·12% to 0·25% for the 1-cm cells and from 0·12% to 5·0% for the 5-cm cells over the entire concentration range of 0 to 120 g/l. The reference cell analysis prediction of 0·31% standard error in these normalised Q values was significantly greater than the above figure of 0·12% for zero uranium concentration Q values. Because sample cells with water only should behave exactly as the reference cell, normalisation actually removed (in addition to the time effects) some of the short term variability classified as random in the reference cell analysis. Implicit in this statement also is that there was no evidence of residual solution contamination in the sample cells or any other loading effect. All 20 averages are plotted as points using a logarithmic scale against uranium concentration in Fig. 7. A linear relationship in these points is in agreement with Beer's law, equation (5) with the scattering parameter $a = 0$. The 1-cm cell data are approximately linear. However, the 5-cm cell data clearly deviate from a linear relationship, indicating the necessity of a scattering parameter in the model.

The modified Beer's law (5) was fitted to the 10 plotted points for each cell size. The details of the estimation are on p. 318. The resulting aqueous calibration functions for the two cell sizes are listed in Table V. These functions are the inverses of the modified Beer's law estimates, expressing uranium concentration explicitly in terms of Q. In Fig. 7 the model appears to fit the data adequately. However, statistical analysis (see p. 318 and Table IV) shows that the model fit is quite poor for two uranium solutions. Errors of 0·200 g/l in the standard values of

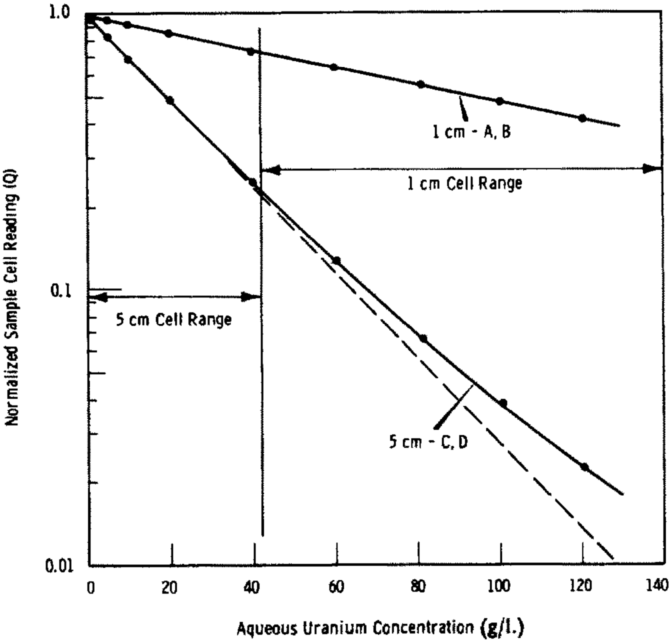

FIG. 7.—Aqueous cell calibration data and modified Beer's law.

TABLE IV.—ANALYSIS OF VARIANCE-SAMPLE CELL CALIBRATION

Source	Sum of squares ($\times 10^6$)		Degrees of freedom	Mean squares ($\times 10^6$)	
	5-cm cell	1-cm cell		5-cm cell	1-cm cell
Uranium					
Calibration	11,308,297·6260	3,444,594·8437	2		
Residual	194·0300	43·0100	7	27·7186	7·1443
Cells	0·6661	0·0500	1	0·6661	0·0500
Interaction	8·7252	21·8525	9	0·9695	2·4281
Replication	84·1700	86·2940	60 56[a]	1·4028	1·5410
TOTAL	11,308,585·2173	3,444,746·0502	79 75		

[a] Four outlier observations were deleted from the 1-cm cell analysis.

TABLE V.—AQUEOUS URANIUM SOLUTION CALIBRATION FUNCTION

Concentration range, *g/l.*	Function, *g/l.*	Accuracy limits,[a] *g/l.*
	For 1-cm path length	
40–120	$U = 127{\cdot}1 \log_e \left(\frac{0{\cdot}9412}{Q - 0{\cdot}0554}\right)$	0·27–0·50
	For 5-cm path length	
0–40	$U = 27.70 \log_e \left(\frac{0{\cdot}9829}{Q - 0{\cdot}0126}\right)$	0·07–0·27

[a] Standard deviation of uranium concentration estimate.

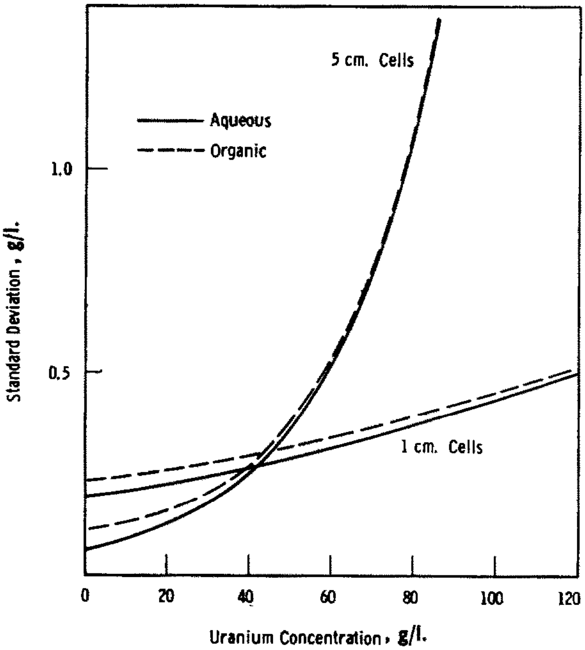

FIG. 8.—Accuracy of aqueous and organic uranium solution analysis using modified Beer's law calibration function.

these solutions would explain the significance. Fig. 8 is a plot of the accuracy of the aqueous uranium solution estimation as a function of uranium concentration. Accuracy is expressed as total standard deviation in g/l., which includes both the random error in an individual Q ratio and the deviation between the model and standard solutions. For both size cells the total standard deviation increases with uranium concentration. The 5-cm cells are more accurate for low concentration and the 1-cm ones for high. The crossover point is about 40 g/l. The accuracy limits for each calibration function over the range of uranium concentration for which it has the smaller total standard deviation are listed in Table V. Using 42 g/l. as the point for switching from 5-cm cells to 1-cm cell gives analysis accuracy of 0·2 g/l. at zero with a monotone increase to 0·5 g/l. at 120 g/l.

Details of statistical analysis

The 100 standard voltage-integration time ratios (V_S/T) obtained from the reference cell analysis, were analysed with a two-factor (loading at 20 levels and sequence

TABLE VI.—ANALYSIS OF VARIANCE—(V_S/T) REFERENCE CELL DATA

Source	Sum of squares ($\times 10^6$)		Degrees of freedom		Mean sum of squares ($\times 10^6$)	
Loading	3·06116		19		0·16111	
Between days		2·03001		2		1·01500
Within days		1·03115		17		0·06066
Sequence position	0·38250		4		0·09563	
Residual	0·09997		76		0·00132	
Error		0·03142		38		0·00087
Remainder		0·06857		38		0·00180
TOTAL	3·54363		99		0·03579	

position at 5 levels) completely crossed analysis of variance. Loading was a random factor and sequence position a fixed factor. Table VI shows the breakdown of the total variation in the (V_s/T) ratios. The 19 degrees of freedom for loading are partitioned into between days and within days effects. Also, 38 degrees of freedom, called *error* are broken out of the residual sum of squares. The error sum of squares measures the variation in the differences between adjacent sequence positions (1–2 and 10–13) across the 20 loadings. This variation should better approximate the variability associated with linearly interpolated values than the residual variance, because the latter is really a measure of the non-additivity of the model rather than a true error estimate.

Clearly, days are the major contribution to the voltage variability. Fig. 3 shows that there is no physical day effect in the loading averages. Both between and within days mean squares are measuring the same voltage drift. Sequence position also is a significant effect as discussed in the main text. The error mean square is significantly smaller than the remainder mean square which indicates that the residual mean square overestimates the short term random fluctuation in the voltage signal. Using the error mean square gives a standard deviation of 0·00003.

The 100 reference cell voltage ratios (V_P/V_s) were analysed in exactly the same manner as the (V_s/T) voltage data discussed above. The analysis of variance breakdown is shown in Table VII. The conclusions from the analysis are similar to those

TABLE VII.—ANALYSIS OF VARIANCE—(V_P/V_S) REFERENCE CELL DATA

Source	Sum of squares ($\times 10^6$)		Degrees of freedom		Mean sum of squares ($\times 10^6$)	
Loading	7371·60		19		387·98	
Between days		5861·53		2		2840·77
Within days		1690·07		17		99·42
Sequence position	198·74		4		49·69	
Residual	40·53		76		7·12	
Error		188·73		38		4·97
Remainder		351·80		38		9·24
TOTAL	8110·87		99		81·93	

for the (V_s/T) data except that the sequence position and error mean squares are, though significant, less significant than for the (V_s/T) data. The error mean square gives a standard deviation of 0·00223 for the short term random fluctuation.

The 80 sample cell normalised Q ratios for A and B 1-cm path length cells and the 80 for the C and D 5-cm path length cells were each analysed with a two factor (uranium at 10 levels and cells at 2 levels) completely crossed analysis of variance with four replicate observations at each of the 20 two-factor level combinations. Uranium was a random factor and cells a fixed factor. Table IV shows the results of the analysis. Four outlier observations from the 1-cm cell data were replaced by three-replicate averages based on significantly large replicate variance. In both analyses the cells main effect and cells-uranium interaction were not significant compared to replicate error. Thus, the A and B cells and the C and D cells could be treated as identical in the calibration. A supplementary analysis which regressed the additive model residuals on loading and sequence position showed that the Q ratio normalisation successfully removed the time effect in the absorptiometer response.

For each cell size the 10 uranium level averaged Q ratios (each average was over eight individual Q values) were fitted to the modified Beer's law (5) by least squares. The least squares parameter estimation was done by an iterative non-linear least squares programme on the Hanford IBM–7090 computer. In Table IV the 9 degrees of freedom for uranium are partitioned by this estimation into 2 explained by the modified Beer's law, called *calibration*, and 7 measuring the variation in the average Q ratios about the calibration function, called *residual*. For both size cells the residual mean square is too large to be explained by random error, so that neither calibration function explains all the uranium level connected variation in the data. The major contributors to the two residual mean squares are the highly significant positive residuals at 10·044 g/l. and negative residuals at 120·642 g/l. A shift of 0·200 g/l. in each of these two standard values would explain the significance.

ORGANIC CELL CALIBRATIONS

Because of the difficulties inherent in preparing organic phase standard solutions, a method to calibrate the absorptiometer for organic solutions was desired which used only aqueous phase standards. The modified Beer's law (5) implies that the absorptiometer response $\log_e (Q_{ORG} - a)$ for organic liquids and the response $\log_e (Q_{AQ} - a)$ for aqueous liquids differ by only a constant due to the incremental change in the solvent mass absorption coefficient (hereafter this effect is termed *organic zero shift*). The following method may be used to check this zero shift theory:

(1) Mix 50 ml of organic solvent with 50 ml of one of the aqueous standard uranium solutions (see Table III). (2) Allow the mixture to equilibrate and separate the two phases. (3) Analyse both phases independently on the absorptiometer using the same sample cell to obtain $\log_e (Q_{AQ} - a)$ and $\log_e (Q_{ORG} - a)$. (4) Repeat 1, 2 and 3 for several different aqueous standards (in the experiment the four standards, distilled water, 40·234 g/l., 81·364 g/l. and 120·642 g/l. were used).

When a mixture equilibrates, the exact uranium concentration of each phase is not known. However, because equal volumes of aqueous and organic went into the mixture, the sum of the uranium concentrations of the two phases is the same as that of the aqueous standard originally used in the mixture. If the zero shift theory is correct, the model

$$\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a) = 2\log_e b + \log_e \varepsilon + cU_T \qquad (7)$$

is applicable for each aqueous standard uranium concentration U_T and should fit the data as well as the modified Beer's law (5) fits the aqueous calibration experimental data. Moreover, the least squares estimate of the slope parameter c obtained by regressing $\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a)$ on U_T should not differ significantly from the slope estimate of c calculated from the aqueous calibration data (see Table V). Once the zero shift theory has been checked, the proper ε parameter is directly estimated from the zero uranium concentration data.

An organic cell calibration experiment was designed to use the above method with the following purposes in mind:

1. Determine whether the organic shift theory is substantiated according to the above criteria.
2. If substantiated, estimate the magnitude of the shift $\log_e \varepsilon$ in equation (7) from the zero uranium data.

3. Calculate the precision of the estimate of $\log_e \varepsilon$.
4. Determine the precision with which uranium concentration in the organic phase can be assayed by gamma absorptiometry, when the calibration is accomplished by zero shifting the aqueous calibration for the same instrument.

The organic-phase solvent used in the pulse column test facility consists of 30% by volume of tributyl phosphate (TBP) in a kerosene-type diluent. The organic liquids for the calibration of the absorptiometer were prepared by taking a 2-l. aliquot of this solvent and scrubbing it in the following manner to remove any possible traces of uranium. First, contact organic with 25 g of sodium carbonate in 500 ml of distilled water and decant the aqueous phase. Second, contact organic with 50 ml of 60% nitric acid in 500 ml of distilled water and decant aqueous phase. Third, wash organic with distilled water. The above process was repeated 4 times to obtain the first organic liquid O_1 and 5 times to obtain the second liquid O_2. The experimental design for the organic calibration included these two organic liquids so that a check was possible on their purity.

The above procedure gave water-saturated organic liquids for calibration. It was necessary to ensure that the organic was saturated with water before the equilibrations with uranium-containing aqueous phase standards because water is soluble to the extent of 0·39 ml in 50 ml of the TBP-kerosene.[4] The solubility of the organic solvent in the aqueous is negligible by comparison, being only $2{\cdot}5 \times 10^{-4}$ ml in 50 ml of aqueous phase.[4]

The experimental design (see Table VIII) for the organic calibration was a complete 2 × 4 factorial with two equilibrations in each cell. The two factors of the factorial were: (1) organic liquid at two levels, O_1 and O_2, and (2) aqueous uranium solution concentrations at the four levels mentioned above which were designated 0, 1, 2, 3. For each pairing of an organic level and a uranium concentration level, a single equilibration and the resulting separated organic and aqueous phases constitute a unit. Two such units were scheduled for each of the eight paired levels of the factorial design so that a check would be possible on the precision of the equilibration-separation process. Thus, the entire experimental schedule involved 16 independent units. In Table VIII, the unit is identified with the equilibration number in the order in which the absorptiometer analyses were performed. The second and third columns in Table VIII give the paired levels for the equilibration.

TABLE VIII.—ORGANIC CALIBRATION EXPERIMENT DESIGN

Equilibration number	Organic liquid	Aqueous uranium standard solution concentration
1	O_1	0
2	O_2	1
3	O_1	2
4	O_2	3
5	O_2	2
6	O_1	3
7	O_2	0
8	O_1	1
9	O_2	3
10	O_1	2
11	O_2	1
12	O_1	0
13	O_1	1
14	O_2	0
15	O_1	3
16	O_2	2

The analysis of an equilibration was always done in the same manner:

(1) Fill the A cell (1-cm path length) and the D cell (5-cm path length) with the separated aqueous phase. (2) Run the analysis sequence RDARADR on the absorptiometer (here, R is the same 5-cm path length distilled water reference cell as used in the aqueous calibration), and record data as for an aqueous calibration loading. (3) Empty, clean and fill A and D cells with separated organic phase. (4) Run the analysis sequence RADRDAR and record as for (2) above.

STATISTICAL ANALYSIS OF ORGANIC CALIBRATION DATA

In order to determine whether the equilibration-separation process was reproducible and whether trace uranium was still being removed from the organic liquid by the fifth scrubbing, a preliminary analysis of variance calculation was performed on the organic calibration data. The details of the analysis are discussed on p. 322 to 323.

The results of the analysis, as summarised in Table IX, indicate that the absorptiometer stability during the organic calibration was similar to that during the aqueous calibration. The 5-cm path length cell data show a significant decrease in the Q ratios for O_2 solvent over corresponding uranium concentration Q ratios for O_1 solvent. In physical units, this decrease corresponds to the removal of 0·04 g/l. uranium during the fifth scrub. A change in uranium concentration of this magnitude could not be detected with the 1-cm path length A cell. Data for both cells show that the ratio of the organic to aqueous uranium concentration is a function of uranium concentration (this effect appears as a solvent-uranium interaction in the analysis of variance Table XI). This was to be expected and was what prompted the addition model (7) analysis. A more subtle effect was that there was a small but significant difference between the ratios for the two organics for the three positive uranium concentration levels. (This effect appears as a solvent-uranium-organic interaction

TABLE IX.—ANALYSIS OF VARIANCE—ORGANIC ZERO SHIFT

Source	Sum of squares ($\times 10^4$)		Degrees of freedom		Mean sum of squares ($\times 10^4$)	
	1-cm cell	5-cm cell	1-cm cell	5-cm cell	1-cm cell	5-cm cell
Regression	20,051·6682	412,382·2937	1	2	20,051·6682	206,191·1468
Residual	0·0988	13·7915	2	5	0·494	2·7583
Sub-total	20,051·7670	412,396·0852	3	7		
Replication	0·2708	1·4574	12	8	0·0226	0·1822
TOTAL	20,052·0378	412,397·5426	15	15		

TABLE X.—ORGANIC URANIUM SOLUTION CALIBRATION FUNCTION[a]

Concentration range, *g/l.*	Function, *g/l.*	Accuracy limits,[b] *g/l.*
	1-cm path length	
45–120	$U\ 127{\cdot}1 \log_e \left(\frac{0{\cdot}9502}{Q - 0{\cdot}0554}\right)$	0·31–0·52
	5-cm path length	
0–45	$U = 27{\cdot}70 \log_e \left(\frac{b}{Q - 0{\cdot}0126}\right)$	0·12–0·31

[a] b = 1·0547 for O_1 solvent,
b = 1·0585 for O_2 solvent.

[b] Standard deviation of uranium concentration estimate.

in the analysis of variance.) This difference did not change with uranium concentration. A simple explanation is that the two organics had different nitric acid concentrations. No attempt was made to determine the organic acid concentration nor to stabilise it during the scrubbing process. Finally, the preliminary analysis indicated that the equilibration-separation process was reproducible; in fact, the difference between the two duplicates was uniformly explainable in terms of the fundamental absorptiometer replication error.

The 128 sample cell normalised Q ratios were split into A and D cell groups. Each group of data was reduced to 16 observations, one for every equilibration. First, the appropriate a scattering parameter was used to calculate $\log_e (Q - a)$ for each Q ratio, then the two replicate analyses for each phase were averaged to give a single $\log_e (Q_{AQ} - a)$ and $\log_e (Q_{ORG} - a)$ for each equilibration. These average logarithms were added to give the single observation,

$$\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a),$$

for each equilibration. The organic distribution ratio interaction present in the individual $\log_e (Q - a)$ readings was summed out of the data by this addition process and did not affect the check on the zero shift theory. The regression model of equation (7) was fitted by least squares to the 16 data points

$$[\log_e (Q_{AQ} - a) + \log_e (Q_{ORG} - a), U]$$

where U, the independent variable, was the aqueous standard uranium concentration. The regression analyses are discussed on p. 19 and summarised in the analysis of variance table of Table IX.

The results of the analysis indicate that the organic calibration data fit the modified Beer's law as well as the aqueous calibration data. The estimates of the attenuation parameter c in the zero shift model (7), given in the form $-1/c$, are 127·3 and 28·05 for the A and D cells, respectively. These are not significantly different from the aqueous calibration function parameters 127·1 and 27·70 of Table V. Thus, both the fit of the zero shift model and the estimates of the attenuation parameter do not refute the organic zero shift theory for either cell.

The organic zero shift parameters $\log_e \varepsilon$ in (7) were estimated from the zero uranium concentration data with the formula,

$$\log_e \varepsilon = \overline{\log (Q_{ORG} - a)} - \overline{\log_e (Q_{AQ} - a)} \qquad (8)$$

Here, the "bar" indicates average over-all appropriate $\log_e (Q - a)$ replicates. For the 1-cm path length A cell the averages each involve eight replicates. For the 5-cm path length D cell individual zero shift parameters were estimated for the two organic solvents O_1 and O_2, so the averages each involved four replicates. The weighted average of these estimates corresponds to $-4·16$ g/l. and $-4·20$ g/l. for the O_1 and O_2 organic solvents, respectively. The standard deviations of the resulting calibration function shifts are 0·14 g/l. for the A cell and 0·90 g/l. for the D cell. The organic uranium solution analysis accuracy of these calibration functions is plotted as the dash curves in Fig. 8. The difference between the dash and solid curves is the additional inaccuracy resulting from the zero shift method of adjusting an aqueous calibration function to give the organic one. From Fig. 8, the change-over point between cells is 45 g/l. for organic analysis. The organic uranium solution functions are listed in Table X along with accuracy limits for their recommended concentration range.

TABLE XI.—ANALYSIS OF VARIANCE—PRELIMINARY ORGANIC ANALYSIS

Source	Sum of squares ($\times 10^4$)		Degrees of freedom	Mean sum of squares ($\times 10^4$)	
	1-cm cell	5-cm cell		1-cm cell	5-cm cell
MODEL					
Uranium	20,051·7670	412,391·4096	3	6,683·9220	137,463·8032
Organic	0·0819	4·3203	1	0·0819	4·3203
Uranium-organic interaction	0·0321	0·3553	3	0·0107	0·1184
Equilibration	0·2387	1·4574	8	0·0298	0·1822
PHASE DISTRIBUTION					
Solvents	273·2753	5,743·9952	1	273·2753	5,743·9952
Solvent-uranium interaction	351·9959	6,986·9578	3	117·3320	2,328·9859
Solvent-organic interaction					
Uranium present	4·7969	100·2786	1	4·7969	100·2786
Residual	0·1941	0·3379	3	0·0647	0·1126
Equilibration	0·2321	1·5129	8	0·0290	0·1891
REPLICATION	1·5758	6·0841	31	0·0493	0·1901

Details of statistical analysis

The 128 sample cell voltage ratios $(V_P/V_s)_{AQ}$ and $(V_P/V_s)_{ORG}$ formed from the organic calibration experiment were normalised with interpolated reference cell voltage ratios $(V_P/V_s)_{REF}$ using (6). The normalised ratios Q_{AQ} and Q_{ORG} were adjusted with appropriate scattering parameters and natural logarithms were calculated to form a set of 32 pairs of $[\log_e (Q_{AQ} - a), \log_e (Q_{ORG} - a)]$ data for each cell size, one pair for every equilibration separation. The model for the sum of the components of each pair is given by (7). The model for difference of the components is

$$\log_e (Q_{AQ} - a) - \log_e (Q_{ORG} - a) = -\log_e \varepsilon + c(U_{AQ} - U_{ORG}) \qquad (9)$$

For each cell size the sums of the 32 pairs and the differences of the 32 pairs were each analysed with a three-factor (uranium at four levels, organic at two levels, and equilibrations at two levels) design. Uranium and organic were crossed and equilibrations nested in each uranium-organic pairing. The analysis of variance breakdown for the design is given in Table XI. The two replicates for each equilibration give 16 degrees of freedom for sums and 16 for differences for each cell size. In the absorptiometer analysis schedule half of one run was not recorded. Therefore, one replicate degree of freedom was lost for differences with each cell. Sums and differences replicate sum of squares were pooled to give a replicate mean square with 31 degrees of freedom. Equation (7) shows that the sums data for a cell should depend linearly on the uranium concentration and the organic shift parameter. The top half of Table XI, marked "MODEL", gives the appropriate variance breakdown. For both cell sizes, equilibration and uranium-organic interaction mean squares are not significant. For the 1-cm cell the organic mean square is not significant but for the 5-cm cell it is very significant. The non-significant interaction implies that equation (7) is an adequate representation of the sum data. The physical interpretation of the organic and equilibration non-significance is discussed in the main text.

Equation (9) shows that the difference data for a cell should depend linearly on the organic shift and on the difference between the equilibrated aqueous and organic-uranium concentrations, the phase distribution. The average difference for a cell should be just a linear combination of the average organic shift and the average phase distribution. The bottom half of Table XI, marked "PHASE DISTRIBUTION", gives the appropriate variance breakdown. The solvent mean square measures the average difference between the phases, *i.e.*, the average value of the model (9). The highly significant result is largely due to the concentration increment $U_{AQ} - U_{ORG}$ because the zero shift $\log_e \varepsilon$ is numerically quite small. The significant solvent-uranium interaction means that the $U_{AQ} - U_{ORG}$ changes with total uranium concentration. In the customary breakdown, the 4 degrees of freedom for solvent-organic interaction would be partitioned into one for solvent-organic interaction and three for solvent-organic-uranium interaction. In such a breakdown both mean squares would be significant. The breakdown of the sums of squares in Table XI places all the significance in 1 degree of freedom, the average solvent-organic interaction over the three positive uranium concentration levels. Thus, when uranium is present, the concentration increment $U_{AQ} - U_{ORG}$ is different for the two organics O_1 and O_2; however, the increment is independent of the exact amount of uranium present.

The non-significance of the equilibration mean square means that the phase distribution was reproducible in the two separate equilibration-separation processes.

For each cell size the 15 degrees of freedom associated with MODEL were fitted by least squares to the regression function (7) with total uranium concentration U as a covariate. For the 5-cm cell a parameter was included for the significant organic effect. Table IX gives the variance breakdown for the regression analysis. For the 5-cm cell the regression-residual partition splits the 7 degrees of freedom associated with uranium, organic, and uranium-organic interaction in Table XI. The replication is measured by the 8 degrees of freedom between equilibrations. For the 1-cm cell the 4 degrees of freedom associated with organic and uranium-organic interaction are pooled with equilibrations to measure replication. The regression-residual partition splits the 3 degrees of freedom associated with uranium. The residual mean squares indicate that the model (7) fits the sum data to 0·2% and 1·7%, respectively, for the 1-cm and 5-cm cells. These percentage figures are in good agreement with the percentage ranges of the aqueous calibration data fit to the modified Beer's law (5).

DISCUSSION OF ERRORS IN CALIBRATIONS

The analysis of the aqueous and organic calibration has demonstrated that the accuracy of the absorptiometer for either organic or aqueous phases varies from 0·1 to 0·5 g/l. over the uranium concentration range of 0 to 120 g/l. This is because of the variability or random noise inherent in an *in situ* uranium estimation.

In order to isolate the source of this variability, the variabilities in the four major components of the absorptiometer system were looked at in more detail. These components are:

1. The integrating picoammeters [which give (V_D) and (V_S)] which includes all variability from capacitance changes, amplifier gain change, non-uniform integration time and integrator transient effects.
2. The phototube, crystal and high voltage supply.
3. The americium source.
4. Removal and replacement of a sample cell.

The phototube was disconnected from the lower integrator and a constant current source was connected to this integrator input. The timer was run through its cycle several times and (V_P) and (V_S) were recorded. The ratios (V_P/V_S) were then computed. The standard deviation of these ratios amounted to 0·01% of the (V_P/V_S) ratio which gives an estimate of the variability of the first component.

The source as a long-lived radionuclide has Poisson statistics. The variability in this component may be directly calculated from the source intensity, the geometry, the reference cell attenuation and the NaI crystal efficiency. Such a calculation gives an effective intensity of $1{\cdot}5 \times 10^7$ γ/min at the phototube with a standard error of 0·026%.

A comparison of sample cell analysis where the sample cell was left in place for varying numbers of analyses and where it was removed and replaced in the normal manner showed there was no detectable positioning effect, transient effect, or effect from phototube hysteresis.

No method was readily available to determine the variability of the phototube-crystal-high voltage supply component. However, it appears, by process of elimination, that the major part of the random noise in the absorptiometer calibration must be attributed to random short term fluctuations in the phototube-crystal system sensitivity or to possible high voltage fluctuations of a magnitude greater than the 1 part in 10^5 quoted by the manufacturer.

CONCLUSIONS

The data-logging absorptiometer described in this paper has been in operation for approximately two years. About 2000 samples have been analysed during this time. An average of 30 samples/8-hr day has been achieved by the laboratory using the apparatus and very few operator errors have been made. When an error has occurred, it has been gross and easily detected. An incorrect setting of the cell-size switch has been the most frequent error. Here, the data point is still salvable by adjusting the data for the capacitance change. The goal of a rapid, foolproof and accurate method of uranium analysis has thus been achieved.

The method developed to calibrate the absorptiometer for organic phase solutions is original with this paper. The method clearly eliminates the necessity of preparing organic phase standards which is, in general, difficult.

Acknowledgements—The processing and statistical analysis of the data were done on the Hanford Atomic Products Operation IBM 7090. The authors are particularly indebted to D. E. Hudson for his handling of the machine calculations.

The efforts of Mrs. Kay Skeie and Mrs. Lena Schock in performing the analyses necessary for the aqueous and organic calibrations were very much appreciated.

Inclusion of the scattering term in the section *Mathematical model of absorption*, which greatly improves the model, was suggested by A. Whittaker.

Zusammenfassung—Urankonzentrationen in wäßrigen und organischen Lösungen werden durch Gamma-Absorptionsmessung bestimmt. Eine ^{241}Am-Quelle, die 60 keV-Quanten emittiert, und ein Szintillationsdetektor werden verwendet. Der von der Photozelle gelieferte Strom wird über eine Minute integriert und liefert ein 2–10 V Gleichstromsignal, das in einer Datenspeicheranlage registriert wird. Mit einer einzigen Methode, die nur wäßrige Standards erfordert, wird das System für wäßrige und organische Uranlösungen geeicht. Eine eingehende statistische Analyse der Versuchsergebnisse ist beigefügt. Eine Abweichung vom Beerschen Gesetz wird durch die Berücksichtigung von Streueffekten im Modell erklärt. Lösungsanalysen mit dieser Anlage sind genauer als ±0,5 g/l bei Urankonzentrationen von 0–120 g/l.

Résumé—Les concentrations en uranium de solutions aqueuses et organiques sont déterminées par absorptiométrie gamma. On utilise une source de ^{241}Am qui émet des photons d'énergie 60 keV, et un détecteur à scintillation. Le courant de sortie du phototube est intégré pendant 1 min, donnant un signal de 2–10 V en courant continu, qui est noté par un système enregistreur. Pour étalonner le système on utilise, tant pour les solutions aqueuses que pour les solutions organiques d'uranium, une méthode unique ne nécessitant que des étalons aqueux. Une analyse statistique détaillée des résultats expérimentaux est incluse. On explique une déviation notée par rapport à la loi de Beer par la présence d'effets de dispersion dans le modèle décrit. Les analyses de solutions faites avec ce modèle donnent des résultats d'une précision supérieure à ±0,5 g/l, pour des concentrations en uranium comprises entre 0 et 120 g/l.

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MUTUAL RADIATION INTERFERENCE EFFECTS OF THE ALKALI ELEMENTS AND HYDROGEN UPON THE RESONANCE LINE INTENSITIES OF THE ALKALI ELEMENTS IN FLAME SPECTROPHOTOMETRY*

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Summary—The mutual interference effects of different concentrations of each of the alkali elements and hydrogen, as the chlorides in solution, on the intensity of the resonance line for four different concentrations of each of the alkali elements have been studied. All concentrations have been expressed in millimoles per litre. The interference effects were greatest on the lowest concentration and least on the greatest concentration of each element. In general, lithium produced the least effect on the other elements, and the other elements had the least effect on lithium. Hydrogen ion, as hydrochloric acid, caused suppression because of the anion effect, with caesium being suppressed the most. Caesium and rubidium caused the greatest enhancement on the other elements. Because of their very low ionisation potentials, the mutual interference effects of rubidium and caesium on each other were found to be very large.

INTRODUCTION

THIS work, which was started several years ago, was designed to be a careful study of the interference effects for a broad concentration range of the alkali chlorides and hydrochloric acid upon the resonance line radiation of each of the alkali elements. Many brief studies on "interferences", usually associated with a procedural development and with limited concentration ranges, have been performed for lithium, sodium and potassium. In comparison, relatively few studies are available for rubidium and caesium. However, it is difficult to evaluate much of the results reported in the literature, because the work was performed with different types of instrument, different types of burner and fuel, and under different and sometimes unstated operating conditions. Very often, insufficient attention was given to such problems as purity of reagents, sources and degree of contamination, and care in the preparation of the solutions. The authors found rubidium and caesium salts from most sources to contain high concentrations of the other element, as well as of potassium. Work done with impure solutions, as indicated above, cannot yield reliable results. Much of the information in the literature is not in agreement, and there are often examples of conflict. For example, sodium and potassium have been reported to suppress[2] and to enhance[24] their respective emission intensity. It has also been reported that excess sodium caused both high and low results for potassium, depending on the potassium

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concentration,[3] and only high results for different potassium concentrations.[19] Higher concentrations of hydrogen chloride have been reported to enhance[21] and to suppress the emission of the lithium 671-mμ line.[16] It has also been reported that these effects were not observed when an optical system of adequate resolving power was used.[17]

This study represents an effort to obtain more reliable interference effects results with respect to the elements of Group I of the Periodic Table, and to examine further some of the factors that effect the equilibrium constant expression:

$$K = \frac{[M^+][e^-]}{[M]} = \frac{[x^2]}{[1 - x]}P \tag{1}$$

when x = degree of ionisation of the metal atoms,

and P = partial pressure for each species in the flame.

The above may also be expressed directly in terms of the partial pressure equilibrium constant

$$K_P = \frac{[P_M{}^+][P_e{}^-]}{[P_M]} \tag{2}$$

Although this paper represents results from a large number of solutions with different concentrations, this and other published results do not appear to be sufficiently quantitative to be reduced to a common correction factor, because there are numerous factors that can effect the partial pressure of the atomic species in the flame. However, because of the range of concentrations examined, the results will serve as a guide to the spectrochemist on the magnitude of the interferences that may be expected.

The present study involved only aqueous solutions, the integral aspirator burner, and the use of oxygen-hydrogen fuel.

EXPERIMENTAL

Equipment and materials

Beckman model DU spectrophotometer equipped with the 9200 flame attachment, oxygen-hydrogen burner, 9200 spectral energy recording attachment, and a Brown electronic recorder with a 0- to 10-mV scale and a ½-second pen response.

Borosilicate glassware was used for all volumetric measurements but not for the storage of any solutions. All volumetric ware used in this study met the requirements as specified in N.B.S. Circular 602 and Federal Specifications DD-V-581a.

Standard platinum tips or *No. 27 hypodermic syringe needles* were used with the 5-ml (sub-divisions, 1/100 ml) semimicro burettes.

Polyethylene bottles were used as containers. These bottles were steamed, then leached with ion-exchange water before they were used. Water stored in these bottles did not show the changes observed by Delhez.[7] When the solutions were stored for a few weeks or longer for future reference, the bottles were sealed with tape, because for small polyethylene bottles a cap screwed on tightly does not necessarily assure a sealed bottle.

All the *alkali chlorides* used in this work were Johnson, Matthey Specpure grade. The *hydrochloric acid* was redistilled. All solutions were prepared with ion-exchange water that had been previously distilled, then passed through a column containing no metal or rubber parts. Attempts were made to use some standard A.C.S.-grade chemicals for some of the solution concentrations. However, these were found to be quite unsatisfactory because of traces of impurities of the analyte, and so were replaced with solutions prepared from Specpure chemicals.

Procedure and precautions

Solutions. Four concentrations of each element; namely, 0·375, 0·75, 1·5 and 3·0 millimoles per litre, were studied in order to cover the usual concentrations that may be found in analytical work. The concentration of the added mutually interfering cations was varied from 0 to 2000 millimoles per litre for the alkali salts and from 0 to 5000 millimoles per litre for the acid. These units of concentration were used instead of parts per million, in order to have all solutions in the same concentration ratios. In addition to the stock solutions, 1340 separate sample solutions were required.

In case of questionable results all the solutions for a series of a given concentration, such as 0·375 millimoles per litre of caesium, were reprepared. To avoid other anion influences, chlorides were used for all solutions.

Testing for impurities. All water used was from an ion-exchange column containing no metal parts and charged with the mixed-bed resin Amberlite IR 400. All water, glassware, polyethyleneware, and stock solutions were checked for contamination before use by looking for the resonance line of each of the alkali elements. This was done by aspirating the water or solution in question into the flame and recording the response for the resonance line of the possible contaminating element. If no response was obtained, the items were considered to be satisfactory.

A series of solutions with concentrations from 0 to 2000 millimoles per litre for each alkali element were prepared from the stock solutions to serve as blanks. Each concentration of the series was checked by scanning the resonance line for each analyte under the same operating conditions as those in which the line intensity of that analyte was determined. These served as an additional check for contamination, as well as for possible line and background interferences.

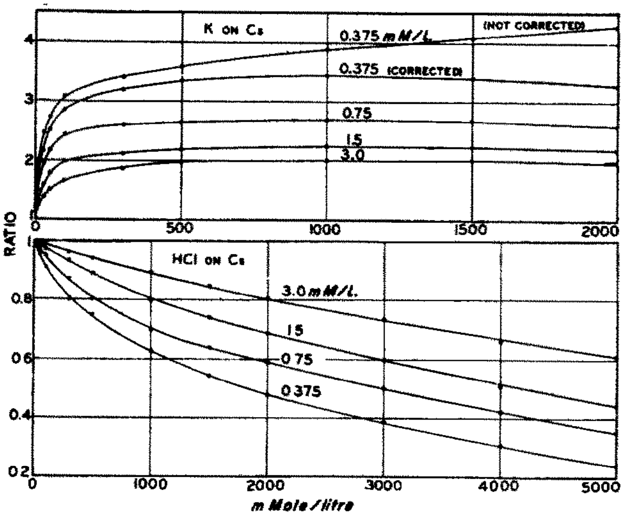

FIG. 1.—Example of mutual interference as a function of concentration of analyte.

If a very small amount of the analyte is present as an impurity in the interferent, or if weak lines of the interferent are closely adjacent to the resonant line of the analyte, it is readily detected in the results unless corrections are made for background and weak-line interferences. This is illustrated in Fig. 1 for the effect of potassium on the concentration 0·375 millimole of caesium per litre. The top curve, uncorrected, shows the effect of a possible minute trace of caesium in the potassium salt which is being added to the caesium solution, and increasing background as the concentration was increased. By spectrographic examination, traces of caesium have been observed in some samples of commercial A.C.S.-grade potassium chloride, but not in others.

The second curve shows the effect of potassium corrected for background interference at 8521·1 A from the potassium chloride solutions. It is doubtful whether the very weak potassium doublet 8503·8 and 8505·2 A produced any influence, because these lines were not observed on sensitive infrared emulsion when potassium chloride was burned in a low current d.c. arc or when a 1*M* potassium chloride solution was aspirated into an oxygen-hydrogen flame for as long as 2 hr.

Ratio of intensities. The samples were aspirated into the flame, and the resulting intensities were recorded on the strip-chart recorder. A pure solution was burned with each solution containing a given concentration of the mutually interfering element, in order to compare the intensities for the pure sample and the sample containing the interfering element. Two or three runs were made on each sample-reference pair at different times, and the intensities were calculated in terms of the ratio:[12]

$$R = \frac{I_{\text{analyte+interferent}}}{I_{\text{analyte}}} \tag{3}$$

By this method it was possible to detect drift or any unusual equipment variation, and to compensate for minor variations, such as slow drift or small variations in instrument settings. The values of R greater than 1 indicate enhancement and those less than 1 indicate suppression of the intensities of the resonance lines for the elements.

The slit widths were adjusted to obtain approximately 0·3–0·4 full-scale responses for each element at each concentration. Changes were made when the enhancement or suppression became very large.

DISCUSSION

The mutual radiation interferences on each of the alkali elements were studied in four concentrations, 0·375, 0·75, 1·5 and 3·0 millimoles per litre. Contamination effects, effects arising from line and band overlapping, and background interferences were examined, and compensations were made on the graphs.

The mutual radiation interference effects of the acid and the other alkali elements on each individual alkali element are summarised in Figs. 1–4 and are tabulated in Table I. At the low concentrations, these results are in general agreement with those listed by Dean.[6] A given concentration of the interfering element has the least enhancement or suppression effect on the most concentrated solutions of the same analyte. This is illustrated in Fig. 1 by the effects of potassium and hydrogen chloride on the four concentrations of caesium. The concentration 1000 mmole/l. of potassium caused a radiation enhancement on the 3·0-mmole/l. concentration of caesium by a factor of 2, and the 0·375-mmole/l. concentration was enhanced by a factor of 3·4. The 2*M* acid concentration caused twice as much suppression of the 0·75-mmole/l. concentration of caesium as of the 3·0-mmole/l. concentration.

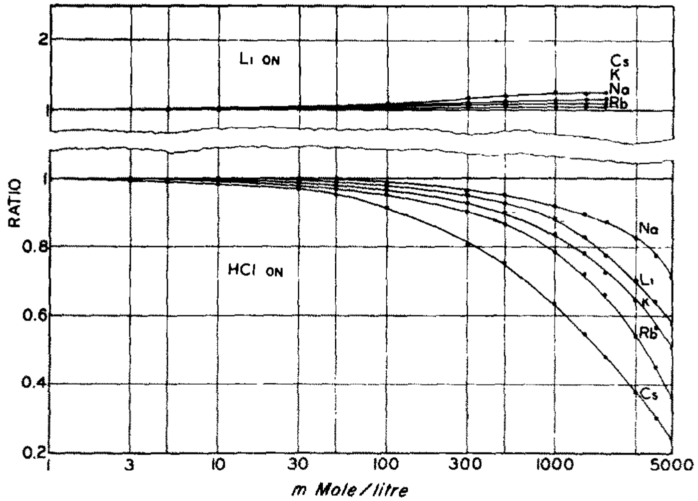

Fig. 2.—Mutual interference effect of lithium and hydrochloric acid.

In order to discuss the experimental results in Figs. 1–4 and Table I, the following equilibrium reactions must be considered, because these are involved in the reactions in the flame and affect the intensities of the resonance lines.

$$\mathrm{M} \leftrightharpoons \mathrm{M}^{+} + \mathrm{e} \tag{4}$$

$$\mathrm{M} + \mathrm{OH} \leftrightharpoons \mathrm{MOH} \tag{5}$$

$$\mathrm{M} + \mathrm{Cl} \leftrightharpoons \mathrm{MCl} \tag{6}$$

$$\mathrm{H} + \mathrm{Cl} \leftrightharpoons \mathrm{HCl} \tag{7}$$

$$\mathrm{H} + \mathrm{OH} \leftrightharpoons \mathrm{HOH} \tag{8}$$

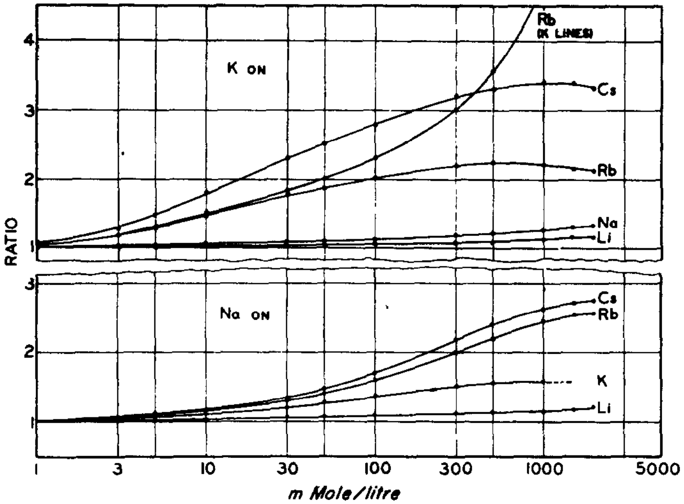

FIG. 3.—Mutual interference effect of potassium and sodium.

Although these probably do not exist in a true equilibrium in the usual chemical sense, a steady state of balanced dissociation and recombination does exist. Thus, from the equilibrium constant values, dissociation energies and other physical constants, the effect of the competing reactions on the resonance line intensities can be estimated. Unfortunately, reliable values are still not available in the literature.

The suppression effect of the aqueous hydrogen chloride results from the formation of the relatively stable chloride,[5,18] the reaction following the mass action law,

$$\frac{[P_M][P_{Cl}]}{[P_{MCl}]} = K_P \tag{9}$$

that reduces the number of free atoms available for excitation.

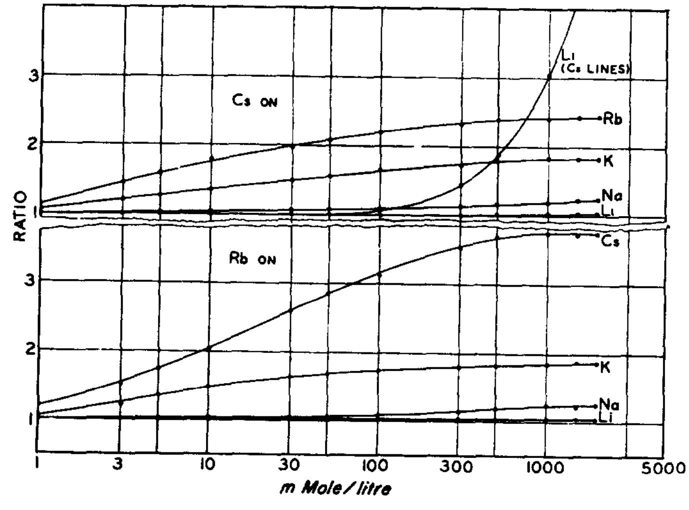

FIG. 4.—Mutual interference effect of caesium and rubidium.

Table I.—Changes in emission intensity because of interference effects

Interferent	Concentration		Analyte	Change in emission intensity, %			
				Concentration			
	mm/l.	*ppm*	Na	0·375	0·75	1·5	3·0 *mm/l.*
Li				8·6	17·2	34·5	69·0 *ppm*
	1	6·94		0	0	0	0
	3	20·8		0	0	0	0
	5	34·7		0	0	0	0
	10	69·4		0·5	1	0	0
	30	208		2	1	0	0
	50	347		2	2	1	−0·5
	100	694		3	2	1	−0·5
	300	2082		6	3·5	2	0
	500	3470		7	5	2	1
	1000	6940		9·5	6	3	1
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Li			K	14·7	29·3	58·6	117·3 *ppm*
	1			0	0	0	0
	3			0	0	0	−1
	5			1	0	0	0
	10			1·5	0	0	0
	30			3	1	0	0
	50			3·5	2	0	0
	100			5	3	1	0
	300			8	5	3	1
	500			9·5	6	3	2
	1000			12	7	4	2
			(Slit width	0·05	0·04	0·04	0·03 *mm*)
Li			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			0	0	0	0
	3			0	0	0	−1
	5			0	0	0	−1
	10			0	0	0	−1
	30			0	0	−1	−1
	50			1	0	−1·5	−2
	100			2	1	−1	−2
	300			3	1·5	−1·5	−3
	500			4	1·5	−1	−3
	1000			5	1	−1	−5
			(Slit width	0·055	0·045	0·035	0·03 *mm*)
Li			Cs	49·8	99·7	194·4	398·8 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			−0·5	−0·5	−0·5	0
	10			1	−1	−1	−1
	30			2	−1	−1	−2
	50			3	−1	−1	−2·5
	100			6	1	−1	−2·5
	300			16	5	−1·5	−3
	500			19	6·5	−3	−3·5
	1000			24	9	−4	−5·5
			(Slit width	0·07	0·05	0·04	0·03 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Li	0·375	0·75	1·5	3·0 *mm/l.*
Na				2·6	5·2	10·4	20·8 *ppm*
	1	23·0		0	0	0	−1
	3	69·0		1	1	1	0·5
	5	115		2·5	2·5	2·5	2
	10	230		4	3	2	2
	30	690		6	5	4	3
	50	1150		8	7	4	3
	100	2299		10	10	6	5
	300	6897		12	10	9	8
	500	11,496		16	12	11	10
			(Slit width	0·1	0·1	0·08	0·06 *mm*)
Na			K	14·7	29·3	58·6	117·3 *ppm*
	1			1	0·5	0	0
	3			4	2·5	1	0
	5			6	4	3·5	1
	10			12	6	4	2
	30			22	13	8	5
	50			30	19	12	8
	100			36	21	13	10
	300			50	32	20	14
	500			55	35	23	17
			(Slit width	0·05	0·04	0·04	0·03 *mm*)
Na			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			2	1	0	0
	3			5	3	1	2
	5			10	5	3	2·5
	10			15	9·5	6·5	5
	30			30	23	16	10
	50			46	33	22	14
	100			70	51	34	20
	300			100	74	54	40
	500			121	87	65	45
			(Slit width	0·055	0·045	0·035	0·03 *mm*)
Na			Cs	49·8	99·7	199·4	398·7 *ppm*
	1			2	1	1	0
	3			6	4	2	2
	5			11	7	4	2
	10			18	14	7	5
	30			42	34	20	11
	50			56	48	26	14
	100			78	70	40	25
	300			120	111	74	38
	500			140	129	87	48
			(Slit width	0·07	0·05	0·04	0·03 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %						
			Analyte	Concentration					
	mm/l.	*ppm*	Li	0·375		0·75	1·5	3·0 *mm/l.*	
K				2·6		5·2	10·4	20·8 *ppm*	
	1	39·1		0·5	1*	0·5	0	0	
	3	117		0·6	1	0·5	0·5	0	
	5	196		1	4·5	1	1	1	
	10	391		2	8	1	1·5	1	
	30	1,173		4·5	10	2·5	2·5	1	
	50	1,955		5·5	16	3	3	2	
	100	3,910		6	22	3	3	2	
	300	11,730		6	40	4	3·5	3	
	500	19,100		8	60	5	3·5	3	
			(Slit width	0·10		0·10	0·08	0·06 *mm*)	
K			Na	8·6		17·2	34·5	69·0 *ppm*	
	1			1		1	0	0	
	3			2		1·5	1	0	
	5			3		2·5	2	0·5	
	10			5		3·5	3	1	
	30			8·5		6	4·5	2·5	
	50			10		7·5	5·5	4	
	100			12·5		9·5	7	4·5	
	300			17		14	10	6	
	500			20		16	12	8	
			(Slit width	0·10		0·08	0·05	0·045 *mm*)	
K			Rb	32·0		64·1	128·2	256·4 *ppm*	
	1			5	6*	4	3	1	2*
	3			15	16	10	10	3	4
	5			27	30	22	16	6	8
	10			48	52	38	26	12	14
	30			77	84	60	44	26	30
	50			87	100	72	54	32	38
	100			98	130	82	68	40	50
	300			120	200	102	80	53	70
	500			124	355	108	84	64	85
			(Slit width	0·045		0·035	0·03	0·03 *mm*)	
K			Cs	49·8		99·7	199·4	398·7 *ppm*	
	1			10	15*	10	6	3·5	
	3			27	45	23	19	9	
	5			45	75	37	22	11	
	10			81	104	58	37	22	
	30			130	151	93	62	40	
	50			152	173	115	78	51	
	100			178	208	142	97	66	
	300			220	240	160	110	85	
	500			230	260	165	118	99	
			(Slit width	0·05		0·04	0·03	0·025 *mm*)	

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*		0·375	0·75	1·5	3·0 *mm/l.*
Rb			Li	2·6	5·2	10·4	20·8 *ppm*
	1	85·5		0	−1	−0·5	−0·5
	3	256·4		1	0	−1	−1
	5	427·4		2	0	−1	−0·5
	10	854·8		2	0	0	0
	30	2,564		3	0	0	0
	50	4,274		3	1	1	0
	100	8,548		4	1	1	1
	300	25,644		4	2	1	1·5
	500	42,740		4	3	1	3
			(Slit width	0·10	0·10	0·08	0·06 *mm*)
Rb			Na	8·6	17·2	34·5	69·0 *ppm*
	1			1	1	0	0
	3			2	1·5	1	1
	5			3·5	2·5	2	2
	10			4	4	2·5	2·5
	30			5·5	4·5	4	2·5
	50			7·5	6	5	3·5
	100			10	7·5	6	5
	300			14	11	9	6
	500			16	13	11	8
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Rb			K	14·7	29·3	58·6	117·3 *ppm*
	1			6	4	2	1
	3			24	13	10	5
	5			38	24	15	9
	10			50	33	19	13
	30			62	44	24	16
	50			66	46	30	19
	100			72	53	34	22
	300			79	58	37	25
	500			81	63	39	25
			(Slit width	0·045	0·04	0·03	0·025 *mm*)
Rb			Cs	49·8	99·7	199·4	398·7 *ppm*
	1			26	20	11	5
	3			55	47	26	13
	5			73	61	39	19
	10			108	91	56	34
	30			160	120	101	54
	50			188	143	116	60
	100			209	165	132	80
	300			252	188	150	93
	500			270	201	159	96
			(Slit width	0·05	0·04	0·03	0·025 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Li	0·375	0·75	1·5	3·0 *mm/l.*
Cs				2·6	5·2	10·4	20·8 *ppm*
	1	132·9		0	0	0	0
	3	398·7		0	0	0	0
	5	664·6		0	0	0	0
	10	1,329		0	0	0	0
	30	3,987		1	0	0	1
	50	6,646		2 5*	0 4*	1 3*	1 1·5*
	100	13,291		2 11	0 8	1 7	1 4
	300	39,873		3 44	1 37	2 20	2 6
	500	66,455		3 87	2 76	2 39	2 12
			(Slit width	0·10	0·08	0·07	0·06 *mm*)
Cs			Na	8·6	17·2	34·5	69·0 *ppm*
	1			1	1	0	0
	3			3	2·5	1	1
	5			4·5	3	2	1
	10			7	5	2·5	1·5
	30			8	6	3·5	2·5
	50			9	6	4	3
	100			12	8	5·5	4·5
	300			15	10	7·5	5·5
	500			17	11·5	9	6·5
			(Slit width	0·10	0·08	0·05	0·045 *mm*)
Cs			K	14·7	29·3	58·6	117·3 *ppm*
	1			8	5	4	2
	3			21	18	12	6
	5			28	24	14	10
	10			38	31	22	13
	30			49	42	33	26
	50			58	46	37	28
	100			70	54	42	35
	300			76	66	49	43
	500			82	70	54	47
			(Slit width	0·045	0·04	0·03	0·025 *mm*)
Cs			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			16	10	6	4
	3			46	29	22	14
	5			57	38	34	18
	10			80	55	45	26
	30			98	68	56	40
	50			106	82	70	47
	100			120	90	82	56
	300			134	98	90	63
	500			139	101	93	70
			(Slit width	0·045	0·035	0·03	0·025 *mm*)

TABLE I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Li	0·375	0·75	1·5	3·0 *mm/l.*
HCl				2·6	5·2	10·4	20·8 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			0	0	0	0
	10			0	0	0	0
	30			0	−0·5	0	0
	50			−1	−1	−1	−0·5
	100			−2·5	−2·5	−1·5	−1·5
	300			−6	−4·5	−4·0	−4
	500			−8	−7·5	−6·5	−5·5
	1000			−13·5	−12·5	−12·5	−10·5
			(Slit width	0·10	0·10	0·08	0·08 *mm*)
HCl			Na	8·6	17·2	34·5	69·0 *ppm*
	1			0	0	0	0
	3			0	0	0	−0·5
	5			0	0	0	0
	10			0	0	0	0
	30			0	0	0	0
	50			−0·5	0	−0·5	0
	100			−1	−0·5	−0·5	0
	300			−3	−2	−1	0
	500			−5	−3	−1·5	−1
	1000			−9	−4·5	−3·5	−2·5
			(Slit width	0·10	0·08	0·06	0·06 *mm*)
HCl			K	14·7	29·3	58·6	117·3 *ppm*
	1			0	0	1	1
	3			0	0	1	1
	5			0	0	0	0·5
	10			0	0	0	0
	30			−1	−0·5	0	0
	50			−2	−1	−1	0
	100			−4	−3	−1·5	−1
	300			−7	−5·5	−3·5	−2·5
	500			−10	−8	−6	−3·5
	1000			−18	−13·5	−9	−7
			(Slit width	0·045	0·045	0·035	0·035 *mm*)
HCl			Rb	32·0	64·1	128·2	256·4 *ppm*
	1			0	0	0	0
	3			0	0	0	0
	5			0	0	0	0
	10			−1	0	0	0
	30			−2	−1	−0·5	0
	50			−3	−2	−1	0
	100			−5	−3	−2	−1
	300			−11	−7	−5	−2·5
	500			−15	−10	−7	−4
	1000			−23	−17	−13	−7·5
			(Slit width	0·04	0·04	0·04	0·04 *mm*)

Table I (*continued*)

Interferent	Concentration		Change in emission intensity, %				
			Analyte	Concentration			
	mm/l.	*ppm*	Cs	0·375	0·75	1·5	3·0 *mm/l.*
				49·8	99·7	199·4	398·7 *ppm*
HCl							
	1			0	0	0	0
	3			−1	0	0	0
	5			−1	0	0	0
	10			−2	−1·5	−1	0
	30			−3	−2	−1	−0·5
	50			−4·5	−3	−1	−0·5
	100			−9	−5	−2·5	−1
	300			−20	−13	−6·5	−4
	500			−25	−20	−11	−6
	1000			−37·5	−30·5	−20·5	−10
			(Slit width	0·05	0·05	0·05	0·05 *mm*)

* Not corrected for background and other interferences; integral aspirator burner; oxygen, 2·6 l./min; hydrogen, 5·6 l./min.

The greatest suppression of resonance line radiation (Fig. 1) is on the lowest concentration of analyte, because at a given concentration of interferent its mass action effect is greater on the available analyte atoms, thus making a greater proportion unavailable for excitation.

The degree of suppression for each of the alkali elements in the presence of hydrochloric acid is illustrated in Fig. 2. Anion effects of both the chloride and the hydroxide are involved. At the low concentrations of hydrogen chloride the ratio M:MOH and Cl:HCl will largely be fixed, because of the high concentration of the OH and H in the flame. With an increase in the hydrogen chloride aspirated into the flame, and the resulting greater concentration of chloride, there is a shift in the metal atom-metal chloride equilibrium accompanied by a decrease in the M:MCl ratio [equation (6)] and a proportional decrease in the intensity of the resonance line radiation. The increasing suppression of the potassium, rubidium and caesium resonance line radiations is a result of the formation of the increasingly stable metal chlorides, with caesium chloride having the highest dissociation energy.

If the formation of the non-dissociated alkali-metal hydroxides is not considered, this is in agreement with the dissociation energies as determined by Bulewicz *et al.*,[4] but not in agreement with the values determined by Somayajulu[22] for caesium and rubidium chloride (Table II). Dissociation energies for the alkali-metal hydroxides are not available. However, based on the deviation of the degree of ionisation as predicted from the Saha equation[23] and a study of hydroxide formation,[14] the stability of the gaseous alkali-metal hydroxides is in the order Na < K < Rb < Cs < Li. Lithium forms a very stable gaseous hydroxide. There was no deviation for sodium, so the gaseous sodium hydroxide is so unstable as to be effectively absent in the flame. The gaseous potassium hydroxide is nearly as unstable as the sodium hydroxide, and the rubidium and caesium hydroxides are progressively a little more stable.

In addition, the MOH:M ratios,[13] of Table II, would indicate that the formation of potassium, rubidium and caesium hydroxide molecules had no effect or only a minor effect on the resonance line radiation-suppression for these elements. The sodium resonance line radiation was suppressed the least, because sodium hydroxide essentially does not exist in the flame and the sodium chloride has the lowest dissociation energy.

The suppression effect of hydrogen chloride on the intensity of the lithium resonance line is only a little greater than that for sodium. Lithium chloride has the greatest dissociation energy (Table II), and the hydrogen chloride should have a similar mass action effect to form lithium chloride as the other alkali chlorides, if the formation of the stable lithium hydroxide could be neglected. This would indicate that the lithium already exists largely as the highly stable lithium hydroxide, and that few lithium atoms are available to form the stable lithium chloride molecule, thus only a small suppression was observed. If the lithium hydroxide were largely dissociated, then there would be a large suppression arising from the mass action effect of the excess hydrogen chloride and the high dissociation energy of the lithium chloride molecule.

TABLE II.—PHYSICAL VALUES FOR GROUP I ELEMENTS

Element	Resonance line, *A*	Excitation potential, *eV*	Ionisation potential, *eV*	* Ionisation in the flame, %*		
				Air-propane (2200°K)	H_2—O_2 (2450°K)	C_2H_4—O_2 (2800°K)
Li	6707·8	1·84	5·39	0·01	0·9	16·1
Na	5890·0	2·10	5·14	0·3	5·0	26·4
	5895·9	2·10				
K	7664·9	1·61	4·34	2·5	31·9	82·1
Rb	7800·2	1·56	4·18	13·5	44·4	89·6
Cs	8521·1	1·39	3·89	28·3	69·6	96·4

Chloride	Dissociation energy				$\frac{MOH}{M}$ Ratio[13]
	Bulewicz *et al.*[4]	Somayajulu[22]	Gaydon[10]		
Li	110·5 ± 3 *kcal.*	4·8 eV.	5·0 ± 0·3 *kcal.*	115 eV.	4·4
Na	97·5 ± 2	4·12	4·24 ± 0·05	97·6	0
K	99·6 ± 2	4·32	4·40 ± 0·05	101·4	0·19
Rb	101·5 ± 2	4·76	4·5 ± 0·2	103	0
Cs	107·2 ± 3	4·38	4·6 ± 0·2	106	0·37

* Based on a partial pressure of 10^{-6} atmos for the metal atoms in the flame.

The addition of a second ionisable substance, interferent, causes an increase in the partial pressure of the free electrons in the flame. This, through the mass action effect, will decrease the M^+:M ratio in the analyte and increase the population of neutral atoms available for excitation. The partial pressure of the free electrons depends on the ionisation potential and concentration of the interferent. In addition the decrease in the ratio of M^+:M is also dependent on the ionisation potential and concentration of the analyte.

Thus, if the ionisation potential of the analyte is high, there will be few ions from any given concentration, so that even though a relatively large population of electrons is supplied from an interferent, the observed enhancement will be small. This is illustrated by the effect of the other alkali elements on lithium (Figs. 3 and 4).

If the ionisation potential of the analyte is low, a relatively large percentage of the atoms will be ionised, so that an appreciable increase in the electron population from the interferent will cause a large mass action effect, and the observed degree of enhancement will be large. This is most strikingly illustrated by the enhancement effect of caesium on rubidium, and rubidium on caesium (Fig. 4). The degree of enhancement will be greatest on the lowest concentration of analyte, as illustrated by the effect of potassium on different concentrations of caesium (Fig. 1), because the mass action effect of the electron population is greater on the analyte ions, thus making a greater proportion of the atoms available for excitation. In addition, a greater degree of ionisation would have taken place at the lower concentrations.

Caesium, with its low excitation potential (3·89 eV) is highly ionised in the oxygen-hydrogen flame (Table II). The relatively high concentration of electrons causes an appreciable decrease in the $M^+:M$ ratio of the analyte. The degree of this change is dependent on the M^+ population of the analyte, which in turn is dependent on its ionisation potential. Thus, at a given concentration of the analyte, a given concentration of caesium has the greatest enhancement on rubidium (excitation potential 4·18 eV), and successively lesser effect on potassium (4·34 eV), sodium (5·14 eV) and lithium (5·39 eV) (Fig. 4). A similar relation is shown for the effect of rubidium on potassium, sodium and lithium, and of potassium on sodium and lithium. This was also observed for caesium and rubidium on the other alkali elements by Farquhar and Hill[8] and by Bernstein.[1]

In the case of two interferents at a given concentration, the interferent with the lowest ionisation potential may be expected to have the greatest enhancement effect on the analytes with higher excitation potentials. Thus, the enhancement effect caused by caesium on the other alkali elements with higher ionisation potentials should be greater than that caused by rubidium, assuming no other factors to be present. These differences were generally observed (Fig. 4, Table I), although they were not always large.

An interferent with a relatively high ionisation potential, such as sodium, will have the greatest enhancement effect on the resonance line radiation of the analyte with the lowest ionisation potential. Although the additional electron population produced by the interferent is not great, its mass action effect and subsequent enhancement will be greater on the analyte which is ionised to the greatest degree in the flame. This is illustrated by the greater enhancement effect of sodium and of potassium on caesium than on rubidium (Fig. 3). This greater enhancement of an analyte with the lowest excitation potential is illustrated by the results showing that the enhancement effect of rubidium on caesium is greater than that of caesium on rubidium; the effect of potassium is greater on rubidium than that of rubidium on potassium; and the effect of sodium is greater on potassium than that of potassium on sodium (Fig. 3 and 4). The enhancement effects of caesium on rubidium and of rubidium on caesium are somewhat greater than those reported in the more limited results by Pro *et al.*[20]

The presence of lithium causes very little radiation effect on the other alkali elements (Fig. 2). In addition, the radiation intensity of its resonance line is least affected by the presence of the other alkali elements. This would be a result of its high ionisation potential (5·37 eV), so that only a very small percentage of the total atom population is ionised, and any mass action effect is very small. It is suggested that the gaseous lithium hydroxide is quite extensively dissociated in the oxygen-hydrogen flame,[11] so that the small mutual radiation effect of lithium on the other elements is a consequence of its high ionisation potential and not because of its hydroxide making atoms unavailable for ionisation.

The effect of caesium on lithium (Fig. 4) results from the relatively weak caesium 6723·3 A line-addition effect on the lithium 6707·8 A line. Recording of caesium radiation in this region indicated the presence of this line but no band structures.

The large enhancement of potassium on rubidium (Fig. 3) results from spectral interferences of the strong potassium 7699·0 A line, and at very high concentrations the 7664·9 A and 7699·0 A doublet. Part of this error was thought to result from the presence of the K_2 band in this spectral region.[15] However, a brief study using a spectrograph with a large reciprocal dispersion did not reveal these bands in any part of the flame. The true enhancement of rubidium is lower than would be expected (Fig. 3), considering the enhancement of sodium on rubidium and the excitation potential values (Table II). This may be the result of subtracting an incorrect value for the blank, because the rubidium line appears on the shoulder of the spectral tracing for the potassium line.

The temperature also influences the degree of the mutual-cation-enhancement effect. In a hot flame the degree of ionisation of an easily ionised analyte is large (Table II). A high concentration of electrons from an interferent will have a large mass action effect, so that the relative enhancement will be large. If the degree of ionisation of the analyte and interferent is less, as in a lower temperature flame, the degree of enhancement will be less.

Zusammenfassung—Die gegenseitigen Störeinflüsse verschiedener Konzentrationen aller Alkalien und Wasserstoff, die sich als Chloride in der Lösung befanden, auf die Intensität der Resonanzlinie wurden für vier verschiedene Konzentrationen aller Alkalien untersucht. Alle Konzentrationen wurden in Millimolen pro Liter ausgedrückt. Die Störungen waren am größten bei der geringsten und am kleinsten bei der höchsten Konzentrationen jedes Elements. Allgemein beeinflußte Lithium die anderen Elemente am wenigsten und andere Elemente das Lithium am wenigsten. Salzsäure bewirkte wegen des Anioneffekts Verringerung, am meisten beim Caesium. Caesium und Rubidium rufen die größte Erhöhung bei den anderen Elementen hervor. Wegen ihrer sehr niedrigen Ionisationspotentiale stören sich Rubidium und Caesium gegenseitig sehr stark.

Résumé—Les effets de l'influence mutuelle des diverses concentrations des éléments alcalins et de l'hydrogène comme les chlorures en solution, sur les intensités des raies de raisonnance pour quatre concentrations de chacun des éléments alcalins ont été étudiés. Toutes les concentrations sont exprimées en millimoles par litre. Les effets de cette interférence se manifestent le plus aux plus faibles concentrations et réciproquement. En général, le lithium produit le plus faible effet sur les autres éléments, et les autres éléments ont le moins d'effet sur le lithium. L'hydrogène, comme l'acide chlorhydrique, supprime cet effet par action de l'anion, principalement sur le césium. Le césium et le rubidium exercent la plus grande exaltation sur les autres éléments. A cause de leurs potentiels d'ionisation très bas, les effets d'interférence mutuelle du rubidium et du césium sont très importants.

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SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM(VII) AFTER EXTRACTION WITH 2-THENOYLTRIFLUORACETONE

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Summary—A new method is proposed for the determination of rhenium(VII) at the microgram level. 2-Thenoyltrifluoracetone in isoamyl alcohol-benzene extracts rhenium(VII) quantitatively from 7–9*N* sulphuric acid. Treatment of this organic extract with tin(II) chloride and potassium thiocyanate gives a yellow coloured product which can be measured at 430 mμ. Beer's law is valid over the concentration range of 0·5–5 μg of rhenium/ml. The effect of diverse ions has been studied.

THE well-known chelating agent 2-thenoyltrifluoracetone (TTA) has been found useful for the extraction of a large number of metals. The review article by De and Khopkar[1] covers the literature up to 1961, since when about another 50 publications have appeared. TTA has now been applied to the extraction of rhenium(VII). With TTA, rhenium(VII) forms a colourless chelate which can be extracted with isoamyl alcohol-benzene from a sulphuric acid medium. For spectrophotometric evaluation of the rhenium(VII) the organic extract is treated with potassium thiocyanate and tin(II) chloride to give a yellow coloured product,[2] which can be measured at 430 mμ. This forms the basis of a new method for the extraction and spectrophotometric determination of rhenium(VII) at microgram level.

Earlier work on the ether extraction of rhenium thiocyanate complex has been described by Sandell.[2] 2,4-Diphenylthiosemicarbazide forms a red coloured product with rhenium and it is extractable into chloroform.[3] Rhenium, reduced with tin(II) chloride, can be extracted with benzildioxime-benzyl alcohol.[4] Tetraphenylarsonium chloride has been used to extract rhenium into chloroform.[5] In 4*M* sodium hydroxide solution rhenium has been extracted with pyridine.[6] Thio-oxine in chloroform can extract rhenium from a strong hydrochloric acid medium.[7] Methyl Violet in toluene[8] and diethylphosphorodithioic acid in benzene[9] have been reported to extract rhenium. Other extractants for this element include 4-methylcyclohexane-1,2-dione dioxime,[10] dimethylglyoxime,[11] α-furildioxime,[12] thiourea and diphenylthiourea[13] and toluene-3,4-dithiol.[14]

EXPERIMENTAL

Apparatus

A Unicam SP 600 spectrophotometer with 1-cm glass cells was used for the absorbance measurements.

Reagents

The reagents used were either chemically pure or reagent grade materials unless otherwise mentioned.

2-Thenoyltrifluoracetone (TTA). An approx. 0·15*M* solution of TTA (Columbia Organic Chemicals, Columbia, S. Carolina, U.S.A.) in isoamyl alcohol was used.

Stock solution of ammonium perrhenate. Prepared by dissolving ammonium perrhenate (Johnson, Matthey & Co. Ltd., London, England) in water containing 0·3N sulphuric acid. The solution, standardised by the nitron method,[15] contained 344 μg of rhenium/ml. Test solutions containing 34.4 μg of rhenium/ml were prepared by ten-fold dilution of the stock solution with 0·3N sulphuric acid.

20% *Potassium thiocyanate solution*

35% *Tin(II) chloride solution.* Prepared by dissolving 35 g of tin(II) chloride in 20 ml of 1:1 hydrochloric acid and diluting to 100 ml.

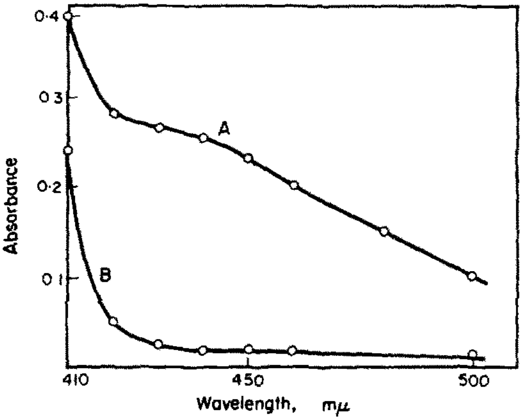


Fig. 1.—A. Absorption spectrum of rhenium thiocyanate [TTA chelate treated with tin(II) chloride-potassium thiocyanate] in isoamyl alcohol-benzene (Re = 1·478 × $10^{-5}M$; TTA = 0·15M; 7·6N sulphuric acid) *vs.* solvent mixture.
B. Reagent blank *vs.* solvent mixture.

General procedure

A suitable aliquot (0·5–4 ml) of ammonium perrhenate solution, containing 34·4 μg of rhenium/ml, was mixed with 10 ml of 7·6N sulphuric acid in a 250-ml separating funnel. For acidity studies, a suitable acid of desired strength was used. For the study of diverse ions, a solution containing the foreign ion was introduced before the addition of acid. Rhenium was extracted with 10 ml of 0·15M TTA in isoamyl alcohol plus 5 ml of benzene (pre-equilibrated with the acid) by shaking for 5 min, then the layers were allowed to settle and separate. The aqueous phase was titrated for the determination of acid when necessary and tested for the presence of rhenium (duplicate runs). To the separated organic phase 25 ml of 1:4 hydrochloric acid, 2 ml of 20% potassium thiocyanate and 1 ml of 35% tin(II) chloride were added and the mixture shaken for 5 min.[9] The resultant organic extract was filtered (to remove traces of water) into a 25-ml volumetric flask and diluted to 25 ml with isoamyl alcohol. The absorbance of this solution was then measured at 430 mμ against a reagent blank.

RESULTS AND DISCUSSION

Absorption curve

The absorption spectrum of a solution of the rhenium(VII)–TTA chelate extracted and processed as under *General procedure*, is shown in Fig. 1. All further measurements were carried out at 430 mμ where minimum reagent absorption occurs. The absorptivity at 430 mμ is 16240 ± 196.

Effect of acidity

The extraction of rhenium starts at an acidity of about 0·5N sulphuric acid, gradually increases and becomes 100% from 7·6N (equilibrium 7·12N) sulphuric acid onwards. This is shown in Fig. 2. The optimum acidity is 7·6–9·5N in sulphuric acid (equilibrium 7·12–9·04N). The distribution ratio in each case was calculated from the amount of rhenium in the organic phase and in the aqueous phase (the latter obtained by difference from the total amount taken), the values being recorded in Table I.

A hydrochloric acid medium is unsuitable because the extraction is incomplete.

The organic phase gave the test of rhenium(VII) only—with thiocyanate, colour was developed only after reduction with tin(II) chloride and furthermore, reaction with nitron gave a positive result. This ruled out the possibility of the existence of lower oxidation states of rhenium. The extracted species is presumably an ion-association compound having the structure:

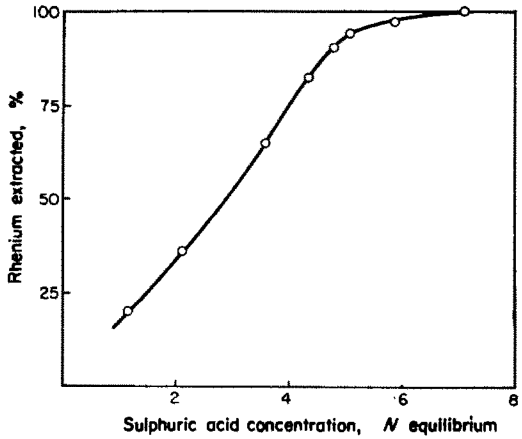
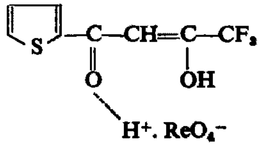


Fig. 2.—Extraction of rhenium-TTA chelate with isoamyl alcohol-benzene as a function of sulphuric acid concentration.



This is analogous to the cupferrate complex of pertechnetate, Cup$^+$. TcO$_4^-$ reported by Elving *et al.*[16]

Calibration curve

The absorbances of different amounts of rhenium were measured at 410, 420, 430, 440 and 450 mμ against a reagent blank. The results prove that Beer's law is valid, as in the ether extraction method,[2] at 430 mμ over the concentration range of 0·5 to 6 μg of rhenium/ml.

The optimum TTA reagent concentration is 0·15*M* and the optimum period of extraction 5 min. The coloured system is stable for up to 2 hr, within which time measurements must be made.

Diverse ions

A number of binary mixtures of rhenium(VII) with other ions were prepared for the examination of interferences in the *General procedure* (7·6*N* sulphuric acid). The tolerance limit for each ion (Table II), represents that concentration of the foreign

Table I.—Extraction of rhenium (68·8 μg) as a function of acid concentration

Sulphuric acid, *N* (equilibrium)	Distribution ratio,[a] *D*
1	0·17
1·17	0·20
2	0·41
2·09	0·45
3	0·86
3·58	1·48
4	2·4
4·34	3·66
4·8	7·28
5·09	13·4
5·88	28·83
6	39·2
6·5	79·2
7·12 to 9·04	100% extraction

[a] $D = \frac{[\mathrm{Re^{VII}}] \text{ per ml of organic phase}}{[\mathrm{Re^{VII}}] \text{ per ml of aqueous phase}}$.

Table II.—Effect of diverse ions on the determination of rhenium (68·8 μg)

Diverse ion	Added as	Tolerance limit, μg
U^{6+}	$UO_2(NO_3)_2.6H_2O$	1000
Fe^{3+}	$FeCl_3.6H_2O$	1000
Cr^{3+}	$Cr_2(SO_4)_3.18H_2O$	5000
Mn^{2+}	$MnSO_4.5H_2O$	5000
Co^{2+}	$CoSO_4.7H_2O$	5000
Ni^{2+}	$NiSO_4.5H_2O$	5000
Cu^{2+}	$CuSO_4.5H_2O$	5000
Zr^{4+}	$ZrOCl_2$	5000
Th^{4+}	$Th(NO_3)_4.4H_2O$	5000
Ta^{5+}	Tantalum tartrate	1000
W^{6+}	Na_2WO_4	1000
PO_4^{3-}	$(NH_4)_2HPO_4$	10,000
F^-	NaF	10,000
Cl^-	NaCl	10,000
SCN^-	KSCN	10,000
EDTA	Disodium salt	10,000
Citrate	Citric acid	10,000
Tartrate	Tartaric acid	10,000
Oxalate	Sodium oxalate	10,000

ion in the presence of which the absorbance of rhenium is obtained within ±2%. It should be noted that silver, zinc, bismuth, aluminium, mercury(II) and manganese(VII) do not show any interference even in large amounts. It is interesting that manganese(VII) is reduced by isoamyl alcohol in TTA solution and hence does not affect the extraction procedure. Thus, 68·8 μg of rhenium(VII) can be extracted in the presence of 100 times its amount of manganese(VII).

Palladium(II), molybdenum(VI), vanadium(V), titanium(IV), cerium(IV) and lead interfere, but moderate amounts of platinum(IV) and niobium(V) can be tolerated.

Molybdenum, if present, must be removed by a preliminary extraction. In the presence of mercury(I) nitrate and potassium thiocyanate,[17] molybdenum can be extracted with ether, then the rhenium can be extracted subsequently from the aqueous phase and measured as in the *General procedure*.

The interference from vanadium(V) and titanium(IV) can be removed by masking them with hydrogen peroxide in the acidic medium used. Cerium(IV) and palladium(II) can be eliminated by prior extraction at pH 6 with 0·5*M* TTA.

It should be possible to determine rhenium in fission residues by the proposed method. Thorium, zirconium, strontium, yttrium and caesium do not interfere. Uranium(VI) can be removed by preliminary extraction at pH 6 with TTA-benzene. Molybdenum and cerium (neodymium) can be removed as above.

With 68·8 μg of rhenium from ten runs, the absorbance measured was 0·24 ± 0·003. The sensitivity is 0·0112 $\mu g/cm^2$ (*cf.* 0·005 $\mu g/cm^2$ in the ether extraction method). The proposed method compares well with the standard ether extraction method as regards speed, accuracy and sensitivity.

It is superior to the standard ether method in that the solvent, *viz.* isoamyl alcohol-benzene, is much less volatile and more stable than ether; also in that the colour of the thiocyanate system is fairly stable and there is no deposition of solid on standing as in the ether method, leading to unsteady readings.

Analysis of an industrial material

Unfortunately, no rhenium-containing industrial material was available to the authors to test the proposed method for determination of rhenium. The method was, therefore, tested by introducing rhenium into a dissolved standard steel sample and ascertaining the recovery of rhenium.

A known weight (*ca.* 0·1 g) of alloy steel No. 64a (Bureau of Analysed Samples Ltd., Newham Hall, Yorks., U.K.; Fe 80%, Cr 4%, V 2%, Mo 4%, W 6%) was dissolved in sulphuric-nitric acids as described before,[18] 860 μg of rhenium (ammonium perrhenate) added and the solution made up to 100 ml. An aliquot of this solution (4 ml) was taken. Iron was first removed by adjusting the pH to 1 and extracting with two 50-ml portions of acetylacetone-chloroform (50%). To the aqueous phase was added concentrated sulphuric acid to make the solution 2*N* in this acid, molybdenum reduced with mercury(I) nitrate and the solution treated with thiocyanate and extracted with ether as described before. The residual aqueous phase was evaporated to about 2 ml, and 20 ml of 12*N* sulphuric acid and 5 ml of 20 vol. hydrogen peroxide added. Vanadium was masked and rhenium extracted with TTA and determined as under *General procedure*. Chromium(III) and tungsten(VI) did not interfere in the analytical range used.

The results from triplicate analysis as above were: 838, 848 and 840 μg of rhenium (rhenium taken: 860 μg).

Zusammenfassung—Eine neue Methode zur Bestimmung von Rhenium-(VII) im Mikrogrammbereich wird vorgeschlagen. 2-Thenoyltrifluoraceton in Isoamylalkohol-Benzol extrahiert Rhenium(VII) quantitativ aus 7–9 n Schwefelsäure. Behandlung des organischen Extrakts mit Zinn(II)-chlorid und Kaliumrhodanid gibt ein gelbes Produkt, das bei 430 mμ photometriert werden kann. Das Beersche Gesetz gilt von 0,5 bis 5 μg Rhenium im ml. Der Einfluß verschiedener Ionen wurde untersucht.

Résumé—On propose une nouvelle méthode de dosage du rhénium(VII) à l'échelle du microgramme. La 2-thénoyltrifluoracétone en alcool isoamylique-benzène extrait quantitativement le rhénium(VII) à partir de ses solutions dans l'acide sulfurique 7–9 N. Le traitement de cet extrait organique par le chlorure stanneux et le sulfocyanure de potassium donne un produit coloré en jaune que l'on peut mesurer à 430 mμ. La loi de Beer est respectée pour des concentrations en rhénium comprises entre 0,5 et 5 μg/ml. On a étudié l'influence de divers ions.

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PRECIPITATION OF ZINC SULPHIDE FROM AMMONIACAL SOLUTIONS BY THIOACETAMIDE*

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Summary—The rate at which thioacetamide precipitates zinc sulphide from ammoniacal zinc solutions is controlled mainly by two types of reaction: reactions between the various zinc species and thioacetamide, and reactions between the zinc and the sulphide produced by an ammonia-thioacetamide reaction; the sulphide from the hydroxide catalysed hydrolysis of thioacetamide is relatively small. The rate expression for reactions of the first type is

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

The rate of precipitation by the second process is controlled by the rate at which sulphide is formed by the ammonia-thioacetamide reaction; this rate expression is

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

INTRODUCTION

STUDIES carried out in these laboratories of the rates of precipitation of various metal sulphides by thioacetamide [TAA] have shown that these precipitation rates are controlled by either or both of two types of reaction process. These studies indicate that one of these processes involves a reaction between the metal and TAA; the second process involves a reaction between the metal and the sulphide produced by reaction of TAA with one or more constituents in the solution. In the cases studied the rate of precipitation by this latter process is the same as the rate of production of sulphide; therefore, the rate expression for the precipitation is identical with that for the production of sulphide. Rate studies have been made of the production of sulphide from TAA by hydrolysis catalysed by acid[1] and by base,[2] by reactions in ammonia-ammonium chloride and in carbonate-hydrogen carbonate buffers[3] and by reaction with hydrazine.[4]

The precipitation of zinc sulphide from acid solutions has been found[5] to proceed by both the direct reaction and the acid catalysed hydrolysis reaction. The rate equation for this precipitation at 90°, in units of moles, litres and minutes, is

$$-\frac{d[Zn^{2+}]}{dt} = 4{\cdot}2 \times 10^{-4}\frac{[Zn^{2+}][CH_3CSNH_2]}{[H^+]^{1/2}} + 0{\cdot}23\,[H^+][CH_3CSNH_2].$$

The present paper extends the study of the precipitation of zinc sulphide by TAA to ammoniacal solutions. Precipitation of metals from ammonia buffer systems is of

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interest because of the high stability of many metal-ammonia complexes, and because by control of the ammonia-TAA reaction one can vary the rate of sulphide formation at constant pH.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. The TAA was Arapahoe Chemical Co. material. Stock solutions were prepared and, when necessary, were standardised by conventional methods. Disodium ethylenediaminetetra-acetate (EDTA) solution, 0·01 *VF* (volume formal), was standardised against metallic zinc.

Procedure

A reaction solution was prepared from distilled water and stock solutions of ammonia, ammonium nitrate and zinc nitrate, and the ionic strength was adjusted to 0·65 with sodium nitrate when necessary. The solution, contained in a 38 × 200 mm-stoppered test tube, was preheated to slightly above 40°, the desired volume of TAA solution at room temperature added and the tube immersed in a water bath at 40 ± 0·5°. At timed intervals a sample of the suspension was removed and rapidly filtered through a fritted glass filter. Duplicate 5.00-ml aliquots of this filtrate were then acidified and boiled to destroy the excess thioacetamide and volatilise the hydrogen sulphide formed. These solutions were adjusted to a pH of about 10 with an ammonia-ammonium chloride buffer, and the zinc was titrated with the EDTA solution; Eriochrome Black T was used as indicator.

The initial over-all rate of precipitation was obtained from the experimental points by graphical methods. The reactions were followed until about 20–30% of the zinc had precipitated.

RESULTS AND DISCUSSION

The symbol [Zn(II)] represents the total (volume formal) concentration of zinc in the solution; therefore, $[\mathrm{Zn(II)}] = \sum_{n=0}^{4} [\mathrm{Zn(NH_3)_n}^{2+}]$. The ammonia concentrations given in the rate expressions are the free ammonia concentrations, *i.e.*, the total concentration of ammonia added less the amount present in zinc ammines.

Ammonia-thioacetamide reaction

Peters and Swift[3] have studied the reactions of thioacetamide in ammonia buffers over the temperature range of 60° to 90°. The rate of production of sulphide is described by the following equation:

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = k[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2$$

where $k = 0{\cdot}055 \pm 0{\cdot}001$ litre^2.mole^{-2}.min^{-1} at 90°, and 0·012 at 60°.

The present work was carried out at 40°, and the corresponding value of k was determined, using a method similar to that of Peters and Swift. Seven experiments gave a mean value of k at 40° of $(5{\cdot}0 \pm 0{\cdot}2) \times 10^{-3}$ litre^2.mole^{-2}.min^{-1}.

The sulphide produced by the ammonia-thioacetamide reaction was assumed to react rapidly and quantitatively to form zinc sulphide. Therefore, the rate of precipitation of zinc sulphide by the ammonia-thioacetamide reaction could be calculated from the expression

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = 5{\cdot}0 \times 10^{-3}[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

Direct reaction

Under the conditions of this study, both the ammonia-thioacetamide reaction and the direct reaction took place to a significant extent. The reaction rate observed was the sum of the two reaction rates, from which the rate of the direct reaction was obtained by difference.

Effect of zinc and thioacetamide concentrations

Table I shows the results of experiments in which the initial thioacetamide concentration was varied from 0·0100*VF* to 0·0500*VF* at initial zinc concentrations of 0·0100 and 0·00250*VF*. When necessary, the total ammonia concentration was so varied as to keep the concentration of uncomplexed ammonia constant. The values in Table I indicate that the rate of the direct reaction is first order with respect to both zinc and thioacetamide.

TABLE I.—EFFECT OF ZINC AND THIOACETAMIDE CONCENTRATIONS ON THE INITIAL RATE OF PRECIPITATION OF ZINC SULPHIDE

TAA, *VF*	Zn(II), *VF*	Observed rate of precipitation, *mole.litre*$^{-1}$*.min*$^{-1}$	Calculated rate of NH_3—CH_3CSNH_2 reaction,[a] *mole.litre*$^{-1}$*.min*$^{-1}$	Calculated rate of direct reaction, *mole.litre*$^{-1}$*.min*$^{-1}$	K'_{direct},[b] *litre.mole*$^{-1}$*.min*$^{-1}$
0·0100	0·0100	1·65 × 10^{-6}	0·07 × 10^{-6}	1·58 × 10^{-6}	0·158
0·0150	0·0100	2·58	0·10	2·48	0·165
0·0200	0·0100	3·44	0·13	3·31	0·165
0·0500	0·0100	8·39	0·32	8·07	0·161
0·0100	0·00250[c]	0·418	0·066	0·352	0·160

(Initial conditions: total NH_3 = 0·154*VF*; calculated free $[NH_3]$ = 0·115*VM*; $[NH_4^+]$ = 0·265*VM*; pH = 8·41, temperature = 40°.)

[a] Calculated from expression $\frac{-d[Zn(II)]}{dt} = 5{\cdot}0 \times 10^{-4}[CH_3CSNH_2][NH_3]^2$.

[b] Calculated from expression $\frac{-d[Zn(II)]}{dt} = K'[CH^3CSNH_2][Zn(II)]$.

[c] Initial total NH_3 = 0·125*VF*; initial free $[NH_3]$ = 0·115*VM*.

Effect of ammonia concentration

Bjerrum[6] has found that zinc forms four ammine complexes in aqueous solutions, and has determined the formation constants. The general equilibrium expression for their formation is

$$\frac{[Zn(NH_3)_n{}^{2+}]}{[Zn(NH_3)_{n-1}^{2+}][NH_3]} = K_n.$$

For each concentration of free ammonia the relative concentration of each zinc-ammine and n̄, the average coordination number of zinc, were calculated. This information is presented in Table II. The concentration of the aquated zinc ion is negligible and not included in the calculations below.

TABLE II.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE CONCENTRATION OF ZINC AMMINES

Free $[NH_3]$, *VM*	Average co-ordination number, n̄	Percentage of total zinc present as			
		$Zn(NH_3)_4{}^{2+}$	$Zn(NH_3)_3{}^{2+}$	$Zn(NH_3)_2{}^{2+}$	$Zn(NH_3)^{2+}$
0·280	3·97	96·0	3·93	0·07	—
0·115	3·89	89·8	9·79	0·47	—
0·0800	3·84	85·5	13·4	0·94	0·08
0·0600	3·79	81·0	17·3	1·66	0·18
0·0400	3·69	73·0	23·1	3·34	0·53

Fig. 1 shows the dependence of the initial precipitation rates, both of the total reaction and of the direct reaction, upon the ammonia concentration. The observed relationship between the ammonia concentration and the rate of the direct reaction may be attributed to different rates of reaction of the various zinc-ammine species with thioacetamide. Individual second-order rate constants, k_n', for each zinc-ammine species were computed from a system of simultaneous equations based on the values in Fig. 1 and Table II. These equations were of the following form:

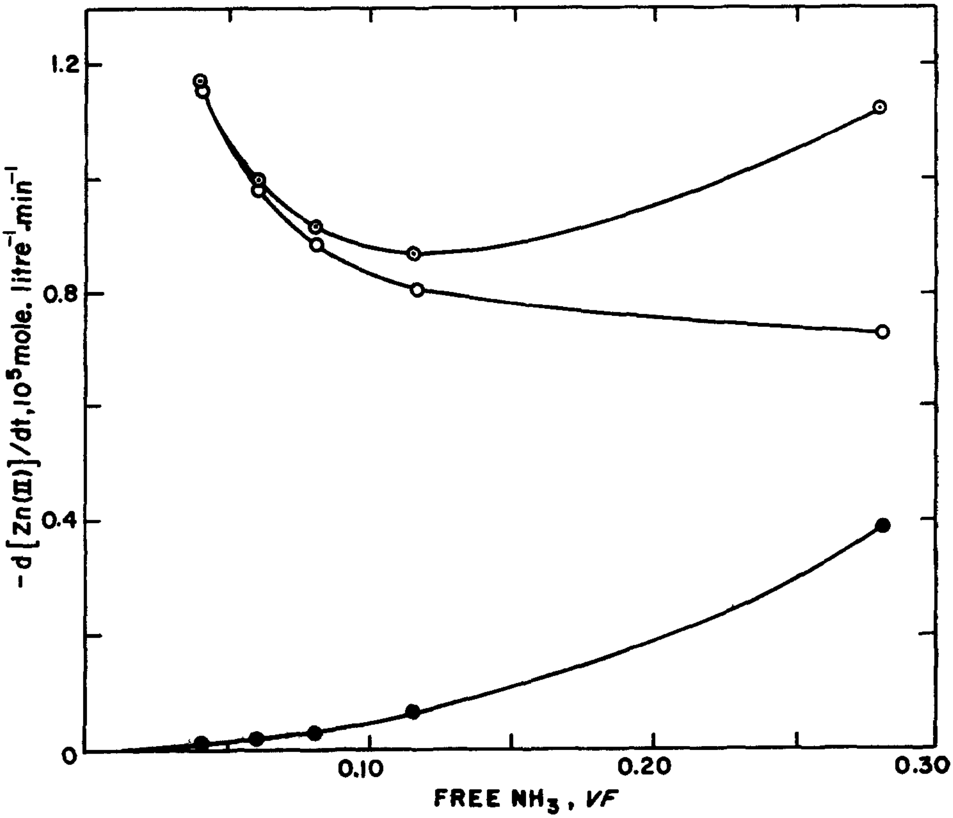

FIG. 1.—Effect of ammonia concentration on rate of precipitation of zinc sulphide (initial conditions: [Zn(II)] = 0·01 *VF*; CH_3CSNH_2 = 0·005 *VF*; pH = 8·41; temperature = 40°):—
⊙—over-all reaction,
○—direct reaction,
●—NH_3–TAA reaction.

$$-\frac{d[Zn(II)]}{dt} = [Zn(II)][CH_3CSNH_2]\left(k_4'\frac{[Zn(NH_3)_4{}^{2+}]}{[Zn(II)]} + k_3'\frac{[Zn(NH_3)_3{}^{2+}]}{[Zn(II)]} + k_2'\frac{[Zn(NH_3)_2{}^{2+}]}{[Zn(II)]} + k_1'\frac{[Zn(NH_3)^{2+}]}{[Zn(II)]}\right).$$

It can be seen that K′, as given in Table I, corresponds to the term in parentheses in the above equation.

The best values of the individual second-order rate constants are:

$$k_4' = 0{\cdot}136, \quad k_3' = 0{\cdot}39, \quad k_2' = 0{\cdot}93, \quad k_1' = 2{\cdot}3 \text{ litre.mole}^{-1}\text{.min}^{-1}.$$

Effect of pH

The effect of pH on the direct reaction was studied over a pH range of 8·12 to 9·13. The results presented in Table III indicate that the rate of the direct reaction is inversely proportional to the two-thirds power of the hydrogen ion concentration.

TABLE III.—EFFECT OF pH ON THE INITIAL RATE OF PRECIPITATION OF ZINC SULPHIDE

pH	Observed rate of precipitation, *mole.litre^{-1}.min^{-1}*	Calculated rate of direct reaction,[a] *mole.litre^{-1}.min^{-1}*	K'_{direct},[b] *litre.min^{-1}.mole^{-1}*	K'',[c] *litre$^{1/3}$.mole$^{-1/3}$.min^{-1}*
9·13	$4{\cdot}75 \times 10^{-5}$	$4{\cdot}62 \times 10^{-5}$	0·462	$3{\cdot}84 \times 10^{-7}$
8·84	3·06	2·93	0·293	3·80
8·41	1·74	1·61	0·161	3·90
8·12	1·12	0·99	0·099	3·85

(Initial conditions: $[\text{Zn(II)}] = 0{\cdot}005\,VF$; $[CH_3CSNH_2] = 0{\cdot}0200\,VM$; total $NH_3 = 0{\cdot}134\,VF$; free $[NH_3] = 0{\cdot}115\,VM$; temperature = 40°.)

[a] Obtained from observed over-all rate by subtracting the rate of the ammonia-thioacetamide reaction, $0{\cdot}13 \times 10^{-5}$ mole.litre^{-1}.min^{-1}.

[b] Calculated from the expression $-d[\text{Zn(II)}]/dt = K'[CH_3CSNH_2][\text{Zn(II)}]$.

[c] Calculated from the expression $-d[\text{Zn(II)}]/dt = K''[CH_3CSNH_2][\text{Zn(II)}]/[H^+]^{2/3}$.

According to Bjerrum[6] the formation constants of the various metal ammines depend on the ammonium nitrate concentration; however, the variation in the ammonium ion concentrations was not large enough to affect significantly the relative concentrations of the various ammines.

Rate expression

The true rate constants, k_n, may be obtained from the second-order constants, k_n', measured at pH 8·41. The values of the true rate constants at 40°, expressed in litre$^{1/3}$.mole$^{-1/3}$.min^{-1}, are:

$$k_4 = 3{\cdot}1 \times 10^{-7}, \quad k_3 = 8{\cdot}9 \times 10^{-7}, \quad k_2 = 21 \times 10^{-7}, \quad k_1 = 53 \times 10^{-7}.$$

It can be seen that as n decreases by 1, the rate constant increases by a factor of about 2·5. Therefore, k_0, the rate constant for the completely aquated zinc ion, may be estimated as $1{\cdot}3 \times 10^{-5}$. Bowersox, Smith and Swift[5] have studied the thioacetamide precipitation of zinc sulphide from non-complexing acidic media at 90°. Extrapolation of their data to 40° yields a value of the direct reaction rate constant of 1×10^{-5}. The agreement between this value and the estimated value of k_0 is surprising in view of the fact that in acidic media the rate varies inversely with the square root of the hydrogen ion concentration, while in the present work the rate varies inversely with the two-thirds root.

The kinetic expression for the over-all rate of precipitation of zinc sulphide from an ammoniacal solution by thioacetamide at 40° is as follows, in units of moles, litres and minutes:

$$\begin{aligned} -\frac{d[\text{Zn(II)}]}{dt} = \frac{10^{-7}[CH_3CSNH_2]}{[H^+]^{2/3}} & (3{\cdot}1[\text{Zn}(NH_3)_4{}^{2+}] \\ & + 8{\cdot}9[\text{Zn}(NH_3)_3{}^{2+}] + 21[\text{Zn}(NH_3)_2{}^{2+}] + 53[\text{Zn}(NH_3)^{2+}] \\ & + 130[\text{Zn}^{2+}]) + 5{\cdot}0 \times 10^{-3}[CH_3CSNH_2][NH_3]^2. \end{aligned}$$

Precipitation at high concentrations of zinc and thioacetamide

At concentrations of zinc and thioacetamide somewhat higher than those in the above experiments, and particularly at the lower ammonia concentrations, the behaviour of the system differed from that previously observed, the most apparent change being the precipitation of as much as four-fifths of the zinc during the mixing process. When this initial rapid precipitation was not observed, the course of the reaction was adequately described by the above rate expression and rate constants. Although the rate data from each experiment with concentrated solutions fit the expression

$$-\frac{d[Zn(II)]}{dt} = K'_{direct}[Zn(II)]$$

the value found for K'_{direct} depended strongly upon the method of addition of thioacetamide to the reaction mixture, the age of the thioacetamide solution and the presence of added seed crystals of zinc sulphide in the reaction mixture. This variation in rate, caused by nucleation effects, has been investigated and will be reported separately.[7]

ANALYTICAL CONSIDERATIONS

The zinc-sulphide precipitate obtained with thioacetamide was relatively dense and granular and, therefore, could be readily separated from the supernatant by filtration or centrifugation.

The results presented here suggest that with suitable modification of procedure thioacetamide may be substituted for hydrogen sulphide as a sulphide precipitant in ammoniacal systems. The dependence of the rates of both the direct reaction and the ammonia-thioacetamide reaction on the ammonia concentration permit the over-all precipitation rate to be varied over rather wide limits, even at constant temperature and pH. This increased control over the precipitation rate would seem to be advantageous in carrying out effective separations in ammoniacal media; however, no definite conclusions concerning separations can be drawn until the behaviour of each combination of elements involved has been studied.

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Zusammenfassung—Die Geschwindigkeit der Fällung von Zinksulfid aus ammoniakalischen Lösungen mit Thioacetamid wird hauptsächlich durch zwei Reaktionstypen kontrolliert: Reaktionen zwischen den verschiedenen Zinkspezies und Thioacetamid und Reaktionen zwischen Zink und dem aus der Reaktion zwischen Ammoniak und Thioacetamid stammenden Sulfid; die aus der durch Hydroxylionen katalysierten Hydrolyse von Thioacetamid stammende Sulfidmenge ist relativ klein. Die Geschwindigkeitsgleichung für Reaktionen des ersten Typs ist

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

Die Fällungsgeschwindigkeit nach dem zweiten Prozeß wird durch Geschwindigkeit der Sulfidbildung aus Ammoniak und Thioacetamid bestimmt; dieser Geschwindigkeitsausdruck lautet

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

Résumé—On contrôle la vitesse à laquelle le thioacétamide précipite le sulfure de zinc à partir de solutions ammoniacales de zinc essentiellement par deux types de réactions: réactions entre les différentes espèces du zinc et la thioacétamide, et réactions entre le zinc et le sulfure produit par une réaction ammoniaque-thioacétamide; le sulfure produit par l'hydrolyse du thioacétamide catalysée par l'hydroxyde est relativement faible. L'équation de vitesse pour les réactions du premier type est:

$$-\frac{d[Zn(II)]}{dt} = \sum_{n=0}^{4} k_n[CH_3CSNH_2][Zn(NH_3)_n{}^{2+}][H^+]^{-2/3}.$$

La vitesse de précipitation selon le second processus est contrôlée par la vitesse à laquelle se forme le sulfure dans la réaction ammoniaque-thioacétamide; cette équation de vitesse est:

$$-\frac{d[CH_3CSNH_2]}{dt} = -\frac{d[Zn(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

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PRECIPITATION OF NICKEL SULPHIDE FROM AMMONIACAL SOLUTIONS BY THIOACETAMIDE†

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Summary—The rate of precipitation of nickel sulphide from ammoniacal solutions by thioacetamide is controlled mainly by two types of reaction: reactions between the various nickel species and thioacetamide, and reactions between the nickel species and the sulphide produced by a thioacetamide-ammonia reaction. The sulphide produced by the hydroxide-catalysed hydrolysis of thioacetamide is relatively small. The rate expressions for these two predominant processes are, respectively,

$$-\frac{d[Ni(II)]}{dt} = \sum_{n=0}^{6} k_n[Ni(NH_3)_n{}^{2+}][CH_3CSNH_2][H^+]^{-2/3}$$

and

$$-\frac{d[Ni(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

INTRODUCTION

PREVIOUS studies of the rates of precipitation of metal sulphides by thioacetamide (TAA) have indicated that two processes are involved in these precipitations. In one of these the TAA reacts with some constituent of the solution to liberate sulphide, which then forms the precipitate; in such cases the rate of sulphide formation limits the rate of the precipitation. Precipitation by the other process occurs without the intermediate formation of sulphide from TAA. In the latter case the reaction appears to take place directly between the metal ion and TAA; this process is called the *direct reaction*.

Within the accuracy of the measurements, the rate of precipitation of nickel sulphide from acidic solutions has been found to be controlled by the direct reaction only.[2] The rate equation for this precipitation at 90°, in units of moles, litres and minutes, is

$$-\frac{d[Ni^{2+}]}{dt} = 2{\cdot}2 \times 10^{-4}\,[Ni^{2+}][CH_3CSNH_2][H^+]^{-1/2}.$$

An experimental study[3] of the precipitation of zinc sulphide by TAA from solutions buffered by ammonia and ammonium ion has indicated that the hydrated zinc ion and the zinc ammines are precipitated *via* both routes. The direct reaction with each zinc species is characterised by a different value of the direct-reaction rate constant.

A study of the precipitation of nickel sulphide by TAA from ammoniacal solutions is presented here. In such solutions, sulphide is produced predominantly by a TAA-ammonia reaction, the rate of which depends upon the square of the ammonia

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concentration. Washizuke[4] has reported that precipitation occurs by a different mechanism in more concentrated ammonia solutions (0·4–1·2*M*); in these solutions the rate of precipitation of nickel sulphide appears to be dependent on the rate of a base-catalysed reaction between TAA, NH_3 and OH. In the present systems, and in those studied by Washizuke, the rate of precipitation by processes other than the direct reaction can be controlled by varying the ammonia concentration.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. The TAA was Arapahoe Chemical Company material. Stock solutions were prepared and, when necessary, were standardised by conventional methods. The reaction solutions were prepared from distilled water and stock solutions of ammonia, ammonium nitrate and nickel(II) nitrate. The ionic strength of the reaction solutions was adjusted to 0·30 with sodium nitrate.

Procedure

The solution, contained in a 38 × 200-mm stoppered test tube, was preheated to slightly above 40°, the appropriate volume of TAA solution at room temperature added and the tube immersed in a water bath at 40° ± 0·5°. At timed intervals a sample of the suspension was removed and filtered through a fritted glass filter into a tube containing solid disodium ethylenediaminetetra-acetate (EDTA). The excess solid EDTA was removed by filtration, and the concentration of nickel in the solution determined colorimetrically. Confirmatory analyses showed that this procedure gave results reproducible to within 3%.

The initial rates of precipitation reported below were obtained graphically from the experimental points. The reactions were followed only until approximately 20% of the nickel was precipitated; this reduced the effect of the increase in ammonia concentration caused by release of ammonia from the nickel ammines.

RESULTS AND DISCUSSION

In the subsequent discussion, the symbol [Ni(II)] represents the total (volume formal) concentration of nickel in solution; therefore

$$[\mathrm{Ni(II)}] = \sum_{n=0}^{6} [\mathrm{Ni(NH_3)_n}^{2+}].$$

The ammonia concentrations shown in the rate expressions are for free ammonia.

Ammonia-thioacetamide reaction

The rate of precipitation of nickel sulphide as a result of this reaction was assumed to be equal to the calculated rate of formation of sulphide. The rate expression is therefore

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = -\frac{d[\mathrm{Ni(II)}]}{dt} = k\,[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2.$$

The value of the rate constant k at 40° has been found[2] to be $5{\cdot}0 \times 10^{-3}$ litre^2. mole^{-2}. min^{-1}.

Effect of nickel and thioacetamide concentrations

Table I presents the results of experiments in which the initial nickel and TAA concentrations were varied at constant pH and free ammonia concentration. The results indicate that the direct reaction rate is dependent on the first order of both Ni(II) and TAA concentration.

Effect of pH

The rate of the direct reaction was studied over the pH range of 8·67 to 9·49. As shown in Table I, at these hydrogen-ion concentrations, the rate appears to be inversely proportional to the two-thirds power of the hydrogen-ion concentration.

TABLE I.—EFFECT OF NICKEL, THIOACETAMIDE AND HYDROGEN-ION CONCENTRATIONS ON THE INITIAL RATE OF PRECIPITATION OF NICKEL SULPHIDE

TAA, *VF*	Ni(II), *VF*	pH	$[H^+]^{2/3}$, *VM*	Observed rate, *mole. litre⁻¹. min⁻¹*	Rate of direct reaction,[a] *mole. litre⁻¹. min⁻¹*	K,[b] *mole. litre⁻¹. min⁻¹*
0·100	0·0100	9·22	$7·1 \times 10^{-7}$	$3·0 \times 10^{-5}$	$2·7 \times 10^{-5}$	$1·9 \times 10^{-8}$
0·200	0·0100	9·22	$7·1 \times 10^{-7}$	$6·3 \times 10^{-5}$	$5·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0200	9·22	$7·1 \times 10^{-7}$	$6·0 \times 10^{-5}$	$5·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·150	0·0100	8·67	$1·7 \times 10^{-6}$	$3·2 \times 10^{-5}$	$2·7 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0100	8·94	$1·1 \times 10^{-6}$	$2·1 \times 10^{-5}$	$1·8 \times 10^{-5}$	$2·0 \times 10^{-8}$
0·100	0·0100	9·49	$4·7 \times 10^{-7}$	$4·7 \times 10^{-5}$	$4·4 \times 10^{-5}$	$2·1 \times 10^{-8}$

(Free NH_3 = 0·080*VM*; temperature = 40°.)

[a] Calculated from observed rate by subtracting the rate of the NH_3–TAA reaction, $5·0 \times 10^{-3} [CH_3CSNH_2] [NH_3]^2$.

[b] Calculated from the expression K = rate of direct reaction multiplied by

$$\frac{[H^+]^{2/3}}{[CH_3CSNH_2][Ni(II)]}.$$

Effect of ammonia concentration

Nickel in aqueous solution forms six ammine complexes, the general equilibrium expression for their formation being

$$\frac{[Ni(NH_3)_n{}^{2+}]}{[Ni(NH_3)_{n-1}][NH_3]} = K_n\,.$$

Bjerrum[1] has determined the values of K_n. Therefore, for each concentration of free ammonia, the relative concentration of each nickel ammine and the average number of ammonia molecules co-ordinated to each nickel ion, $\bar{n}$, could be computed. This information is presented in Table II.

Table III shows the dependence of the initial rates of the over-all precipitation and the direct reaction on the free ammonia concentration. At free ammonia concentrations greater than approximately 0·3 molal, the rate of the ammonia–TAA reaction becomes so fast that the direct reaction process makes a relatively small contribution to the over-all precipitation rate. The observed relationship between rate and ammonia concentration for the direct reaction may be explained by assuming that each nickel species reacts at a different rate. In principle, therefore, a series of simultaneous equations of the form

$$-\frac{d[Ni(II)]}{dt} = [CH_3CSNH_2](k_0'[Ni^{2+}] + k_1'[Ni(NH_3)^{2+}] \\ + k_2'[Ni(NH_3)_2{}^{2+}] + \ldots + k_6'[Ni(NH_3)_6{}^{2+}])$$

could be set up and solved for the value of k_n'. It was observed in the analogous case of zinc,[3] however, that the ratios of successive rate constants were approximately constant, *i.e.*, that $k_0'/k_1' = k_1'/k_2' = k_2'/k_3'$, *etc.* In order to simplify the computations, the assumption was made that the ratios of successive rate constants are also

TABLE II.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE RELATIVE CONCENTRATIONS OF NICKEL AMMINES

Free $[NH_3]$, *VM*	Average ammonias per nickel, $\bar{n}$	$[Ni^{2+}]$	$[Ni(NH_3)^{2+}]$	$[Ni(NH_3)_2{}^{2+}]$	$[Ni(NH_3)_3{}^{2+}]$	$[Ni(NH_3)_4{}^{2+}]$	$[Ni(NH_3)_5{}^{2+}]$	$[Ni(NH_3)_6{}^{2+}$
0·060	3·13	0·00121	0·0286	0·204	0·436	0·268	0·0596	0·00254
0·080	3·38	0·00048	0·0155	0·143	0·405	0·332	0·0986	0·00558
0·110	3·64	0·00016	0·00702	0·0884	0·345	0·389	0·158	0·0125
0·150	3·90	0·00005	0·00296	0·0509	0·272	0·418	0·232	0·0247
0·200	4·14	—	0·00124	0·0286	0·203	0·416	0·309	0·0436
0·250	4·32	—	0·00061	0·0174	0·154	0·396	0·367	0·0650

TABLE III.—EFFECT OF FREE AMMONIA CONCENTRATION ON THE INITIAL RATE OF PRECIPITATION OF NICKEL SULPHIDE

Free $[NH_3]$, *VM*	Ni(II), *VF*	$\overline{\text{TAA}}$, *VF*	Observed rate, *mole. litre^{-1}. min^{-1}*	Rate of direct reaction,[a] *mole. litre^{-1}. min^{-1}*	K′,[b]	Computed rate,[c]
0·050	0·0100	0·0500	$2·9 \times 10^{-5}$	$2·8 \times 10^{-5}$	$5·6 \times 10^{-2}$	$2·8 \times 10^{-5}$
0·060	0·0100	0·100	$4·5 \times 10^{-5}$	$4·3 \times 10^{-5}$	$4·3 \times 10^{-2}$	$4·3 \times 10^{-5}$
0·080	0·0100	0·100	$3·1 \times 10^{-5}$	$2·8 \times 10^{-5}$	$2·8 \times 10^{-2}$	$2·8 \times 10^{-5}$
0·110	0·0100	0·150	$3·6 \times 10^{-5}$	$2·7 \times 10^{-5}$	$1·8 \times 10^{-2}$	$2·5 \times 10^{-5}$
0·150	0·0300	0·100	$4·4 \times 10^{-5}$	$3·3 \times 10^{-5}$	$1·1 \times 10^{-2}$	$3·3 \times 10^{-5}$
0·200	0·0200	0·200	$6·9 \times 10^{-5}$	$2·9 \times 10^{-5}$	$0·72 \times 10^{-2}$	$2·9 \times 10^{-5}$
0·250	0·0300	0·200	$7·4 \times 10^{-5}$	1×10^{-5}	$0·18 \times 10^{-2}$	3×10^{-5}
0·200[d]	0·0200	0·100	5×10^{-5}	3×10^{-5}	—	2×10^{-5}
0·293[d]	0·0200	0·200	13×10^{-5}	4×10^{-5}	—	4×10^{-5}

(pH = 9·22; temperature = 40°)

[a] Computed from observed rate by subtracting the rate of the NH_3–TAA reaction; $5·0 \times 10^{-3}$ $[CH_3CSNH_2]$ $[NH_3]^2$.

[b] Computed from the expression $K' = \dfrac{\text{Rate of direct reaction}}{[CH_3CSNH_2]\,[Ni(II)]}$.

[c] Computed from the second-order rate constants for each nickel ammine species.

[d] pH = 10·04.

constant for the nickel ammines. Based on this assumption the best values of the individual second order rate constants, k_n', expressed in litre. mole^{-1}. min^{-1}, are

$$
\begin{aligned}
k_0' &= 2·9\\
k_1' &= 5·0 \times 10^{-1}\\
k_2' &= 8·6 \times 10^{-2}\\
k_3' &= 1·5 \times 10^{-2}\\
k_4' &= 2·5 \times 10^{-3}\\
k_5' &= 4·4 \times 10^{-4}\\
k_6' &= 7·5 \times 10^{-5}.
\end{aligned}
$$

The rates of the direct reaction calculated on the basis of these rate constants are also presented in Table III.

Rate expression

The true rate constants, k_n, were obtained from the second order constants, k_n', measured at pH 9·22 and 40°. The best values for these constants, in units of moles, litres and minutes, are incorporated into the following equation, which describes the over-all rate of precipitation of nickel sulphide from ammoniacal solution by thioacetamide at 40°.

$$-\frac{d[\mathrm{Ni(II)}]}{dt} = 5{\cdot}0 \times 10^{-3}[\mathrm{CH_3CSNH_2}][\mathrm{NH_3}]^2 + \frac{[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{2/3}}(2{\cdot}1 \times 10^{-6}[\mathrm{Ni^{2+}}] + 3{\cdot}5 \times 10^{-7}[\mathrm{Ni(NH_3)^{2+}}] + 6{\cdot}0 \times 10^{-8}[\mathrm{Ni(NH_3)_2{}^{2+}}] + 1{\cdot}0 \times 10^{-8}[\mathrm{Ni(NH_3)_3{}^{2+}}] + 1{\cdot}8 \times 10^{-9}[\mathrm{Ni(NH_3)_4{}^{2+}}] + 3{\cdot}0 \times 10^{-10}[\mathrm{Ni(NH_3)_5{}^{2+}}] + 5{\cdot}3 \times 10^{-11}[\mathrm{Ni(NH_3)_6{}^{2+}}]).$$

Effect of temperature

To determine the dependence of the precipitation on temperature, experiments were performed at 25°, 40°, 50°, 60° and 70° with solutions in which the initial concentrations of the reagents were as follows: [Ni(II)] = 0·0200*VF*; $\mathrm{CH_3CSNH_2}$ = 0·0500*VF*; $\mathrm{NH_4Cl}$ = 0·060*VF*; total initial $\mathrm{NH_3}$ = 0·38*VF*; and calculated free ligand $\mathrm{NH_3}$ = 0·29*VM*. The initial rates for each temperature are given in Table IV. Because of uncertainties concerning the values of the formation constants of the nickel ammines at the higher temperatures, and because of the likelihood of volatilisation of some of the ammonia, no attempts were made to calculate the temperature dependence of the ammonia-TAA or the direct-reaction processes.

TABLE IV.—EFFECT OF TEMPERATURE ON RATE OF PRECIPITATION

Temperature, °*C*	Initial over-all rate of precipitation, $\times 10^5$
25	0·9
40	4·5
50	8
60	18
70	50

Initial Conditions: Ni(II) = 0·020*VF*; $\mathrm{CH_3CSNH_2}$ = 0·050*VF*; $\mathrm{NH_4Cl}$ = 0·060*VF*; free ligand $\mathrm{NH_3}$ = 0·29*VM*; total initial $\mathrm{NH_3}$ = 0·38*VF*.

ANALYTICAL CONSIDERATIONS

These studies have shown that the rate of precipitation of nickel sulphide by thioacetamide can be varied over a wide range by the proper selection of the reaction temperature and the concentrations of the reagents. For example, calculations indicate that in a solution initially 0·01*VF* in nickel(II), 0·10*VF* in thioacetamide, 0·30*VF* in free ammonia and having a pH of 10, the quantitative precipitation of nickel sulphide should require about 700 min at 40°; however, at 90° the precipitation should be quantitative within about 5 min.

The use of thioacetamide for the precipitation of nickel sulphide appears to have several advantages over the conventional hydrogen sulphide or ammonium sulphide precipitations. When a solution containing nickel nitrate, aqueous ammonia, ammonium chloride and thioacetamide is heated at 90°, a dense, granular precipitate of nickel sulphide is obtained and the clear, colourless supernatant can be easily separated from the precipitate by decantation. Thus, the precipitation of nickel sulphide by thioacetamide avoids the troublesome aspects of the ammonium sulphide precipitation, namely (1): the voluminous precipitate which can be filtered only with great difficulty, (2) the yellowish to black colour of the filtrate caused by the presence of colloidal nickel sulphide, and (3) the lengthy procedure required to coagulate this precipitate. However, when thioacetamide is employed for the precipitation of sulphides and where subsequent operations are to be made with the same solution, the effects of the excess thioacetamide together with its hydrolysis and reaction products must be considered.

It seems possible that thioacetamide could be used to advantage as a substitute for hydrogen or ammonium sulphide in the separation of zinc, nickel and cobalt as sulphides from ammoniacal solutions in which aluminium, chromium and in some cases manganese, are present as tartrate[5] or oxalate[6] complex ions. Before thioacetamide can be employed for such separations, however, it will be necessary to determine experimentally the behaviour of each of the elements involved under the conditions to be used for the separation.

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Zusammenfassung—Die Geschwindigkeit der Fällung von Nickelsulfid aus ammoniakalischen Lösungen mit Thioacetamid wird hauptsächlich durch zwei Reaktionstypen kontrolliert: Reaktionen zwischen den verschiedenen Nickelspezies und Thioacetamid und Reaktionen zwischen Nickel und dem aus der Reaktion zwischen Ammoniak und Thioacetamid stammenden Sulfid; die aus der durch Hydroxylionen katalysierten Hydrolyse von Thioacetamid stammende Sulfidmenge ist relativ klein. Die Geschwindigkeitsausdrücke für die beiden vorherrschenden Prozesse sind

$$-\frac{d[Ni(II)]}{dt} = \sum_{n=0}^{6} k_n[Ni(NH_3)_n{}^{2+}][CH_3CSNH_2][H^+]^{-2/3}$$

und

$$-\frac{d[Ni(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2.$$

Résumé—On contrôle la vitesse de précipitation du sulfure de nickel à partir de solutions ammoniacales au moyen de thioacétamide essentiellement par deux types de réactions: réactions entre les différentes espèces du nickel et la thioacétamide, et réactions entre le nickel et le sulfure produit par une réaction thioacétamide-ammoniaque. (Le sulfure produit par l'hydrolyse du thioacétamide catalysée par l'hydroxyde est relativement faible.) Les expressions de la vitesse pour ces deux processus prédominants sont, respectivement:

$$-\frac{d[Ni(II)]}{dt} = \sum_{n=0}^{6} k_n[Ni(NH_3)_n{}^{2+}][CH_3CSNH_2][H^+]^{-2/3}$$

et

$$-\frac{d[Ni(II)]}{dt} = k[CH_3CSNH_2][NH_3]^2 .$$

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EFFECT OF NUCLEATION ON RATE OF PRECIPITATION OF METAL SULPHIDES BY THIOACETAMIDE[*]

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Summary—Observations have shown that the number of nuclei formed in thioacetamide precipitations of metal sulphides is usually dependent on the first power of the thioacetamide concentration, and is essentially independent of pH, temperature and metal ion concentration. Under certain conditions a second nucleation process has been observed, in which the number of nuclei formed is proportional to the third power of the thioacetamide concentration, and to the inverse first power of the hydrogen ion concentration. The rate of the *direct reaction* between metal ions and thioacetamide is directly proportional to the number of nuclei formed, and the rate expression is otherwise of zero order in thioacetamide. A partial explanation of this effect is proposed.

INTRODUCTION

IN a previous study[1] of the precipitation of zinc sulphide from ammonia buffers by thioacetamide (TAA), it was observed that the rate of precipitation conformed to the equation

$$-\frac{d[\mathrm{Zn(II)}]}{dt} = K[\mathrm{Zn(II)}][\mathrm{TAA}]\,[\mathrm{H}^+]^{-2/3}\,.$$

The symbol [Zn(II)] represents the total formal concentration of zinc. Precipitations conforming to equations of this form have been observed previously and the process has been termed the *direct reaction*[2] because the rate equation suggests a reaction between the metal and TAA directly, without an intermediate reaction of TAA to yield sulphide. In the case of zinc, this equation was followed only at relatively low concentrations of TAA; at higher concentrations precipitation proceeded so rapidly that essentially all the zinc precipitated during mixing. The precipitate obtained under these conditions was much more finely divided than that obtained at lower TAA concentrations, suggesting that the phenomenon could be attributed to nucleation processes.

This paper reports a preliminary study of nucleation in the TAA precipitation of several metal sulphides, the bulk of the information having been obtained from systems in which zinc was precipitated from ammonia buffered solutions. The factors affecting nucleation can be most simply elucidated by studying the variation in the number of

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precipitate particles with varying conditions. This variation in the number of particles can be conveniently studied by measuring the turbidity of the precipitate suspension. The ratio of the intensities of the incident and transmitted beam is given by

$$\frac{I}{I_0} = e^{-\tau l}$$

where τ is the turbidity and l is the path length. The relationship between turbidity and particle size and number is complex, but for particles larger than the wavelength of light used, τ is approximately proportional to Nr^2, where N is the number of particles per unit volume and r is the particle radius.[3] Because τ is proportional to the measured absorbance of the solution

$$A \propto Nr^2.$$

The volume of precipitate per unit volume is proportional to Nr^3, and also to C, the moles of metal precipitated per unit volume, so that

$$C \propto Nr^3.$$

Combining these two equations and solving for N, one obtains

$$N \propto A^3/C^2.$$

In the discussion below, the ratio A^3/C^2 will be termed N_{relative}.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used throughout. Stock solutions were prepared and, when necessary, were standardised by conventional methods.

Apparatus

A Bausch and Lomb Spectronic 20 colorimeter was used to measure absorbances. Preliminary investigation revealed that over the range of concentrations employed, the suspensions obtained in this study gave measurements reproducible to within 5–10%.

Procedures

When rates of precipitation were determined, the general procedure followed in previous TAA precipitation studies was employed. The concentration of metal ion in solution at various times was determined by EDTA titration, either of a filtered aliquot of solution or of the precipitate obtained upon filtration of an aliquot.

When the effects of varying the concentrations of the reaction constituents upon the number of nuclei were studied, stock solutions were used to prepare series of four to six reaction solutions, which were identical except for the concentration of the constituent under examination. Except where otherwise noted these precipitations were carried out at room temperature with constant mechanical shaking. After the precipitation had proceeded to a suitable extent, an aliquot of the suspension was taken for the colorimetric determination of turbidity. Simultaneously, another aliquot was analysed to determine the amount of material precipitated. From this information, A^3/C^2, proportional to N, was computed.

RESULTS AND DISCUSSION

Effect of thioacetamide concentration on number of zinc sulphide nuclei

The effect of TAA concentration on the number of particles formed was studied in a series of experiments in which varying amounts of solid TAA were added to stock buffer solutions and agitated thoroughly for 10 sec, after which a fixed volume of zinc nitrate solution was added to each. The relative number of particles formed in each precipitating solution was then determined as outlined above. Because the method of mixing the components of the reacting system affects the number of particles formed, the above method was followed closely except where otherwise noted. Fig. 1 shows the results of these experiments in a plot of log N *vs.* log ([TAA] × 10^2). It can be seen that at low concentrations of TAA, N is directly proportional to [TAA], and at high concentrations N is proportional to $[\mathrm{TAA}]^3$. The two nucleation processes distinguished in this way will subsequently be referred to as the *first order nucleation* and the *third order nucleation*, and will be discussed separately.

First order nucleation process

Additional experiments similar to those outlined above on the precipitation of nickel sulphide from ammonia buffers, and of zinc, cadmium and nickel sulphides from formate buffers (pH about 5) showed that the first order nucleation is predominant. Further experiments showed that the number of particles formed by this process is independent of the concentration of metal ion, of ammonia, of pH and of temperature. These results indicate that nucleation was taking place on insoluble impurities in the TAA. In such cases the number of nuclei formed by this process should then depend only on the number of impurity particles, and hence on the quantity of a given sample of TAA and should be independent of other reaction conditions.

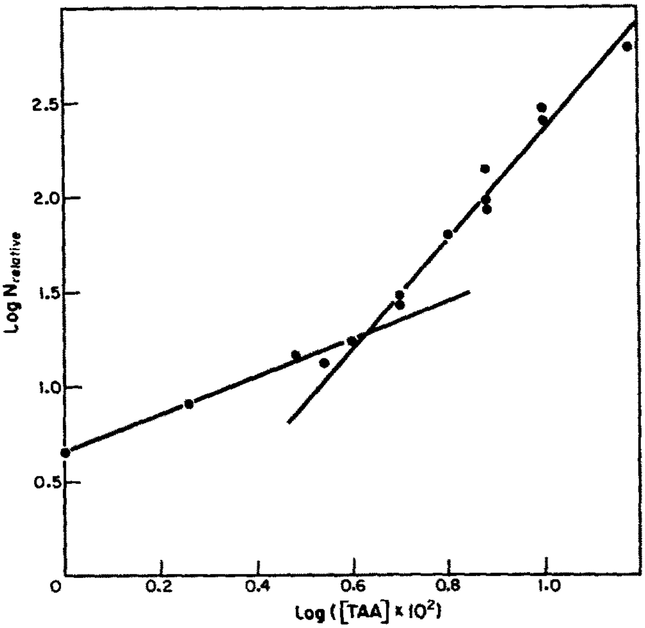

FIG. 1.—Effect of thioacetamide concentration on number of zinc sulphide nuclei (initial conditions: [Zn(II)] = 0·010*VF*, $\mathrm{NH_{3}}_{\mathrm{total}}$ = 0·115*VF*, NH_4NO_3 = 0·230*VF*, pH = 9·02, temperature *ca.* 25°)

This hypothesis was tested by carrying out the following experiments:

(1) Six different samples of solid TAA, from four commercial sources, were employed to precipitate zinc sulphide. Three of the samples were obtained from the same source and differed only in lot number: these three samples produced an essentially constant number of particles. The samples from the other source yielded from two to four times as many particles as did the first set of samples. These results indicate that

the number of nucleating particles present in any sample of TAA depends upon the prior history of the TAA.

(2) The variation of *N* with TAA concentration was observed, using a TAA solution which had been filtered through a membrane filter (pore size 100 mμ), and for comparison, an unfiltered TAA solution. The results, shown in Fig. 2, indicate that filtration inhibits the first order nucleation, and only third order nucleation is observed.

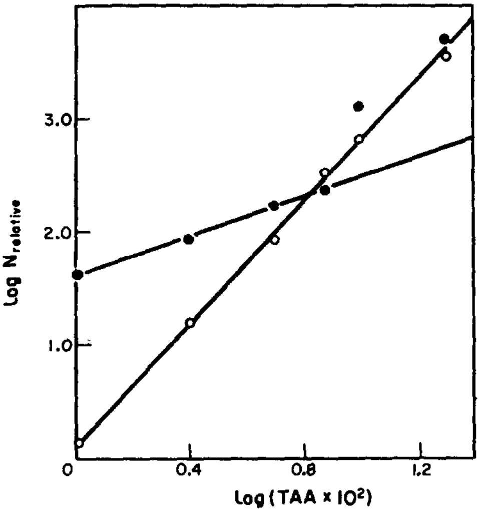

FIG. 2.—Effect of filtration on number of zinc sulphide nuclei [initial conditions: [Zn(II)] = 0·0050*VF*, $NH_{3\,total}$ = 0·099*VF*, NH_4NO_3 = 0·040*VF*, pH = 9, temperature *ca.* 25° (room temperature)].
● TAA unfiltered, ○ TAA filtered.

Third order nucleation process

A previous study of the TAA precipitation of nickel sulphide from ammonia buffered solution[4] did not reveal the very rapid precipitation observed in the analogous precipitation of zinc sulphide, nor had the rapid precipitation been obtained in the precipitation of zinc sulphide from acidic solutions.[5] Consequently, experiments were carried out to determine whether the third order nucleation process related to this rapid precipitation is a specific phenomenon occurring only with zinc ammines, or whether it occurs more generally.

Accordingly, the variation of *N* with TAA concentration was studied in the precipitation of nickel sulphide from an ammonia buffer (pH) 9, with TAA concentrations from 0·074*VF* to 1·00*VF*. These experiments show that a third order nucleation does take place, but not to a significant extent unless the TAA concentration is above about 0·6*VF*. In the previously noted studies of the precipitation of zinc sulphide from ammonia buffers, the third order nucleation became predominant at TAA concentrations above about 0·06*VF*.

In experiments in which zinc sulphide was precipitated from formate buffers, pH about 5, only first order nucleation was observed, even at TAA concentrations as high as 1·1*VF*. When the first order nucleation was inhibited by prior filtration of the TAA solution through a membrane filter, first order nucleation was not observed, and the third order process prevailed down to the lowest TAA concentration employed, 0·01 *VF*. Analogous experiments with filtered TAA have not been carried out with other metals.

Precipitation of zinc sulphide from ammoniacal solutions was used to study the dependence of the third order nucleation process on concentrations of the reaction constituents. The number of particles formed at a given concentration of TAA was independent of the concentrations of zinc and ammonia, but was inversely proportional to the concentration of hydrogen ion over the pH range 8·6 to 10·2. The temperature dependence of the third order nucleation was not studied. Current concepts of homogeneous nucleation require some metal ion dependence; therefore, this process also appears to be heterogeneous, possibly involving particles different in nature from those responsible for the first order process.

Nature of direct reaction between thioacetamide and metal ions

The precipitation of metal sulphides by TAA in general follows one or both of two reaction paths. The TAA may react to give sulphide, which then precipitates the metal ion; in previous experiments the rate of this precipitation has been found to be the same as the rate of formation of sulphide. The second process, the *direct reaction* previously discussed, does not involve prior formation of sulphide; the rate of this precipitation reaction has been found to conform to the following equation for a number of dipositive metals:

$$-\frac{d[M]}{dt} = k\,[M][TAA]\,[H^+]^{-1}\;{}^{2} \qquad (1)$$

Mechanistically, the rate of a precipitation is fixed by the rate at which the precipitating ions can diffuse to the surface of the precipitate particles, or by the rate at which the ions at the surface are incorporated into the particles, *i.e.*, the over-all rate of precipitation is dependent upon either a diffusion process or an interface process, or both. In certain cases of precipitations from homogeneous solution, the rates of these processes are limited by the rate at which precipitant is generated, so that the over-all rate of the precipitation will be controlled by the rate of generation of precipitant, with deviations only at the beginning and end of the precipitation, where the concentration of one of the precipitating ions is quite small.

Because the direct reaction does not involve prior formation of sulphide, equation (1) must describe either a diffusion process or an interface process. Diffusion-limited precipitation cannot be described by a rate equation of the form of equation (1);[6] therefore, the observed kinetics of the direct reaction can be attributed to an interfacial process. The rate at which an interfacial reaction proceeds depends upon the area of the interface. In a precipitating system this interfacial area is the product of the number of particles and the area per particle. Although the actual surface area per particle increases as precipitation proceeds, the effective growth area of the particles need not increase; it has frequently been observed[7] that each growing particle apparently contains only a fixed number of sites which are active in growth. In this case the precipitation rate will depend only on the number of growing particles in the system, and not on the surface area.

Equation (1), with slight modification, fits this model, where the number of sites is proportional to the number of particles, and the number of particles is that number formed by the first order nucleation process, and so is proportional to the TAA concentration. Equation (1) may now be rewritten

$$-\frac{d[M]}{dt} = k\,[TAA]_0[M]\,[H^+]^{-1/2} \tag{2}$$

where $[TAA]_0$, the original TAA concentration, is directly proportional to the number of active growth sites. This modification of the observed rate equation predicts that the direct reaction is kinetically of zero order in TAA, *i.e.*, that the rate of the precipitation will not decrease as TAA is consumed by the reaction.

In previous studies[1,2,4,5] of the direct reaction where equation (1) was observed, TAA was present in large excess. Thus, the concentration of TAA remained essentially constant during the precipitation, and the dependence of the precipitation rate on TAA concentration was determined by varying the initial concentration of TAA, a procedure which also varies the number of nuclei, and thus cannot determine whether the precipitation is described by equation (1) or (2). Experiments involving the precipitation of cadmium sulphide from acidic solution, and of zinc sulphide from ammoniacal solution, were carried out, and the results indicate that the precipitation is described by equation (2). In these experiments, the metal ion and TAA were present in equivalent amounts, or the metal was present in excess. Results from one of these experiments are presented in Table I.

Table I.—Dependence of rate of precipitation of cadmium sulphide on concentration of thioacetamide in solution

Time, *min*	CdS precipitated, *mole. litre*$^{-1}$	k_1,[a] *litre. mole*$^{-1}$. *min*$^{-1}$	k_2,[b] *litre. mole*$^{-1}$. *min*$^{-1}$
6	0·0020	0·028	0·029
24	0·0077	0·027	0·033
34	0·0101	0·026	0·033
49	0·0162	0·028	0·048
60	0·0190	0·026	0·055
72	0·0230	0·027	0·107
89	0·0234	—	—

(Initial conditions: $[Cd^{2+}] = 0{\cdot}50\,VM$, TAA $= 0{\cdot}0235\,VF$,
pH = 5·78 (formate buffer), temperature = 80°)

[a] Calculated from $-\frac{d[Cd^{2+}]}{dt} = (k_1[TAA]_0)[Cd^{2+}]$.

[b] Calculated from $-\frac{d[Cd^{2+}]}{dt} = k_2[TAA][Cd^{2+}]$.

In order to form metal sulphide by the direct reaction, a reaction between the metal ion and TAA must take place. Because, according to equation (2), the solution concentration of TAA does not affect the rate, the metal-TAA reaction must take place under conditions such that the TAA concentration is constant. This will be the case when TAA is present as an adsorbed layer on the precipitate, provided that a large fraction of the available adsorption sites is occupied by TAA even at low TAA concentrations.

It is now possible to propose the following process to describe the TAA precipitation of metal sulphides by the direct reaction. Nucleation takes place on particles introduced into the system with the thioacetamide, the number of such particles usually being directly proportional to the quantity of thioacetamide added. Each nucleus formed in this way adsorbs TAA until essentially all its adsorption sites are filled. Metal ions diffuse rapidly to the surface of the particles, but are incorporated into the precipitate only slowly, by reaction with the adsorbed TAA molecules. Such a reaction can occur only at specific areas of the particle surface, each particle having a fixed number of these active growth areas. The role of hydrogen ion in the direct reaction is not explained by this process. The inverse half order hydrogen ion dependence of the direct reaction may indicate either a pH-sensitive adsorption of the metal on TAA or an effect of pH on the number of active growth areas.

Zusammenfassung—Es wurde beobachtet, daß die Anzahl der bei Thioacetamidfällungen von Metallsulfiden gebildeten Keime im allgemeinen von der Thioacetamidkonzentration linear abhängt und im großen und ganzen von pH, Temperatur und Metallionenkonzentration unabhängig ist. Unter bestimmten Bedingungen wurde ein zweiter Keimbildungsprozeß beobachtet, bei dem die Keimzahl proportional zur dritten Potenz der Thioacetamidkonzentration und umgekehrt proportional zur ersten Potenz der Wasserstoffionenkonzentration ist. Die Geschwindigkeit der "direkten Reaktion" zwischen Metallionen und Thioacetamid ist direkt proportional zur Keimzahl; im übrigen ist der Geschwindigkeitsausdruck nullter Ordnung bezüglich Thioacetamid. Eine teilweise Erklärung für diesen Effekt wird vorgeschlagen.

Résumé—Des observations ont montré que le nombre de germes formés dans les précipitations de sulfures métalliques au moyen de thioacétamide dépend habituellement de la puissance première de la concentration en thioacétamide, et est essentiellement indépendant du pH, de la température et de la concentration en ion métallique. Dans certaines conditions, on a observé un second processus d'amorçage, dans lequel le nombre de germes formés est proportionnel à la puissance troisième de la concentration en thioacétamide, et inversement proportionnel à la puissance première de la concentration en ion hydrogène. La vitesse de la "réaction directe" entre les ions métalliques et le thioacétamide est directement proportionnelle au nombre de germes formés, et l'équation de vitesse est autrement d'ordre zéro dans le thioacétamide. On propose une explication partielle de cet effet.

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SELEKTIVE TRENNUNG VON SELEN(IV) DURCH EXTRAKTION MIT METHYLÄTHYLKETON

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Zusammenfassung—Selen(IV) wird mit Methyläthylketon in salzsaurem Medium extrahiert und hierbei die optimale Acidität bestimmt, bei der die Extraktion vollständig ist. Ferner wird die Assoziationskinetik der Selenchloridkomplexe mit Methyläthylketon sowie die Extraktionskinetik des Assoziats mit Chloroform untersucht. Hierbei wird auf die Möglichkeit hingewiesen, Selen in Gegenwart zahlreicher, in beträchtlicheren Mengen vorhandener Stoffe, darunter auch Tellur, durch Extraktion zu trennen. Bestimmt wurde auch der Selengehalt in Kupferkonzentraten. Abschliessend folgen statistische Bearbeitung der Ergebnisse und Bewertung der Genauigkeit der Methode.

DIE Trennung des Selens von anderen Elementen ist in der analytischen Praxis stets mit erheblichen Schwierigkeiten verknüpft. Ein Teil der üblichen Methoden[1-6] beruh auf der Reduktion von Selen(IV) zu Elementarselen, das mit Tellur oder einem anderen geeigneten Fällungsmittel mit zur Fällung gebracht wird. Diese Methoden können jedoch die vollständige Trennung von Selen nicht gewährleisten. Anderen Methodent liegt die Extraktion zugrunde. Zur Anwendung gelangen unterschiedliche Extraktionsmittel wie Triphenylarsoniumchlorid,[7] *N*-Dodecyltrioktylmethylamin, Tribenzylamin,[8] Ditizon,[9] Methylisobutylketon,[10]Tributylphosphat,[11] Diäthyldithiophosphorsäure,[12] Triphenylblei,[13] Tri-*N*-oktylphosphinoxyd,[14] 3,3′-Diaminobenzidin[15-20] u.a. Auch diese Methoden vermögen nicht eine ausreichend vollständige, selektive und anspruchslose Trennung des Selens von anderen Elementen zu verwirklichen.

In der vorliegenden Arbeit weisen wir auf einen Weg der Selenextraktion hin, der den erwähnten Erfordernissen in weitgehendem Masse Rechnung trägt.

EXPERIMENTELLER TEIL

Nachdem wir eine Reihe von Extraktionsmitteln auf deren Wirksamkeit bei Selen geprüft hatten, entschieden wir uns für das Methyläthylketon, das uns am geeignetesten erschien. Es stellte sich nämlich heraus, dass sowohl reines Methyläthylketon als auch seine stark verdünnte Chloroformlösung extraktionsfähig sind.

Man könnte erwarten, dass die Extraktion nach dem Oxonium-Mechanismus vor sich geht. In diesem Fall würden die günstigsten Extraktionsbedingungen dann eintreten, wenn Selen in einem negativ geladenen Komplex vorliegt.

In salzsaurem Medium hat man die Bildung von Selen(IV)-chlorid-Komplexen beobachtet.[21-27] Nach Petzold[28] stellen sich je nach der Konzentration der Salzsäure nachstehende Gleichgewichte ein:

$$H_2SeO_3 + 4HCl \rightleftharpoons SeCl_4 + 3H_2O$$
$$SeCl_4 + 2HCl \rightleftharpoons H_2SeCl_6.$$

Durch spektrophotometrische Untersuchung der Komplexbildung im System Selen(IV)/Chlorionen stellten Babko und Mitjurewa[29] fest, dass bei 4,5M HCl die Bildung von Chloridkomplexen einsetzt, denen die Autoren die wahrscheinliche Zusammensetzung $Se(OH)_2Cl_2$ zuschreiben.

Untersuchungen über den Einfluss der Acidität auf die Extraktion von Selen

Zu 1 ml einer Lösung, die 100 μg Se enthält, geben wir jeweils 9 ml Salzsäure von unterschiedlicher Normalität und anschliessend 0,5 ml Methyläthylketon hinzu. Die Lösung wird kräftig geschüttelt, 10 Min. liegen gelassen und nachher mit 10 ml Chloroform extrahiert. Abb. 1 veranschaulicht den Zusammenhang zwischen Extraktionsgrad und Acidität. Man sieht, dass die Extraktion bei 4,5M HCl merklich zunimmt, was mit den Untersuchungsergebnissen von Babko und Mitarbeitern im Einklang steht. Bei 6,5M HCl ist die Extraktion des Selens nahezu vollständig. Rückschlüsse auf die Selenverteilung konnten wir ziehen, indem, wir seinen Gehalt in beiden Phasen bestimmten. Zu diesem Zweck bedienten wir uns der photometrischen Methode, der die Messung der optischen Dichte einer Kolloidlösung zugrundeliegt, die durch Reduktion von Selen(IV) mit Zinn(II)-chlorid in Gegenwart von Wismutnitrat und Gelatine gewonnen wurde.

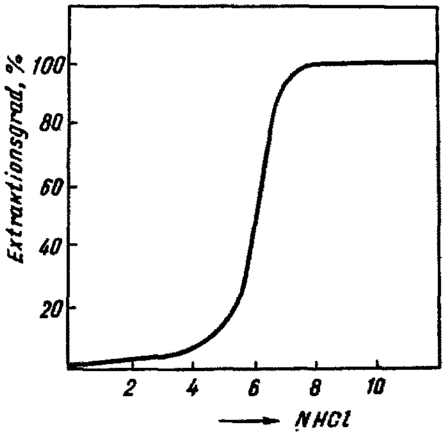

ABB. 1

Untersuchung der Assoziations- und Extraktionskinetik

Unter Voraussetzung des vermutlichen Oxonium-Mechanismus der Extraktion und Berücksichtigung des Umstandes, dass Methyläthylketon sich ziemlich leicht in Wasser löst, hielten wir es für zweckmässig, zunächst einmal die Assozierung des Selen(IV)-chlorid-komplexes mit dem Methyläthylketon in salzsaurem Medium durchzuführen und dann das erhaltene Assoziat mit Chloroform zu extrahieren. Die Angaben über die Assoziationskinetik sind aus Abb. 2 zu ersehen. Demnach

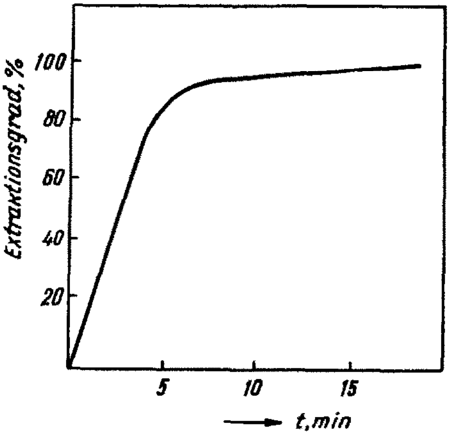

ABB. 2

ist die Geschwindigkeit der Assoziation nitch sehr gross. Beträgt die Konzentration des Selens $1{,}2 \cdot 10^{-4}$M und die des Methyläthylketons 0,35M, so vollzieht sich die vollständige Assozierung innerhalb von 15 Min. Die Extraktion mit Chloroform geht viel schneller vor sich.

Untersuchungen über die Rückextraktion von Selen

Zwecks analytischer Anwendung der Methode ist es von Belang, einen Weg zur quantitativen Rückextraktion des Selens zu suchen. Versuchsweise wurden zwar zahlreiche einschlägige Mittel angewendet, doch ohne Erfolg. Schliesslich wurde diese Frage in nachstehend geschilderter Weise gelöst. Der Chloroformauszug wurde in einem Messkolben gesammelt und nach Zugabe von 2 ml Wasser und 0,5 ml konz. Salpetersäure im Wasserbad erhitzt. Es entwich zuerst das Chloroform, dann trat die Zersetzung des Methyläthylketons ein. Man erhitzt bis zum Aufhören der Gasentwicklung und völligen Entfärben der Lösung. Eigens angestellte Versuche ergaben, dass bei diesen Umsetzungen kein Verlust an Selen zu verzeichnen war.

Untersuchung über die Störende Wirkung anderer Stoffe

Konzentrationen bis 0,6M für die Schwefelsäure und 0,5M für die Salpetersäure stören die Extraktion nicht. Diese wird praktisch nicht gestört auch von vielen anderen, in den Auszug nicht übergehenden Stoffen, wenn diese in nachstehend angegebenen Mengen (Tabelle I) vorhanden sind.

TABELLE I

Fe(III)	50 mg	Bi(III)	50 mg	Sb(III)	50 mg
Al(III)	50 mg	Ni(II)	50 mg	Sb(V)	50 mg
Cu(II)	100 mg	Co(II)	50 mg	Au(III)	1,5 mg
Mn(II)	50 mg	V(V)	30 mg	Mo(VI)	50 mg
Cd(II)	50 mg	As(III)	1 mg	Mg(II)	50 mg
Zn(II)	50 mg	As(V)	50 mg	Te(IV)	50 mg

Auch geringe Mengen von Tl, In, Ga, Ge, W und Th stören die Extraktion nicht, während das Vorhandensein starker Oxydationsmittel, vermutlich durch Oxydation von Selen(IV) zu Selen(VI), störend wirkt. Ist die Menge der Begleitstoffe grösser als die in Tab. I angegebene, so werden sie teilweise mit extrahiert und manche von ihnen wirken dann störend bei der weiteren Bestimmung des Selens. In diesem Falle wird empfohlen, die organische Phase mit 3–4 ml gesätiger lösung von Natrium Chlorid bzw mit derselben Menge von 7M HCl zurück zu extrahieren.

Die Klärung der mit dem Mechanismus der Extraktion verknüpften Fragen der Komplexbildungs- und Assoziierungsprozesse sowie der selektiven Extraktionswirkung des Methyläthylketons in Chloroform soll unseren nachträglichen Forschungen vorbehalten sein.

Anwendung der Methode

Erforderliche Reagenzien

Standartlösung von Selen. Man löst 1,4050 g über Phosphorpentoxyd getrocknetes Selenoxyd in Wasser bis auf 1 L. Diese Lösung enthält 1000 μg Se/ml. Durch entsprechende Verdünnung entstehen Lösungen, die 100 bzw. 10 μg Se/ml enthalten.

Zinn(II)-chlorid, 25%ige Lösung. Man löst 125 g $SnCl_2$ in 100 ml konz. HCl, erwärmt im Wasserbad bis zum Klarwerden und verdünnt dann mit Wasser auf 500 ml.

Wismut(III)-nitrat, 1%ige Lösung. 5 g $Bi(NO_3)_3$ wird in 150 bis 200 ml Wasser gelöst; man säuert dann mit Salpetersäure an bis zum Klarwerden der Lösung und verdünnt mit Wasser auf 500 ml.

Gelatine, 0,5%ige Lösung. 1 g reiner Gelatine wird in 100 ml heissem Wasser gelöst, mit 1 ml konz. HCl angesäuert und auf 200 ml verdünnt.

Konzentrierte Salz-, Schwefel- und Salpetersäure

Methyläthylketon p.a.[*]

Chloroform p.a.

Analysengang

0,5 bis 3,0 g des Probegutes (Kupfer- und Bleikonzentrate, Blei/Silber-Legierung, schwarzes Kupfer u.a.) werden in 5 bis 15 ml konz. Salpetersäure gelöst. Man erhitzt und dampft die Lösung auf einige ml ein. Nach Zagabe von 2 ml konz. Schwefelsäure wird weiter erhitzt bis zur Entwicklung von Dämpfen (SO_3). Man Kühlt ab, setzt 3 bis 4 ml Wasser hinzu und erwärmt abermals bis zur

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[*] Methyläthylketon wird bei der trockenen Holzdestillation gewonnen und ist deshalb oft gelb gefärbt. Dann muss es abdestilliert und als farbloses Produkt gesammelt werden.

Zersetzung der Schwefelsäure. Der Rückstand wird mit 20 ml 7M HCl versetzt und filtriert. Das Filtrat wird in einem Messkolben von 50 ml gesammelt. Den Niederschlag wäscht man mit derselben Säure aus und den Kolben füllt man bis zur Marke. 10 ml der Lösung bringt man in einen Scheide trichter, setzt 0,3 ml Methyläthylketon hinzu, schüttelt und lässt dann die Lösung 15 Min. lang liegen. Nachher wird 3 Min. lang mit 10 ml Chloroform extrahiert. Die organische Phase wird in einem 50 ml-Messkolben gesammelt, die wässerige Phase mit 2 bis 3 ml Chloroform gewaschen und dann in denselben Kolben gebracht. Nach Zugabe von 2 ml Wasser und 0,5 ml konz.Salpetersäure erwärmt man vorsichtig im Wasserbad bis zur Entfernung des Chloroforms; die Erwärmung wird dann längere Zeit fortgesetzt bis zur völligen Zersetzung des Ketons. In die farblose Lösung bringt man 20 ml Wasser, 6 ml konz.Salzsäure, 1 ml Wismutnitratlösung und verdünnt dann mit Wasser auf etwa 40 ml. Nach Zusatz von 0,5 ml Zinn(II)-chlorid-Lösung wird energisch gerührt, worauf die Lösung 15 Min. lang stehen gelassen wird. Nachher setzt man 4 ml Gelatinelösung hinzu, füllt mit Wasser bis zum Strich und photometriert bei $\lambda = 450$ mμ. Man benutzt eine Küvette mit Stärke der absorbierenden Schicht 5 cm. Als Bezugslösung wird Wasser verwendet.

Die Bestimmung des Selengehalts erfolgt nach vorgezeichneter Standardkurve. Zu dem Zweck werden 10 bis 100 μg Selen extrahiert. Der Auszug wird in vorstehend beschriebener Weise aufgearbeitet und die optische Dichte der jeweiligen Lösung bestimmt.

Statistische Bewertung der Genauigkeit der Methode

Die Bewertung der Genauigkeit der Methode erfolgt durch statistische Bearbeitung der Ergebnisse, die wir bei der Bestimmung von 30 μg Selen unter reinen Bedingungen und bei der Ermittlung des Selengehalts im Kupferkonzentrat erhielten.*

$$\text{I}\quad 30\,\mu\text{g Se}\,.\ N = 10,\ E = 0{,}181,\ s = 0{,}0063,\ v = \frac{S}{E}\,.\,100 = 3{,}46\%.$$

$$\text{II Kupferkonzentrat.}\ N = 10,\ \bar{x} = 225{,}7\ \text{g Se/t},\ s = 3{,}38,\ v = \frac{s}{\bar{x}}\,.\,100 = 1{,}59\%.$$

Summary—Selenium(IV) may be extracted by methyl ethyl ketone in a hydrochloric acid medium. The optimum acidity for the extraction has been determined. The kinetics of the association of the selenium chloride complex with methyl ethyl ketone, and of the extraction of the association complex by chloroform, have been examined. In consequence it is possible to separate selenium from considerable amounts of other materials, including tellurium, by extraction. The selenium content of copper concentrates can be determined. A statistical examination of the results, and an estimate of the accuracy of the method are included.

Résumé—On peut extraire le sélénium(IV) par la méthyl-éthyl-cétone en milieu acide chlorhydrique. On a déterminé l'acidité optimale pour l'extraction. On a examiné la cinétique de l'association du complexe chlorure de sélénium avec la méthyl-éthyl-cétone, et celle de l'extraction du complexe d'association par le chloroforme. En conséquence, il est possible de séparer le sélénium-quantités considérables d'autres produits, y compris le tellurium, par extraction. On peut déterminer la teneur en sélénium de concentrats de cuivre. On a inclus dans cette étude un examen statistique des résultats, et une estimation de la précision de la méthode.

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* Die Rückextraktion des Selens aus der organischen Phase mit Wasser und verdünnter Lösung von Salzsäure haben wir zwar geprüft doch mit negativen Ergebnissen. Das läßt sich durch die Irreversibilität der Prozesse der Komplexbildung und Assoziierung erklären. Nachträgliche Untersuchungen zeigten daß das Assoziat zwischen dem Chloridkomplex des Selens und dem Methyläthylketon ziemlich stabil ist. Hierzu kommt es, daß die Assoziation durch die Salzsäure insofern gefördert wird, als sie die Dielektrizitätskonstante des Mediums herabsetz. In dieser Hinsicht ist das Methyläthylketon maßgeblicher, das in der Wasserphase in weitgehendem Maße löslich ist.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—III*

CHELOMETRIC DETERMINATION OF IRON(III) USING AN INDICATION SYSTEM OF TWO CARBON ELECTRODES

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Summary—Two carbon (graphite) electrodes have been used for indicating the end-point in the biamperometric titration of iron(III). Satisfactory results are obtained over a wide range of applied potentials. The absolute current values are related linearly to the values of the applied potential. At a potential of 0·6–2·0 V the current differences during the titration are from several μA to ten times these values. The influence of pH, applied potential and temperature on the titration have been studied; the effect of interfering elements has been investigated. Under optimal conditions the determination is highly selective and accurate. It is possible to determine 1–150 mg of iron(III).

In a preliminary communication,[1] the possibility of using two carbon (graphite) electrodes for biamperometric detection of the end-point in titrations with EDTA was mentioned. Previously, the carbon electrode had been used as an indicator electrode in potentiometric and amperometric titrations[2] and also in polarography.[4] For biamperometric titrations with two polarisable electrodes ("dead-stop" method) an electrode system of two carbon electrodes has not yet been applied.[5]

In the present paper the results are reported of a study of the conditions for the biamperometric titration of iron(III) with EDTA using an indication system of two carbon electrodes. Recently, this titration was investigated with an electrode system of two platinum electrodes.[6]

EXPERIMENTAL

Reagents

Unless otherwise stated, all solutions were prepared from reagent-grade chemicals.

Foreign ion solutions. Solutions of Ni^{2+}, Cu^{2+}, Th^{4+}, Zr^{4+}, Al^{3+}, Ti^{4+}, UO_2^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, Pb^{2+}, Mg^{2+} and Sn^{2+} were prepared from salts soluble in water.

Buffer solutions (pH 1–4·2). Prepared from 1*M* trichloracetic acid (pH 1·1–1·5), monochloracetic acid (pH 2–2·8) and formic acid (pH 4·2–5·3) by neutralisation with aqueous ammonia under potentiometric control of pH with a glass electrode.

Standard iron(III) *solution.* Prepared by dissolution of behanite (99·8% Fe) in a minimum amount of hydrochloric acid (1:1) and a little 30% hydrogen peroxide. After dissolution, the hydrogen peroxide was decomposed and the cooled solution diluted with redistilled water to 1000 ml. The amount of iron in this solution was determined gravimetrically [1 ml ≡ 1·027 mg of Fe(III)], and the value checked regularly.

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* Part II: see reference 7.

0·05M EDTA solution. Prepared by dissolution of 33·22 g of Chelaton 3 (Lachema, Brno, Czechoslavakia) and dilution to 2000 ml with redistilled water. The titre was determined by titration against standard lead nitrate solution with Xylenol Orange as indicator.[8]

Apparatus

For indication of the end-point a "dead-stop" instrument was used.[9] Two spectrographic carbon electrodes of 5-mm diameter (KABLO, Bratislava, Czechoslovakia, 99·99% carbon) were used. They were placed in glass tubes and covered with plastic (dentacryle) so that only 10 mm of their length remained exposed (Fig. 1). When not in use, the electrodes were kept immersed in water.

The pH was measured with a glass electrode and an electronic pH meter Multoscop III (Laboratorní potřeby, Prague, Czechoslovakia). Polarographic measurements were carried out with a polarograph LP 55 (Laboratorní přístroje, Prague, Czechoslovakia).

Procedure

The chosen amount of iron(III) was diluted to about 150 ml with redistilled water in a 250-ml beaker and the pH adjusted under potentiometric control with hydrochloric acid or sodium hydroxide or with 15 ml of a suitable 1*M* buffer solution. The titrations were carried out at pH 1·5–2·0 in unbuffered solution at 20° with intensive stirring (1600 rpm) using 0·05*M* EDTA solution. All titrations were started 2–3 min after inserting the electrodes into the solution. During this time the "equilibrium" of the electrode reactions was established. The change of current was read after each addition of titrant during the titration. The stabilisation of current values is satisfactory mainly at the end-point and after it.

All data given in this paper are the arithmetical mean of three determinations.

RESULTS AND DISCUSSION

Influence of pH

It is well known that the chelometric titration of iron(III) takes place in a relatively acidic medium. From the point of view of selectivity, the optimum condition for this titration is, of course, the maximum possible acidity. The influence of pH on the biamperometric titration of iron(III) was studied in buffered (Fig. 2) and unbuffered (Fig. 3) media. Titration proceeds satisfactorily at pH 1·1–2·5 in the unbuffered medium and pH 1·1–4·2 in the buffered solution. At other values of pH, detection of the end-point is impossible.

Influence of applied potential

The influence of the applied potential was investigated over the range 0·6–2·0 V (Fig. 4). Satisfactory results can be obtained even at an applied potential lower than 0·6 V, but in this case the amperometer used must be more sensitive. This phenomenon had previously been encountered in the biamperometric titration of thallium(III).[7] For measurements in the range 0·6–2·2 V of applied potential, a microammeter with full-scale deflection of 0–750 μA was used. The mean relative error of the determination of 15 mg of iron(III) was ±0·1%.

Influence of temperature

Although the titration proceeds very well at room temperature, the influence of temperature was studied. It was found that at higher temperatures the stabilisation of current at the beginning of the titration is somewhat faster; no other differences were found.

"Passivation" of electrodes

The aim of the following experiments was to find the appropriate influence of the products of the electrode reactions. These products can cover the surface of the electrode and change the indicator properties of the electrode couple. From this point of

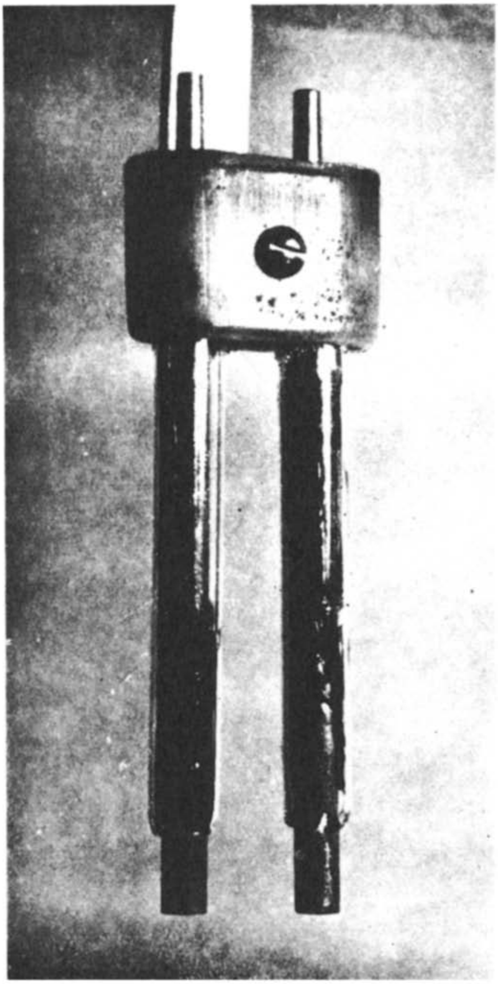

FIG. 1.—Carbon (graphite) indicator electrodes for biamperometric titration of iron(III).

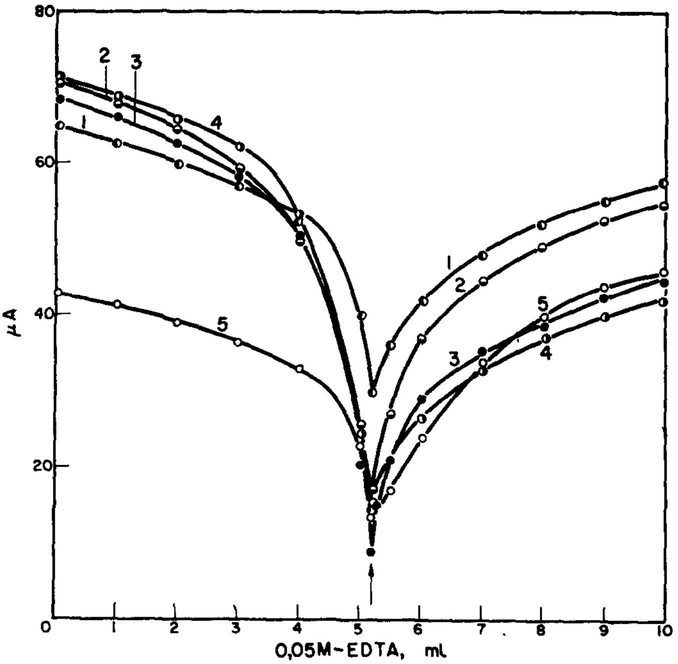

FIG. 2.—Influence of pH on the titration curves in buffered solution:— *1*—pH 1·1; *2*—1·5; *3*—2·0; *4*—2·8; *5*—4·2. [15·41 mg of Fe(III); total volume: 150 ml; temperature: 20°; applied potential: 1·0 V.]

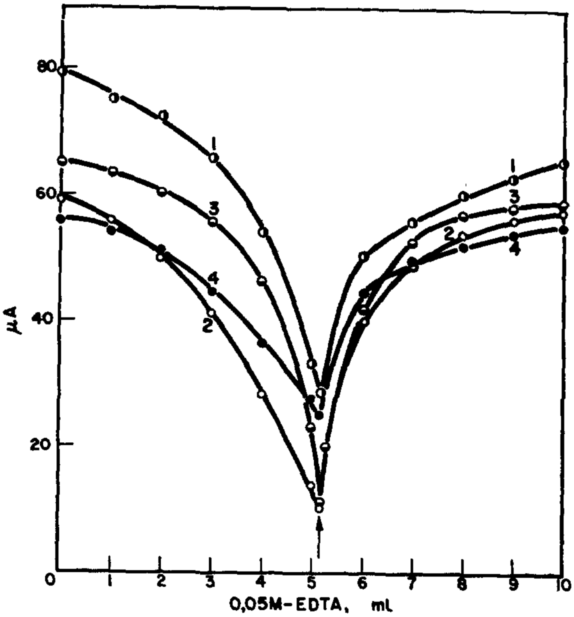

FIG. 3.—Influence of pH on the titration curves in unbuffered solution:— *1*—pH 1·1; *2*—1·5; *3*—2·0; *4*—2·5. [15·41 mg of Fe(III); total volume: 150 ml; temperature: 20°; applied potential: 1·0 V.]

view. 50 determinations of iron were carried out under identical conditions over 24 hr. After each titration the electrodes were only washed with distilled water. Fig. 5 shows the spread of the 50 titration curves. The relative error in these titrations was not greater than ±0·2%.

Subsequently, attention was paid to the decrease of the current at the moment when the electrodes were inserted into the titration solution. In Fig. 6 is given the dependence of the current on time, where the start of the time axis is the time of inserting the electrodes. Curve 1 shows this dependence for the system of two carbon electrodes: in this case the electrodes were first soaked for 144 hr in 0·1*M* potassium chloride solution. Curve 2 shows the dependence when the electrodes were first soaked for the same time in distilled water. These curves show that saturation of the carbon electrodes with potassium chloride has practically no influence on stabilisation of the current. In both cases, after 5 min, only a small decrease of the current occurs. For analytical application it is enough to wait 2–3 min after inserting the electrodes

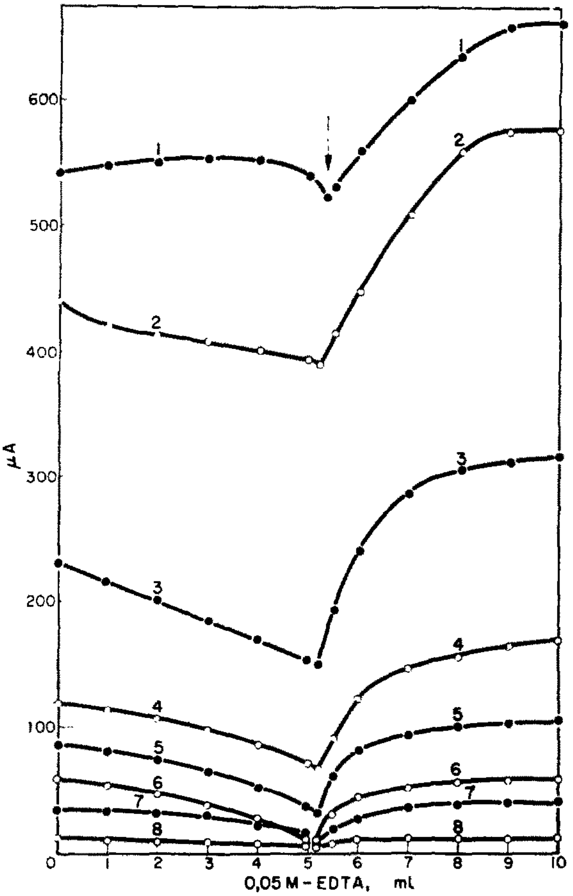

Fig. 4.—Influence of applied potential on the titration curves:— *1*—2·0 V; *2*—1·8 V; *3*—1·6 V; *4*—1·4 V; *5*—1·2 V; *6*—1·0 V; *7*—0·8 V; *8*—0·6 V. [15·41 mg of Fe(III); total volume: 150 ml; pH: 1·7 (unbuffered); temperature: 20°].

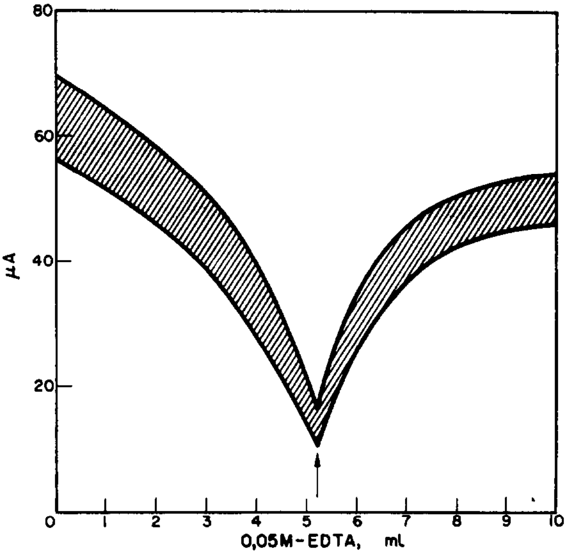

FIG. 5.—Spread of titration curves in 50 titrations [15·41 mg of Fe(III); total volume: 150–180 ml; temperature: 20°; pH: 1·5–2·0; theoretical consumption: 5·20 ml of 0·05*M* EDTA; applied potential: 1·0 V].

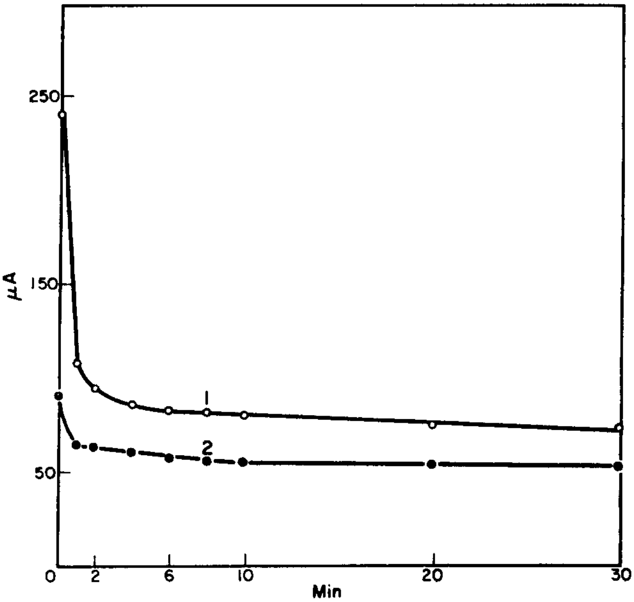

FIG. 6.—Current-time curves at the stabilisation of current values:— *1*—0·1*M* KCl; *2*—distilled water. [15·41 mg of Fe(III); total volume: 150 ml; pH: 1·7 (unbuffered); temperature: 20°; applied potential: 1·0 V].

into the titration solution. However, when one starts the titration immediately, no great differences in the course of the titration are found.

The decrease of the current just after the potential is applied is caused by polarisation of the electrodes; this does not proceed immediately under the given conditions.

Accuracy

The proposed end-point indication of the chelometric determination of iron(III) permits the determination of 1–150 mg of iron in a volume of 150 ml with reliable accuracy. The results of some titrations are summarised in Table I. The results from this table (with the exception of the results of the titration of 1–2 mg of iron, when the error is greater) give a mean relative error of ±0·8%.

Table I

Fe(III), *mg*		0·05*M* EDTA, *ml*		Difference	
Present	Found	Theory	Found	mg	%
1·03	1·06	0·33	0·34	+0·03	+2·91
2·06	2·09	0·66	0·67	+0·03	+1·46
6·18	6·12	1·98	1·96	−0·06	−0·97
15·41	15·41	5·20	5·20	0·00	0·00
30·83	30·68	10·40	10·35	−0·15	−0·52
51·38	51·53	17·35	17·40	+0·15	+0·29
82·21	81·62	27·70	27·50	−0·59	−0·73
102·76	103·40	34·68	34·90	+0·64	+0·63
154·14	155·53	52·03	52·50	+1·39	+0·90

Selectivity

The selectivity of the proposed titration was verified by the titration of 15·41 mg of iron(III) under defined conditions (pH 1·3–2·5; 20°; 1·0 V) in the presence of a series of foreign ions. The results have shown that even a high concentration of nitrate, sulphate, phosphate, acetate, chloride and borate does not interfere. Also, many metals do not interfere, *e.g.*, cobalt, lead, zinc, cadmium, calcium, barium, strontium, magnesium, manganese, uranium(VI), iron(II) and titanium(IV). On the other hand, even small concentrations of thallium(III) interfere in the titration of iron(III). Indium, gallium, zirconium, thorium and aluminium are titrated together with iron and thus interfere in the determination. Greater amounts than 50 mg of nickel and 80 mg of copper also interfere. Some metals can be masked with fluoride ions, particularly aluminium and also thorium and zirconium,[10] as in the titration of iron(III) with two platinum electrodes.[6]

Analytical application

The described chelometric titration has a similar analytical application to the titration with an indication system of two platinum electrodes.[6] The described procedure is probably best applied to the determination of iron(III) in the presence of iron(II) in various metallurgical materials.[10]

CONCLUSION

The present study has shown the possibility of replacing the two platinum electrodes with two graphite electrodes in the biamperometric titration of iron(III) with

EDTA. The obtained results are of the same accuracy and of the same selectivity. In an unbuffered medium the determination can be carried out at pH 1·1–2·5 and in a buffered medium at pH 1·1–4·2. If a microammeter is used for indicating the end-point, a higher applied potential than 0·6 V should be used.

The graphite electrodes are much cheaper than the platinum ones, which is an advantage in routine analysis. Another advantage is the possibility of determining iron(III) in an acidic medium at room temperature, which was impossible using two platinum electrodes.

Future papers in this series will present the utilisation of amperometry with two identical electrodes for the chelometric determination of some other metals which can be titrated with EDTA, *e.g.*, thorium, indium, gallium, zirconium, copper and rare earths.

As in the case of the titration of iron(III) with EDTA using two platinum indicator electrodes, it is not yet possible to give an exact explanation of the electrode reactions involved in the titration with two carbon electrodes.

In particular, the decrease of current during the titration before the equivalence point cannot yet be explained satisfactorily. An increase of current after the equivalence point was found in the chelometric titration of all metals, provided that indication with two identical electrodes of platinum or of carbon was used and, of course, the pH was kept at the optimum value for each titration. This phenomenon extends the previous presumption that the described biamperometric titrations with EDTA are possible only with metals forming redox systems. Metals which do not form redox systems have a different character in their titration curves. Because the metal ion and also its complex do not give the electrode reaction over a wide potential interval, there are no changes of current before the equivance point. Immediately after the equivalence point the presence of a minimum amount of free EDTA (which takes part in the electrode reaction) causes an increase in the current.

Zusammenfassung—Zur Anzeige der biamperometrischen Titration von Eisen(III) mit EDTA wurden zwei Kohle-(Graphit-) elektroden verwendet. Befriedigende Ergebnisse wurden in einem weiten Bereich der angelegten Spannung erhalten. Die absoluten Stromwerte hängen linear von der angelegten Spannung ab. Bei 0,6 bis 2,0 V gehen die Stromdifferenzen während der Titration von einigen μA bis zum Zehnfachen davon. Der Einfluß von pH, Spannung und Temperatur auf die Titration wurden untersucht sowie der Einfluß von Störelementen. Unter optimalen Bedingungen ist die Bestimmung sehr selektiv und genau. Man kann 1–150 mg Eisen(III) bestimmen.

Résumé—Pour l'indication du dosage biampérométrique du fer(III) au moyen d'EDTA, on a utilisé deux électrodes de carbone (graphite). Des résultats satisfaisants ont été obtenus dans un large domaine de potentiels appliqués. Les valeurs absolues du courant sont liées linéairement aux valeurs du potentiel appliqué. A un potentiel de 0,6–2,0 V, les différences de courant durant le dosage vont de plusieurs μA à dix fois ces valeurs. On a étudié les influences du pH, du potentiel appliqué et de la température sur le dosage; on a examiné l'influence des éléments interférents. Dans des conditions optimales, le dosage est hautement sélectif et précis. Il est possible de doser 1–150 mg de Fe(III).

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XVIII*

MASKING OF IRON WITH FLUORIDE

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Summary—Very simple conditions have been found for the quantitative precipitation of iron in an acidic medium as K_3FeF_6. This facilitates the complexometric determination of a number of elements, such as copper, lead, nickel, cobalt, zinc and cadmium, in the presence of iron, aluminium, titanium and the rare earths.

TRIETHANOLAMINE has been used[1,2] to mask iron and aluminium in the determination of manganese, nickel, calcium and magnesium in ores, rocks and minerals, but it screens iron completely only in alkaline solution. It cannot be used if copper or cobalt are to be determined because its complexes with these metals are sufficiently stable to prevent complete reaction with EDTA. Flaschka and Püschel[3] have screened iron(II) with cyanide, but the method is unselective and has not found application in routine work.

The problem of screening iron in an acidic medium has not hitherto been satisfactorily solved. Doornbos, Ab and Faber[4] precipitated iron as potassium hexafluoroferrate(III) and then titrated copper with EDTA using Glycinethymol Blue as indicator,[5] but some of the copper was adsorbed on the precipitate and a double titration was required to overcome this difficulty. The literature contains conflicting statements about the screening and interference effects of fluoride in the determination of iron with EDTA. Accordingly, we examined the masking of iron(III) with ammonium, sodium and potassium fluorides in the presence of nitrate. We found that ammonium fluoride was without effect on the indirect determination of iron by back-titration of an excess of EDTA, whereas sodium and potassium fluorides gave precipitates of the hexafluoroferrate(III) which were sufficiently stable not to react with EDTA. This means that with a mixture of aluminium and iron it is possible to screen aluminium alone with ammonium fluoride or both aluminium and iron with a mixture of potassium and ammonium fluorides. A detailed study has yielded a simple method for the screening of iron, aluminium, titanium and lanthanides, which can be used for the analysis of alloys, *etc*., containing these elements.

EXPERIMENTAL

Reagents

Solutions of EDTA, DCTA, iron(II), lead(II), aluminium(III), zinc(II), cadmium(II) and copper(II) were made $0{\cdot}05M$ and their concentrations were checked complexometrically. The following solutions were also prepared:— $0{\cdot}1M$ sodium fluoride, $1M$ potassium hydrogen fluoride, $2M$ ammonium fluoride, $1M$ nitric acid, 25% potassium carbonate and 0·2% Xylenol Orange. Solid urotropine and ammonium fluoride were also used.

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* Part XVII: *Talanta*, 1964, **11**, 1613.

Procedure

Add ammonium fluoride to 50–100 ml of the acid solution (0·3–0·5*M* HNO_3) containing up to 60 mg of iron. Cover the vessel containing the solution with a watch-glass and add 25% potassium carbonate solution. Adjust the pH to 5·0–5·5 with solid urotropine, and let the solution stand for 5 minutes with occasional stirring. Add a known volume of EDTA or DCTA, and titrate the solution with 0·05*M* lead nitrate, using Xylenol Orange as indicator. If all the iron has been precipitated, the amounts of EDTA or DCTA taken and found are the same. The results are shown in Table I, from which the optimum concentrations of ammonium fluoride, potassium hydrogen fluoride and potassium carbonate to be added can be deduced.

TABLE I.—PRECIPITATION OF IRON WITH FLUORIDES

Taken	Added		Back-titration		Found
Fe(III), *mg*	F, *ml*	25% K_2CO_3, *ml*	0·05*M* complexan, *ml*	0·05*M* Pb(II), *ml*	Fe(III), *mg*
2·87	10[a]	5	3·00 E[c]	1·98	2·87
			2·96 D	1·99	2·72
2·87	10[a]	10	3·00 E	2·21	2·20
			2·96 D	2·15	2·36
2·87	10[a]	20	3·00 E	2·05	2·65
			2·96 D	1·98	2·78
2·87	10[a]	30	3·00 E	2·10	2·51
			2·96 D	2·10	2·51
2·87	20[a]	5	3·00 E	2·50	1·40
			—	—	—
2·87	20[a]	10	3·00 E	2·78	0·61
			2·96 D	2·98	—
2·87	20[a]	20	3·00 E	2·98	0·06
			2·96 D	2·99	—
2·87	20[a]	30	3·00 E	2·97	0·08
			—	—	—
2·87	20[b]	30	3·00 E	3·00	—
			—	—	—
14·34	10[a]	10	9·86 D	9·25	1·70
14·34	10[b]	20	10·00 E	9·83	0·47
14·34	20[b]	10	10·00 E	9·95	0·14
14·34	20[b]	20	10·00 E	10·03	—
14·34	20[b]	30	10·00 E	9·98	0·06
57·36	10[a]	10	25·00 E	7·90	34·88
57·36	10[a]	20	25·00 E	26·90	0·28
57·36	20[b]	—	24·66 D	27·70	—
57·36	20[b]	10	25·00 E	24·93	0·20

[a] 2*M* NH_4F; [b] 1*M* KHF_2; [c] E = EDTA, D = DCTA.

It was found that the iron must be precipitated from a volume not greater than 100 ml, and the amount of precipitant needed was constant, irrespective of the amount of iron present; this meant that larger amounts of iron were more easily precipitated than small ones. Addition of sodium or potassium hydroxide also resulted in precipitation, but potassium carbonate seemed to be the best reagent to use because the carbon dioxide liberated appeared to promote the precipitation. The ammonium salt could not be precipitated. Once the iron had been precipitated, dilution of the solution to as much as 300 ml had no significant effect on the precipitate.

Determination of zinc, lead, cobalt, copper, etc., in presence of iron (aluminium)

Follow the procedure given above: to the acid solution add 2·5 g of ammonium fluoride neutralised with 25 ml of 25% potassium carbonate as described. Determine all elements indirectly by back-titration of excess of DCTA with lead nitrate using Xylenol Orange as the indicator. In Table II some typical results are given.

TABLE II.—DETERMINATION OF SOME ELEMENTS AFTER MASKING OF OF IRON AND ALUMINIUM

Taken, *mg*		$0{\cdot}05M$ complexan, *ml*	Back-titration	Found, *mg*	Difference, *mg*
Fe	Metal ion		$0{\cdot}05M$ $Pb(NO_3)_2$, *ml*	Metal ion	Metal ion
2·87	10·36 Pb(II)	2·96 DCTA	2·00	9·95 Pb(II)	−0·41 Pb(II)
2·87	207·21 Pb(II)	25·00 EDTA	4·98	207·41 Pb(II)	+0·20 Pb(II)
2·87	2·89 Ni(II)	3·00 EDTA	1·99	2·96 Ni(II)	+0·07 Ni(II)
2·87	68·39 Zn(II)	22·00 EDTA	1·13	68·12 Zn(II)	−0·17 Zn(II)
2·87	3·14 Cu(II)	4·93 DCTA	4·05	2·77 Cu(II)	−0·47 Cu(II)
2·87	57·98 Ni(II)	25·00 EDTA	5·25	57·97 Ni(II)	−0·01 Ni(II)
2·87	5·66 Cd(II)	5·00 EDTA	3·98	5·73 Cd(II)	+0·07 Cd(II)
2·87	113·31 Cd(II)	25·00 EDTA	4·83	113·35 Cd(II)	+0·04 Cd(II)
28·68	10·36 Pb(II)	5·00 EDTA	4·01	10·26 Pb(II)	−0·10 Pb(II)
28·68	3·42 Zn(II)	4·93 DCTA	4·00	3·14 Zn(II)	−0·28 Zn(II)
28·68	3·14 Cu(II)	2·96 DCTA	1·99	3·09 Cu(II)	−0·05 Cu(II)
57·36	10·36 (PbII)	3·00 EDTA	1·92	11·18 Pb(II)	+0·82 Pb(II)
57·36	3·14 Cu(II)	3·00 EDTA	1·98	3·24 Cu(II)	+0·10 Cu(II)
2·81	1·40 Al(III)	5·00 EDTA	3·99	2·82 Fe(III)	+0·01 Fe(III)
2·81	27·99 Al(III)[a]	2·94 DCTA	1·93	2·82 Fe(III)	+0·01 Fe(III)
1·41	34·99 Al(III)[a]	3·00 EDTA	2·50	1·39 Fe(III)	−0·02 Fe(III)
28·11 13·99	3·14 Cu(II)	2·94 DCTA	2·00	2·99 Cu(II)	−0·13 Cu(II)
2·81 1·40 Al(III)	103·91 Pb(II)	15·00 EDTA	4·96	104·05 Pb(II)	+0·14 Pb(II)
20·13 Fe(III)[b] 20·75 Al(III)[b]	1·00 Ni(II)	25·00 EDTA	3·80	21·20[b] Fe(III) + Ni(II)	—

[a] Al masked by 1 g of NH_4F before addition of EDTA; in this case the determination of Fe(III) or another element is carried out.

[b] Ml of $0{\cdot}05M$ solution.

RESULTS AND DISCUSSION

Precipitation of iron with fluoride

The fluoride complexes of iron(III) are less stable than the EDTA or DCTA complexes. Iron can be determined by the addition of an excess of EDTA and back-titration with lead, even in $1M$ ammonium fluoride solution, without difficulty. If sodium or potassium ions are present, however, precipitation of the alkali metal hexafluoroferrate(III) takes place. The addition of sodium fluoride will mask moderate amounts of iron in this way, but the low solubility of sodium fluoride (4% at room temperature) limits the amount of iron that can be screened. Furthermore, the presence of large amounts of fluoride in the solution causes the end-point of the back-titration to be rather indistinct. Potassium fluoride is more suitable as a reagent, giving a white microcrystalline precipitate, but again a large amount must be added. We have found, however, that the fluoride can be introduced by addition of ammonium fluoride, and the potassium added subsequently, either as the fluoride or some other salt. The precipitate gives no reaction with thiocyanate, hexacyanoferrate(III), ammonia, EDTA or DCTA, but on standing with sodium hydroxide it gives a brown precipitate of hydrous iron(III) oxide.

Interference

It has already been pointed out that aluminium, titanium and the rare earths are also masked. Aluminium (or titanium) can be selectively masked with ammonium fluoride alone (neutralise with aqueous ammonia) and the iron determined. These combined procedures have been used for the analysis of various copper alloys.

The masking of iron fails only in the presence of magnanese. We have observed an unexpected phenomenon: manganese is coprecipitated with fluoride. Probably it comes down as a double fluoride iron, which is more reactive than pure hexafluoroferrate(III) and which always gives a positive reaction for iron with thiocyanate, hexacyanoferrate(III) and ammonia. This unfavourable effect of manganese will be studied further.

Zusammenfassung—Sehr einfache Bedingungen zur quantitativen Fällung von Eisen als K_3FeF_6 in saurem Medium wurden gefunden. Das erleichtert die komplexometrische Bestimmung einer Anzahl von Elementen wie Kupfer, Blei, Nickel, Kobalt, Zink und Cadmium in Gegenwart von Eisen, Aluminium, Titan und seltenen Erden durch Zugabe überschüssiger ÄDTA und Rücktitration mit Blei unter Verwendung von Xylenol orange als Indikator.

Résumé—On a trouvé des conditions très simples pour précipiter quantitativement le fer à l'état de K_3FeF_6 en milieu acide. Ceci facilite le dosage complexométrique d'un certain nombre d'éléments tels que le cuivre, plomb, nickel, cobalt, zinc et cadmium, en présence de fer, aluminium,titane, et des terres rares, par addition d'un excès d'EDTA et dosage en retour au moyen de plomb, le Xylénol Orangé servant d'indicateur.

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DETERMINATION OF MINOR AND TRACE ELEMENTS IN NICKEL BY X-RAY SPECTROMETRY

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Summary—The authors have investigated the applicability of X-ray spectrometry to the analysis of nickel for several elements in the ppm range. Results of the investigation are presented and compared with optical spectrographic analysis as regards sensitivity, precision and accuracy, speed and convenience.

INTRODUCTION

X-RAY spectrometry has become almost commonplace for the determination of major and minor constituents of alloys. It has also been used to determine trace amounts of metals in light matrices, such as rocks, slags, petroleum and solutions. However, when trace element concentrations are to be determined in metals, optical emission spectrography is normally used, even though an overlap in ranges of the two methods is recognised.

Little has been published about the determination of trace concentrations in metals by X-ray spectrometry. Michaelis, Alvarez and Kilday[1] investigated detection limits and interferences and developed analytical curves for twenty elements in low-alloy steels. They found that detection limits for most of these elements were below 100 ppm, but those for silver, arsenic and zirconium were 9, 7 and 6 ppm, respectively. Campbell and Thatcher[2] calculated theoretical limits of detectability for several elements in iron. These ranged from 1 to 8·5 ppm for such elements as manganese, copper, chromium and titanium.

X-ray spectrometry offers some advantages, even in this range; a greater amount of sample contributes to the analysis in a shorter time, and compared with optical emission spectroscopy the spectra are simpler with fewer line interferences. The results reported here compare the X-ray method with an already well-established optical emission method for nickel analysis.

EXPERIMENTAL

Apparatus

Quantometer. An Applied Research Laboratories Vacuum X-Ray Quantometer was used in this work. This instrument comprises a multichannel spectrometer, a power supply, a control cabinet for power to the X-ray tube and an electronic read-out console. Fig. 1 shows a schematic diagram of the spectrometer. Mounted around the sample and X-ray tube are nine channels, each with its own crystal and detector. The six fixed channels are: iron, nickel, aluminum, magnesium, scattered radiation at 0·6*A* and copper. Each of these channels is equipped with the optimum arrangement of crystal; air or vacuum path; detector type, size and window; and slit setting for the particular wavelength involved. Three scanning channels together cover the range from 8·27*A* to 0·36*A*; *i.e.*, silicon and elements of higher atomic number. The wavelength ranges of these scanning channels overlap to some extent (Fig. 1), allowing a choice of vacuum or air channel for some elements. A tenth channel, known as the external standard channel, has a small copper disk in a position to be irradiated by the primary beam; the undispersed radiation from this disk is integrated until a preselected voltage is accumulated. Simultaneously, all channels integrate radiation at their particular wavelengths.

The detectors are Multitrons (non-proportional gas-amplification detectors) and Minitrons (flow Geiger detectors); the signal voltage developed by each is stored in a capacitor. At the completion of integration, as signalled by the external standard channel, the capacitors are discharged sequentially at a rapid rate, driving the chart pen to give readings proportional to the fluorescence radiation intensities.

This array is in a research instrument which is used for many tasks. For the work described, only the copper and iron fixed channels and the vacuum scanner covering the 1·07*A* to 3·77*A* range were used.

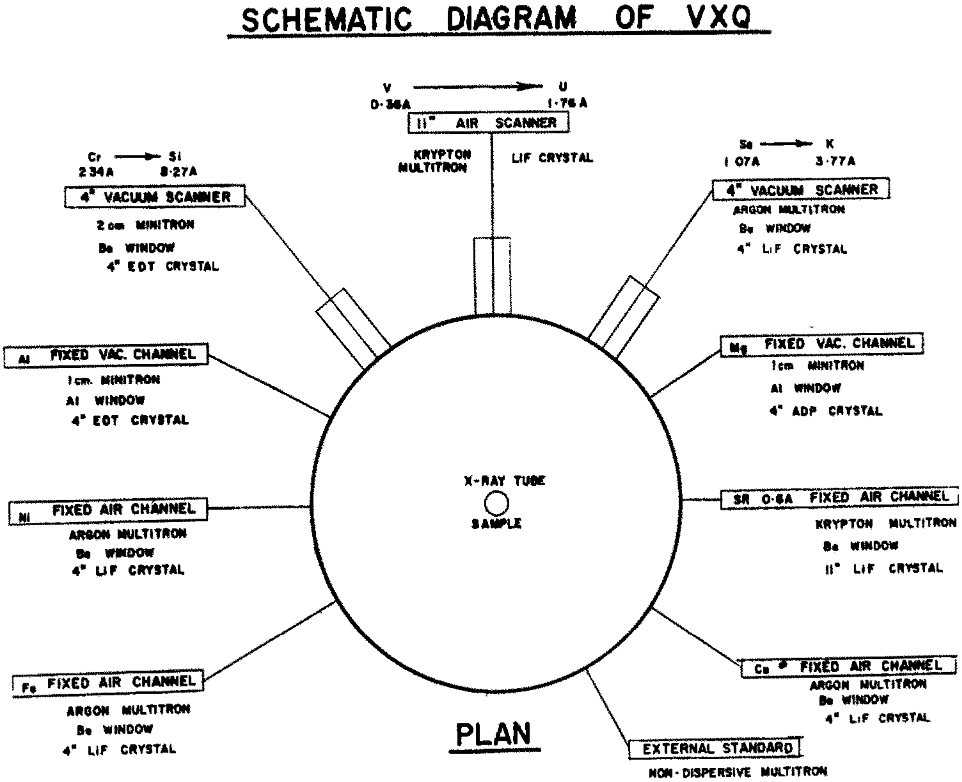

FIG. 1

Mortars and pestles. The mortars and pestles used for this work were fabricated from vacuum-melted nickel ingots. They were originally made for use in the optical emission method, particularly to avoid contamination from magnesium, silicon, aluminium and boron. Although nickel is softer than conventional mortar materials, these mortars have served the purpose very well. They are cleaned by grinding a little high purity nickel powder and the inner surfaces are occasionally polished on a lathe with diamond-impregnated plastic on a cloth backing.

Preparation of samples and standards

Few nickel standards are available commercially. The National Bureau of Standards issues three nickel oxide standards containing several elements in concentrations useful for the X-ray technique,[3] and four secondary standards of Nickel 200 are available from the Huntington Alloy Products Division of the International Nickel Company.[3]

Synthetic standards are useful and can be prepared by adding impurity element solutions to a nickel nitrate solution, evaporating to dryness and reducing the oxides to sponge by heating in hydrogen. Alternatively, oxides, carbonates or other compounds of impurity elements may be added to powdered nickel sponge to make a master standard which can be diluted with pure nickel sponge powder for analytical standards.

Clean samples of millings, drillings, chips, *etc*., with warm 10% hydrochloric acid to remove surface contamination. Powders or salts are not cleaned. Dissolve 10 g of sample in about 50 ml of

1:1 nitric acid in a platinum dish. Add 20 ml of concentrated nitric acid in 5-ml increments and evaporate the solution slowly on a hot plate at 250°. When the solution has evaporated nearly to dryness, place the dish in a muffle furnace and heat at 400° until the sample has dried and mostly oxidised. Leave the furnace door ajar to allow in air to flush out fumes of nitrogen oxides.

Loosen the sample from the platinum dish, transfer to a porcelain boat and place it in a hinged tube furnace. Pass hydrogen through the tube at about 500 ml/min and raise the temperature to 400°. Maintain this temperature for 20 min to allow complete reduction of the nickel oxide to nickel sponge. Remove the tube assembly from the furnace but maintain the hydrogen flow until the sample has cooled to room temperature. This decreases the danger of pyrophoricity.

Grind the nickel sponge to uniformly fine powder in a mortar.

Prepare briquettes in one of two ways:

(a) Press about 10 g of nickel sponge in a 1⅜″ i.d. mould at about 34,000 psi for 30 sec.

(b) Place about 4 g of boric acid in the mould and tamp with a hardwood plunger to form a flat suface.

Distribute a minimum of 2·5 g of nickel sponge evenly over the boric acid and press at 34,000 psi for 30 secs.

The first method provides a solid nickel disk about 2·5 mm thick. It is the safer method but requires more sample, reagents and time than the other. In the second method, the nickel must be distributed evenly to avoid formation of thin places in the surface, but the smaller amount of sample makes preparation quicker and easier. It is also better when the amount of sample is limited.

Good agreement was found in analyses of the two types of briquette. Density variations might be expected to cause some differences but this was not found critical in the present work. Samples sliced from nickel rods, for example, gave results that agreed reasonably well with those from briquettes.

Thus, one set of curves may be applied to solid or sponge samples. A solid sample must be free from surface contamination and the surface should be ground and polished. The boric acid-backed briquettes are generally used for sponge prepared fromd rillings, chips, powders or irregular samples. Nickel sponge powder, prepared as described here, is composed of irregular particles that bond together well whereas powders composed of spherical particles may crumble when briquetted.

Development of analytical curves

Only the iron and copper fixed channels and one scanning channel were used for this work. General parameters are:

X-ray tube—Tungsten target, end window
Power—50 KV, 35 MA
Collimator—1·25″ diameter
Crystals—Lithium fluoride, 4″ radius of curvature
Detectors—Non-proportional gas-amplification
Mode—Vacuum; sample chamber, X-ray chamber,
and scanning channel evacuated.

Air mode can be used for iron and copper at the higher concentration levels, but vacuum is required for titanium and for high sensitivities for other elements.

Calibration curves for different elements and concentration ranges are prepared in the following way. Draw a trial curve on linear co-ordinates with chart readings from zero to one hundred as abscissae and elemental concentrations over the desired range as ordinates. Obtain the desired low and high chart readings from this curve for the low and high standards. Then take actual readings on low and high standards and correlate these mathematically with the desired readings to allow the desired curve to be approximated closely. Make adjustments to attenuators which vary detector sensitivity and to potentiometers which control the zero position and sensitivity of each channel. Analyse all the standards and plot the true curves.

Good straight line curves were obtained for the following elements in nickel (the most suitable concentration ranges given in brackets):—manganese (10–80 ppm, 25–220 ppm and 0·02–0·40%), iron (20–330 ppm, 0·02–0·14% and 0·10–1·20%), cobalt (25–200 ppm, 0·01–0·10% and 0·1–1·0%), chromium (30–350 ppm and 0·02–0·14%), copper (25–500 ppm and 0·01–0·25%) and titanium (30–330 ppm and 0·01–0·10%). The K_α radiation was used except in the case of copper when $K_{\alpha 2}$ radiation was used for the lower concentration range and K_α for the higher. The NiK_α radiation interfered at low concentrations but the $K_{\alpha 2}$ was found to be more sensitive than NiK_β radiation. It is possible to obtain extra zero and sensitivity controls for the channels so that the correct range is automatically available or to provide separate channels for measurement of different ranges, but in the present work, the samples were simply re-analysed under different conditions as required.

Tests were made using ratios of the elements to nickel and to scattered radiation but these appeared to offer no advantage over the use of elemental radiation intensity alone.

Precision

The method used in estimating precision is shown in Table I. Five briquettes were prepared from the same sample and each was analysed five times. Thus, the vertical columns show the reproducibility of sampling and the horizontal columns show the reproducibility of sample orientation and of the instrument itself. In most cases the precision of sampling was as good as instrumental precision.

TABLE I.—PRECISION OF THE DETERMINATION OF MANGANESE IN NICKEL

Run Sample	1	2	3	4	5	$\bar{X}^a$	S^a	V^a
2717-1	39	40	40	41	39	40	0·7	1·8%
-2	42	41	41	41	42	41	0·7	1·7%
-3	41	38	39	41	40	40	1·3	3·3%
-4	42	41	43	42	39	41	1·6	3·9%
-5	42	40	42	43	41	42	1·2	2·9%
$\bar{X}^b$	41	40	41	42	40	41 41		
S^b	1·3	1·2	1·6	1·0	1·3		1·1 1·3	
V^b	3·2%	3·1%	3·9%	2·4%	3·3%			2·7% 3·2%

[a] Instrumental precision

[b] Sampling precision

$\bar{X}$ = Arithmetic mean

S = Standard deviation = $\sqrt{\dfrac{\Sigma(x-\bar{x})^2}{n-1}}$

V = Coefficient of variation = $\dfrac{100S}{\bar{X}}$

All figures but V are in ppm.

DISCUSSION

No attempt was made in this work to define or determine limits of detection. Michaelis *et al.*[1] define detectability as "that concentration at which the coefficient of variation is equal to 100%". Campbell and Thatcher[2] define the minimum detectable amount for the trace concentration range as "that concentration or amount that results in a line intensity above background equal to three times the square root of background for counting times that are not to exceed 10 min."

The maximum coefficient of variation encountered here was 20·9% for iron at 73 ppm. It is believed that the analytical ranges for all of the elements studied can be extended at the lower end with suitable standard samples. However, the limits reached are generally lower than were expected at the outset.

It is not expected that limits of detection by the X-ray method will surpass or even match those that can be obtained by optical emission spectrography for these elements. On the other hand, it may be possible to reach lower detection limits for some refractory elements, such as tantalum or zirconium, by direct X-ray analysis than by direct optical emission analysis.

Precision data for the six elements determined in two samples are presented in Table II. A fairly high order of precision is indicated. A comparison of precision data, made by analysing seventeen pellets of a nickel sample by optical emission analysis and seven briquettes of the same sample by the X-ray method, showed no definite advantage of one method over the other.

TABLE II.—PRECISION OF X-RAY ANALYSIS

Element	Instrumental			Sampling		
	$\bar{X}$	S	V	$\bar{X}$	S	V
	Sample no. 4597					
Manganese	1992	10	0·5%	1996	137	6·9%
Iron	1040	32	3·2	1050	193	18·4
Cobalt	880	13	1·5	880	12	1·3
Copper	330	10	3·0	330	10	3·0
Chromium	107	4·2	4·0	107	8·6	8·0
Titanium	127	7	5·8	127	21	16·0
	Sample no. 1091					
Manganese	136	2·2	1·6%	136	2·6	1·9%
Iron	73	14	20·1	73	16	20·9
Cobalt	75	6	8·4	75	6	8·6
Copper	100	6	5·9	100	6	6·0
Chromium	60	4·9	8·1	60	5·7	9·3
Titanium	75	7·6	10·8	75	7·3	9·8

Average determination, $\bar{X}$, and the standard deviation, S, are given in ppm.
Coefficient of variation, V, is in %.

TABLE III.—ACCURACY OF X-RAY ANALYSIS

Element	X-ray	Optical emission	Chemical
	Sample no. 4597		
Manganese	0·199%	0·195%	0·200%
Iron	0·105%	0·115%	0·120%
Cobalt	0·088%	0·090%	0·093%
Copper	0·033%	0·032%	0·030%
Chromium	0·011%	0·012%	0·013%
Titanium	0·013%	0·012%	0·012%
	Sample no. 1091		
Manganese	136 ppm	128 ppm	140 ppm
Iron	73 ppm	82 ppm	74 ppm
Cobalt	75 ppm	67 ppm	64 ppm
Copper	100 ppm	81 ppm	72 ppm
Chromium	60 ppm	59 ppm	67 ppm
Titanium	75 ppm	78 ppm	81 ppm
	Miscellaneous samples		
Manganese	16 ppm	12 ppm	—
Iron	26 ppm	25 ppm	—
Cobalt	59 ppm	59 ppm	64 ppm
Copper	45 ppm	40 ppm	—
Chromium	30 ppm	27 ppm	—
Titanium	26 ppm	22 ppm	—

Accuracy is indicated by comparing X-ray, optical emission and chemical analyses made on the same samples (Table III). Except for copper in sample 1091, where contamination is suspected, agreement is surprisingly good.

It is difficult to compare the speed of the X-ray method with others for the analysis of nickel because of the variety of determinations involved. There are circumstances, however, in which the X-ray method can be most rapid. For example, it allows simultaneous determination of one or more major elements and one or more minor or trace constituents in the same sample when both chemical and spectrographic methods would otherwise be required. The non-destructive nature of X-ray analysis allows re-use of the same sample briquette many times.

Finally, while it is a distinct advantage for those with both types of equipment to be able to check one method against the other, it is perhaps even more important for the X-ray spectrographer to know that the usefulness of his method can be extended to these lower limits.

Zusammenfassung—Die Autoren untersuchten die Anwendbarkeit der Röntgenspektrometrie auf die Analyse mehrerer Elemente in Nickel im ppm-Bereich. Ergebnisse werden vorgelegt und bezüglich Empfindlichkeit, Genauigkeit und Richtigkeit sowie Geschwindigkeit und Bequemlichkeit mit der optischen spektrographischen Analyse verglichen.

Résumé—Les auteurs ont étudié la possibilité d'application de la spectrométrie de rayons X à l'analyse de divers éléments dans le nickel, dans le domaine des parties par million. On présente les résultats de cette étude, et les compare à l'analyse spectrographique optique des points de vue sensibilité, précision et justesse, vitesse et commodité.

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FRONTAL SOLUBILISATION CHROMATOGRAPHY

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Summary—The behaviour of three non-electrolytes has been studied in both frontal and elution chromatography with an ion-exchange resin as stationary phase and an aqueous solution of ethanol as the mobile phase. On the basis of the plate-equilibrium theory, an equation is derived for the breakthrough graph in frontal chromatography. This is simply the integral of the equation for the graph in elution chromatography. Good agreement is found between the experimental breakthrough results and the equation, as well as between the distribution ratios and plate numbers as evaluated by the two chromatographic methods.

INTRODUCTION

ONE of the research projects of this laboratory is the chromatographic resolution of racemic substances with optically-active ion-exchange resins as the stationary phase. Ion-exchange, salting-out[1,2] and solubilisation[2,3] chromatography are included in this project. In preliminary resolutions, frontal chromatography has been more successful than elution chromatography. Because frontal salting-out and solubilisation chromatography had not been studied from either a practical or theoretical point of view, it was desired to perform such an investigation with optically-inactive resins and solutes before attempting further experiments on chromatographic resolutions. In this paper, an equation is derived on the basis of the plate-equilibrium theory for the breakthrough graph in frontal solubilisation chromatography; also, the elution behaviour of three compounds taken singly and in pairs is compared with their frontal behaviour with the aid of the plate-equilibrium theory.

EQUATION FOR FRONTAL SOLUBILISATION CHROMATOGRAPHY

From previously published equations[4] of elution chromatography

$$M = M^* \exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right]$$

$$M^* = \frac{J}{V}\sqrt{\frac{p}{2\pi C(C+1)}}$$

$$V = \frac{U^*}{C+1} \tag{1}$$

it can readily be shown that

$$M = \frac{J}{U^*}\sqrt{\frac{p(C+1)}{2\pi C}}\exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right] \tag{2}$$

where M is the molarity of the migrant solute in any fraction of the eluate;
M^* is the maximum value of M;
U is the volume of eluate collected from the beginning of the addition of the sample;
U^* is U when $M = M^*$;
p is the number of plates in the column;
C is the distribution ratio of the migrant;
V is the interstitial volume of the column;
and J is the quantity (mmol) of sample.

In frontal chromatography

$$J = M_F{}^* \int_{U=0}^{U=U} dU \tag{3}$$

where $M_F{}^*$ is the molarity of the solute in the sample solution and hence the ideal final value of M_F, the molarity of the solute in any fraction of the eluate.

If the solute molecules in the first small increment of sample in frontal chromatography are tagged with a radioactive tracer, these molecules would be distributed in the eluate fractions in the same manner as in elution chromatography; the presence or absence of other solute molecules in the portions of liquid subsequently added to the column would not alter the chromatographic behaviour of the tagged molecules. The same statement is true of any subsequent small increment of sample solution, and is also true whether the solute molecules in any increment are tagged or not. Therefore, it follows that the frontal graph is simply the integral of the elution graph. This has previously been found to be true for gas–liquid chromatography.[5–7] Now by writing M_F for M in equation (2) and substituting the value of J from equation (3), we get the equation of the frontal graph

$$M_F = \frac{M_F{}^*}{U^*} \sqrt{\frac{p(C+1)}{2\pi C}} \int_{U=0}^{U=U} \exp\left[\frac{-p}{2}\left(\frac{C+1}{C}\right)\left(\frac{U-U^*}{U^*}\right)^2\right] dU \tag{4}$$

In the theory of probability

$$t = \frac{x}{\sigma}.$$

Also from the equations[4]

$$x = U - U^*$$

$$\sigma = U^* \sqrt{\frac{C}{p(C+1)}}$$

it follows that

$$U = U^* + tU^* \sqrt{\frac{C}{p(C+1)}} \tag{5}$$

$$dU = U^* \sqrt{\frac{C}{p(C+1)}}\, dt.$$

Substitution of the last two equations into equation (4) yields

$$Y = \frac{M_F}{M_F{}^*} = \frac{1}{\sqrt{2\pi}} \int_{U=0}^{U=U} \exp\frac{-t^2}{2}\, dt \tag{6}$$

Values of the integral can be found in probability tables after converting the desired values of U to the corresponding values of t by equation (5). When $U = 0$

$$t \cong -\sqrt{\frac{p(C+1)}{C}} = -\infty.$$

For any reasonable values of p and C, the approximation is valid within the accuracy of the data in probability tables.

It should be noted that the area under the Gaussian graph to be found in probability tables is the area from $t = -\infty$ to $t = t$. Some probability tables give the area from $t = 0$ to $t = t$. These tables can be used by adding 0·5000 to the listed values.

In applying the foregoing equations to the interpretation of a symmetrical experimental breakthrough graph, it should be noted from equation (5) that when $U = U^*$, $t = 0$ and $Y = 0{\cdot}500$. C can then be evaluated by equation (1) after V is determined experimentally or estimated from published data.[8] To determine p, any convenient value of Y is selected, and the corresponding value of U is read from the experimental graph. The value $Y = 0{\cdot}900$ is recommended because the breakthrough curve has a moderate slope at this point, permitting an accurate reading of the corresponding U; then $t = 1{\cdot}282$. By substitution of this value and the appropiate values of U, U^* and C in equation (5), the value of p is calculated. It is desirable to repeat the calculation at $Y = 0{\cdot}100$, $t = -1{\cdot}282$ to test the symmetry of the graph; a symmetrical graph will give identical values of p.

EXPERIMENTAL

A column, 6·25 cm × 3·80 cm², of Dowex 50-X4, 200–400 mesh, was used. The resin had been previously conditioned by successive passages of 1M hydrochloric acid, water, 95% ethanol, water, 1M sodium hydroxide and water, with several repetitions of the cycle, ending with the resin in the hydrogen form. Finally, a sufficient volume of aqueous ethanol solution (3·00 volumes of 95% ethanol plus 7·00 volumes of water) was passed through the column to equilibrate it. The interstitial volume of the column was 7·85 ml.

Acetophenone, nitrobenzene and β-naphthol of the best available grade were used without further purification. Each of these compounds was subjected to both elution and frontal chromatography with aqueous ethanol of the foregoing composition as eluent or solvent, respectively. In frontal chromatography the concentrations of solutes were between 4×10^{-5} and $3 \times 10^{-4}M$. Eluate fractions of 3·60 ml were collected automatically and analysed by ultraviolet spectrophotometry. Elution or breakthrough graphs were plotted in all cases and used to evaluate C and p for the solute(s) present. A less extensive investigation was also made of the behaviour of β-naphthol in both elution and frontal chromatography with Dowex 50-X8 as the stationary phase.

RESULTS

In most of the breakthrough graphs, the final concentration of the eluate fell a little short of the concentration of the feed solution. This may be the result of the presence in each of the three solutes investigated of a small percentage of a more tenaciously absorbed impurity. If M_F^* in equation (6) is taken as the concentration on the plateau after the breakthrough, the experimental curves follow equation (6) very closely. A typical example of the breakthrough graphs of two solutes in one solution is shown in Fig. 1. The maximum difference between the concentration of any fraction of eluate and the value calculated by equation (6) from the values of C and P of experiments 8 and 19 of Table I was only $3 \times 10^{-6}M$.

The elution graphs were nearly perfect Gaussian curves. A comparison of the

TABLE I.—SUMMARY OF CHROMATOGRAPHIC RESULTS

No.	Compound studied	Other compound present	Resin[a]	Type	Flow rate, *cm/min*	*C*	*P*
1	$C_6H_5NO_2$	None	B	elution	0·18	8·06	42
2	$C_6H_5NO_2$	None	B	frontal	0·18	7·82	38
3	$C_6H_5NO_2$	β-$C_{10}H_7OH$	B	elution	0·18	8·04	41
4	$C_6H_5NO_2$	β-$C_{10}H_7OH$	B	frontal	0·18	8·10	38
5	$C_6H_5COCH_3$	None	B	elution	0·18	5·72	31
6	$C_6H_5COCH_3$	None	B	frontal	0·18	5·50	32
7	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	B	elution	0·18	5·68	33
8	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	B	frontal	0·18	5·59	33
9	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·18	5·67	24
10	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·25	5·32	23
11	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·31	5·23	22
12	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·46	5·08	18
13	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	frontal	0·46	5·18	19
14	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	elution	0·70	5·08	13
15	$C_6H_5COCH_3$	β-$C_{10}H_7OH$	A	frontal	0·70	5·28	12
16	β-$C_{10}H_7OH$	None	B	elution	0·18	17·7	33
17	β-$C_{10}H_7OH$	None	B	frontal	0·18	18·3	33
18	β-$C_{10}H_7OH$	$C_6H_5COCH_3$	B	elution	0·18	17·7	31
19	β-$C_{10}H_7OH$	$C_6H_5COCH_3$	B	frontal	0·18	18·3	33
20	β-$C_{10}H_7OH$	$C_6H_5NO_2$	B	elution	0·18	17·4	31
21	β-$C_{10}H_7OH$	$C_6H_5NO_2$	B	frontal	0·18	17·9	33
22	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·18	17·9	23
23	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·18	17·6	28
24	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·25	16·0	19
25	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·31	16·0	17
26	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·31	17·2	15
27	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·46	15·3	12
28	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	elution	0·70	15·2	8
29	$C_{10}H_7OH$	$C_6H_5COCH_3$	A	frontal	0·70	16·5	7
30	$C_{10}H_7OH$	None	B	elution	0·46	15·7	18
31	$C_{10}H_7OH$	None	B	frontal	0·46	16·7	16
32	$C_{10}H_7OH$	None	B	elution	0·70	15·3	13
33	$C_{10}H_7OH$	None	B	frontal	0·70	16·8	13

[a] Resins A and B refer to two different columns of Dowex 50-X4.

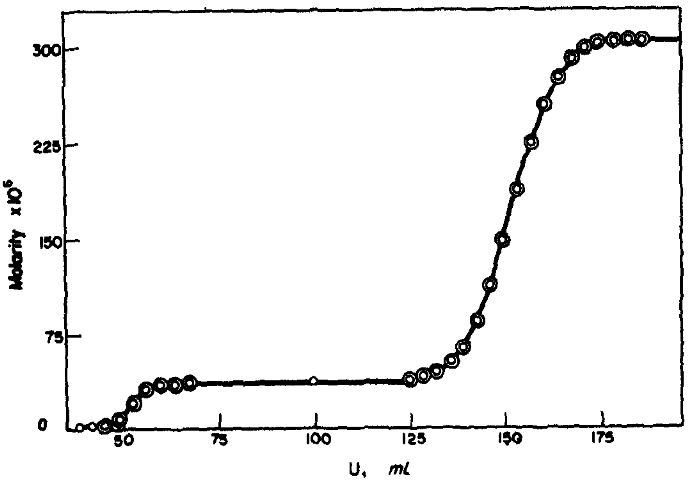

FIG. 1.—Frontal graph of a solution 36·2 × $10^{-6}M$ in acetophenone and 271·0 × 10^{-6} *M* in β-naphthol at 0·18 cm per min (see text for other experimental details). Small circles represent experimental points. Large circles represent points calculated

values of C and P, the number of plates per cm of column height, is given in Table I.

The C values and the P values of experiments 1–4 agree within the experimental error, indicating that these parameters may be evaluated for nitrobenzene by either of the chromatographic techniques with equal reliability. These results also indicate that β-naphthol, which emerges from the column after nitrobenzene, does not affect the chromatographic behaviour of nitrobenzene, in the concentrations used in these experiments.

Experiments 5–8 confirm the same observations in regard to acetophenone in the presence or absence of β-naphthol. Experiments 9–15 show that C and P for acetophenone are slightly influenced by changes in the flow rate. This is an indication of lack of equilibrium.

Experiments 13–33 show slightly larger C values for frontal chromatography than for elution experiments. The differences may be within the experimental error. The presence of acetophenone or nitrobenzene, both of which emerge from the column before β-naphthol, does not affect the behaviour of β-naphthol. Experiments 22–33 indicate again the effect of increasing flow rate.

The experiments, both frontal and elution, with β-naphthol and Dowex 50-X8 yielded P values between 10 and 12 and C values of 12·2.

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Zusammenfassung—Das Verhalten dreier Nichtelektrolyte bei Frontal- und Elutionschromatographie mit einem Ionenaustauscherharz als stationärer und einer wäßrigen Alkohollösung als beweglicher Phase wurde untersucht. Auf Grund der Theorie des Bodengleichgewichts wurde eine Gleichung für den Durchbruchsverlauf bei der Frontalchromatographie abgeleitet. Diese ist einfach das Integral der Gleichung für den Verlauf bei der Elutionschromatographie. Es wurde gute Übereinstimmung zwischen den experimentellen Durchbruchsdaten und der Gleichung gefunden, ebenso zwischen den Verteilungsverhältnissen und Bodenzahlen, die nach den beiden chromatographischen Methoden gefunden wurden.

Résumé—On a étudié le comportement de trois non-électrolytes en chromatographie frontale et en chromatograhie d'élution, avec une résine échangeuse d'ions comme phase stationnaire et une solution aqueuse d'alcool comme phase mobile. Sur la base de la théorie d'équilibre des plateaux, on a déduit une équation pour le graphique d'"affleurement" en chromatographie frontale. Celle-ci est simplement l'intégrale de l'équation du graphique de la chromatographie d'élution. On a trouvé un bon accord entre les données expérimentales d'"affleurement" et l'équation, et entre les coefficients de distribution et les numéros des plateaux, ainsi qu'ils sont évalués par les deux méthodes chromatograhiques.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—IX*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF BISMUTH

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Summary—A simple radiochemical separation of bismuth has been developed, based on two dithizone extraction steps, the second of which is a substoichiometric extraction. When copper, gold, mercury, palladium, platinum and silver are not present in interfering amounts, only the substoichiometric dithizone extraction is necessary. The method has been applied to the determination of bismuth by activation analysis in granite and in silicon.

BISMUTH is a mono-isotopic element: on irradiation with thermal neutrons ^{210m}Bi and ^{210}Bi are formed according to following nuclear reactions:

$$^{209}\text{Bi}\,(\text{n}, \gamma)\,^{210m}\text{Bi} \quad \sigma = 0{\cdot}019 \text{ barn, t/2} = 5{\cdot}0 \text{ day}$$

$$^{209}\text{Bi}\,(\text{n}, \gamma)\,^{210}\text{Bi} \quad \sigma = 0{\cdot}014 \text{ barn, t/2} = 2{\cdot}1 \times 10^{6} \text{ year.}$$

Of these isotopes only ^{210m}Bi is suitable for activation analysis. Because gamma spectrometry cannot be used for measuring the activity of this beta-emitter (β: 1·15 MeV; $1{\cdot}7 \times 10^{-4}\%$ α), radiobismuth must be isolated in a radiochemically pure state. Of various organic reagents which form extractable chelates with bismuth, such as thenoyltrifluoracetone, thio-oxine, diethylammonium diethyldithiocarbamate and dithizone, the two latter reagents are probably the most suitable for the substoichiometric separation of bismuth. However, in the case of dithizone the quantitative extraction data (log K) of a number of metal dithizonates are well known (Table I).

Reproducibility

Substoichiometric separation is reproducible only when the organic reagent used (dithizone in carbon tetrachloride in the present case) is consumed completely, forming an extractable chelate with the element under investigation. This condition is fulfilled if the pH of the extracted solution corresponds to the value calculated according to the formulae:[2,3]

$$\text{pH} \geqslant -\frac{1}{\text{N}} \log \text{K} - \log 0{\cdot}001\, c_{\text{HA}} \tag{1}$$

$$\text{pH} \leqslant \text{pK}_{\text{HA}} + \log q_{\text{HA}} + \log \frac{\text{V}_{\text{org}}}{\text{V}} \tag{2}$$

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For carbon tetrachloride extraction ($V_{CCl_4}:V_{H_2O} = 1:10$), and for the case when 0·1% of the original concentration of dithizone remains unreacted (0·001 c_{HA}), the pH of the treated solution must lie in the region 2·7 to 8; when 1% of dithizone remains unreacted, $1{\cdot}7 < \text{pH} > 8$ ($K_{HA} = 2{\cdot}8 \times 10^{-5}$; $q_{HA} = 1{\cdot}1 \times 10^{-4}$; $c_{HA} \simeq 10^{-3}$ M). The good agreement of this theory with experimental results can be seen from Figs. 1 and 3.

TABLE I.—EXTRACTION DATA OF METAL DITHIZONATES[1]

Metal	log K[a]	Metal	log K[a]	Metal	log K[a]
Ag^+	7·18	Fm^{3+}	N	Pr^{3+}	N
Al^{3+}	N	Ga^{3+}	1·3	Pu^{3+}	N
				Pu^{4+}	N
Am^{3+}	N	Gd^{3+}	N	PoO_2^{2+}	N
Ba^{2+}	N	Hg^{2+}	26·85	Sc^{3+}	N
Be^{2+}	N	In^{3+}	4·84	Sm^{3+}	N
Bi^{3+}	9·98	La^{3+}	N	Sr^{2+}	N
Bk^{3+}	N	Lu^{3+}	N	Tb^{3+}	N
Ca^{2+}	N	Mg^{2+}	N	Th^{4+}	N
Cd^{2+}	2·14	Mn^{2+}	P	Tl^+	−3·3
Ce^{3+}	N	H_2MoO_4	N	U^{4+}	N
Cf^{3+}	N	Nd^{3+}	N	UO_2^{2+}	N
Co^{2+}	1·53	Np^{3+}	N	Y^{3+}	N
Cu^{2+}	10·53	Ni^{2+}	1·19	Yb^{3+}	N
Dy^{3+}	N	Pb^{2+}	0·44	Zn^{2+}	2·3
Eu^{3+}	N	Pd^{2+}	27	Zr^{4+}	N
Fe^{3+}	N	Pm^{3+}	N		

[a] N = metal not extracted; P = metal partially extracted.

Selectivity

The selectivity of the substoichiometric separation of bismuth with dithizone (H_2Dz) can be evaluated from the data given in Table I. Palladium, mercury, copper and silver (as well as gold and platinum, for which log K values are not known), interfere in the determination, being extracted simultaneously with bismuth even when a substoichiometric amount of dithizone is used. On the other hand, at pH > 9 in the presence of cyanide ions only Bi^{3+}, In^{3+}, Pb^{2+}, Sn^{2+} (log K value not known precisely) and Tl^+ are extracted as dithizonates into carbon tetrachloride.[1] Of these ions, the extraction constant of $In(HDz)_3$ is the closest one to that of $Bi(HDz)_3$, and

$$\frac{[Bi(HDz)_3]\,\text{org}}{[In(HDz)_3]\,\text{org}} = 1{\cdot}4 \times 10^5 \frac{[Bi^{3+}]}{[In^{3+}]}.$$

Accordingly, indium will not interfere in the determination of bismuth.[2] From the above it follows that a highly selective radiochemical separation of bismuth, based on the preliminary extraction of bismuth from cyanide solution at pH > 9 using an *excess* of dithizone in carbon tetrachloride, is possible. The bismuth is then stripped from the organic phase with an aqueous solution of mineral acid and substoichiometric extraction of the bismuth carried out with a second portion of dithizone after adjusting the pH to 4 ± 2.

EXPERIMENTAL

Apparatus

Geiger–Müller end-window-counter
pH meter. Radiometer TTT1 (Copenhagen, Denmark).
Spectrophotometer. Zeiss Universal (Jena, DDR).
Separatory funnels. 50- and 150-ml volume.

Reagents

Bismuth carrier. Prepared by dissolving analytical reagent grade metallic bismuth in a small volume of nitric acid, evaporating nearly to dryness, then diluting to an appropriate volume with water (200 μg of bismuth/ml).

Dithizone solution. $7 \times 10^{-4}M$ in carbon tetrachloride.

Acetate buffer (pH 5·6). 0·2M acetic acid plus 0·2M sodium acetate (1:9).

Borax buffer (pH 10). 0·1M sodium hydroxide plus 0·05M sodium tetraborate (2:3).

Radiobismuth tracer. The RaE used as a tracer in preliminary experiments was prepared by dithizone extraction from an RaD preparation.

Irradiation

The test samples (*ca.* 0·5–1 g) of granite were sealed in quartz ampoules and irradiated in a neutron flux of $7{\cdot}5 \times 10^{12}$ neutrons . cm^{-2} . sec^{-1} for 100 hr in a nuclear reactor. The bismuth standard (containing 2 mg of bismuth) was sealed in a quartz ampoule and irradiated simultaneously with the test samples.

Development of Method

Reproducibility

The optimum pH range for substoichiometric separation of bismuth was first investigated. To a series of separatory funnels containing 20 ml of water and 0·5 ml of 10% ascorbic acid, 200 μg of bismuth were added and the pH adjusted (with nitric acid or aqueous ammonia) to different values in the range from 0 to 12. After adding 1·5 ml of dithizone solution (a substoichiometric amount), the extraction was carried out for 3 min and the amount of bismuth present in the organic extract measured either spectrophotometrically at 490 mμ or radiometrically (bismuth carrier labelled with RaE used and the activity of the evaporated organic phase measured by a Geiger–Müller counter). From the curve obtained (Fig. 1) a suitable acidity (pH 2–6) can be seen.

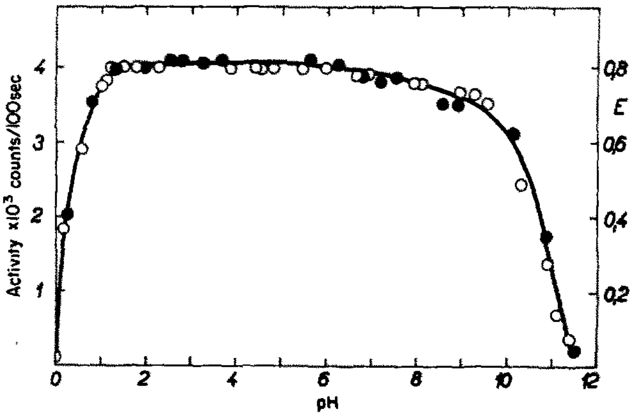

FIG. 1.—Influence of pH on the extraction of bismuth (200 μg) using a substoichiometric amount of dithizone in carbon tetrachloride:

○—spectrophotometric measurements,
●—radiometric measurements.

The time necessary for reaching extraction equilibrium has been tested by extraction of a solution of the following composition: 10 ml of water, 200 μg of bismuth carrier, 5 ml of acetate buffer, 0·5 ml of 10% ascorbic acid; the pH was adjusted to 5 ± 1 with dilute aqueous ammonia. This solution was shaken with 1·5 ml of dithizone solution and the amount of $Bi(HDz)_3$ extracted measured spectrophotometrically; the amount of bismuth extracted was plotted against the time of shaking

(Fig. 2). The extraction was repeated with a second substoichiometric portion of dithizone. An extraction time of 2 min is quite satisfactory.

The reproducibility of the substoichiometric separation was tested in the following way. The acidity of a series of solutions, containing known, increasing amounts of bismuth carrier and 0·5 ml of 10% ascorbic acid, was adjusted to pH 5 ± 1. These solutions were simultaneously extracted with 2·00 ml of dithizone solution for 3 min and the amount of extracted bismuth measured spectrophotometrically (Fig. 3). The same curve has been obtained by means of radiometric measurements using RaE as a tracer.

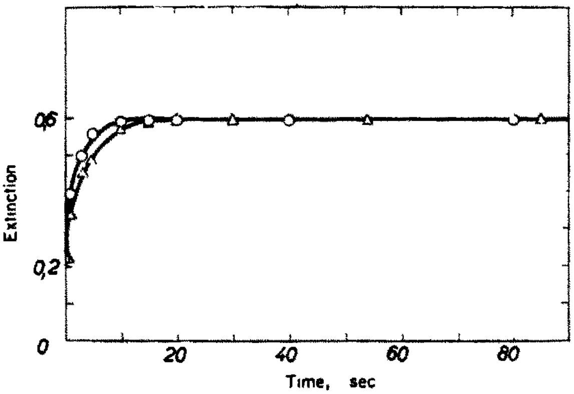

FIG. 2.—Time necessary for reaching extraction equilibrium. Extraction of 200 μg of bismuth with two successive substoichiometric portions of dithizone in carbon tetrachloride at pH *ca.* 4 (spectrophotometric measurements):
○—first extract,
△—second extract.

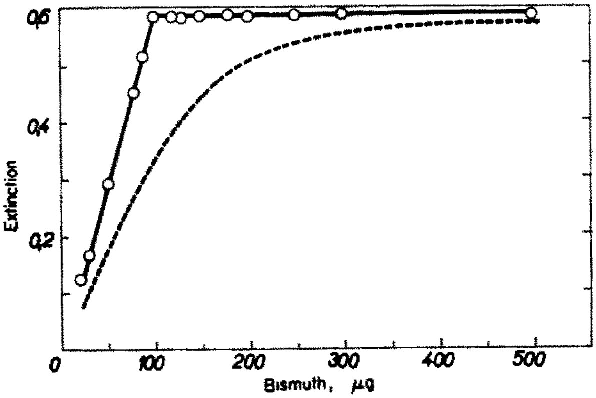

FIG. 3.—Reproducibility of the substoichiometric extraction of bismuth with dithizone at pH *ca.* 4. The dotted line illustrates the influence of a higher acidity (pH < 2).

Selectivity

The selectivity of the substoichiometric separation was investigated by means of microgram amounts of radioisotopes of possible interfering ions. These radioisotopes are mixed with bismuth carrier (400 μg of bismuth) and the proposed radiochemical separation carried out (see *Procedure*). The selectivity of the separation steps is evaluated from the activities of the organic and aqueous phases, respectively. From Table II it can be seen that only indium, if present in large amounts, interferes in the substoichiometric determination of bismuth by activation analysis. However, this interference is not serious for well known nuclear reasons.

The influence of various anions, which can be present in the extracted solution from dissolution of the test samples or as a component of buffer and masking solutions, has been studied spectrophotometrically. If present in 0·2*M* concentration, the following salts do not interfere in the extraction of $Bi(HDz)_3$ at pH *ca.* 10 (percentage extraction stated in parenthesis): ammonium acetate (95%), sodium tartarate (95%), ammonium citrate (95%), sodium sulphate (95%) ammonium chloride (75%), sodium phosphate (80%), ammonium fluoride ($0{\cdot}1M$ — 60%), ammonium fluoride and boric acid ($0{\cdot}1M + 0{\cdot}01M$; —95%), potassium cyanide (95%) and sodium tetraborate (95%).

TABLE II.—INTERFERENCE WITH THE EXTRACTION OF BISMUTH CAUSED BY THE ADDITION OF RADIOACTIVE TRACERS[a]

Radioisotope added	^{204}Tl	^{72}Ga	^{114}In	^{110}Ag	^{203}Hg	^{64}Cu
Total activity added,[b] *cpm*	54,560	16,020	15,300	20,220	25,300	18,210
Activity of dithizone extract from cyanide medium, *cpm*	48,720	30	15,120	18	150	60
Activity of HNO_3 strip solution, *cpm*	32,880	0	11,520	0	0	(5)
Activity of substoichiometric extract, *cpm*	0	0	81	0	0	0
%	0	0	0·5	0	0	0

[a] 400 μg of bismuth present as carrier, interferring metals present in microgram amounts.

[b] Only one-tenth of the total activity was actually measured.

Procedure

Dissolve the finely pulverised irradiated sample of granite in a mixture of nitric, hydrofluoric and sulphuric acids in the presence of bismuth carrier (200 μg of bismuth). Evaporate the solution to the appearance of fumes of sulphuric acid (nearly to dryness). Add 20 ml of hot $0{\cdot}1M$ nitric acid and transfer to a 150-ml separatory funnel, then add 10 ml of $2M$ tartaric acid (to prevent the hydrolysis of aluminium) and 5 ml of 10% ascorbic acid, followed by $6M$ aqueous ammonia dropwise to pH 6–10.

Add 10 ml of 10% potassium cyanide and 5 ml of borax buffer (pH now *ca.* 10). Extract with three successive 5-ml portions of dithizone solution for 2 min. Wash the combined organic extracts with water, transfer to a 50-ml separatory funnel, then strip the bismuth with 5 ml of $2{\cdot}8M$ nitric acid and 1 ml of 10% ascorbic acid by shaking for 2 min. Add 5 ml of acetate buffer to the separated aqueous phase and adjust the pH to 5 ± 1. Finally, carry out the substoichiometric extraction using 1·5 ml of dithizone solution for 2 min. Evaporate to dryness 1·0 ml of the organic extract on a counting tray on which a disc of filter paper has been placed, and mount for counting.

An appropriate amount of bismuth standard is treated and counted in the same way. The amount of bismuth (y) present in the test sample is calculated from the relationship[3]

$$y = y_s \frac{a}{a_s}$$

where y_s is the amount of bismuth present in the standard sample, and a and a_s are the activities isolated substoichiometrically from the test and standard samples, respectively.

Pure silicon can be treated in a similar way to that described above for samples of granite.

RESULTS AND DISCUSSION

The results of the analysis of granites and pure silicon by the developed procedure are summarised in Table III. The radiochemical purity of the substoichiometric extract was checked by decay measurements (Fig. 4) and by the method of successive substoichiometric extracts. The latter uses two successive, substoichiometric (1·5-ml) portions of extracting agent. In this way two extracts are obtained from the test sample for measuring activities a' and a''. If these activities are equal, it can be judged that not only the reproducibility of the substoichiometric separation (see also Fig. 3) but also the radiochemical purity of the extracts obtained is satisfactory.

Previous radiochemical separations of bismuth developed by different authors[4–8] for the activation analysis of various materials are rather complicated and time consuming. In comparison, the radiochemical procedure now described is simpler, because it is based on two dithizone extraction steps, the second being the substoichiometric one. The selectivity of this method has been demonstrated by its application to the analysis of granite and silicon. When silver, copper, mercury, gold, palladium and platinum are not present in interferring amounts in the test material, the proposed procedure can be further simplified by using only the final substoichiometric dithizone extraction.

TABLE III.—SUBSTOICHIOMETRIC DETERMINATION OF BISMUTH IN GRANITES AND SILICON

Sample	Granite I[a]	Granite II[a]	Granite II[a]	Silicon[c]
Weight, *g*	0·9237	0·5480	0·5482	4·5033
Amount (y_s) of Bi present in standard, *μg*	8·0	8·0	8·0	8·0
Activity obtained from test sample,[b] *a′*	518	263	207	131
a″	534	219	212	—
Activity obtained from standard sample, a_s	456	456	456	5461
Amount of bismuth found, *μg*	9·1	4·6	3·6	0·19
	9·4	3·8	3·7	—
%	1·0 × 10^{-3} [d]	7·7 × 10^{-4} [d]	6·7 × 10^{-4} [d]	4·2 × 10^{-6}

[a] Activities, expressed in c/100 sec, are mean values from 10 measurements corrected for background and decay.

[b] *a′* = first substoichiometric extract; *a″* = second substoichiometric extract.

[c] Activity expressed in c/1000 sec.

[d] Of the order of 10^{-3}% of bismuth was found spectrographically.

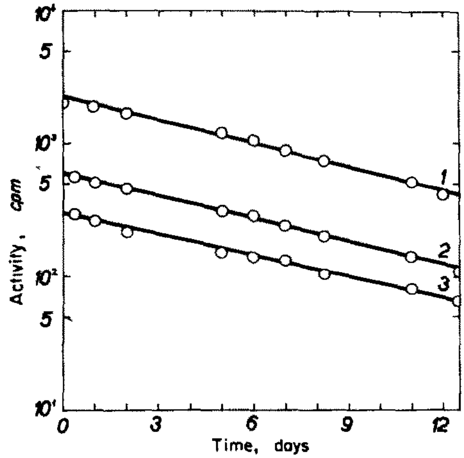

FIG. 4.—The decay curves of dithizonate extracts obtained from irradiated samples of:
1—bismuth standard,
2—granite I,
3—granite II.

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Zusammenfassung—Eine einfache radiochemische Methode zur Abtrennung von Wismut wurde entwickelt. Sie beruht auf Extraktion mit Dithizon in zwei Stufen; bei der zweiten Stufe wird unterstöchiometrisch extrahiert. Wenn Kupfer, Gold, Quecksilber, Palladium, Platin und Silber nicht in störenden Mengen anwesend sind, ist nur die unterstöchiometrische Extraktion mit Dithizon notwendig. Die Methode wurde auf die aktivierungsanalytische Bestimmung von Wismut in Granit und in Silicium angewandt.

Résumé—On a mis au point une méthode simple de séparation radiochimique du bismuth, basée sur deux stades d'extraction à la dithizone, la seconde étant une extraction substoechiométrique. Celle-ci est seule nécessaire lorsque cuivre, or, mercure, palladium, platine et argent ne sont pas présents en quantités susceptibles d'interférer. On a appliqué la méthode au dosage du bismuth par analyse par activation dans le granit et le silicium.

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DETERMINATION OF COPPER IN SEA WATER BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary—A commerical atomic absorption spectrophotometer is used without modification to establish the most suitable operating conditions for the determination of copper. Using the direct method of spraying aqueous solutions of copper into the flame, the minimum copper which can be determined is about 25 μg/litre. However, this method is not suitable for determining copper in sea water. A method based on the extraction of the copper-ammonium pyrrolidine dithiocarbamate complex into ethyl acetate and spraying of the organic extract into the flame is satisfactory, and it gives a marked increase in sensitivity.

INTRODUCTION

THE determination of trace metals has in recent times gained considerable analytical significance. Many methods and techniques have been applied to this end with varying degrees of success. The development of atomic absorption spectroscopy by Walsh,[1,2] however, provided a technique which has been particularly useful in the determination of trace metals because of its reduced susceptibility to interference. In this respect it is superior to emission spectroscopy and flame photometry, two techniques of great value in trace metal determination.

In the short time since its innovation, a large volume of literature has appeared on the application of this technique to the determination of small amounts of metals in various materials.[3] Allan[4] used the technique successfully for the determination to trace metals in agricultural materials, while Menzies[5] reported on its use for the analysis of industrial alloys and Erinc and Magee[6] used it for the determination of palladium in platinum metal alloys.

Sea water contains very small concentrations of metals such as copper, zinc and nickel. Fabricand *et al.*[7] employed atomic absorption spectroscopy for the determination of metal concentrations in water from the Pacific and Atlantic Oceans. However, investigations of this type are not numerous and the lack of reliable measurements on trace constituents has been pointed out by several authors.[8] The present work was undertaken to investigate the minimum amount of copper which could be determined by atomic absorption spectroscopy, with the purpose of using the method for the determination of copper in sea water.

EXPERIMENTAL

Apparatus

A standard Uvispek H 700 spectrophotometer, fitted with a Hilger H 1100 atomic absorption attachment, was used. For the line source a standard Hilger and Watts copper hollow-cathode lamp was employed. Although trends in the results indicated that modification of the spraying chamber might be an advantage, no alterations were made to the standard commercial equipment.

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The regular arrangement of equipment and method of operation were used throughout. These have been described often, elsewhere, and will not be repeated here. Gatehouse and Willis[9] established conditions for the determination of copper by the atomic absorption method. However, the instrument used was different to that in the present work and experience has shown that conditions are very much dependent on the apparatus used. The optimum conditions for the particular instrument used n the present work were, therefore, investigated.

RESULTS AND DISCUSSION

Effect of lamp current

In their work Gatehouse and Willis[9] found that the spectral line at 3248 Å was the most sensitive for measurement of the absorption of copper. In investigations on the lamp current, therefore, this wavelength was used. An aqueous solution of copper sulphate ($CuSO_4 \cdot 5H_2O$), containing 100 μg atom of copper/litre,* was sprayed into the flame. The results are shown in Table I. Maximum response was obtained at a lamp current of 4·5 mA, which was, therefore, used in subsequent investigations.

TABLE I.—EFFECT OF LAMP CURRENT

Lamp current, *mA*	Response (optical density)
4·5	0·112
10·0	0·105
14·5	0·102
19·5	0·095
24·0	0·094
28·5	0·092
34·0	0·085

(Slit width: 0·25 mm; air pressure: 20 lb/in.^{2}; propane gas pressure: 2 lb/in.^{2})

Effect of slit-width

In the instrument used by the earlier workers,[9] a slit-width of 3 mm was considered best for maximum absorption by copper at 3248 Å. The spectrophotometer used in the present work, however, provided for slit-widths up to a maximum of 2 mm. It was necessary, therefore, to determine the optimum slit-width. The results (average values for a number of readings) are shown in Table II. Although the response

TABLE II.—EFFECT OF SLIT-WIDTH

Slit width, *mm*	Response (optical density)
0·50	0·108
0·45	0·108
0·40	0·110
0·35	0·110
0·30	0·110
0·25	0·111
0·20	0·111
0·15	0·111
0·10	0·120

(Wavelength: 3248 Å; lamp current: 4·5 mA; air pressure: 20 lb/in.^{2}; propane gas pressure: 2 lb/in.^{2}; solution sprayed: 100 μg of copper atom/litre.)

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* μg atom/litre = μg × atomic weight/litre

increases at lower slit-widths, it was not considered desirable to use these because results below a slit-width of 0·25 mm were not easily reproducible. For a lamp current of 4·5 mA, the best results were always obtained using a slit-width of 0·25–0·30 mm.

Effect of air/propane gas pressures

An air/propane gas flame was used throughout the work. Investigation of the gas pressure was considered necessary because, according to Elwell and Gidley,[3] the time for a droplet to pass through 1 cm of flame is about 10 msec, so that lowering the gas pressure should decrease the velocity of the gases and, consequently, the velocity at which the droplets pass through the flame, thereby enhancing the sensitivity. The results for air and propane gas pressures are shown in Tables III and IV, respectively.

TABLE III.—EFFECT OF AIR PRESSURE

Air pressure *lb/in.²*	Response (optical density)
20	0·124
22	0·125
24	0·132
25	0·134
27	0·137
29	0·138
30	0·137
32	0·134
34	0·132

(Slit-width: 0·25 mm; lamp current: 4·5 mA; propane gas pressure: 2 lb/in.²; wavelength: 3248 Å; solution sprayed: 100 μg atom of copper/litre.)

TABLE IV.—EFFECT OF PROPANE GAS PRESSURE

Propane gas pressure, *lb/in.²*	Response (optical density)
1	0·126
1·5	0·129
2	0·134
2·5	0·134
3	0·133

(Slit-width: 0·25 mm; air pressure: 29 lb/in.²; lamp current: 4·5 mA; wavelength: 3248 Å; solution sprayed: 100 μg atom of copper/litre.)

Increase in the propane gas pressure above 3 lb/in.² produced a tendency to luminosity in the flame. From the point of view of response and reproducibility an air pressure of 29 lb/in.² and a propane gas pressure of 2 lb/in.² were found to be the most suitable for aqueous solutions of copper.

Effect of absorbance path

In spraying aqueous solutions of copper, the height of the *absorbance path** in the flame relative to the base of the flame was found to have a marked influence on

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* This is more fundamental than the *burner position*.

the response (Table V). It will be seen that an aqueous solution of copper sprayed into the flame gives maximum response at high absorbance path.

TABLE V.—EFFECT OF ABSORBANCE PATH

Absorbance path	Response (optical density)
Low	0·040
Low medium	0·046
High medium	0·052
High	0·053

(Slit-width: 0·25 mm; air pressure: 29 lb/in.^{2}; lamp current: 4·5 mA; wavelength: 3248 Å; solution sprayed: 40 μg atom of copper/litre).

Analytical results

Using the above optimum conditions for maximum response, a series of copper solutions, prepared from copper sulphate, was sprayed into the flame and the response recorded (Table VI).

TABLE VI.—RESPONSE FOR VARYING AMOUNTS OF COPPER

Copper present, *μg/litre*	Response (optical density)
250	0·006
200	0·005
150	0·004
100	0·003
50	0·002
25	0·002
10	—

The values shown for the response are an average of a number of readings at each concentration. Below 50 μg of copper/litre the sensitivity decreases and below 25 μg/litre a sensible response was not obtained.

For different amounts of copper a calibration curve was obtained and is shown in Fig. 1 (curve A).

Copper in sea water

The method was applied to the determination of copper in sea water drawn from the Belfast Lough. Satisfactory results could not be obtained, however, because of interference from other elements present in the sea water, principally sodium. In order to overcome this difficulty with the direct method, a new approach was made by way of copper complexes and their selective extraction into organic solvents.

Behaviour of copper complexes

The use of metal complexes sprayed into the flame from organic solvents is not extensive in atomic absorption spectroscopy. Erinc and Magee[6] determined palladium by extracting the palladium pyridine thiocyanate complex in hexone and spraying the organic extract into the flame. More particularly, Allan[10] formed the ammonium pyrrolidine dithiocarbamate complex of copper and extracted it into ethyl acetate. This extract, sprayed into the flame, gave an enhancement in sensitivity for the copper absorption.

In the present work, the reagent ammonium pyrrolidine dithiocarbamate could not be readily obtained, so that preliminary investigations were begun with the widely used complexing agent for copper, sodium diethyldithiocarbamate. With copper this reagent forms complexes which are readily soluble in carbon tetrachloride, chloroform and xylene. However, all the extracts of the copper complex were found to be unsuitable. Spraying into the flame resulted in an unstable, sooty flame giving inconsistent responses. Further, in the case of carbon tetrachloride, a large volume of chlorine was evolved in the flame. The reagent used by Allan, ammonium pyrrolidine dithiocarbamate was prepared after the method of Malissa and Schoffman.[11] Results using this reagent showed that the copper complex in the ethyl acetate, when sprayed into the flame, yielded an increase 4–6 times that for the same concentration sprayed from aqueous solution. A procedure which was found to operate satisfactorily is as follows.

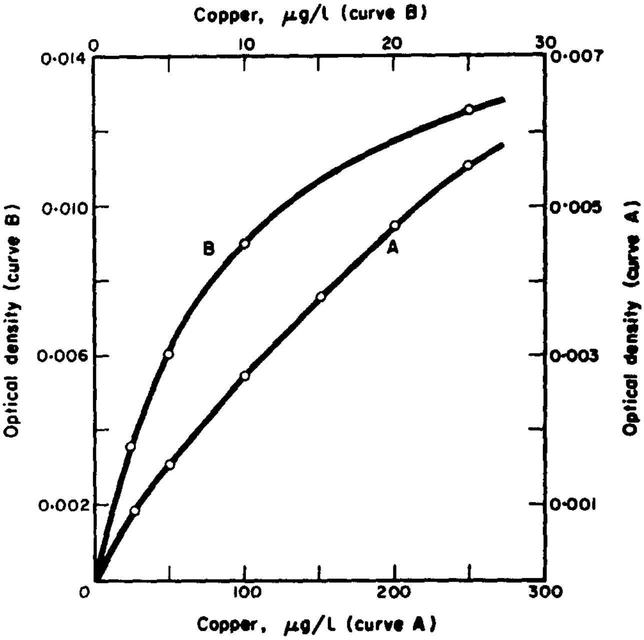

FIG. 1.—Calibration curve for copper:
A—Up to 250 μg of copper/litre (without extraction procedure),
B—Up to 25 μg of copper/litre (with extraction procedure).

Procedure

To 25 ml of an aqueous solution of copper in a 50-ml separating funnel, add 1 ml of 1 % ammonium pyrrolidine dithiocarbamate solution. Shake the mixture well for 15–20 sec, then add 10 ml of ethyl acetate. Shake again for 1 min. After separation of the phases, remove the lower aqueous phase. Filter the acetate phase into a 10-ml volumetric flask and make up to the mark. Employing the conditions derived above for operation of the atomic absorption spectrophotometer (*Note*), spray the acetate extract into the flame and record the response.

Note. Investigations showed that all the conditions determined for aqueous solutions of copper gave optimum response with the acetate extract except for the absorbance path. Results for a 40 μg atom/litre solution of copper extracted into ethyl acetate as the complex are shown in Table VII.

TABLE VII

Absorbance path	Response (optical density)
Low	0·215
Low medium	0·200
High medium	0·130
High	0·110

It will be seen that, unlike the aqueous solution, maximum response occurs at low absorbance path.

Analytical results

Using this procedure the response for copper concentration in the range 2·5 to 250 μg/litre was measured. Results are shown in Table VIII. The results shown at each concentration represents an average value of a number of readings. A calibration curve was prepared for the range of concentrations and is shown in Fig. 1 (curve B).

TABLE VIII.—RESPONSE FOR VARYING AMOUNTS OF COPPER USING EXTRACTION PROCEDURE

Copper present, *μg/litre*	Response (optical density)
2·5	0·011
5	0·014
10	0·017
25	0·021
50	0·026
100	0·033
250	0·051
Blank (Background reading)	0·008

Determination of copper in sea water

It was indicated above that difficulties arise in the direct determination of copper in sea water because of the interference from other elements, particularly sodium.

Before applying the extraction method to the determination of copper in sea water, the influence of large excesses of sodium and magnesium on the method was investigated. To copper solutions of known concentration (2·5–250 μg/litre), sufficient sodium chloride and magnesium chloride were added to make the solutions 16% in the former and 1% in the latter. The solution was then complexed, extracted in the recommended manner and sprayed into the flame. Results are shown in Table IX. Figures in parenthesis are those obtained for solutions of the same concentration of copper, but without the addition of sodium and magnesium chlorides. The result shown at each concentration represents the average of a number of readings

In the presence of sodium and magnesium only, a very small increase in the response was observed. It was supposed that the small increase in the response was

TABLE IX.—EFFECT OF SODIUM AND MAGNESIUM CHLORIDE ON RESULTS FOR COPPER

Copper concentration, *μg/litre*	Response (optical density)
2·5	0·012 (0·011)
5	0·014 (0·014)
10	0·017 (0·017)
25	0·021 (0·021)
50	0·026 (0·026)
100	0·033 (0·033)
250	0·051 (0·051)

from the presence of traces of heavy metal impurities complexed and extracted in the same way as copper. Ethylenediaminetetra-acetic acid (EDTA) was added as a masking agent to the test solution in Table IX before formation of the copper complex and the determinations repeated. In this way the small increase in the response was eliminated. For the determination of copper in sea water the procedure just discussed was used, with the addition of EDTA to the samples before complexing and spraying into the flame.

The sea water was drawn from the Belfast Lough at a depth of 2 ft below the surface and, after sampling, was analysed with the following results:

(a) 2·00 μg/litre.
(b) 1·75 μg/litre,
(c) 1·75 μg/litre,
(d) 2·00 μg/litre,
(e) 1·75 μg/litre.

The average value for these 5 samples is 1·85 μg of copper/litre.

The values obtained are very similar to those obtained by Fabricand *et al.*[7] for sea water drawn from the Altantic and Pacific Oceans and to those of Chow and Thompson.[12] The latter workers used a spectrophotometric method for the determination, while the former employed atomic absorption spectroscopy. It would appear, therefore, that the copper content of the water in the Irish Sea does not vary markedly from that of the Pacific Ocean.

Acknowledgements—The authors wish to thank D.S.I.R. for a grant which permitted the Hilger Uvispek-spectrophotometer to be purchased, and the Central Dockyard Laboratory, H.M. Dockyard, Portsmouth, England, for providing the copper hollow-cathode lamp. One of us (A. K. M. R.) also wishes to thank the Central Testing Laboratories, Government of Pakistan, for granting study leave.

Zusammenfassung—Ein handelsübliches Spektralphotometer für atomare Absorptionsmessungen ohne Änderungen wird zur Ermittlung der geeignetsten Arbeitsbedingungen zur Kupferbestimmung verwendet. Mit der direkten Methode, bei der wäßrige Kupferlösungen in die Flamme gesprüht werden, ist die Nachweisgrenze für Kupfer etwa 25 μg/Liter. Diese Methode ist aber nicht zur Bestimmung von Kupfer in Meerwasser geeignet. Dieses Problem wird zufriedenstellend gelöst durch Extraktion des Kupfer-Ammoniumpyrrolidindithiocarbamat-Komplexes in Äthylacetat und Versprühen des organischen Extraktes in der Flamme. Mit dieser Arbeitsweise erzielt man eine bemerkenswerte Steigerung der Empfindlichkeit.

Résumé—Afin d'établir le meilleur mode opératoire pour le dosage du cuivre, on a employé sans modification un spectrophotomètre d'absorption atomique commercial. En utilisant la méthode directe de pulvérisation de solutions aqueuses de cuivre dans la flamme, la quantité minimale de cuivre dosable est d'environ 25 μg/litre. Toutefois, cette méthode ne convient pas au dosage du cuivre dans l'eau de mer. Une méthode, basée sur l'extraction du complexe cuivre-pyrrolidine dithiocarbamate d'ammonium en acétate d'éthyle, et pulvérisation dans la flamme de l'extrait organique, est satisfaisante, et offre un accroissement notable de la sensibilité.

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SHORT COMMUNICATIONS

A modification of Leithe's method for determining nitrate

(*Received* 9 *November* 1964. *Accepted* 4 *January* 1965)

IN the Leithe method,[1] nitrate is reduced with a known amount of iron(II) solution (55 g of $FeSO_4 \cdot 7H_2O$, 20 g of NaCl and 900 ml of 1:1 H_2SO_4/litre) and the excess iron(II) is then back-titrated using ferroïn as indicator.

Although freshly-prepared Leithe reagent gives excellent results, we have found that within 1–2 hr a precipitate appears in the solution, and the blank values begin to decrease in an erratic manner. This experience contrasts with that of Leithe who prepared solutions stable for 1 day or longer.

A reagent stable for at least 5 or 6 days can be simply prepared by dissolving the appropriate amount of $FeSO_4 \cdot 7H_2O$ in 1 litre of water containing HCl; the NaCl and H_2SO_4 necessary to effect the reduction are added separately. Because the reduction depends upon reaction conditions, it has been necessary to determine conditions under which this reagent would give the most satisfactory results.

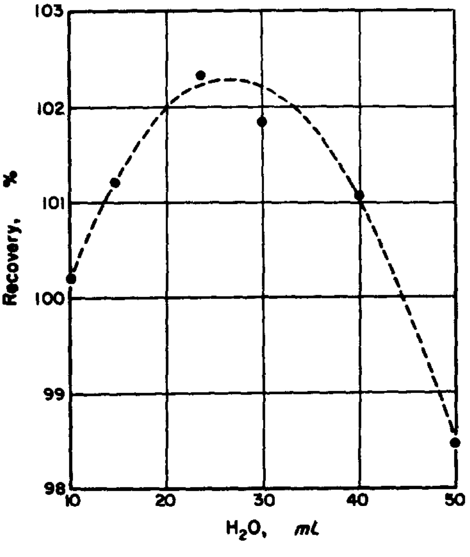
EXPERIMENTAL

Reagents and solutions

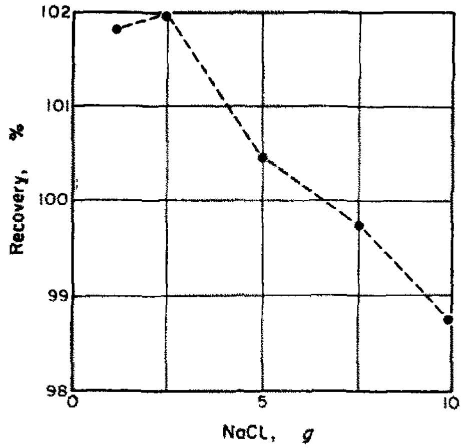
Reagent-grade chemicals were used throughout.

Standard solutions of nitrate were prepared by weighing out the desired amount of either KNO_3 or $NaNO_3$ and diluting to volume.

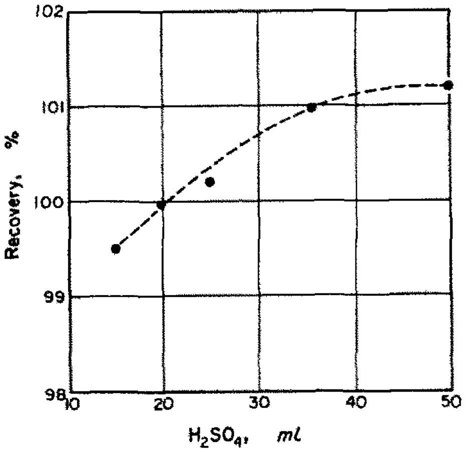
The $FeSO_4$-HCl solution was prepared by dissolving 92 g of $FeSO_4 \cdot 7H_2O$ in 200 ml of water, containing 20 ml of concentrated HCl, and diluting to 1 litre.



a—Effect of H_2O: 5 g of NaCl, 25 ml of H_2SO_4, 40 mg of $NaNO_3$ present.



b—Effect of NaCl: 25 ml of H_2SO_4, 20 ml of H_2O, 40 mg of $NaNO_3$ present.



c—Effect of H_2SO_4: 5 g of NaCl, 20 ml of H_2O, 40 mg of $NaNO_3$ present.

FIG. 1.—The effect of reaction conditions on the determination of nitrate using $FeSO_4$-HCl.

Procedure

The details of the Leithe procedure both for solutions of nitrate and for mixtures of nitrate and nitrite have been described in detail elsewhere.[1] They were followed exactly.

To study the conditions in which the $FeSO_4$-HCl reagent would be a satisfactory substitute for the Leithe reagent, a 10-ml aliquot of $NaNO_3$ solution (4·00 g/litre) was placed in a 250-ml Erlenmeyer flask. A known volume of H_2O, a known weight of NaCl, a 15-ml aliquot of the $FeSO_4$-HCl reagent and a known volume of H_2SO_4 were added in that order. The resulting solution was boiled for 3 min and cooled; 100 ml of H_2O were added and the excess iron(II) titrated with standard dichromate to the ferroin end-point.

On the basis of the results obtained from the above experiments, known amounts of nitrate were titrated in the following manner: the sample was dissolved in 20 ml of H_2O, and 5 g of NaCl, a 15-ml aliquot of the reagent and 20 ml of concentrated H_2SO_4 were added; from this point on, the sample solutions were treated as previously described. To determine nitrate in mixtures of nitrate and nitrite, only one additional modification was necessary to remove the nitrite interference. After the sample was dissolved in water, 2 g of urea were added; 0·5 ml of concentrated H_2SO_4 was added drop-wise and with vigorous shaking; the nitrate was then determined as before.

RESULTS AND DISCUSSION

The results in Fig. 1(a, b, c) show the effect of reaction conditions on the reduction of the nitrate to $FeNOSO_4$ using the $FeSO_4$-HCl reagent. The effect of chloride on this reagent is similar to the chloride effect on the Leithe reagent.[2] That the amount of water and acid affect the recoveries should come as no surprise, considering the rigorous conditions necessary in the Leithe procedure. Increasing the amounts of NaCl and H_2SO_4 improves the sharpness of the end-point; increasing the amount of water initially present decreases the sharpness of the end-point, and after 50 ml have been added the end-point colour-change is from orange to yellowish-brown, not from orange to *aqua*.

Table I shows the results obtained using this procedure. Urea, recommended by Leithe for removal of nitrite, is effective; but, as the table shows, its effect is limited to about the equivalent of 46 mg of $NaNO_2$. We have not found it necessary to add unglazed porcelain when using our procedure, although Leithe recommends it for his.

TABLE I.—DETERMINATION OF NITRATE

$NaNO_2$, *mg*	$NaNO_3$, *mg*	
	Added	Found
0·00	20·0[b]	20·2
	39·7	39·7 ($n = 4, s = 0·3$)[d]
	40·0[b]	39·9
	59·7[a]	60·1 ($n = 3, s = 0·7$)
	60·0[b]	59·9
	79·6[a]	80·4 ($n = 4, s = 0·8$)
	80·0[b]	80·6
18·1	39·7[a]	39·8 ($n = 3, s = 0·3$)
30·2	39·7[a]	39·5 ($n = 3, s = 0·2$)
40·4	40·0[b]	39·8
46·0	46·8[b]	46·9
60·0	30·8[b]	31·8
		29·6[c]

[a] Two different analysts analysed the same standard.

[b] A second standard analysed by a third analyst.

[c] 4 g of urea used instead of 2.

[d] *n* represents the number of determinations, *s* the standard derivation.

An X-ray diffraction pattern of the precipitate which formed in the Leithe reagent showed it to be $FeSO_4 \cdot H_2O$ (szomolnokite). If the reagent was prepared in the manner described by Leithe, *i.e.*, by dissolution of the $FeSO_4 \cdot 7H_2O$ and NaCl in 100 ml of H_2O followed by the addition of sufficient cold 50% H_2SO_4 to give 1 litre of solution, precipitation was gradual and, as noted above, did not begin for an hour or so. If the $FeSO_4 \cdot 7H_2O$ and NaCl were dissolved in 550 ml of H_2O and 450 ml of concentrated H_2SO_4 were added, a copious precipitate of $FeSO_4 \cdot H_2O$ formed immediately; cooling the reaction mixture effected no apparent reduction in the amount of precipitate.

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Summary—A more stable reagent, $FeSO_4$-HCl, can be effectively substituted for the $FeSO_4$-NaCl-H_2SO_4 reagent originally proposed by Leithe for the determination of nitrate. The NaCl and H_2SO_4 necessary to effect a quantitative reaction are added separately to the sample and blanks, rather than being incorporated in the reagent.

Zusammenfassung—Das ursprünglich von Leithe zur Nitratbestimmung vorgeschlagene $FeSO_4$-NaCl-H_2SO_4-Reagens kann mit Erfolg durch eine stabilere Lösung von $FeSO_4$ in HCl ersetzt werden.

Résumé—Le réactif $FeSO_4$-NaCl-H_2SO_4, proposé à l'origine par Leithe pour le dosage des nitrates, peut être efficacement remplacé par un réactif plus stable, $FeSO_4$ en HCl.

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Applications de la chelatometrie—XVI:* Emploi du complexe cuivrique de l'E.D.T.A. pour le dosage volumetrique du glucose

(*Reçu le* 19 *Decembre* 1964. *Accepté le* 26 *Janvier* 1965)

L'EMPLOI des réactifs cuivriques est très répandu pour le dosage des sucres réducteurs; récemment, plusieurs méthodes chélatométriques ont été suggérées pour le dosage du cuivre contenu, soit dans un excès de réactif après réaction, soit dans le précipité d'oxyde cuivreux.

Street[1] est, à notre connaissance, le premier à avoir employé l'E.D.T.A. pour doser le cuivre II dans un réactif utilise en excès; le réactif était de formule classique stabilisé à l'acide tartrique; Knight et Allen[2] puis Roche,[3] reprennent successivement la même technique; le dosage est pratiqué sans filtration en utilisant la murexide comme indicateur. Jäschke[4] filtre le milieu réactionnel pour pouvoir conduire le dosage en tampon ammoniacal sans être gêné par le cuivre I "soluble" dans ces conditions et facilement réoxydé par l'oxygène atmosphérique. Ce procédé est voisin de celui que nous avons indiqué précédemment[5] mais nous opérions alors en milieu tampon pyridiné avec le violet de pyrocatéchine comme indicateur.

En 1954, Bultasova et Horakova,[6] ont décrit une technique dans laquelle l'oxyde cuivreux, isolé, était repris par l'acide nitrique pour permettre son dosage volumétrique par l'E.D.T.A.; une méthode semblable a été mise en oeuvre récemment par Tamura et Miyazaki;[7] ces auteurs utilisent également un réactif cuivrique classique à l'acide tartrique.

En 1953, cependant, l'étude des conditions de réduction par les sucres du complexe cuivrique de l'E.D.T.A. avait été faite par Reiner et Preiss,[8] d'une part, et par Wagreich et Harrow,[9] d'autre part. En 1957, Doss[10] utilisait ce réactif, alcalinisé par la soude, pour réaliser des dosages directs, l'indication du point final étant donnée par le Bleu de Méthylène.

En 1954, Potterat et Eschmann[11] exposent une technique utilisant ce même complexe cuivrique, avec redissolution de l'oxyde cuivreux dans l'acide nitrique suivie d'une mesure volumétrique au moyen de l'E.D.T.A.; diverses applications sont décrites ensuite par ces mêmes auteurs[12–15] puis par Raymond,[16] par Malkus et Fara[18] et par Rentschler *et al.*[19] Hadorn et Biefer[20] étudient l'influence des acides aminés; Hadorn et Suter[21] examinent celle des dextrines et Kupferschmid[22] celle des peptides, peptones et protéines. Malkus[23] suggère une variante dans laquelle la murexide est remplacée par le Bleu de Glycine-Thymol. Hadorn[24] compare la technique originale à celle de la "double polarisation" et à la méthode de Luff-Schoorl;[25–27] après les avoir fait essayer toutes trois par 18 laboratoires sur 8 échantillons de chocolat, il conclut qu'elle est la plus fidèle des trois.

Potterat et Eschmann[11] n'avaient pas manqué de remarquer qu'à chaque atome de cuivre précipité à l'état d'oxyde cuivreux correspondait une molécule d'E.D.T.A. libérée et donc dosable au moyen d'une solution titrée de sulfate de cuivre.

Toutefois, ces auteurs s'étaient heurtés à plusieurs difficultés et avaient définitivement abandonné cette voie. Les difficultés étaient dûes à la présence d'impuretés métalliques, une couleur trop prononcée de la solution et un mauvais virage.

Etant donné l'intérêt présenté par un dosage évitant la séparation et la reprise du précipité, nous avons voulu essayer si, au moins dans le cas d'un sucre "propre", cette voie ne pouvait pas être exploitée. Après précipitation, la mesure de la quantité d'E.D.T.A. libéré a d'abord été tentée au moyen d'un sel de zinc ou de manganèse en milieu tamponné par le chlorure d'ammonium et en présence de Zincon ou de Noir Eriochrome suivant Kinnunen et Merikanto[28] ou Kinnunen et Wennerstrand,[29] mais l'incertitude du virage avec ces sels nous a fait revenir finalement au sulfate de cuivre.

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* Article précédent: *Talanta*, 1962, **9**, 97.

Zusammenfassung—Das ursprünglich von Leithe zur Nitratbestimmung vorgeschlagene $FeSO_4$-NaCl-H_2SO_4-Reagens kann mit Erfolg durch eine stabilere Lösung von $FeSO_4$ in HCl ersetzt werden.

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Street[1] est, à notre connaissance, le premier à avoir employé l'E.D.T.A. pour doser le cuivre II dans un réactif utilise en excès; le réactif était de formule classique stabilisé à l'acide tartrique; Knight et Allen[2] puis Roche,[3] reprennent successivement la même technique; le dosage est pratiqué sans filtration en utilisant la murexide comme indicateur. Jäschke[4] filtre le milieu réactionnel pour pouvoir conduire le dosage en tampon ammoniacal sans être gêné par le cuivre I "soluble" dans ces conditions et facilement réoxydé par l'oxygène atmosphérique. Ce procédé est voisin de celui que nous avons indiqué précédemment[5] mais nous opérions alors en milieu tampon pyridiné avec le violet de pyrocatéchine comme indicateur.

En 1954, Bultasova et Horakova,[6] ont décrit une technique dans laquelle l'oxyde cuivreux, isolé, était repris par l'acide nitrique pour permettre son dosage volumétrique par l'E.D.T.A.; une méthode semblable a été mise en oeuvre récemment par Tamura et Miyazaki;[7] ces auteurs utilisent également un réactif cuivrique classique à l'acide tartrique.

En 1953, cependant, l'étude des conditions de réduction par les sucres du complexe cuivrique de l'E.D.T.A. avait été faite par Reiner et Preiss,[8] d'une part, et par Wagreich et Harrow,[9] d'autre part. En 1957, Doss[10] utilisait ce réactif, alcalinisé par la soude, pour réaliser des dosages directs, l'indication du point final étant donnée par le Bleu de Méthylène.

En 1954, Potterat et Eschmann[11] exposent une technique utilisant ce même complexe cuivrique, avec redissolution de l'oxyde cuivreux dans l'acide nitrique suivie d'une mesure volumétrique au moyen de l'E.D.T.A.; diverses applications sont décrites ensuite par ces mêmes auteurs[12–15] puis par Raymond,[16] par Malkus et Fara[18] et par Rentschler *et al.*[19] Hadorn et Biefer[20] étudient l'influence des acides aminés; Hadorn et Suter[21] examinent celle des dextrines et Kupferschmid[22] celle des peptides, peptones et protéines. Malkus[23] suggère une variante dans laquelle la murexide est remplacée par le Bleu de Glycine-Thymol. Hadorn[24] compare la technique originale à celle de la "double polarisation" et à la méthode de Luff-Schoorl;[25–27] après les avoir fait essayer toutes trois par 18 laboratoires sur 8 échantillons de chocolat, il conclut qu'elle est la plus fidèle des trois.

Potterat et Eschmann[11] n'avaient pas manqué de remarquer qu'à chaque atome de cuivre précipité à l'état d'oxyde cuivreux correspondait une molécule d'E.D.T.A. libérée et donc dosable au moyen d'une solution titrée de sulfate de cuivre.

Toutefois, ces auteurs s'étaient heurtés à plusieurs difficultés et avaient définitivement abandonné cette voie. Les difficultés étaient dûes à la présence d'impuretés métalliques, une couleur trop prononcée de la solution et un mauvais virage.

Etant donné l'intérêt présenté par un dosage évitant la séparation et la reprise du précipité, nous avons voulu essayer si, au moins dans le cas d'un sucre "propre", cette voie ne pouvait pas être exploitée. Après précipitation, la mesure de la quantité d'E.D.T.A. libéré a d'abord été tentée au moyen d'un sel de zinc ou de manganèse en milieu tamponné par le chlorure d'ammonium et en présence de Zincon ou de Noir Eriochrome suivant Kinnunen et Merikanto[28] ou Kinnunen et Wennerstrand,[29] mais l'incertitude du virage avec ces sels nous a fait revenir finalement au sulfate de cuivre.

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* Article précédent: *Talanta*, 1962, **9,** 97.

D'autre part, nous avons vite renoncé à l'addition de chlorure d'ammonium dont la présence améliorait le virage, mais occasionnait en "dissolvant" l'oxyde cuivreux une réoxydation très rapide de celui-ci même en opérant sous une couche de paraffine comme le conseille Peska.[30] Comme indicateur, nous avons retenu la murexide qui a donné satisfaction à la plupart des auteurs et évite de modifier le pH de la solution après réaction. Nous avons toutefois, observé que, si la concentration de 1 à 2 mmoles par litre indiquée par Schwarzenbach et Flaschka,[17] et rappelée par Potterat et Eschmann,[11] pouvait être portée à une concentration cinq à dix fois plus forte en milieu ammoniacal, elle devait, par contre, être considérée comme un maximum dans le milieu sodique dans lequel nous devions travailler. Une dilution importante s'avérant nécessaire, nous avons résolu le problème en effectuant la réduction dans une fiole jaugée de 100 ml qu'il suffit de compléter ensuite avec de l'eau distillée; un prélèvement de 20 ml additionné d'eau avant titrage nous a permis de satisfaire les conditions de dilution et d'obtenir un virage tout à fait net; cette manière de faire présente, en outre, l'avantage d'éliminer la presque totalité de l'oxyde cuivreux, cette élimination ajoutant encore à la qualité du virage.

PARTIE EXPERIMENTALE

Réactifs utilisés

Réactif cuivrique 0,1 M: nous avons utilisé le réactif décrit par Eschmann[14] mais, en raison de la méthode mise en oeuvre, nous avons dû adopter un procédé de préparation permettant d'écarter tout risque de présence d'E.D.T.A. ou sulfate cuivrique en exces dans la solution. Une fiole jaugée à deux graduations est nécessaire pour cette préparation: celle-ci peut être effectuée dans une fiole de capacité correspondant à l'importance de la consommation de réactif mais nous nous sommes limités à une fiole de 200/220 ml qui offrait l'avantage d'être disponible dans le commerce; pour des capacités plus grandes, la fiole pourrait être obtenue en modifiant le col d'une fiole à simple jauge. 8,4 g d'éthylène-diaminotétracétate disodique bien sec sont dissous avec 64,5 g de carbonate de sodium décahydraté dans le minimum d'eau distillée nécessaire; 5,4 g de sulfate cuivrique pentahydraté, préalablement dissous dans un peu d'eau distillée, sont ajoutés et, lorsque la dissolution est totale, on complète à 200 ml au moyen d'eau distillée.

D'autre part, une solution environ 0,1 M de sulfate cuivrique est préparée en dissolvant 2,5 g du même sulfate pour faire 100 ml; on prélève exactement 5 ml sur les 200 ml de la première solution; on introduit cette prise d'essai dans une fiole avec 250 ml d'eau distillée et un peu de murexide préparée comme indiqué plus loin; On place la solution de sulfate cuivrique 0,1 M dans une burette de 5 ou 10 ml graduée en 0,02 ml et fait couler cette solution goutte à goutte dans la fiole jusqu'au virage de la murexide. Le volume de solution utilisé, multiplié par 39, donne celui à ajouter dans les 195 ml de réactif restant; ceci fait, on complète le tout à 220 ml au moyen d'eau distillée.

Murexide: on sait que les solutions aqueuses de murexide ne sont que très brièvement utilisables[31] et que la solution alcoolique à 70° se décompose lentement;[32] nous avons choisi une solution à 0,15% dans l'éthylène-glycol suivant les recommandations de Brunisholz *et al.*;[33] on peut toutefois remplacer cette solution par un mélange sec avec le chlorure de sodium[34–35] ou avec le sulfate de potassium.[36]

Sulfate cuivrique 0,01 M: 2,5 g de sulfate cuivrique pentahydraté sont dissous dans l'eau distillée de façon à obtenir un litre de solution. Le titre de ce réactif est établi au moyen d'une solution d'E.D.T.A disodique 0,01 M en présence de murexide à un pH compris entre 8 et 10. Nous avons utilisé un poids connu de magnésium pur "dissous" dans l'acide chlorhydrique pour étalonner la solution d'E.D.T.A. avec le Noir Eriochrome comme indicateur et en opérant à un pH voisin de 10.

Eau distillee: nous avons employé une eau distillée fraîchement bouillie pour la préparation des solutions ci-dessus aussi bien que pour la mise en oeuvre de toutes les opérations de la présente technique.

Mode opératoire

Dans une fiole jaugée de 100 ml en verre Pyrex surmontée d'un tube de verre servant de condenseur, placer quelques très petits fragments de verre ou de porcelaine et introduire 10 ml de réactif cuivrique mesurés exactement au moyen d'une pipette; ajouter 10 ml de la solution de glucose à doser mesurés avec la même précision; placer la fiole dans un chauffe-ballon électrique et porter à douce ébullition; maintenir celle-ci pendant 10 min puis ajouter 25 ml d'eau distillée froide par le tube condenseur; refroidir à température ambiante, retirer le tube condenseur et compléter à 100 ml au moyen d'eau distillée; agiter pour homogénéiser et laisser reposer pendant quelques minutes.

Dès que l'oxyde cuivreux s'est déposé, ce qui a lieu très rapidement, prélever exactement 20 ml du liquide surnageant au moyen d'une pipette; les introduire dans une fiole d'Erlenmeyer de 250 ml; ajouter 80 à 100 ml d'eau distillée et une quantité de murexide juste suffisante pour obtenir une légère coloration violacée.

Ajouter la solution de sulfate cuivrique, au moyen d'une burette de 10 ml graduée en 0,02 ml, jusqu'au virage de l'indicateur; ce virage est très brusque et parfaitement net; il a lieu du violacé au vert plus ou moins jaunâtre en passant par une teinte grisâtre paraissant presque incolore lorsque l'indicateur est peu abondant; nous avons choisi cette teinte intermédiaire comme point final de dosage. La solution de sulfate cuivrique n'étant jamais exactement centimolaire, il nous a paru plus commode d'exprimer les mesures en nombre de millimoles d'E.D.T.A. libéré plutôt qu'en volume de réactif utilisé; ce nombre est calculé au moyen de la formule ci-dessous:

$$E = V \times N' \times 5$$

V = nombre de millilitres de solution de sulfate cuivrique utilisé, N' = molarité exacte de cette solution.

La technique a été experimentée sur des poids de glucose compris entre 5 et 25 mg; les résultat-obtenus correspondent, avec des différences minimes, aux valeurs indiquées par le tableau d'Eschs mann.[14] Ce tableau peut servir au calcul du nombre de mg de glucose présent dans les 10 ml de solution essayée; nous avons remarqué, toutefois, que ce nombre pouvait être calculé, pour les poids compris entre 5 et 25 mg que nous avons essayés, au moyen d'une seule formule que nous donnons ci-après:

$$P = E(5{,}75E + 36{,}1) + 0{,}26.$$

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CLAUDE HENNART

Résumé—Le glucose peut être dosé par chelatométrie en mesurant la quantité d'E.D.T.A. libéré de son complexe cuivrique après réduction du cuivre II en oxyde cuivreux; la mesure est faite, sans filtration, au moyen d'une solution titrée de sulfate cuivrique en présence de murexide.

Summary—Glucose can be determined chelatometrically by measuring the amount of EDTA liberated from its copper(II) complex after reduction of copper(II) to copper(I) oxide. The EDTA is measured, without filtration, by titration with a standard solution of copper(II) sulphate using Murexide as indicator.

Zusammenfassung—Glucose kann chelatometrisch bestimmt werden durch Messung der EDTA-Menge, die aus ihrem Kupfer(II)-Komplex frei wird, wenn Kupfer(II) zu Kupfer (I)-oxyd reduziert ist. Die EDTA wird ohne Filtration durch Titration mit eingestellter Kupfer(II)-sulfatlösung und Murexid als Indikator bestimmt.

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LETTERS TO THE EDITOR

Determination of sulphate with barium chloranilate

SIR,

A recent paper by Agterdenbos and Martinius[1] leaves the impression with the reader that the widely used spectrophotometric method for determining sulphate with barium chloranilate is of limited usefulness. The conclusions drawn by these authors were based on a mathematical treatment of the equilibria existing in solutions containing extremely small amounts of sulphate. The absorbance-concentration relationship for the reaction:

barium chloranilate + sulphate → acid chloranilate + barium sulphate

becomes non-linear at low concentrations of sulphate because of the solubility of the barium salts and the dissociation of the acid, and because of the changes in the ionic strength.

These problems were considered by the developers of the method, and they were discussed in a paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in March 1957.[2] Because the deviations from linearity were caused by easily understood relationships discussed in elementary textbooks of physical chemistry, this discussion was omitted from the publication.[3]

Examination of the equations presented by Agterdenbos and Martinius reveals that the deviations from linearity caused by solubility and equilibria relationships are significant only below about 0·2 μg/ml (0·2 ppm) of sulphate if 4-cm cells are used, or below 0·05 ppm in the more commonly used 1-cm cells. This concentration is well below the range of sulphate concentrations for which the method is used. However, Fig. 2 of their paper clearly shows that the method can be used at a concentration of 0·2 μg/ml in 4-cm cells.

The results in Table IV of the paper purport to show the effect of the ionic strength on the error obtained in the measurement of absorbance. However, no direct relationship between ionic strength and the magnitude of the error can be obtained from the results in this table, other than the well-known positive error at high ionic strengths. Furthermore, the spread in the experimental values in Fig. 2 suggests that the error of one of the authors' single measurements may be as high as ±0·04 absorbance unit.

Several criticisms may be offered about the authors' experimental results and their theoretical treatment. The method used by them to prepare barium chloranilate (*i.e.*, by adding an excess of chloranilic acid to barium chloride solution) will surely produce a compound which is contaminated with chloranilic acid, so that high, inconsistent blanks will be obtained. They also gave no reason for using urotropine as a buffer rather than the highly satisfactory acetic acid-sodium acetate mixture.[4] Furthermore, the absorbance of blank solutions of barium chloranilate was not given by the authors. All of the commerical and experimental samples of barium chloranilate examined by the developers of the method gave absorbances of at least 0·6 in 1-cm cells at pH 4·5 at 332 mμ. Because absorbance of the blank increases as the pH increases, the blank solutions studied by the authors in 4-cm cells must have had extremely high absorbances.

The authors infer that previous workers have assumed that the calibration curve passes through the origin. Careful examination of Fig. 1 of reference 4 and the slides presented in reference 3 reveals that the developers of the method did not represent the calibration curve in this manner. Also, the authors have incorrectly neglected the contribution of the acid chloranilate ion to the total absorbance of the solution.

In conclusion, the authors have correctly described some obvious but trivial limitations of the spectrophotometric method for determining sulphate with barium chloranilate These limitations should be apparent to chemists familiar with chemical equilibrium theory. They may be important for other exchange reactions used in analytical chemistry. The spectrophotometric method for sulphate is useful for most systems, and the calibration curve is linear in the practical range of absorbance.

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16 *October* 1964

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SIR,

When we saw Dr. Barney's letter[1] we were appreciative that he, who should be a specialist in this respect because he was the first investigator who applied barium chloranilate to the determination of small amounts of sulphate, had read our paper[2] and given some comments on our work. After we had read his letter, however, it seemed useful for us to reply to his comments.

1. Dr. Barney suggests that the results of our calculations are so self-evident that it is unnecessary to publish them. We cannot agree with this view. Of course, qualitatively, they are self-evident, but they are so in many analytical determinations where equilibria play an important role. Fortunately, however, the magnitude of the effect is not large enough in many cases to cause a significant change of the calibration curve from linearity and significant influence of ionic strength on the curve. In the problem we studied, the magnitude of the deviations proved to be sufficiently large to be discussed quantitatively. We believe that our calculations give a good insight into the scope and limitations of the method. We are afraid that some error is involved in Dr. Barney's statement that some figures from his references 3 and 4 give information on the calibration curves he obtained. We regret that we could not find any information of the kind suggested in these references. (Unfortunately no report was available of the lecture. From the footnote to his paper in reference 3 and from our reference 1 in this letter we conclude, however, that his reference 3 should be regarded largely as a written report of this lecture.)
2. Dr. Barney's conclusions on the error made in the determination of the blank values in our Table IV are not well founded for at least two reasons. Firstly, he makes his conclusions from the values found in our Fig. 2. However, the experiments made to obtain the values in this figure were much more complicated than those used to obtain the values of Table IV. Secondly, the value of 0·04 he gives for the error in the absorbance is rather pessimistic. Our Fig. 2 clearly shows that the range found at the highest concentration level is about 0·05 or 0·06 extinction unit, obtained from 6 or 7 determinations. This gives a most probable value of about 0·02 for the value of the standard deviation. An error of 0·04 may, of course, be found, but it may be expected only in a few cases, even in the more complicated experiments.
3. We cannot agree with Dr. Barney's conclusions on the preparation of the reagent. The fact that we did not obtain satisfactory results when it was prepared according to Dr. Barney's directions (with a *large* excess of barium) may arise from slight differences in the preparation procedure. Without further experimental evidence, however, we cannot see that our procedure (using a *small* excess of chloranilate) should surely give rise to less satisfactory results than Dr. Barney's procedure, because an excess of barium may give inconsistently *low* results. In fact, our investigation included a large variation in the amount of reagent used for determination of the blank. No influence of such a variation on the blank value was found and it was, therefore, concluded that the contamination of our reagent was not important.

   Dr. Barney's conclusions on the value of our blanks are badly founded by his comparison with his own values, because we clearly showed the influence of alcohol concentration and ionic strength and both were quite different in his and in our experiments. In fact, our value was about 0·88 in a 4-cm cell, which seems favourable when compared with his value of at least 0·6 in a 1-cm cell!
4. Regarding the use of urotropine, we prefer the use of this buffer to acetate because it may be assumed that under our experimental conditions it has a lower ionic strength at the same buffering capacity.
5. From the values we cited for the dissociation constants of chloranilic acid in water ($pK_1 = 0{\cdot}85$, $pK_2 = 3{\cdot}18$), it follows that no significant contribution of the acid chloranilate may be expected in this solvent at about pH 5·2. It is difficult to predict the apparent pH required to fulfil this condition in about 70% alcohol, but the fact that a small change in apparent pH did not influence the value of ε (page 881 of our paper) makes it probable that no significant amount of acid chloranilate were present in our experiments.
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relationship between ionic strength and extinction. The values given indicate that theory and experiment agree well, and Table IV on page 881 gives the information which Dr. Barney wishes for some practical conditions!

7. We do not believe that in practice the problem of the determination of small amounts of sulphate is restricted to samples with low and well known ionic composition. We cannot, therefore, agree with his conclusion on the usefulness of the method. In samples with favourable ionic composition, however, the method is useful (as we said on page 884 of our paper).

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Concerning a certain international experiment

Sir,

In a paper by Cook *et al.*, which appeared in this journal,[1] results were given of an international comparison of analytical methods, designed to show the accuracy and precision of some techniques of routine trace analysis for nuclear materials. This interesting and, in its way, original work was arranged in order to compare the analytical results of some relatively common materials (aqueous solutions containing the nitrate salts of copper, chromium, manganese and mercury), obtained by four different methods in nine representative laboratories in various countries. The extensive and important material accumulated during the investigation has been subjected by the authors to an elementary statistical treatment:[2] in particular, mean values were calculated, also standard deviations and confidence limits of single determinations and of the average results; all this data was presented in the paper as tables and figures. The reduced data shows clearly that some of the methods compared are preferable from the point of view of precision and accuracy. In this way, the importance of the work carried out by the co-operation of international research workers is obvious and has been pointed out more than once[3,4] in reviews.

However, in our opinion, the method chosen by the authors[1] of presenting the results of the research is not the best, because the points of many important conclusions of the work are not made or remain obscure. It is necessary to point out separately that the vast experimental material accumulated by the international researches (551 results in all) could serve as a source of far greater extent and variety of information (or international interest!), than the information which the reader can find in the paper in question. In particular, it does not seem to be quite correct to incorporate results (for their subsequent statistical treatment), some of which may possibly not appertain to the same population. Besides, when dealing with samples of analysed results of different sizes (n) and different origins, it seems that for the sake of clarity the values of standards (s) should be given rather than confidence limits (ts), *etc.*

Most probably in the treatment of such statistical material a multifactor analysis of variance would be very useful.[5-13] Such mathematical treatment would allow the clear revelation of errors of repeatability and reproducibility, as well as errors which are inherent in the different methods within the same technique, *etc.* Also, it would be useful to clear up these questions whether the accumulated results are submitted to the law of normal distribution, or whether they are to fulfil some other statistical procedure for "squeezing out" the maximum information from the results.

Undoubtedly, it would hardly be possible for each reader to present his own "account" to the authors and to satisfy all claims of this type. That is why we should not judge the authors severely and this is not the purpose of our letter. Slips are almost inevitable in any new matter, and to criticise is always somewhat easier than to do the job.

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relationship between ionic strength and extinction. The values given indicate that theory and experiment agree well, and Table IV on page 881 gives the information which Dr. Barney wishes for some practical conditions!

7. We do not believe that in practice the problem of the determination of small amounts of sulphate is restricted to samples with low and well known ionic composition. We cannot, therefore, agree with his conclusion on the usefulness of the method. In samples with favourable ionic composition, however, the method is useful (as we said on page 884 of our paper).

Analytisch Chemisch Laboratorium
der Rijksuniversiteit te Utrecht
Croesestraat 77a
Utrecht, Netherlands.
15 *January* 1965

J. AGTERDENBOS
N. MARTINIUS

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[2] J. Agterdenbos and N. Martinius, *ibid.*, 1964, **11**, 875.

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Sincere thanks are expressed to our friends and colleagues, Miss K. Moloshnikova for her kindly assistance, Dr. I. V. Krivoshei for interesting evening discussions and Mrs. H. G. Klausnitzer for the English translation.

A. B. BLANK
RUDOLPH ALEXANDER GEITZ

Department of Analytical Chemistry
A.M. Gorky Khar'kov State University
Ukraine, U.S.S.R.
22 *October* 1964

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[1] G. B. Cook, M. B. A. Crespi and J. Minczewski, *Talanta*, 1963, **10**, 917.
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[3] I. P. Alimarin, *Zhur. Analit. Khim.*, 1963, **18**, 1412; *cf. Pure Appl. Chem.*, 1963, **7**, 455.
[4] A. K. Babko, *Zavodskaya Lab.*, 1964, **8**, 910.
[5] C. Bennett and N. L. Franklin, *Statistical Analysis in Chemistry and the Chemical Industry*. J. Wiley & Sons Inc., New York, 1954.
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SIR,

The letter of Drs. Blank and Geitz raises, apart from specific points related to our paper, a very general problem of science today, and that is the ever increasing number of scientific papers submitted for publication each year. Editors of journals, faced with this problem, exercise the right to reduce the length of a submission, if, in their opinion, unnecessary or unsuitable material is included. In our case, the preliminary report which included all results was considered by the Editor-in-Chief, who, however, preferred not to publish individual values which made up laboratory averages. We did not press this point further because we believe that it is normal scientific practice for an interested worker to apply to authors of published papers for further clarification or additional data, which is normally freely given. In fact, as we knew that further statistical data could be derived from the collected results, we anticipated that such requests might be made; we were and still are very willing to supply all the data (except the identification of the individual laboratories) to anyone wishing it.*

On the specific points raised by Drs. Blank and Geitz we comment as follows.

1. The statistical treatment given in the paper was considered by us to be sufficient for our purposes, which was to obtain an estimate, in a comparatively simple analytical situation, of the relative value of the techniques as they are normally performed in a routine laboratory. It was hoped that the information obtained on these general aspects would be useful to analytical chemists in their everyday work and we believe this was so.

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3. The use of ts instead of s in our expressions for the mean values allowed all data of different origin to be put on the same footing, considering that some of the means were derived from sets containing only 2 or 3 results, against the average of 5. It is obvious that ts contains not only the information on precision given by s but also the intrinsic quality of this information. We could have assigned a weight to the different sets, but we thought that the use of ts gave a more objective basis.

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4. It should also be pointed out that no results were rejected, although we believed that systematic errors were included. In this respect our assumption was that the random distribution of systematic errors could be treated mathematically as if it were a proper distribution of random errors because the causes of these biases were not known.

5. Finally, we wish to point out that our treatment is only *one* of those possible and claim in its favour only that it filled our needs at the time of writing and that its results were not of merely mathematical interest but proved to be useful to chemists working in the field.

G. B. Cook*
M. B. A. Crespi†
J. Minczewski‡

International Atomic Energy Agency
Seibersdorf Laboratory, Seibersdorf
Niederösterreich, Austria.
15 *February* 1965

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† Present address: Comision Nacional de Energia Atomica, Buenos Aires, Argentina.
‡ Present address: Institute of Nuclear Research, Warsaw, Poland.

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REACTIONS OF METALLOCHROMIC INDICATORS ON MICELLES—I

GENERAL OBSERVATIONS*

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Institute of Pure Chemicals, Brno, Czechoslovakia

(*Received* 7 *July* 1964. *Accepted* 5 *January* 1965)

Summary—Purple-red alkaline solutions of Xylenol Orange are decolourised by the addition of cationic long-chain quaternary salts. A definite minimal ratio of the detergent to the indicator is necessary to bring about the full decolourising effect. The formation of micellar aggregates is supposed. In these one dye molecule is surrounded by at least five molecules of cetylpyridinium bromide and six molecules of cetyltrimethylammonium bromide, respectively. According to absorption spectra, the electronic structure of the Xylenol Orange in this state is that normally found at pH 6.4. Xylenol Orange, bounded in these aggregates, is capable of forming coloured complexes with a number of cations over a wider pH range than usual. Some ions, such as calcium and magnesium, not usually determined complexometrically with Xylenol Orange as an indicator may be successfully titrated using the modified indicator.

IT has been known for more than forty years that acid-base indicators have altered their colour in the presence of micelle-forming detergents.[1,2] This phenomenon, which takes place near the critical micelle concentration, has been explained by the preferential adsorption of one dissociation form of the indicator onto the detergent micelles, with the consequent displacement of the acid-base equilibrium in favour of this form.[3] Studying the effects of anionic, cationic and non-ionic detergents on a large number of dyes, Hartley[3] has found that the greatest colour change occurs when the charge on the detergent micelles is opposite to that of the indicator ions. In agreement with this "sign rule", the most marked effect has been observed for the interaction between an indicator with several charge points and an oppositely charged micelle.[4] However, for simple acid-base indicators, which exist in the appropriate pH-ranges at most as bi- or tervalent ions, the largest effect alters the apparent pKa by about 1·5 units. Metallochromic indicators of the complexan-type are in aqueous solutions present, depending on the pH, as anions whose charge may vary from one to six.[5,6] Because of the relatively high charge within certain pH-ranges, an extremely large colour effect could be expected from the interaction of these dyes and cation-active detergents.[4] Preliminary experiments, carried out with Xylenol Orange and cetylpyridinium bromide (CPB) and cetyltrimethylammonium bromide (CTAB), respectively, have confirmed this assumption. The addition of relatively small amounts of the above mentioned quaternary salts to the deeply coloured solutions of Xylenol Orange at pH 10–11 causes a marked colour change corresponding to a shift in pH of about 4 units towards the acid region. The addition of some cations

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* Presented in part before the Section of Analytical Chemistry at the XXth Meeting of the Czechoslovak Chemical Society, Žilina, July, 1963.

to this "decolourised" solution of Xylenol Orange results in the formation of intensely coloured (bright red to pure blue) complexes. Other complexan-type indicators behave in a similar manner.

This paper presents a more detailed study, undertaken in order to establish some general conditions of this phenomenon and to assess the analytical worth of the reaction. Xylenol Orange has been used as a model indicator.

EXPERIMENTAL

Reagents

All chemicals used throughout this work were of reagent grade purity.

Xylenol Orange. A $10^{-3}M$ standard solution was prepared by dissolving the calculated amount of the indicator (Lachema, Czechoslovakia) in redistilled water. This solution was prepared daily because of its low stability.[7] The working solutions were prepared by appropriate dilution of this stock solution.

Cetylpyridinium bromide and cetyltrimethylammonium bromide. Commercial products (Lachema) were used in the form of a $0{\cdot}01M$ solution in 20% methanol (v/v). The solutions were standardised by argentometric determination of the bromide ion content.

Buffer solutions. Ammonia-ammonium chloride buffer of pH 10·5 and a series of Sörensen's buffer solutions were used.

$0{\cdot}05M$ EDTA and $0{\cdot}01M$ metal solutions were prepared in the usual manner from appropriate salts.

Apparatus

Spectrophotometer. All absorbance measurements were made with either a spectrophotometer SF-4 (U.S.S.R.) using matched silica cells of 10-mm light-path, or a Pulfrich photometer (C. Zeiss, Jena, DDR) with 5-mm cells.

pH *meter.* pH values were determined with a glass electrode and a pH-meter Acidimetr AK (Kovodružstvo, Prague, Czechoslovakia).

RESULTS

Absorption spectra

The absorption spectra of the alkaline Xylenol Orange solutions show a characteristic absorption maximum at 580 mμ. After the addition of CPB (or CTAB), this maximum decreases, whilst a second absorption peak appears at 440 mμ. Visually, this change represents a discolouration of the original purple-red solution to pale greyish-pink, or in more dilute solutions to almost colourless.

Fig. 1 shows the absorption spectra of a solution of Xylenol Orange at pH 10·5 and on the same solution in the presence of CPB; to both solutions 2 drops of a $0{\cdot}05M$ EDTA solution have been added in order to avoid interference from any cations. Except for a small bathochromic shift of the absorption band at 580 mμ, the second curve agrees well with the dissociation form of Xylenol Orange at pH 6·4.[6]

The change of the absorption spectrum of Xylenol Orange occurs gradually, depending on the amount of quaternary salt added. In Fig. 2, the absorbance of Xylenol Orange at 580 mμ is plotted against the concentration of CPB and CTAB, respectively. All the curves obtained have three sections; the first, short horizontal section is caused by the influence of mineral salts added in the form of buffer solution; the second, descending section, represents the successive effect of the detergent on the indicator up to the point at which the additional increase of the quaternary salt concentration does not further diminish the absorbance of the dye.

It may be inferred from these curves that this point and hence the full decolourising effect is reached at the minimal ratio of the detergent to Xylenol Orange of 4·94 in the case of CPB and 5·96 for CTAB. When this ratio has been exceeded, the absorbance of Xylenol Orange remains unaltered even when an excess of several orders of magnitude of quaternary salts has been added.

It may also be noted that short-chain quaternary salts, such as tetramethylammonium bromide, do not affect the absorption spectra of Xylenol Orange.

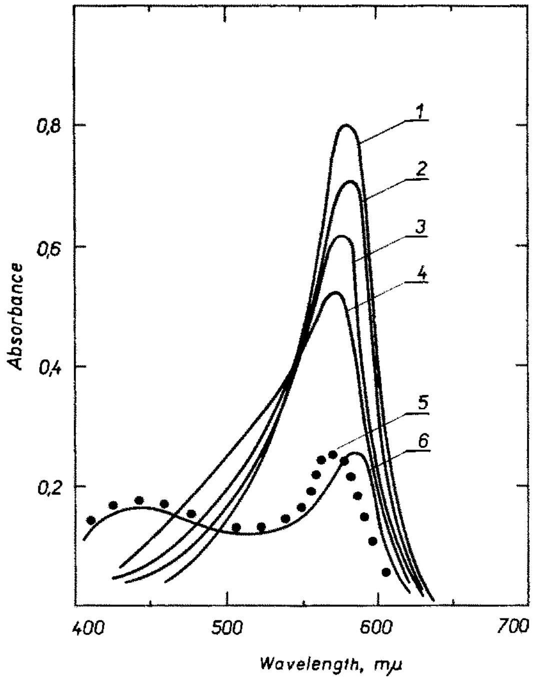

FIG. 1.—Absorption spectra of Xylenol Orange:—2·0 × $10^{-5}M$ XO at pH 10·5 (3); at pH 6·4 (5); at pH 10·5 with 5·0 × $10^{-4}M$ CPB (6); and excess of Ca (1); Zn (2) and Mn (4).

Effect of mineral salts

The presence of higher amounts of mineral salts disturbs the effect of the cationic detergents on the absorption spectra of Xylenol Orange. This negative influence may be seen in Fig. 2 where the length of the first horizontal branches of the curves is proportional to the amount of buffer solution added. Quantitatively, this effect is shown in Fig. 3, where the absorbance of the "decoloured" indicator solutions is plotted against the concentration of alkaline nitrates, chlorides and ammonium sulphate. The rate of increase in the absorbance caused by these salts depends mainly on the nature of the inorganic anion, the most marked one being brought about by the addition of nitrates. The individual cations, sodium, potassium and ammonium ion, have less effect on the absorption spectra of the dye. In the case of nitrates, the differences in the action of particular cations are virtually negligible. However, on addition of larger amounts of nitrates, a salting-out effect has been noticed; with the alkaline nitrates, whose concentrations exceed 0·2M, a reddish flocculant precipitate has been separated.

All these effects could be observed in the presence of long-chain quaternary

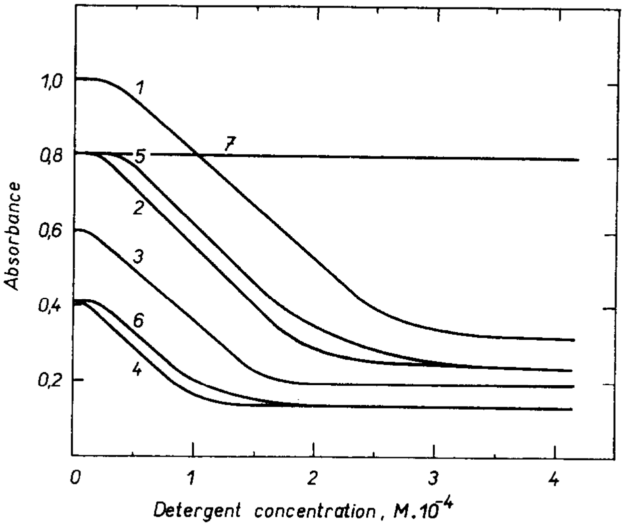

FIG. 2.—Effect of detergents absorbance of XO solutions at 580 mμ in the presence of CPB:—conc. XO = 5·4 × $10^{-5}M$ (1); 4·1 × $10^{-5}M$ (2); 3·0 × $10^{-5}M$ (3) and 2·1 × $10^{-5}M$ (4); in the presence of CTAB:—conc. XO = 4·1 × $10^{-5}M$ (5); 2·1 × $10^{-5}M$ (6); 4·1 × $10^{-5}M$ XO with tetramethylammonium bromide (7); pH of all solutions 10·5.

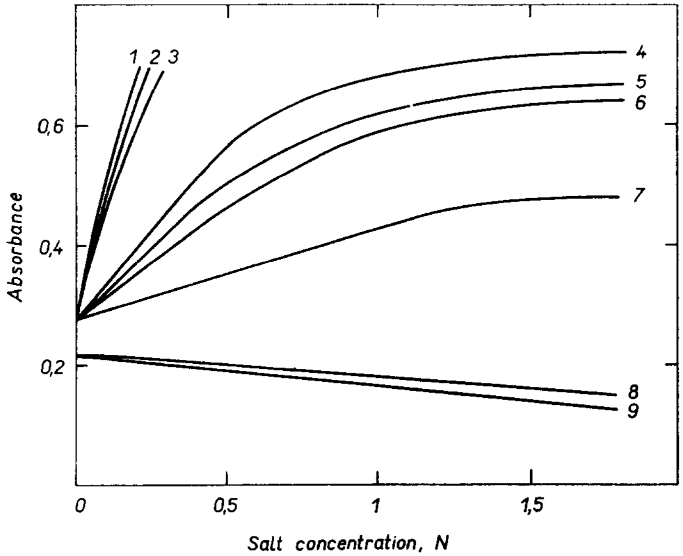

FIG. 3.—Effect of mineral salts—absorbance of XO at pH 10·5, 580 mμ, conc. of XO 4·1 × $10^{-5}M$ with 5 × $10^{-4}M$ CPB:—Effect of NH_4NO_3 (1); $NaNO_3$ (2); KNO_3 (3); NH_4Cl (4); NaCl (5); KCl (6); $(NH_4)_2SO_4$ (7); 4·1 × $10^{-5}M$ XO at pH 6·4 without CPB, with NH_4NO_3 (8) and NH_4Cl (9).

salts only. Xylenol Orange, when alone at pH 6·4, shows at high concentrations of ammonium nitrate and ammonium chloride, only a slight decrease in absorbance associated with the normal "salt error" of acid-base indicator.

Complex formation

Xylenol Orange decolourised by the cationic detergent forms, in an alkaline medium, with numerous metal cations deep-coloured, water-soluble complexes. From the analytical viewpoint, the complexes of Ca(II), Ba(II), Sr(II), Mg(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II) and La(III) are the most interesting. The colours of most of these complexes range from bright red to bluish violet, whilst the complex of tervalent lanthanum is pure blue. Absorption spectra of the complexes with Ca(II), Zn(II) and Mn(II) are shown in Fig. 1.

The addition of EDTA to the solutions of these complexes brings about a decolouration to the original pale-pink colour. This colour change is instantaneous and sharp with the complexes of Ca(II), Ba(II), Mg(II), Cu(II), Cd(II), Zn(II) and Mn(II), but the complexes of Sr(II), Ni(II), Co(II), La(III) and other cations react slowly.

These complexes do not diffuse through a cellophane membrane into another detergent solution, whereas Xylenol Orange and its complexes in the absence of cationic detergents do.

Effect of temperature

No change in the absorbance of Xylenol Orange solutions in the presence of detergent could be observed in the temperature range from 20° to 60°.

DISCUSSION

All our attempts to isolate a product from the interaction of Xylenol Orange and detergent failed; the product is very soluble in water, and from the concentrated solutions, a mixture of detergent crystals and amorphous dye particles was always isolated. This mixture gave the individual components when washed out with an appropriate solvent. These results indicate that the interaction product exists in aqueous solutions as micellar aggregates.

The fact that the formation of micellar aggregates occurs at lower detergent concentrations than the critical micelle concentration (estimated in pure solutions by various methods) does not disagree with this supposition. It is well known that in the presence of an appropriate dye, the induced micelle formation occurs even with concentrations at which the detergent alone does not form micelles.[8]

From the experiments carried out it is not evident which of the groups of the indicator are involved in the bond with the detergent. However, the change in absorption spectra of Xylenol Orange, on addition of the detergent, suggests that the bond must involve the phenolic group.[9] Further, because the absorption spectra of the aggregates and that of free Xylenol Orange at pH 6·4 are identical, a similar resonance structure of the indicator may be assumed in both instances. The metal ion is able to react with the indicator which, however, still remains involved in the micellar aggregates, as evidenced by its inability to pass through cellophane membranes.

High concentrations of mineral salts prevent the formation of dye-detergent micelles. This is probably caused by the inorganic anion displacing the dye as a counter-ion.

Although the theory is incomplete, the practical consequences in analytical chemistry are of some interest. The complexan-type metallochromic indicators of the sulphonphthalein series, which are superior because of their excellent colour properties, have had no previous application in an alkaline medium. The use of a suitable cationic detergent enables these indicators to be used over practically the whole pH range. This fact may be exploited in the field of complexometric titrations as well as in the spectrophotometric analysis of some metal cations. Both these possibilities are the subject of further detailed studies.

Acknowledgment—The authors wish to express their thanks to Mr. J. Körbl (Biochemical and Pharmaceutical Research Institute, Prague, Czechoslovakia) for his helpful discussion of this work.

Zusammenfassung—Purpurrot gefärbte alkalische Lösungen von Xylenolorange werden durch den Zusatz von kationaktiven langkettigen quaternären Salzen entfärbt. Ein bastimmtes Grenzverhältnis des oberflächenaktiven Mittels zum Indikator ist erforderlich um den Entfärbungseffekt voll zur Geltung zu bringen. Es wird die Bildung von mizellenartigen Aggregaten vorausgesetzt. In diesen Aggregaten ist jedes Farbstoffmolekül mit mindestens fünf Molekülen Cetylpyridiniumbromid, beziehungsweise mit sechs Molekülen Cetyltrimethylammoniumbromid umgeben. Absorptionsspektren zeigen, dass die Elektronenstruktur von Xylenolorange in diesem Zustand der üblichen, bei pH 6,4 vorgefundenen Struktur entspricht. Xylenolorange in der Form solcher Aggregate besitzt die Fähigkeit gefärbte Komplexe mit gewissen Kationen in einem breiteren pH-Bereich zu bilden als in der normalen Form. Einige Ionen, wie zum Beispiel Kalzium und Magnesium, welche gewöhnlich nicht mit Xylenolorange als Indikator bestimmt werden, können, erfolgreich mit Hilfe des modifizierten Indikators titriert werden.

Résumé—Les solutions alcalines rouge-pourpre de Xylénol Orangé sont décolorées par l'addition de sels quaternaires cationiques à longue chaîne. Un rapport minimal défini entre le détergent et l'indicateur est nécessaire pour apporter l'effet décolorant total. On suppose la formation d'agrégats micellaires. Dans ces agrégats, une molécule de colorant est entourée par au moins cinq molécules de bromure de cétylpyridinium et six molécules de bromure de cétyltriméthylammonium, respectivement. Selon les spectres d'absorption, la structure électronique du Xylénol Orange dans cet état est celle que l'on trouve normalement à pH 6,4. Le Xylénol Orangé, lié dans ces agrégats, est capable de former des complexes colorés avec un certain nombre de cations dans un domaine de pH plus grand que d'ordinaire. Quelques ions, comme le calcium et le magnésium, que l'on ne dose pas habituellement avec le Xylénol Orangé comme indicateur, peuvent être dosés avec succès en employant l'indicateur modifié.

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REACTIONS OF METALLOCHROMIC INDICATORS ON MICELLES—II†

APPLICATION OF XYLENOL ORANGE TO CHELATOMETRIC TITRATIONS IN AN ALKALINE MEDIUM*

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Summary—Xylenol Orange in the presence of cetylpyridinium bromide has been applied as a metallochromic indicator for the complexometric determination of some metal cations in an alkaline medium. Precise successive determinations of some pairs of metals in the same solution are possible.

IN the introductory communication of this series,[1] the behaviour of alkaline Xylenol Orange solutions in the presence of micelle-forming cationic detergents has been described. From the analytical point of view, the most interesting property of the aggregates formed is their ability to form coloured complexes with various cations. Some of them react practically instantaneously with EDTA solution, so that their successful application in complexometric titrations could be expected. In preliminary experiments, among the metals forming sufficiently stable complexes with EDTA in the alkaline region, the most promising results have been obtained in the titration of calcium(II), magnesium(II), cadmium(II), zinc(II) and manganese(II). The extension of the working range of Xylenol Orange to alkaline solutions allows the successive determination of some pairs of metals in the same solution. The results of such determinations are presented in this paper.

EXPERIMENTAL

Reagents

EDTA. 0·025 and 0·05*M* solutions were prepared from disodium ethylenediaminetetra-acetate (Chelaton 3, Lachema, Czechoslovakia) and standardised in the usual manner.

Metal ions. 0·025*M* solutions of calcium, magnesium, cadmium, zinc lead and manganese were prepared from appropriate salts and standardised by means of conventional EDTA titrations.

Buffers. Ammoniacal buffer solution of pH 10·5 and solid hexamethylenetetramine were used for pH adjustment.

Indicator. Xylenol Orange was used as a 1:100 solid mixture finely ground with potassium chloride.

Cetylpyridinium bromide. Used in the form of a saturated solution in 20% aqueous methanol.

Nitric acid. 10% Aqueous solution.

All chemicals used in this work were of reagent-grade purity.

Procedure

Determination of single metal ions. Dilute the sample solution to 100 ml, and add 10 ml of pH 10·5 buffer solution followed by 1 ml of detergent solution and Xylenol Orange mixture. Titrate with EDTA to the end-point colour change.

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† Part I: see reference 1.

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Determination of pairs of metal ions. The metal ion pairs are selected so that one ion may be titrated in acid and the other in alkaline solution. Acidify the solution to be titrated with a few drops of nitric acid, then add the indicator and solid hexamethylenetetramine. Titrate with EDTA till the solution changes from dark red to clear lemon-yellow.[2,3] Adjust the pH to 10·5 with 10 ml of ammoniacal buffer solution, add 1–2 ml of detergent solution and titrate the second cation with EDTA.

RESULTS

Determination of single metal ions

The results of the determination of individual cations in an alkaline medium are given in Table I. All the tabulated values are the means of ten determinations.

TABLE I.—TITRATION OF INDIVIDUAL CATIONS

Ion	Taken, *mg*	Found, *mg*	Standard deviation, *mg*
Ca^{2+}	5·06[a]	5·06	±0·011
	10·11[a]	10·11	±0·010
	20·33[b]	20·32	±0·017
Zn^{2+}	5·62[a]	5·62	±0·014
	11·24[a]	11·23	±0·016
	33·10[b]	33·09	±0·028
Mn^{2+}	5·84[a]	5·86	±0·007
	11·71[a]	11·71	±0·010
	28·25[b]	28·25	±0·029
Mg^{2+}	6·14[b]	6·14	±0·006
	12·28[b]	12·28	±0·007
Cd^{2+}	12·71[b]	12·69	±0·042
	31·78[b]	31·80	±0·053

[a] 0·025*M* EDTA used.
[b] 0·05*M* EDTA used.

The average recoveries of the determined cations agree well with the amounts taken. The standard deviations, show, especially in the case of determinations of calcium, magnesium and manganese, the excellent reproducibility of individual results. The results obtained for cadmium(II) are less satisfactory; nevertheless, even in this case the results compare favourably with those from previously published methods.

In all the determinations, the end-point colour change was distinct and sharp, within 1-2 drops of the titrant solution. The colours of the indicator-metal complexes vary with the metal ion; those of magnesium and zinc are red; that of manganese is violet; and those of calcium and cadmium are blue-violet. At the equivalence-point these colours change to colourless or pale grey, depending upon the amount of the indicator added. With calcium and cadmium, the colour change passes through a sky-blue shade close to the equivalence-point, which makes the colour change more remarkable.

Determination of pairs of metals

The presence of a metal of the alkaline earth metal group does not interfere with the first determination in acid solution, and the accuracy is unimpaired.

As described in the preceding paper,[1] mineral salts affect the formation of the indicator-detergent complex. Therefore, in these determinations, after the adjustment of pH, a greater amount of the detergent solution is necessary in order to obtain satisfactory results.

In all the titrations of the second cation in the alkaline region, the end-point colour change of the indicator is much better than that obtained when the corresponding metal ions are alone. This phenomenon is probably explained by the following reaction taking place, at least to some extent,

$$\text{Pb-EDTA} + \text{Ca-In} \rightleftharpoons \text{Pb-In} + \text{Ca-EDTA}$$

so that at the end-point the lead-indicator complex is being titrated with consequent improvement in colour change.

TABLE II.—TITRATION OF PAIRS OF METALS

Taken, *mg*		Found, *mg*		95% Confidence interval, *mg*	
Zn	Mg	Zn	Mg	Zn	Mg
3·31	10·99	3·31	10·98	±0·016	±0·012
9·92	8·55	9·87	8·54	±0·033	±0·012
16·53	6·11	16·54	6·11	±0·033	±0·012
23·15	3·66	23·16	3·66	±0·016	±0·012
29·76	1·22	29·78	1·23	±0·033	±0·012
Pb	Ca	Pb	Ca	Pb	Ca
10·58	18·13	10·51	18·13	±0·055	±0·041
31·55	14·10	31·57	14·11	±0·053	±0·021
52·58	10·07	52·56	10·07	±0·105	±0·020
73·61	6·04	73·60	6·05	±0·053	±0·020
94·64	2·01	94·63	2·02	±0·160	±0·020

Table II shows the results of titrations of the metal pairs zinc-magnesium and lead-calcium. The titrations were performed for various ratios of cations. The values given in the table are averages of five determinations. The Dean-Dixon method,[6] which has been recommended for the statistical evaluation of data based on a small number of observations, was used. As may be seen from the tabulated values of confidence intervals, the results of individual titrations of the second cation have good precision.

DISCUSSION

Among the large number of metallochromic indicators used in complexometric titrations, Xylenol Orange is outstanding. However, its application has been limited by its own acid-base indicator properties, to the acid region. The interaction of Xylenol Orange with cation-active detergents permits the extension of its useful range to pH 11, where it behaves like its "acid" form, giving with many cations "normal" complexes (*cf.*[4,5]).

The titrations described in this communication represent only a few examples of the cases in which Xylenol Orange can be used in the presence of cationic detergents. For most of these determinations, of course, other, more or less suitable indicators have been proposed todate. Nevertheless, because of the excellent colour properties of Xylenol Orange which are retained even in these instances, one can suppose that these new possibilities will find a very wide practical application in complexometric analysis.

Zusammenfassung—Xylenolorange wurde als Metallfarbindikator in Gegenwart von Cetylpyridiniumbromid zur komplexometrischen Bestimmung einiger Kationen in alkalischer Lösung angewendet. Es ist möglich gewisse Metallpaare in derselben Lösung aufeinander folgend sehr genau zu bestimmen.

Résumé—Le Xylénol Orangé en présence de bromure de cétylpyridinium a été appliqué, en tant qu'indicateur métallochrome, au dosage complexométrique de quelques cations dans un milieu alcalin. Il est possible d'effectuer les dosages successifs précis de quelques paires de métaux dans la même solution.

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REFLECTANCE SPECTRA OF TWO SOLVATED URANIUM 8-HYDROXYQUINOLATES

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Summary—On precipitation of uranyl 8-hydroxyquinolate from homogeneous solution, two different chelates are obtained.

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$

is dark red whereas $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ is orange. On grinding, the dark-red chelate becomes orange. Reflectance spectra are used to explain the initial colour difference as well as the change in colour of the dark-red compound to orange on grinding.

IN 1961 Bordner *et al.*[1] precipitated two uranium 8-hydroxyquinolates from homogeneous solution with 8-hydroxyquinoline (HQ) generated by hydrolysis of 8-acetoxyquinoline. Table I summarises the properties of the two precipitates. When the dark-red compound, $UO_2Q_2 \cdot HQ$, is ground, it assumes an orange colour very similar to that of $(UO_2Q_2)_2 \cdot HQ$. To explain the colour differences and colour change on grinding the compound $UO_2Q_2 \cdot HQ$, a study of the reflectance spectra of the different compounds was undertaken.

TABLE I.—PROPERTIES OF THE URANIUM 8-HYDROXYQUINOLATES PRECIPITATED FROM HOMOGENEOUS SOLUTION

Formula	$UO_2Q_2 \cdot HQ$	$(UO_2Q_2)_2 \cdot HQ$
Colour of precipitate	dark red	orange
pH of precipitation	5·0	6·8
Excess of reagent used in precipitation procedure	*ca.* 20-fold[1]	2-fold[1]

Reflectance and eye response spectra

The reflectance spectra of the various compounds were obtained with a Cary 14 Spectrophotometer and are shown in Fig. 1b. In general appearance the spectra are very similar. All exhibit high reflectance in the red region around 750 mμ. Sample 1 (orange) has a smaller reflectance in this region whereas the reflectances of sample 2u (dark red) and sample 2g (orange), which are chemically identical, are larger and close to each other. Between 500–600 mμ, or the yellow-orange region of the spectrum, a decrease in reflectance is observed in the order 2g > 1 > 2u. At the ultraviolet end of the spectrum all three show very small but identical reflectance.

To explain these colour phenomena, it is first necessary to consider eye sensitivity. As a measuring instrument for luminosity, the eye is very selective in that it does not respond equally to radiations of different wavelengths. In the region 500–600 mμ, where colours range from green to yellow-orange, the eye is very sensitive, but in the

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region around 750 mμ (red) it is remarkably insensitive. A measure of eye sensitivity at normal brilliance levels for radiation of different wavelengths is given by the *Relative Luminosity Factor* (Eye Response). A part of the values for this factor given by the I.E.S. Nomenclature and Photometric Standards, American Standards Association, ASA C-42, 1941, is reproduced in Table II. The eye exhibits its maximum response at a wavelength of 555 mμ and the values for other wavelengths are given relative to this.

Because of the insensitivity of the eye in the red region around 750 mμ, it requires a large difference in reflectance for the eye to observe the difference. Further, in the region 500–600 mμ, where peak eye sensitivity occurs, small differences in reflectance will have a considerable effect on the eye. Thus, samples 1 and 2g, despite high reflectance around 750 mμ as shown in Fig. 1b, appear predominantly orange to the eye because of moderate reflectance in the eye-sensitive region, whereas sample 2u, which has a reflectance as great as 2g in the red, appears red because its contribution to the reflectance in the eye-sensitive region is much less in comparison to samples 1 and 2g.

TABLE II.—RELATIVE LUMINOSITY FACTOR (Eye Response)

Wavelength of radiation, mμ	Factor
500	0·323
510	0·503
520	0·710
530	0·862
540	0·954
550	0·995
555	1·000
560	0·995
570	0·952
580	0·870
590	0·757
600	0·631
.	.
.	.
.	.
700	0·0041
710	0·0021
720	0·00105
730	0·00052
740	0·00025
750	0·00012
760	0·00006

The significance of the colour phenomena becomes more apparent by converting the reflectance-spectra values obtained with the spectrophotometer to *eye-response* spectra, which corresponds to what the eye actually sees. This is done by plotting the product of the relative luminosity factor and the reflectance at a particular wavelength *versus* the wavelength. The results are shown in Fig. 1a.

From the graphs it will be seen that sample 2g shows its highest reflectance at 575 mμ (orange) with a smaller contribution at 625 mμ (red-orange). To the eye, therefore, this substance will appear predominantly orange but with a reddish tinge to it. Sample 1 will appear orange in colour. Sample 2u, on the other hand, with its major peak at 600–625 mμ appears quite red because its reflectance in the yellow-orange region is much lower than for the other two samples.

The reddish tinge in sample 2g can be seen in Plate 1 of Fig. 1, where 1 is the orange precipitate obtained at pH 6·8 [$(UO_2Q_2)_2 \cdot HQ$] and 2u the dark-red precipitate obtained at pH 5·0 ($UO_2Q_2 \cdot HQ$). The small difference in colour between samples 1 and 2g could be related to a slight difference in structure.

The importance of the eye-response spectra becomes quite evident in that differences in the red region (750 mμ), which looked significant in Fig. 1b, now become insignificant to the eye and that small differences in the yellow-orange region (500–600 mμ) in Fig. 1b become significant.

Effect of particle size on reflectance

While the foregoing discussion gives an explanation for the colour of the precipitate as seen by the eye, it does not offer an explanation for the change in colour of dark-red sample 2u to orange on grinding. The particle size is the principal factor involved in this phenomenon.

Johnson[2] has shown that a strong increase in reflectance takes place when the particle size of a sample decreases. An electron microscopic examination of sample 2u (dark red) showed it to be comprised of particles very much larger than those in sample 1 (orange). Thus, when 2u is ground, there is an increase in reflectance in the eye-sensitive yellow-orange region around 525 mμ (*cf.* reflectance values for 2u and 2g in Fig. 1b). Hence, 2g looks more orange to the eye. However, there is no similar increase in reflectance around 750 mμ on grinding 2u, but this is in agreement with Johnson's[2] views that deductions about reflectance increases on grinding are not accurate where the reflectance values are greater than 0·8, as in the present case.

When samples 1 and 2g are ground to exactly the same particle size, their reflectance spectra curves are coincident in the yellow-orange region and differ only in the red region.

Effect of precipitation conditions on formation of uranium chelates

In the simpler uranyl compounds, *e.g.*, uranyl nitrate, the uranium atom is octa-co-ordinate. The central atom forms 6 bonds, partly covalent, which are in a plane orthogonal to the O—U—O plane. Thus, the uranyl group will show sexa-covalent character and involve the use of f-orbitals.[3] Evidence in favour of this assumption is based on the strong tendency of the uranyl group to co-ordinate molecules of water in the solid state and solution.[4] Sacconi *et al.*[5] have also shown that the uranyl group, even when bonded to two diketone radicals, tends to co-ordinate donor molecules. It would appear, therefore, that the uranyl group, even after reacting with two molecules of 8-hydroxyquinoline, is *co-ordinatively unsaturated* and capable of adding further molecules of solvation. In such circumstances, the rate of precipitation and the number of molecules of reagent available might determine the particular chelate formed.

As seen in Table I, the dark-red compound $UO_2Q_2 \cdot HQ$ is precipitated at pH 5·0 with a calculated excess of reagent of about 20-fold present, whereas at pH 6·8 for the orange precipitate $(UO_2Q_2)_2 \cdot HQ$ there is a 2-fold excess of reagent present. For comparison, two precipitations were carried out with the amounts of reagent used reversed, *i.e.*, where formerly a 2-fold excess of reagent was employed, a 20-fold excess was now used and *vice versa*; all other conditions were maintained as before. The results were that, whereas previously at pH 6·8 an orange precipitate had been obtained, a dark-red precipitate now formed. The precipitate obtained at pH 5·0 was still red, although the amount of precipitate formed was quite small because of the higher acidity and the lack of precipitant. The results thus confirm that the number of available molecules of reagent has a determining influence on the particular uranium chelate formed.

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Zusammenfassung—Bei der Fällung von Uran-8-hydroxychinolat aus homogener Lösung erhält man zwei verschiedene Chelate.

$$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$$

ist dunkelrot, $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ dagegen orange. Beim Mahlen wird das dunkelrote Chelat orange. Mit Hilfe von Reflexionsspektren wird der anfängliche Farbunterschied sowohl als auch die Farbänderung der dunkelroten Verbindung nach orange beim Mahlen erklärt.

Résumé—Lors de la précipitation du 8-hydroxyquinolinate d'uranyle en milieu homogène, on obtient deux chélates différents.

$$UO_2(C_9H_6NO)_2,C_9H_6NOH$$

est rouge foncé, cependant que $[UO_2(C_9H_6NO)_2]_2,C_9H_6NOH$ est orangé. Par broyage, le chélate rouge foncé devient orangé. On utilise les spectres de réflexion pour expliquer la différence de couleur initiale ainsi que le changement de couleur du composé rouge foncé en orangé lors du broyage.

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INFRARED SPECTRA OF CHELATE COMPOUNDS—IV†

A STUDY OF THE URANYL CHELATES OF 8-HYDROXYQUINOLINE IN THE REGION 5000–250 cm^{-1}

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Summary—Previous investigations have shown that two different uranium chelates of 8-hydroxyquinoline can be precipitated from homogeneous solution. Dark red $UO_2(C_9H_6NO)_2{\cdot}C_9H_6NOH$ is obtained at pH 5·0 and orange $[UO_2(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH$ at pH 6·8; the *normal* chelate $UO_2(C_9H_6NO)_2$ is green. The infrared spectra of the solvated compounds have been examined in the range 5000–250 cm^{-1} and that of the normal chelate in the range 5000–650 cm^{-1}. From this it is concluded that the solvated chelates have very similar structures.

IN earlier parts of this series[1–3] the results of infrared investigations of bivalent and tervalent metal chelates of 8-hydroxyquinoline in the region 5000–250 cm^{-1} were reported. In the present work the uranium chelates have been studied.

In 1933 Frere[4] precipitated the uranium chelate of 8-hydroxyquinoline by conventional means and obtained a deep brick-red precipitate for which the formula $UO_2Q_2{\cdot}HQ$ (where $Q = C_9H_6NO$) was given. Since then it has been recognised that uranium forms two compounds with 8-hydroxyquinoline, a red compound with the above structure and the green *normal* chelate UO_2Q_2.[5] However, in 1961 Bordner *et al.*[6] precipitated two different uranium(VI) 8-hydroxyquinolates from homogeneous solution with 8-hydroxyquinoline generated by the hydrolysis of 8-acetoxyquinoline. One of the precipitates was dark red in colour while the other was orange. The analytical data indicated the composition of the two uranium chelates to be different. For the dark-red precipitate, obtained at pH 5·0, the formula $UO_2Q_2{\cdot}HQ$ fitted the data and for the orange chelate, precipitated at pH 6·8, $(UO_2Q_2)_2{\cdot}HQ$ was appropriate.

EXPERIMENTAL

Infrared measurements

The precipitates were obtained by the procedures referred to above. Both the potassium bromide disc technique and the Nujol-mull technique were used to obtain the infrared spectra. In the former the discs were prepared using a Perkin-Elmer die in conjunction with an Elmes hydraulic press capable of delivering 23,000 lb total load on a ram 3" in diameter. Before use, spectroscopic-grade potassium bromide was dried at 150° for 24 hr and ground to pass 100 mesh.

All spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer with a caesium bromide prism. Polystyrene was used for calibration purposes.

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RESULTS

The spectra obtained for the solvated metal chelates are shown in Figs. 1–4 (the spectrum for 8-hydroxyquinoline has been reported previously[1,2]). The principal absorption peaks (μ) in these spectra are as follows:

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ and $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$. 33·85, 28·5, 23·11, 20·55, 19·77, 18·29, 16·6, 16·01, 15·5, 13·68, 13·32, 13·0, 12·73, 12·54, 12·46, 12·3, 12·17,

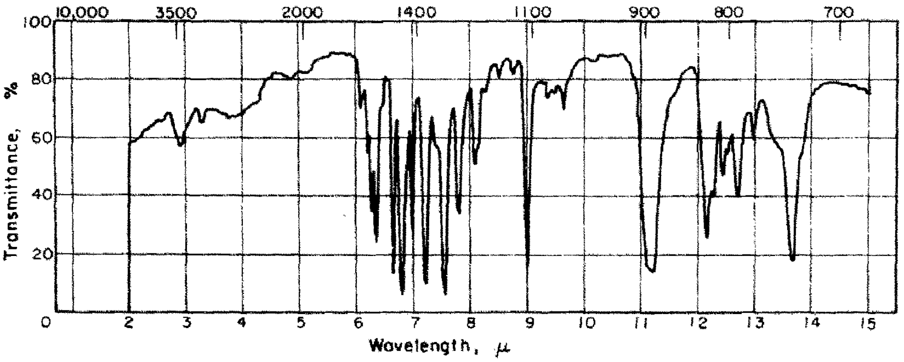

FIG. 1.—The infrared spectrum of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ obtained at pH 5·0 in the region 2–15 μ [1 mg of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ in 400 mg of KBr].

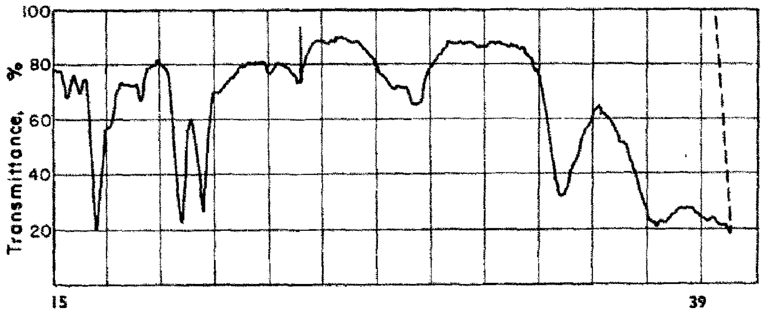

FIG. 2.—The infrared spectrum of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ obtained at pH 5·0 in the region 15–40 μ [2 mg of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ in 400 mg of KBr].

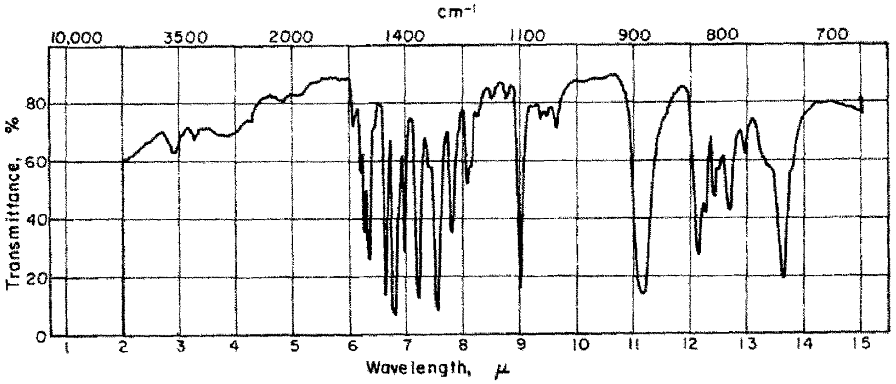

FIG. 3.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ obtained at pH 6·8 in the region 2–15 μ (1 mg of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ in 400 mg of KBr).

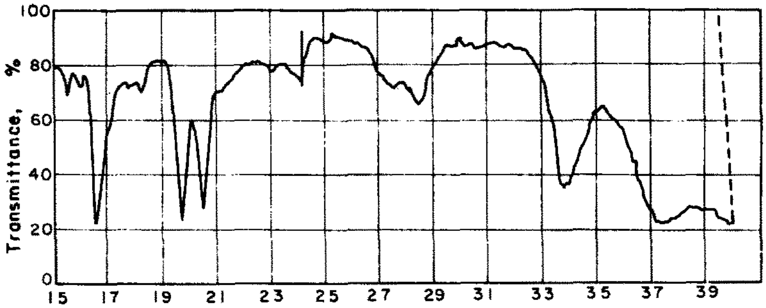

FIG. 4.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ obtained at pH 6·8 in the region 15–40 μ (2 mg of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ in 400 mg of KBr).

11·22, 9·66, 9·5, 9·37, 9·02, 8·78, 8·52, 8·3, 8·16, 8·1, 7·82, 7·56, 7·24, 7·0, 6·8, 6·66, 6·36, 6·28, 6·22, 6·09, 5·14, 4·87, 3·27, 2·92.

Only the principal peaks for the uranium chelate precipitated at pH 5·0 are given, because those for the precipitate obtained at pH 6·8 appeared to be identical. However, in the region between about 9 μ (1100 cm^{-1}) and 14 μ (700 cm^{-1}), it looked as if small differences in the spectra might exist. To investigate more closely if these tendencies were real or imaginary the spectra of the two metal chelates were obtained at improved resolution on the Beckman IR-7 instrument between 650 and 1100 cm^{-1}. The Nujol-mull technique was employed, the concentration of the chelate being adjusted until the best resolution was obtained. The spectrum of the dark-red precipitate obtained at pH 5·0 is shown in Fig. 5 and that of the orange precipitate obtained at pH 6·8 in Fig. 6.

Between the two spectra minor differences arise:

(1) A small peak always occurs at 678 cm^{-1} in the spectrum of the dark-red sample (Fig. 5) which is absent in that of the orange sample (Fig. 6).

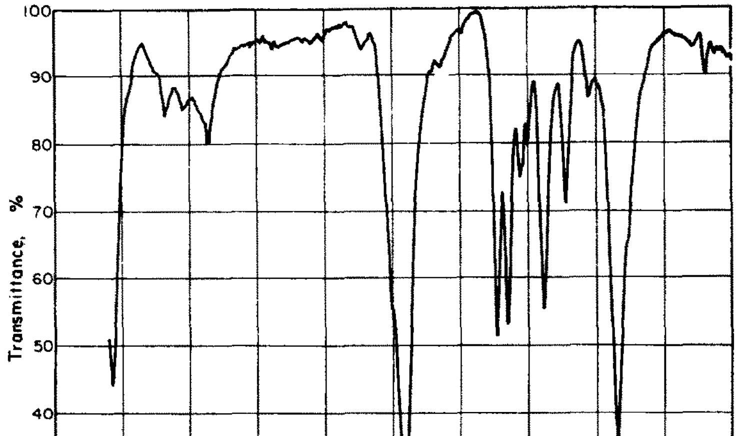

FIG. 5.—The infrared spectrum of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ obtained at pH 5·0 in the region 9–15·5 μ ($[UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ in a Nujol mull].

(2) The lengths of the major peaks at 823 and 813 cm^{-1} are reversed in the spectra of the two chelates.

(3) In the major peak at 888 cm^{-1} a shoulder occurs in both spectra, but it was always more clearly resolved in that of the orange sample.

To investigate more closely the shoulders on the peak at 888 cm^{-1} as indicated in (3) above, a closer examination was carried out, at the greatest sensitivity available, in the spectral region 820–910 cm^{-1}. Little improvement was obtained except that, in the spectrum of the dark-red chelate, the major peak occurred at 891 cm^{-1} (888 cm^{-1} in the orange compounds) and the shoulder in the spectrum of the dark-red chelate appeared to be resolved more clearly.

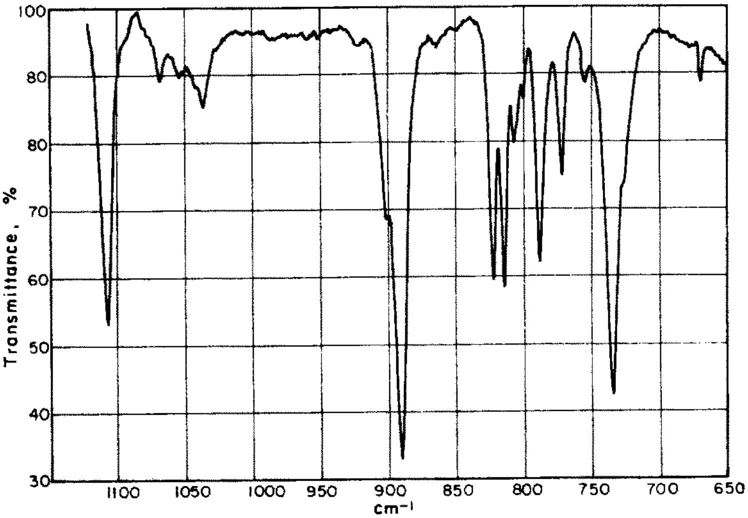

FIG. 6.—The infrared spectrum of $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ obtained at pH 6·8 in the region 9–15·5 μ ($[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ in a Nujol mull).

$UO_2(C_9H_6NO)_2$. The unsolvated chelate, UO_2Q_2, is obtained by heating $UO_2Q_2 \cdot HQ$ at 210–215°.[7] The infrared spectrum is shown in Fig. 7. It will be seen that the spectrum differs in many respects from those of the dark-red chelate and the orange chelate (Figs. 5 and 6). If the three spectra are checked peak by peak it will be found that the differences between UO_2Q_2 and the other two are based principally on the disappearance or shifts of peaks from the latter. The principal differences are as follows:

(1) The peaks at 1056 and 1068 cm^{-1} occurring in the spectra of the dark-red and orange compounds have disappeared from the spectrum of UO_2Q_2.

(2) The peak around 890 cm^{-1} attributed to UO_2^{2+} stretching in the spectrum of the dark-red and orange compounds has shifted to 920 cm^{-1} in the spectrum of UO_2Q_2 and the shoulders on this peak which were so clearly indicated in the former have disappeared.

(3) In the spectra of the dark-red and the orange compounds two peaks occurred at 823 and 813 cm^{-1} and the lengths of the peaks differed clearly in the two spectra. In the case of the spectrum of UO_2Q_2 these peaks are shifted, occurring at 878

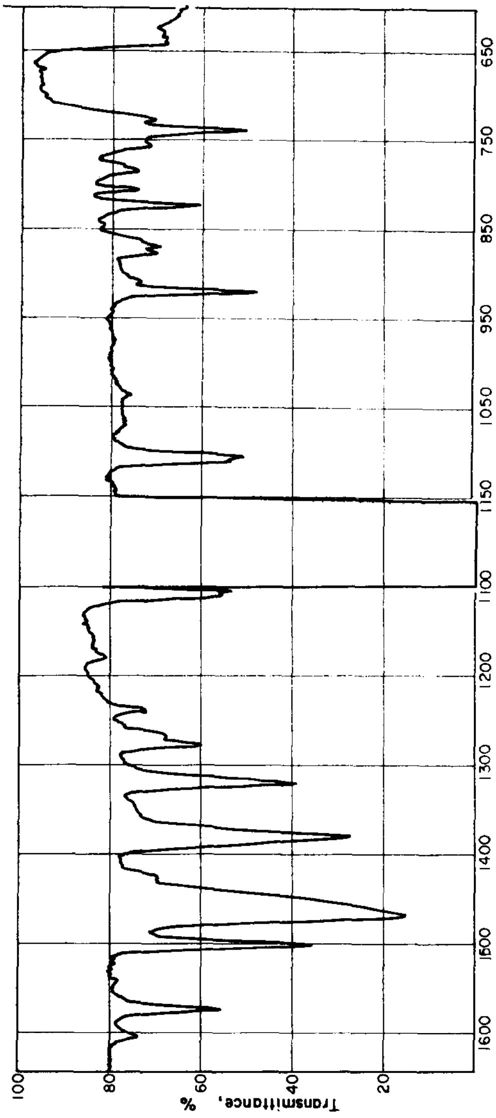

FIG. 7.—The infrared spectrum of the *normal* $UO_2(C_9H_6NO)_2$ in the region 6–15 μ [$UO_2(C_9H_6NO)_2$ in a Nujol mull].

and 869 cm^{-1}, respectively, and the lengths of the peaks again differ, being in the same order as for the orange compound.

CONCLUSION

The structure of the dark-red compound, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, has been discussed by several groups of authors,[5,8,9] but no mention is made by any of them of the orange chelate, $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$. In the present work it was hoped that the infrared investigation might reveal sufficient differences to allow a definite conclusion to be drawn about the structures of the two compounds. However, as the above results show, the spectral differences are small, so that the only conclusion possible is that the two chelates are structurally similar and that differences, if they do exist, are very small. This similarity of the two chelates has also been demonstrated by a study of their reflectance spectra.[10]

It is felt that more positive conclusions may be obtained by a crystal structure determination, as carried out on the red compound by Hall *et al.*[9] Work in this direction is being undertaken and will be reported later.

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)582.

Zusammenfassung—Frühere Untersuchungen zeigten, daß aus homogener Lösung zwei verschiedene Uranchelate von 8-Hydroxychinolin gefällt werden können. Bei pH 5,0 erhält man dunkelrotes

$$UO_2(C_9H_6NO)_2 \cdot C_6H_6NOH,$$

bei pH 6,8 orangefarbiges $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$; das *normale* Chelat $UO_2(C_9H_6NO)_2$ ist grün. Die Infrarotspektren der solvatisierten Verbindungen wurden im Bereich 5000 – 250 cm^{-1}, das des normalen Chelats von 5000 – 650 cm^{-1} aufgenommen. Aus den Spektren wird geschlossen, daß die solvatisierten Chelate sehr ähnliche Struktur besitzen.

Résumé—Des recherches antérieures ont montré qu'à partir de solutions homogènes, on peut précipiter deux chélates d'uranium et de la 8-hydroxyquinoléine différents. Le précipité rouge foncé $UO_2(C_9H_6NO)_2,C_9H_6NOH$ est obtenu à pH 5,0, l'orange

$$[UO_2(C_9H_6NO)_2]_2,C_9H_6NOH$$

à pH 6,8; le chélate *normal* $UO_2(C_9H_6NO)_2$ est vert. On a examiné les spectres infra-rouges des composés solvatés entre 5000 et 250 cm^{-1}, et celui du chélate normal entre 5000 et 650 cm^{-1}. La conclusion en est que les chélates solvatés ont des structures très semblables.

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THE OXIMATION OF BIACETYL

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Summary—Spectrophotometric evidence indicates that the reaction of biacetyl with hydroxylamine proceeds through the formation of two carbinolamine intermediates. The second of these intermediates is also encountered in the reaction of biacetyl monoxime with hydroxylamine. The rate-limiting step in the oximation of biacetyl is the slow dehydration of the initially formed intermediate, as is evidenced from the various rate constants obtained for the two reactions over the range 0–10°. When nickel(II) is present in the biacetyl-hydroxylamine system, the formation of nickel dimethylglyoximate proceeds by two independent mechanisms, whereas only a single mechanism is responsible for precipitate formation in the biacetyl monoxime-hydroxylamine system.

INTRODUCTION

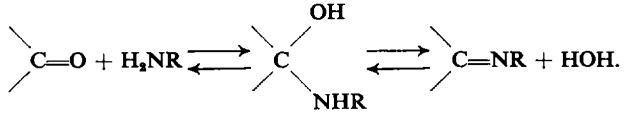
PREVIOUS studies[1–3] on the precipitation from homogeneous solution of nickel dimethylglyoximate have indicated the necessity of further study of the reaction of biacetyl and hydroxylamine to form biacetyl monoxime and dimethylglyoxime:

$$CH_3COCOCH_3 + NH_2OH \xrightarrow{k_1} CH_3C(:NOH)COCH_3 + H_2O \quad (1)$$

$$CH_3C(:NOH)COCH_3 + NH_2OH \xrightarrow{k_2} CH_3C(:NOH)C(:NOH)CH_3 + H_2O \quad (2)$$

Since the classical studies of Barrett and Lapworth,[4] Olander,[5] Conant and Bartlett[6] and Westheimer,[7] there have been many subsequent studies of the reactions between nitrogen bases and carbonyl compounds. The results of these experiments show striking maxima in the rate-pH profiles of these reactions. This effect has been attributed to the opposing effects of the decrease in the concentration of the free nitrogen base at low pH and general acid catalysis.

Jencks[8] has shown that the rate-limiting step in the formation of oximes at neutral pH is not the attack of the nitrogen base on the carbonyl, but is the acid-catalysed dehydration of an addition compound. The reaction mechanism proposed by Jencks is:



$$>C{=}O + H_2NR \rightleftharpoons >C(OH)(NHR) \rightleftharpoons >C{=}NR + HOH.$$

Salesin, Abrahamson and Gordon[3] have studied the effect of pH on the reaction of hydroxylamine with biacetyl at 15·0°. These investigators found that the specific rate constants for reactions (1) and (2) were highly pH dependent, with the rates being faster at lower pH values.

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The present investigation was undertaken to determine the existence of and to study the properties of intermediates formed during the reaction between biacetyl and hydroxylamine, to determine the temperature dependence of the reaction rate constants and to note the effect of nickel(II) on the reaction sequence.

EXPERIMENTAL

Reagents

Biacetyl. PF/HS-grade biacetyl (Burdick and Jackson Laboratories, Muskegon, Mich., U.S.A.) was purified by the method of Salesin *et al.*[3]

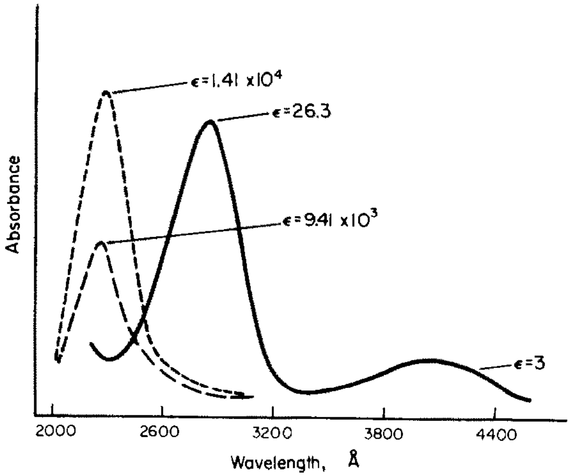


Fig. 1.—Spectra of biacetyl, biacetyl monoxime and dimethylglyoxime in aqueous NH_4Cl solution:

(pH = 7·00—adjusted with NH_3
t = 5°
$[NH_4Cl] = 7{\cdot}1 \times 10^{-2}M$)
———— Biacetyl
– – – – – Biacetyl monoxime
- - - - - - - Dimethylglyoxime.

Biacetyl monoxime. Highest-Purity-Grade biacetyl monoxime (Fisher Scientific Co., Cleveland, Ohio, U.S.A.) was triply sublimed at 35° and 1 mm of mercury.

Hydroxylamine hydrochloride. Analytical Reagent-Grade hydroxylamine hydrochloride (Fisher Scientific Co., Cleveland, Ohio, U.S.A.) was recrystallised from 95% ethanol.

All other chemicals used in the investigation were reagent grade.

Apparatus

All pH measurements were determined with a Beckman Model 9600 pH meter calibrated with a pH reference buffer solution (pH 7·00 ± 0·01) at 25° (Fisher Scientific Co.).

The spectrophotometric studies were made with a Cary Model 14 recording spectrophotometer equipped with a thermostatted cell compartment.

A Burroughs 220 computer was utilised in data-fitting computations.

Procedures

The following spectrophotometric procedures used in studying the biacetyl-hydroxylamine and the biacetyl monoxime-hydroxylamine systems in the absence and in the presence of nickel(II) utilised the spectra of Fig. 1 in order to follow the various species in the reaction solution. (The ultraviolet spectra of aqueous biacetyl monoxime, dimethylglyoxime and nickel dimethylglyoximate solutions have been reported previously.[3]) In correspondence with the conditions employed in the precipitation of nickel dimethylglyoximate,[1] the amount of hydroxylamine used in all reactions was in large excess compared to the oximes.

Series 1: The same procedure as reported by Salesin *et al.*[3] for studying the reaction between biacetyl and hydroxylamine was used in this series of experiments with the exceptions that (*a*) the pH was held constant at 7·00 ± 0·02, at 25°, and (*b*) the temperature was varied over the range 5·0° to 35·0°. The time required from mixing of reagents to the recording of the results was about 4 min.

Series 2: Exactly 0·5000 g of hydroxylamine hydrochloride was dissolved in 90 ml of water, and the pH was adjusted to 7·00 ± 0·02, at 25°; the final volume was 100·0 ml.

A portion of the hydroxylamine solution was used as the reference solution; exactly 16·00 ml, at 25°, were placed in the 5·0-cm sample cell, and the cell was placed in the thermostatted sample compartment of the Cary 14 until temperature equilibrium was reached.

A biacetyl solution was prepared by dissolving 1·545 ml, at 25°, of pure biacetyl in 100·0 ml of solution. The kinetic experiment was started when 0·050 ml of this solution (25°) was added to the hydroxylamine solution in the sample cell in the Cary 14.

The wavelength was held constant at 2838 Å. The temperature for the series was varied over the range 0·5–10·0°. The time required from mixing of reagents to the recording of the results was 0·10–0·15 min.

Series 3: The same procedure was used as described in *Series* 2 above, except that the hydroxylamine solution was replaced by an equivalent NH_4Cl-HCl solution (pH 7·00).

Series 4: The hydroxylamine solution, prepared as described in *Series* 2 above, was used as the reference solution. Exactly 3·150 ml of the solution were added to a 1·0-cm cell, and the cell was then placed in the thermostatted sample compartment.

A solution of biacetyl monoxime was prepared by dissolving 0·1497 g of the solid in 250·0 ml of solution. The kinetic experiment was started when 0·050 ml of this solution was added to the hydroxylamine solution in the sample cell.

The wavelength was held constant at 2250 Å. The temperature for the series was varied over the range 0·5–10·0°.

Series 5: The same procedure was used as described in *Series* 4 above with the modification described in *Series* 3 above.

Series 6: Exactly 1·2500 g of hydroxylamine hydrochloride were dissolved in 225 ml of water, and 4·146 ml of $1·674 \times 10^{-2}M$ nickel(II) solution were added. The pH of this solution was adjusted to 7·00 ± 0·02, at 25°, and the solution was diluted to 250·0 ml.

A portion of the hydroxylamine-nickel solution was used as the reference solution. Exactly 16·00 ml, at 25°, of the hydroxylamine-nickel solution were placed in a 5·0-cm cell, and the cell was placed in the thermostatted sample compartment.

The experiment was started when 0·050 ml of a biacetyl solution, prepared as previously described, was added to the hydroxylamine-nickel solution in the sample cell in the Cary 14.

The wavelength was held constant at 3600 Å. The temperature for the series was varied over the range 0·5–10·0°.

Series 7: Exactly 0·5000 g of hydroxylamine hydrochloride was dissolved in 90 ml of water, and 0·281 ml of $1·674 \times 10^{-2}M$ nickel(II) solution was added. The pH of this solution was adjusted to 7·00 ± 0·02, at 25°, and the solution was diluted to 100·0 ml.

A portion of this solution was used as the reference solution. Exactly 3·150 ml of it were placed in a 1·0-cm cell, and the cell was then placed in the thermostatted sample compartment.

The experiment was started when 0·050 ml of a solution of biacetyl monoxime, prepared as previously described, was added to the hydroxylamine-nickel solution in the sample cell in the Cary 14.

The wavelength was held constant at 2250 Å. The temperature for the series was varied over the range 0·5–10·0°.

RESULTS AND DISCUSSION

Series 1

The results of the experiments are shown in Fig. 2 and Table I. The values of k_1 and k_2 [the rate constants of equations (1) and (2)] were calculated using the mathematical model and approximations previously proposed.[3]

As can be seen from Table I, the values of the rate constants, obtained by the use of approximations, show deviations at each temperature. To eliminate the approximations, a computer programme was utilised in which the best values of the rate constants were determined by numerically fitting the experimental results. The results of the re-analysis again confirmed the values of k_1 shown in Table I. Further, (*a*) the changes in k_2 were even more random with respect to temperature change and (*b*) the numerical fit to the curves of Fig. 2 became poorer as the temperature was lowered. Reliable values of k_2 simply could not be obtained by numerical analysis because of the insensitivity of the calculated absorbance values to changes in the trial values of this parameter. However, a direct way to arrive at values for k_2 was to arrange a series of experiments, similar to the biacetyl-hydroxylamine series, with the biacetyl replaced by biacetyl monoxime. From the previous model, one would predict the absorbance *versus time* dashed curve shown in Fig. 3, whereas the solid curve of Fig. 3 shows the results observed at 5·0°.

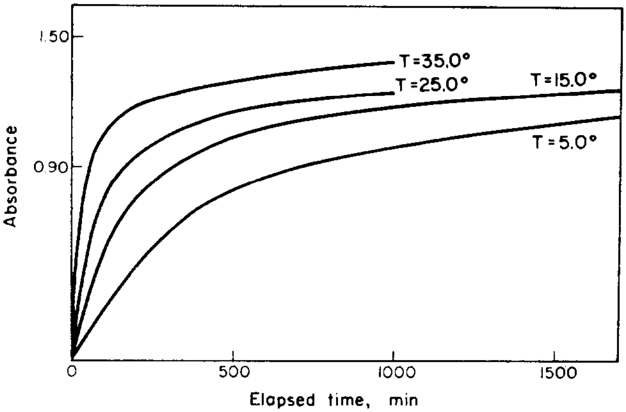


FIG. 2.—Absorbance *versus* time for the continuous spectrophotometric monitoring of the biacetyl-hydroxylamine system

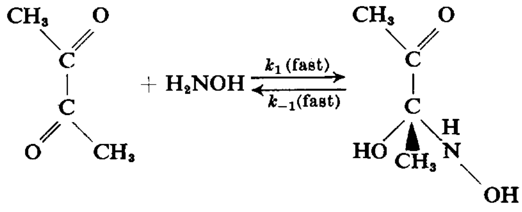
([Biacetyl] = $1{\cdot}080 \times 10^{-4}M$
[Hydroxylamine] = $7{\cdot}194 \times 10^{-2}M$
$\lambda = 2250$ Å).

The observation of Fig. 3, coupled with (*a*) the poorer numerical fit of the results as the temperature was lowered and (*b*) a non-linear Arrhenius plot for the specific rate constant k_1 of *Series* 1, indicated that the model[3] used for the biacetyl-hydroxylamine system was inadequate to explain the observed results.

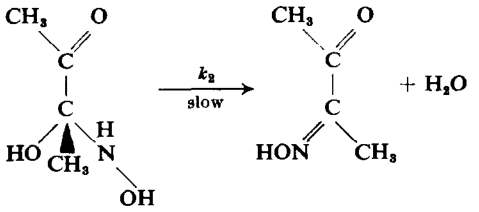
Series 2 *and* 3

Because it was not possible to obtain reliable values of k_1 and k_2 from the observations of *Series* 1, the experiments of *Series* 2 and 3 were devised to follow the concentration of biacetyl rather than biacetyl monoxime and dimethylglyoxime. The results are shown in Fig. 4.

To explain qualitatively the observations shown in Fig. 4, the following model, incorporating Jencks' concept of a reaction intermediate, was formulated:



(3)



(4)

or in abbreviated notation:

$$B + H \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{fast})}{\rightleftharpoons}} I_1 \qquad (3a)$$

$$I_1 \xrightarrow[\text{slow}]{k_2} M + H_2O \qquad (4a)$$

Initially, the concentration of I_1 is zero. If the extinction of I_1 is larger than that of biacetyl at 2838 Å, then the rapid initial increase of the absorbance can be explained

Table I.—Results of the preliminary kinetic studies in the biacetyl-hydroxylamine system

Temp., °*C*	$k_1(\times 10^1)$, *l.mole*$^{-1}$.*min*$^{-1}$	$k_2(\times 10^3)$, *l.mole*$^{-1}$.*min*$^{-1}$
5·0	0·195	8·47
	0·236	7·90
	0·393	5·73
15·0	0·975	5·87
	0·870	4·37
	0·790[a]	2·80[a]
25·0	1·81	8·81
	1·75	8·55
35·0	3·99	6·44
	8·09	26·3

[a] Calculated from the results of Salesin *et al.*[3]

by the rapid formation of I_1 (see Fig. 4, part A of curve). However, as the concentration of I_1 increases, the reverse rate increases and the over-all rate formation of I_1 decreases. Thus, the rate of absorbance-increase decreases (see Fig. 4, part B of curve). When the rate of formation of I_1 becomes less than the rate of formation of biacetyl monoxime [near equilibrium for reaction (3)] the absorbance of the system decreases (see Fig. 4, part D of curve).

Attempts to extract the postulated long-lived intermediate carbinolamine into several organic phases were unsuccessful. However, direct proof of the presence of the intermediate was obtained by observing an absorbance maximum in the ultraviolet spectrum not associated with any of the known reactants or products. The position of this absorbance maximum, initially at 2320 Å, varied with time, the shift being toward shorter wavelengths. The extinction coefficient, ε_{I_1}, of the intermediate and the rate constant, k_1, associated with equation (3) were obtained by the following numerical analysis.

From equations (3) and (4) the following may be written:

$$\frac{dA}{dt} = l\left[\varepsilon_B \frac{dB}{dt} + \varepsilon_{I_1} \frac{dI_1}{dt} + \varepsilon_M \frac{dM}{dt}\right] \qquad (5)$$

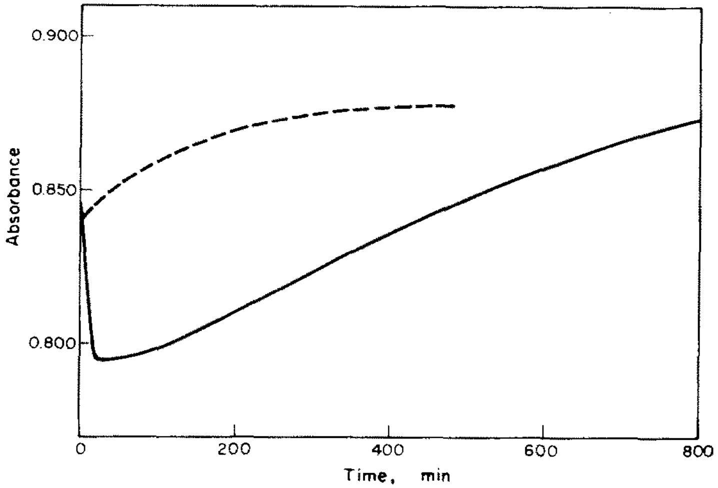


FIG. 3.—Absorbance *versus* time, expected and found, for the biacetyl monoxime-hydroxylamine system

([Biacetyl monoxime] = $8.94 \times 10^{-5}M$
[Hydroxylamine] = $7{\cdot}19 \times 10^{-2}M$
t = 5·00°
λ = 2275 Å
pH = 7·0).

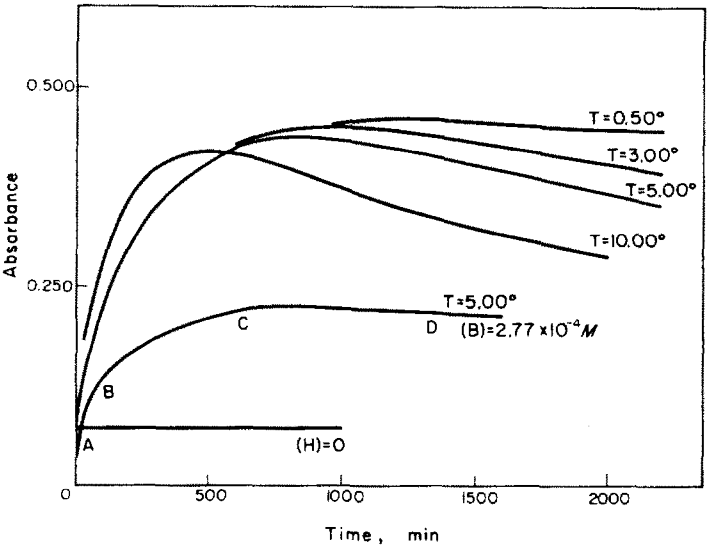


FIG. 4.—Absorbance *versus* time for the biacetyl-hydroxylamine system

([Biacetyl] = $5{\cdot}537 \times 10^{-4}M$
[Hydroxylamine] = $7{\cdot}193 \times 10^{-2}M$
λ = 2838 Å).

where B, I_1 and M = solution concentrations of biacetyl, intermediate I_1 and biacetyl monoxime, respectively;
ε_B, ε_{I_1}, and ε_M = extinction coefficients of biacetyl, intermediate I_1 and biacetyl monoxime, respectively;
A = total absorbance of the solution;
l = path length of the solution in cm;
t = time in min;
k_1, k_{-1}, k_2 = specific rate constants for reactions (3) and (4).

When t is very small, the value of dM/dt and the rate of the reverse reaction (3) will be zero. Further, it was experimentally noted that the initial rapid absorbance increase is first order with respect to biacetyl, *i.e.*, $(dA/dt)_B = 2(dA/dt)_{B/2}$ and $(dA/dt)_H = 2(dA/dt)_{H/2}$. Therefore, equation (5) can be integrated as follows:

$$A = l\{B_0[1 - \exp(-k_1't)]\varepsilon_{I_1} + [B_0 \exp(-k_1't)]\varepsilon_B\} \tag{6}$$

where B_0 = initial concentration of biacetyl.

Equation (6) contains two unknowns, *i.e.*, k_1' and ε_{I_1}. To obtain their values another equation was derived from equation (5) by neglecting $(\Delta B/\Delta t)\varepsilon_B$, the smaller term, because ε_B is much smaller than ε_{I_1},

$$k_1' = \frac{\Delta A}{(\Delta t)(\varepsilon_{I_1})(\bar{B})l} \tag{7}$$

where $k_1' = k_1(H)$;

$\bar{B}$ = average concentration of biacetyl over the time interval Δt.

Then, equations (6) and (7) were used in an iterative calculation to arrive at k_1' and ε_{I_1}, the best values for which are 0·053/min, at 5·0°, and $\frac{200(\text{Abs units})(\text{litre})}{(\text{cm})(\text{mole})}$, respectively.

With this value for ε_{I_1} and with the averaged results (5 runs) obtained at 3·0°, the value of k_1' at 3·0° was calculated to be 0·0509/min from equation (6).

At 0·5°, the results were too uncertain during the initial minutes of the reaction to be used for calculations of k_1'. At 10·0°, the initial reaction took place too quickly to gain reliable results with the experimental techniques employed in this investigation.

If it is assumed that the concentration of the biacetyl monoxime is zero during the early stages of the reaction, the following equation for k_{-1} can be derived from equations (5) and (6):

$$k_{-1} = \frac{\dfrac{\frac{\Delta A}{\Delta t}}{(\varepsilon_{I_1} - \varepsilon_B)l} - k_1'\left[\dfrac{\bar{A} - B_0\varepsilon_{I_1}l}{(\varepsilon_B - \varepsilon_{I_1})l}\right]}{\dfrac{\bar{A} - B_0\varepsilon_{I_1}l}{(\varepsilon_B - \varepsilon_{I_1})l} - B_0} \tag{8}$$

Table II shows the results of the calculation of k_{-1} obtained by using the averaged values at 3·0° and 5·0° over various reaction time intervals.

The calculation of k_2 [*cf.* equation (4)] is based on the assumption that the absorbance change during part D of the curve shown in Fig. 4 results from reaction (4) only. The following equations are based on this assumption:

$$\ln I_1 = -k_2 t + \ln (I_1)_0 \tag{9}$$

TABLE II.—RESULTS OF THE CALCULATION OF k_{-1} AT 3·0° AND 5·0°

Temp. = 3·0°		Temp. = 5·0°	
min	k_{-1}, *min*$^{-1}$	*min*	k_{-1}, *min*$^{-1}$
7·5	0·00292	8·0	0·00494
10·0	0·00480	10·0	0·00519
12·5	0·00590	12·0	0·00478
17·5	0·00685	20·0	0·00811
20·0	0·00875	22·0	0·00816
22·5	0·01120	24·0	0·00648
27·5	0·01120	32·0	0·00755
30·0	0·01010	34·0	0·00805
32·5	0·01118	36·0	0·00686
37·5	0·01006	52·5	0·00550
40·0	0·00951	55·0	0·00552
42·5	0·00918	57·5	0·00555
47·5	0·00912	65·0	0·00559
50·0	0·00884	67·5	0·00532
52·5	0·00819	70·0	0·00524
57·5	0·00870	77·5	0·00516
60·0	0·00831	80·0	0·00539
62·5	0·00727	82·5	0·00520
67·5	0·00792	110·0	0·00500
70·0	0·00725	115·0	0·00479
72·5	0·00673	120·0	0·00493
77·5	0·00680		
80·0	0·00647	mean = $0\cdot0058_7$	
82·5	0·00615		
87·5	0·00626		
90·0	0·00651		
92·5	0·00692		
97·5	0·00637		
100·0	0·00637		
102·5	0·00638		
105·0	0·00632		
110·0	0·00601		
115·0	0·00565		
120·0	0·00573		
125·0	0·00566		
mean = $0\cdot0074_8$			

where $(I_1)_0$ = initial concentration of I_1
Because $A = kI_1$

$$\ln A = -k_2 t + \ln A_0 \tag{10}$$

Thus, as can be seen from equation (10), a plot of the *logarithm of the absorbance versus time* should be linear with a slope equal to $-k_2$. Fig. 5 shows such plots for the results obtained at 0·5, 3·0, 5·0 and 10·0° with values of k_2 given in Table III. [The plots shown in Fig. 5 can also be used to obtain a value of ε_{I_1}. By extrapolating to time zero, where $A_0 = \varepsilon_{I_1}(I_1)_0 l$, and assuming $(I_1)_0 = B_0$, the value of ε_{I_1} found was 199, in good agreement with the value of 200 found previously.]

Table III shows the energy of activation calculated from the temperature dependence of the various specific rate constants. The value of the energy of activation obtained from the specific rate constant, k_1, of the Salesin model is 16 Kcal per mole. A comparison of the two models for the system is shown below:

Model by Salesin et al.[3]

$$\mathrm{B} + \mathrm{H} \xrightarrow{\Delta E_1{}^* = 16\mathrm{Kcal/mole}} \mathrm{I_A}^* \rightarrow \mathrm{M} \tag{11}$$

Present model

$$\mathrm{B} + \mathrm{H} \xrightarrow{\Delta E_2{}^* = 3.1\ \mathrm{Kcal/mole}} \mathrm{I_B}^* \xrightarrow{\Delta E_3{}^* \cong 0}$$

$$\mathrm{I_1} \xrightarrow{\Delta E_4{}^* = 12.9\ \mathrm{Kcal/mole}} \mathrm{I_C}^* \rightarrow \mathrm{M} \tag{12}$$

where $\mathrm{I_n}^*$ = an activated complex (n = A, B, C);
$\Delta \mathrm{E_n}^*$ = energy of activation (n = 1, 2, 3, 4).

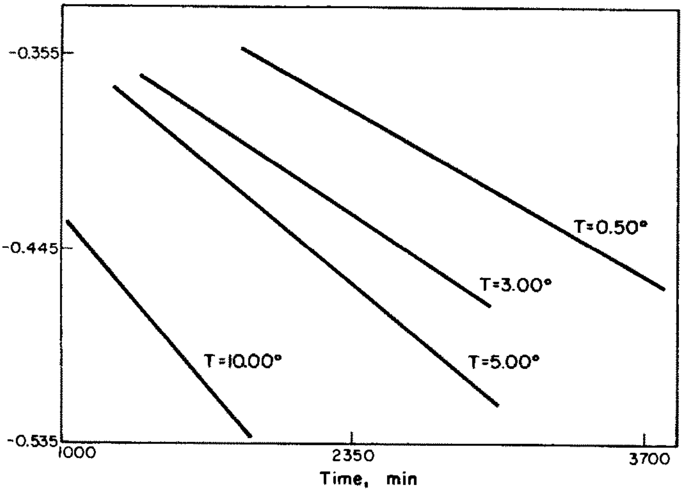
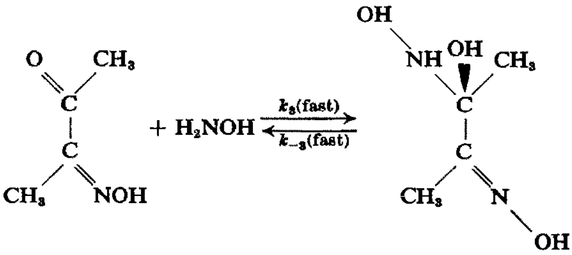


FIG. 5.—$\mathrm{Log_{10}}$ absorbance *versus* time for the biacetyl-hydroxylamine system.

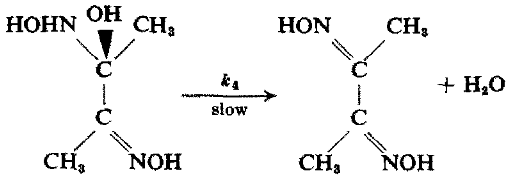
Within the limits of experimental error, $\Delta \mathrm{E_3}^*$ was found to be nearly zero. Thus, the total energy barrier in the formation of biacetyl monoxime from biacetyl and hydroxylamine is the same for both models. Furthermore, the activated complexes $\mathrm{I_A}^*$ and $\mathrm{I_C}^*$ must be identical, and they represent the structure with the highest energy in the system.

Series 4 *and* 5

The results of these series, shown in Fig. 6, can be qualitatively explained by again using the proposed carbinolamine intermediate as shown below:



(13)



(14)

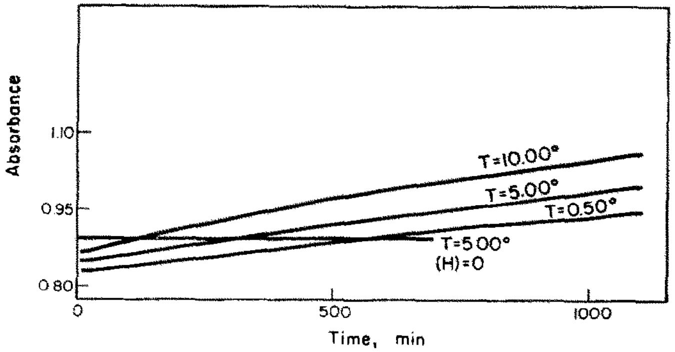


FIG. 6.—Absorbance *versus* time for the biacetyl monoxime-hydroxylamine system ([Biacetyl monoxime] = 9·254 × $10^{-5}M$ [Hydroxylamine] = 7·082 × $10^{-2}M$ λ = 2250 Å).

or in abbreviated form:

$$\mathrm{M} + \mathrm{H} \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} \mathrm{I}_2 \tag{13a}$$

$$\mathrm{I}_2 \xrightarrow[\text{slow}]{k_4} \mathrm{D} + \mathrm{H_2O} \tag{14a}$$

where I_2 and D = solution concentrations of intermediate I_2 and dimethylglyoxime, respectively;

k_3, k_{-3} and k_4 = specific rate constants for reactions 13 and 14, respectively.

The proposed reaction sequence for the biacetyl monoxime-hydroxylamine system was again tested by scanning the ultraviolet spectrum just after mixing the reactants, and an absorbance maximum, not associated with biacetyl monoxime or dimethylglyoxime, was observed. The position of the peak, initially at 2300 Å, varied with time, the shift being towards shorter wavelengths. A method suitable for the calculation of k_3 and k_{-3} was not found. Because of the very large values of the various extinction coefficients, the approximations used in the biacetyl-hydroxylamine system were not applicable to the biacetyl monoxime-hydroxylamine system. The calculation of k_3 must be done from observations made during the initial rapid drop in the absorbance. In as much as most of the initial absorbance change has taken place before the first results are observed, reliable values of k_3 could not be obtained. Without k_3, k_{-3} cannot be calculated from the results observed at a later and more accessible reaction time interval.

During the latter stages of the reaction, reaction (14) becomes predominant. Thus. the absorbance change is caused primarily by the changes in concentration of the intermediate, I_2, and dimethylglyoxime. The total absorbance of the reaction mixture at any time can be expressed as:

$$A = l[\varepsilon_M M + \varepsilon_{I_2} I_2 + \varepsilon_D D] \tag{15}$$

where ε_{I_2} and ε_D = extinction coefficients of intermediate I_2 and dimethylglyoxime, respectively.

If the concentration of biacetyl monoxime is some small fixed amount after 1000 min of reaction, equation (15) can be rewritten as

$$I_2 = \frac{A - C_1}{C_2} \tag{16}$$

where $C_1 = M_0\varepsilon_D l + M(\varepsilon_M l - \varepsilon_D l)$
$C_2 = \varepsilon_{I_2} l - \varepsilon_D l$

A plot of $log\left[\frac{A - C_1}{C_2}\right]$ *versus time* should be a straight line with a slope of $-k_4/2{\cdot}303$. Such a plot is shown in Fig. 7 with the values of k_4 given in Table III.

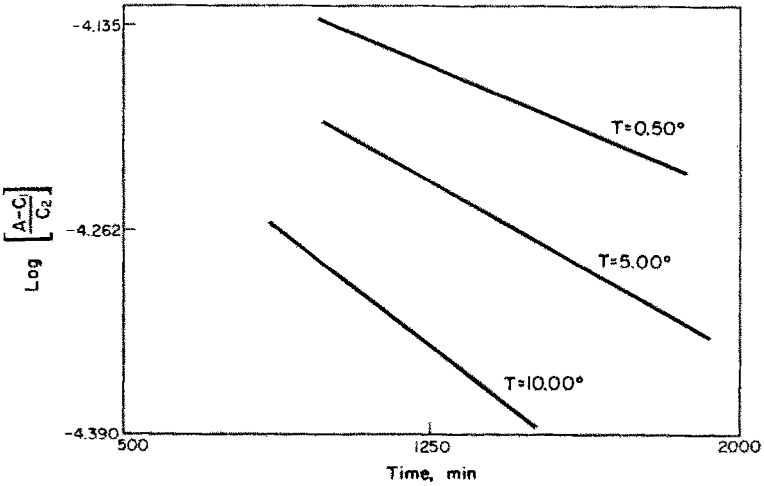


Fig. 7.—Log $\left[\frac{A - C_1}{C_2}\right]$ *versus* time for the biacetyl monoxime-hydroxylamine system.

TABLE III.—RESULTS OBTAINED DURING THE STUDY OF THE FORMATION OF DIMETHYLGLYOXIME

Rate constant, *min⁻¹*	Temperature, °*C*				E*, *Kcal/mole*
	0·5	3·0	5·0	10·0	
$k_1'(\times 10^2)$	—	5·09	5·30	—	3·1
$k_{-1}(\times 10^3)$	—	7	6	—	—
$k_2(\times 10^4)$	1·28	1·46	1·89	2·63	12·9
$k_4(\times 10^4)$	2·1	—	3·3	4·6	13

A summary of all the kinetic results obtained during the study of the formation of dimethylglyoxime from biacetyl and hydroxylamine in the absence of nickel(II) is shown in Table III.

Salesin *et al.*[3] reported that the over-all rate of the formation of biacetyl monoxime was faster than the rate of formation of dimethylglyoxime in the biacetyl-hydroxylamine system. Accordingly, the solution concentration of the biacetyl monoxime should increase to some maximum value and then decrease as the dimethylglyoxime is formed.[9] However, this was not observed in the present investigation, and the difference can be easily explained. To determine biacetyl monoxime and dimethylglyoxime, Salesin used a separational procedure in which the reaction mixture was acidified.[3] As a result, all of the I_1 present in the mixture was immediately converted to biacetyl monoxime[8] and thus reported as such. (The same reasoning also applies to the intermediate I_2 and dimethylglyoxime.)

Series 6 and 7

The results are shown in Figs. 8 and 9, respectively. The two absorbance maxima at t = 3·00° in Fig. 8 are the "nucleation bursts" (appearance of nickel dimethylglyoximate) reported by Salesin.[3] At 5·00° these maxima have overlapped so that only a break appears in the curve. In Fig. 9, a single nucleation burst is evident by the change of slope at about 170 min in the curves obtained at $\lambda = 2250$ Å; this is confirmed even more strikingly at 3600 Å, where only nickel dimethylglyoximate absorbs.

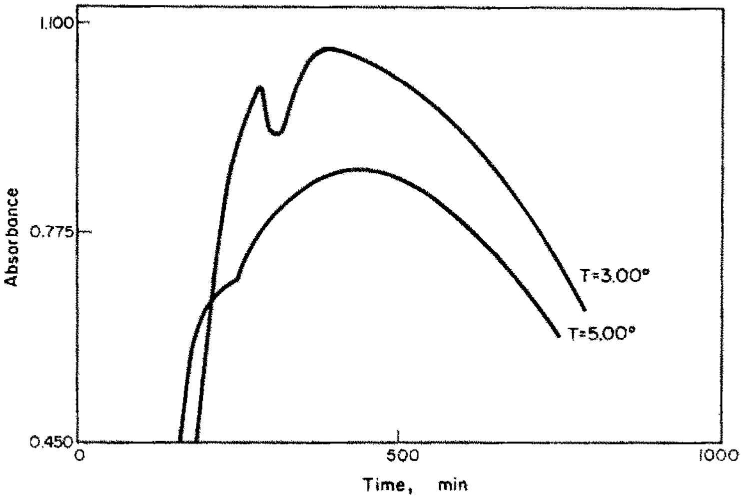


FIG. 8.—Absorbance *versus* time for the biacetyl-hydroxylamine-nickel system ([Biacetyl] = $5·537 \times 10^{-4}M$ [Hydroxylamine] = $7·193 \times 10^{-2}M$ $\lambda = 3600$ Å) [Ni(II)] = $2·77 \times 10^{-4}M$.

A comparison of the large initial absorbance of the system in Fig. 6, where nickel(II) is absent, with the comparably large initial absorbance of the system in Fig. 9, where nickel(II) is present, shows the virtual absence of the lesser absorbing nickel monoxime complex. Further, a change in the nickel concentration by a factor of one-half in the two systems of Figs. 8 and 9 had no effect on the absorption curves, and hence on the rate-controlling reaction. Thus, it was concluded from these two observations that the absorbance change of the system of Fig. 9 was the result of the following reaction sequence:

$$M + H \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} I_2 \qquad (13a)$$

$$I_2 \xrightarrow[\text{slow}]{k_4} D + H_2O \qquad (14a)$$

$$2D + Ni(II) \xrightarrow{\text{fast}} NiD_2 + 2H^+ \qquad (17)$$

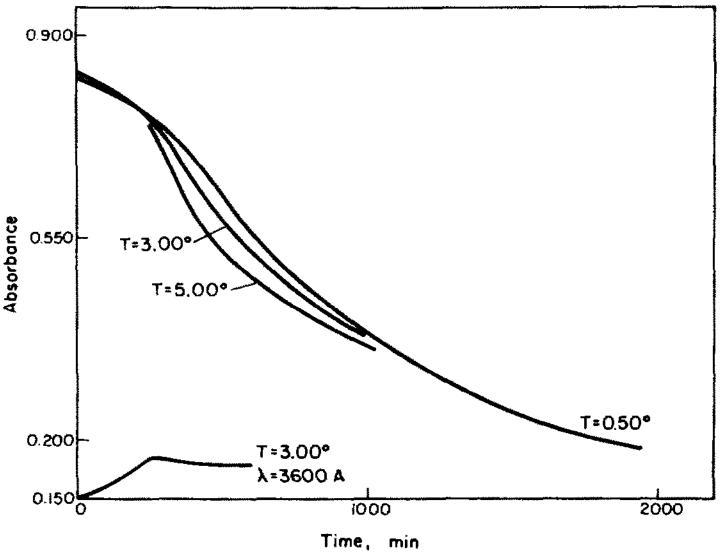


FIG. 9.—Absorbance *versus* time for the biacetyl monoxime-hydroxylamine-nickel system

([Biacetyl monoxime] = $9{\cdot}254 \times 10^{-5}M$
[Hydroxylamine] = $7{\cdot}082 \times 10^{-3}M$
[Ni(II)] = $4{\cdot}625 \times 10^{-5}M$
λ = 2250 Å).

the last equation being responsible for the over-all absorbance decrease. Values of k_4 were obtained from the slope of *log absorbance* (*2250 Å*) *versus time* from the first 170-min portion of two of the curves of Fig. 9. These compare with previous values as shown in Table IV:

TABLE IV

Temperature, °*C*	k_4, *min*$^{-1}$	
	Ni(II) absent	Ni(II) present
0·5°	$2{\cdot}1 \times 10^{-4}$	$2{\cdot}5 \times 10^{-4}$
5·0°	$3{\cdot}3 \times 10^{-4}$	$3{\cdot}3 \times 10^{-4}$

The very close agreement of the values of k_4 in the two systems shows that nickel(II) has no effect on the dehydration of the carbinolamine intermediate I_2, *i.e.*, the rate-controlling reaction.

Extension of this conclusion to the biacetyl-hydroxylamine-nickel(II) system leads in a similar way to the following reaction sequence,

$$B + H \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{fast})}{\rightleftarrows}} I_1 \tag{3a}$$

$$I_1 \xrightarrow[\text{slow}]{k_2} M + H_2O \tag{4a}$$

$$M + H \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} I_2 \tag{13a}$$

$$I_2 \xrightarrow[\text{slow}]{k_4} D + H_2O \tag{14a}$$

$$2D + Ni(II) \xrightarrow{\text{fast}} NiD_2 \downarrow + 2H^+ \qquad (17)$$

where the slowest step is the dehydration of I_1 (*cf.* Table III). If the reaction sequence is valid, then a plot of *log absorbance (3600 Å) versus time* for the first 120 min of Fig. 8 should be linear with slope equal to k_2. The values of k_2 thus obtained compare with previous values as shown in Table V:

TABLE V

Temperature, °*C*	k_2, *min*$^{-1}$	
	Ni(II) absent	Ni(II) present
3·0°	$1{\cdot}46 \times 10^{-4}$	$1{\cdot}2 \times 10^{-2}$
5·0°	$1{\cdot}89 \times 10^{-4}$	$2{\cdot}2 \times 10^{-2}$

The change in the values of k_2 by a factor of 100 shows clearly that nickel(II) must play a significant role in the previous reaction sequence, *i.e.*, numbers [(3a) to (14a) inclusive], in as much as nickel dimethylglyoximate is produced at a rate far faster than is indicated by the rate of formation of dimethylglyoxime from biacetyl and hydroxylamine only.

Because nickel(II) has already been shown to have little effect on the biacetyl monoxime-hydroxylamine part of the reaction sequence, it must then exert its influence by complexing with the intermediate I_1. From the following results from Table III and the previous values of k_2, (repeated in Table VI),

TABLE VI

Temperature	k_1', *min*$^{-1}$	k_2, *min*$^{-1}$
	Ni(II) absent	Ni(II) present
3°	$5{\cdot}09 \times 10^{-2}$	$1{\cdot}2 \times 10^{-2}$
5°	$5{\cdot}30 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$

it can be seen that the over-all rates of formation of I_1 and nickel dimethylglyoximate are comparable in the two systems, *i.e.*, biacetyl-hydroxylamine and biacetyl-hydroxylamine-nickel(II), respectively. Thus, in the latter system, the rate-limiting step must be the formation of I_1 [*cf.* equation (3a)]; I_1 is then immediately complexed by nickel(II). Furthermore, the complex must then proceed, by a series of very fast reactions, all involving nickel complexes, to the end product, nickel dimethylglyoximate. These conclusions now provide an explanation for the multiple nucleation bursts initially reported by Salesin[3] (*cf.* two absorption maxima of Fig. 8); this is in contrast to the single burst observed in the system of Fig. 9.

In the biacetyl-hydroxylamine-nickel(II) system, there is not only the complex between nickel(II) and I_1 as follows,

$$Ni^{2+} + I_1 \rightleftharpoons NiI_1^+ + H^+ \qquad (18)$$

but also likely the following complex.

$$NiI_1^+ + I_1 \rightleftharpoons Ni(I_1)_2 + H^+ \qquad (19)$$

Some of the NiI_1^+ complex may be converted, by dehydration of the intermediate and further reaction with hydroxylamine, to NiD^+. The latter complex will have to wait for additional dimethylglyoxime to be produced by the slow reaction sequence involving biacetyl and hydroxylamine in order to precipitate nickel dimethylglyoximate. The $Ni(I_1)_2$ complex is also converted by dehydration to NiD_2. In addition to this over-all path in which the two nickel carbinolamine intermediates are involved in the precipitation of nickel dimethylglyoximate by equations (18) and (19), there is another independent path. This path involves precipitation of the solid red chelate by equation (17). Thus, there are at least two independent paths giving rise to the two nucleation bursts. In contrast to this, there can be only one path, hence one nucleation burst, with the reaction sequence involving biacetyl monoxime and hydroxylamine.

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Zusammenfassung—Spektralphotometrische Ergebnisse zeigen, daß die Reaktion von Biacetyl mit Hydroxylamin über zwei Carbinolamin-Zwischenstufen verläuft. Das zweite von diesen Zwischenprodukten findet man auch bei der Reaktion von Bicetylmonoxim mit Hydroxylamin. Der geschwindigkeitsbestimmende Schritt bei der Oximierung von Biacetyl ist die langsame Dehydratation des ersten Zwischenprodukts, wie aus den verschiedenen Geschwindigkeitskonstanten für die zwei Reaktionen zwischen 0 und 10° hervorgeht. Bei Gegenwart von Nickel im Biacetyl-Hydroxylamin-System geht die Bildung von Nickel-Dimethyl-glyoximat nach zwei unabhängigen Mechanismen vor sich; dagegen ist nur ein Mechanismus für die Neiderschlagsbildung im Biacetylmonoxim-Hydroxylamin-System verantwortlich.

Résumé—Des preuves spectrophotométriques montrent que la réaction du diacétyle avec l'hydroxylamine passe par la formation de deux carbinolamines intermédiaires. On rencontre également le second de ces intermédiaires dans la réaction de la diacétyle-monoxime avec l'hydroxylamine. Le stade qui limite la vitesse d'oximation du diacétyle est la déshydratation lente de l'intermédiarie initialement formé. Ceci est mis en évidence par les diverses constantes de vitesse obtenues pour les deux réactions entre 0 et 10°. Lorsque le nickel(II) est présent dans le système diacétyle-hydroxylamine, la formation de diméthylglyoximate de nickel procède par deux mécanismes indépendants, cependant qu'un seul mécanisme est responsable de la formation du précipité dans le système diacétyle-monoxime-hydroxylamine.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH POLYAMINOCARBOXYLIC ACIDS

ETHYLENEDIAMINE-N,N′-DI-α-PROPIONIC ACID

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Summary—A new method for the spectrophotometric determination of copper with polyaminocarboxylic acids is presented. The ligand chosen is ethylenediamine-N,N′-di-α-propionic acid (EDDPA) which compares favourably, in sensitivity and selectivity, with all the other similar compounds previously proposed. The copper complex absorbs at 670 mμ with a molar extinction coefficient of 140 at any pH between 3 and 8. Beer's law is obeyed over the range 0–400 ppm of copper and the temperature and ionic strength do not adversely affect the method. Nickel interferes when present in comparable or greater amounts than copper.

INTRODUCTION

Several methods for the spectrophotometric determination of copper with polyaminocarboxylic acids have been proposed in the past few years. These methods have several advantages over the spectrophotometric procedures using diethyldithiocarbamate, dithio-oxamide or dithizone, such as greater simplicity and rapidity, few interferences, wide range of suitable pH, high stability and solubility of the complexes formed. The main inconvenience is their low sensitivity, the limit being about 10 ppm of copper, but this is not very important in routine problems of copper analysis, when this element is present in appreciable percentages.

Nitrilotriacetic acid (NITA),[1] ethylenediaminetetra-acetic acid (EDTA),[2] 1,2-diaminocyclohexanetetra-acetic acid (DCTA),[3] ethyleneglycol-bis(β-aminoethylether)-tetra-acetic acid (EGTA)[4] and 2,2′-diaminodiethylethertetra-acetic acid (EEDTA)[5] have all been suggested as spectrophotometric reagents for copper. These substances are all potentially hexadentate ligands, excepting NITA, which is tetradentate and forms tetrahedral complexes if it is the sole ligand in the co-ordination sphere.

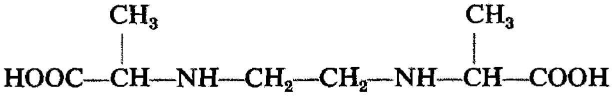
Although the intensity of the colour is not directly related to the type of structure, it is somewhat surprising that no complexan has been suggested with the property of forming square-planar complexes when completely co-ordinated, because it is known that the cupric ion has a marked tendency to such arrangements.

The obvious choice would be ethylenediamine, N,N′-diacetic acid (EDDA), (I), which is, however, rather difficult to prepare, because of the easy replacement of the hydrogen atoms bonded to nitrogen

$$HOOC{-}CH_2{-}HN{-}CH_2{-}CH_2{-}NH{-}CH_2{-}COOH$$

I

Not long ago, Irving, Shelton and Evans studied a sterically hindered complexing reagent derived from EDDA[6] and differing from it by having α-propionate instead of acetate groups (II)



$$\mathrm{HOOC{-}\overset{\overset{\Large CH_3}{|}}{C}H{-}NH{-}CH_2{-}CH_2{-}NH{-}\overset{\overset{\Large CH_3}{|}}{C}H{-}COOH}$$

II

This reagent, ethylenediamine-N,N′-di-α-propionic acid (EDDPA), gives complexes only slightly less stable than EDDA and is far easier to prepare. Indeed, the two α-methyl groups hinder the replacement of the remaining hydrogen atoms bonded to nitrogen and furthermore the compound is easily obtained in a fair state of purity.

Ethylenediamine-N,N′-di-α-propionic acid intensifies the blue colour of dilute copper solutions more strongly than similar complexing agents.

COMPARISON WITH OTHER METHODS

The sensitivity of the present method relative to procedures using other polyaminocarboxylic acids is best appreciated by examining the maximum values of the molar extinction coefficients of the respective copper complexes. We have investigated the variation of absorbance with pH for several complexans, using 100% excess of each compound relative to copper, and have calculated the required $\varepsilon_{\max}$ values without taking into account the possibility of equilibria between different complexes. The calculated extinction coefficients are summarised in Table I; the absorption curves of several of the copper complexes, at a suitable value of pH, are presented in Fig. 1.

TABLE I.—MOLAR EXTINCTION COEFFICIENTS OF COPPER COMPLEXES

Ligand	pH	$\lambda_{\max}$(mμ)	$\varepsilon_{\max}$
NITA	—	775 880	54* 60
EDTA	7	735	91
MEDTA	6	735	106
DCTA	2·5	680	118
EEDTA	1·5	720	59
EGTA	6	700	68
HCEDTA	12·5	735	133
EDDPA	6	670	140

* From ref. 9.

The following abreviations are used:

EDTA	ethylenediaminetetra-acetic acid
MEDTA	1,2-diaminopropanetetra-acetic acid (methyl-EDTA)
DCTA	1,2-diaminocyclohexanetetra-acetic acid

EGTA	ethyleneglycol-bis(β-aminoethylether)tetra-acetic acid
HCIDA	2-hydroxycyclohexyliminodiacetic acid
HCEDTA	N-hydroxycyclohexylethylenediaminetriacetic acid
EEDTA	ethyletherdiaminotetra-acetic acid
EDDPA	ethylenediamine-NN′-di-α-propionic acid
ADA	anthranyldiacetic acid
IMDA	iminodiacetic acid
UDA	uramildiacetic acid
NITA	nitrilotriacetic acid

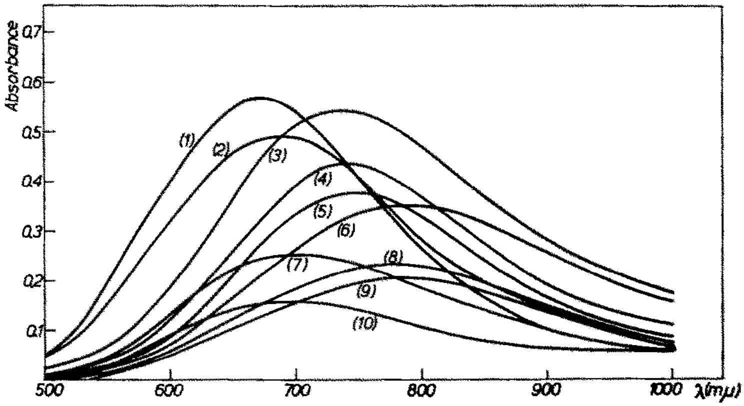


FIG. 1.—Absorption curves of the copper complexes of some polyaminocarboxylic acids (concentration of copper 0·004*M*; concentration of the ligand 0·008*M*): (1) EDDPA, (2) DCTA, (3) HCEDTA, (4) MEDTA, (5) EDTA, (6) HCIDA, (7) EGTA (8) ADA, (9) UDA, (10) IMDA.

Although the extinction coefficients found are not very accurate, because the commercial complexans were not further purified and the instrument used is not adequate for precise measurements, the values obtained confirm our hypothesis by showing that EDDPA is indeed the most sensitive of all the reagents studied. DCTA and HCEDTA also have interesting possibilities, at low and high pH values, respectively.

Bermejo-Martínez and Blas-Pérez[5] have pointed out the advantages of EEDTA for work at low pH, but the extinction coefficient of the copper complex of this ligand is small, and the method, consequently, not very sensitive. Hence, although the limit of pH when using DCTA cannot be so low and needs a rather accurate adjustment, this reagent, also proposed by the same authors, still seems to have advantages relative to EEDTA.

HCEDTA seems to be the appropriate complexan for work at high pH and it will be dealt with in a future paper. The increasing absorption with pH probably results from the ionisation of the phenolic hydrogen which alters the environment of the copper atom. The same is found for the HCIDA-copper-complex.

The absorption curves in Fig. 1 seem to fall into three groups, absorbing in limited ranges of wavelength, corresponding to a definite type of complexan.

Thus, EDDPA probably forms planar complexes and its copper complex absorbs at 670 mμ; EDTA, MEDTA and HCEDTA probably form weakly tetragonal complexes and absorb between 725 and 745 mμ; ADA, UDA and HCIDA absorb between 770 and 790 mμ and may form copper complexes more close to cubic symmetry; finally, EGTA behaves like IMDA, both absorbing at 690 mμ which is close to the value found for EDDPA; they probably also form planar complexes having one co-ordination site occupied by a water molecule. In the case of EGTA this should be ascribed to the 2:1 complex.[7] The maximum of absorption at 680 mμ found for DCTA at pH 2·5 may also correspond to the planar complex with two free carboxylic acid groups.

The behaviour of NITA resembles that of other similar tetradentate ligands, as expected, but its 1:1 copper complex has two broad bands of absorption with maxima at 775 and 800 mμ which were discussed by Jørgensen,[9] who has also commented on the copper complex of EDTA, among other ligands. This author has proposed an empirical parameter equal to the ratio between the observed wave numbers $\bar{\nu}_{Cu}/\bar{\nu}_{Ni}$, which is a measure of the relative tetragonality of the copper complex, because the nickel(II) spectra are very little affected by deviation from cubic symmetry.[8,9] This parameter can be used as a further confirmation for the configurations of the copper complexes considered above.

TABLE II.—DECREASE IN LOG K UNITS FOR METAL COMPLEXES WHEN EDTA IS REPLACED BY EDDMA

	log K EDDPA	log K EDTA	Δ log K
Mg^{2+}	2·8	8·7	5·9
Ca^{2+}	$\sim$1	10·7	9·7
Co^{2+}	10·2	16·31	6·1
Ni^{2+}	12·2	18·62	6·4
Cu^{2+}	15·2	18·8	3·6
Zn^{2+}	10·1	16·5	6·4
Cd^{2+}	8·1	16·6	8·5
La^{3+}	5·8	15·4	9·6

There is still another factor favouring ethylenediamine-N,N′-di-α-propionic acid as a reagent for the spectrophotometric determination of copper. It derives from the fact that being a tetradentate ligand, the stability of most of its complexes is much lower than that of the corresponding complexes formed by the above mentioned complexans, but the decrease for copper is far smaller than for the other metals.

Taking EDTA as an example, these conclusions are summarised in Table II.

Relative to EDTA the decrease in stability for the copper complex is about 1,000 times smaller than for other metals. This is expected to reduce considerably the interferences, because the formation of the copper complex becomes preferential in relation to most, if not all the common metals. The study of the interfering elements, described below, confirms this hypothesis.

EXPERIMENTAL

Apparatus

A Beckman model B spectrophotometer with 1-cm corex cells was used for absorbance measurements. A Radiometer TTTc 1 pH meter, with a combined electrode GK-2025 was used.

Reagents

Ethylenediamine-N,N′-di-α-*propionic acid.* This reagent was prepared by condensation of ethylenediamine with α-chloropropionic acid in an alkaline medium, following the instructions of Irving, Shelton and Evans.[6] A white product, melting with decomposition at 278–280° (*lit.* 260–265°), was obtained in 60% yield.

$0{\cdot}01M$ and $0{\cdot}1M$ solutions of the monosodium salt of the reagent were prepared by dissolving the calculated amount of the acid in a solution containing the corresponding amount of sodium hydroxide.

Copper. Electrolytic copper was dissolved in AnalaR nitric acid, the excess acid evaporated and the solution diluted to the required volume.

Other reagents. Sodium hydroxide, nitric acid, sulphuric acid, sodium and other metal salts for the study of the interferences were all of analytical grade.

The polyaminocarboxylic acids used for comparison were either commercial products or were previously synthesised in our laboratory.

Procedure

The following procedure is recommended for general application and especially for the analysis of alloys.

Dissolve 0·1000–0·5000 g of the sample (for percentages of copper between 100% and 10%) with 20 ml of dilute nitric acid (1:2). Expel nitrogen oxides, transfer to a volumetric flask and dilute to 100 ml with distilled water. Pipette 5·0 ml of the solution to a small beaker, add 2·5 ml of $0{\cdot}1M$ EDDPA (sodium salt) and adjust to pH 3–9 if necessary. Transfer the solution to a volumetric flask and dilute to 25 ml. Check the pH. Read the absorbance with a spectrophotometer at $\lambda = 670$ mμ. Calculate the percentage of copper in a calibration curve obtained from electrolytic copper using the same technique.

STUDY OF THE ANALYTICAL PROCEDURE

Influence of external variables in formation of copper-EDDPA complex

Colour. The reaction of copper with ethylenediamine-N,N′-di-α-propionate is practically instantaneous. The complex has a deep blue colour ($\lambda_{\max} = 670$ mμ) (Fig. 1) which is stable for several days.

pH. The influence of pH is shown in Fig. 2.

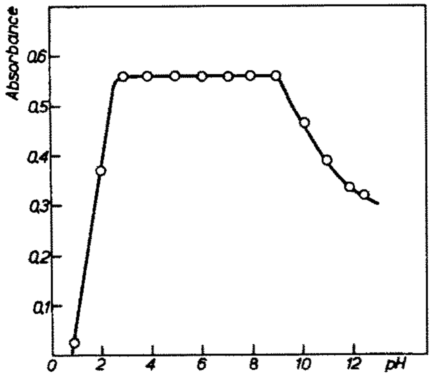


FIG. 2.—Variation of absorbance with pH for the copper-EDDPA complex (concentration of copper $0{\cdot}004M$; concentration of ligand $0{\cdot}008M$).

Below pH 3 the formation of the complex is incomplete and above pH 9 its hydrolysis causes the absorbance to decrease. Between pH 3 and 9 the concentration of the absorbing species is constant and, for analytical purposes, any value of pH between these limits is suitable.

Temperature. A temperature between 10° and 50° has no appreciable effect on the extinction coefficient of the complex.

Ionic strength. The effect of the ionic strength was studied using a 30% solution of potassium nitrate as the upper limit of concentration. The differences in absorbance do not exceed 0·005 unit for the extremes and the solubility of the complex is not affected.

Reagent concentration. The molar ratio method[10] was used to determine the stoichiometry of the complex (Fig. 3). This curve shows that the complex is formed in equimolar proportions of metal and ligand, as expected. A 100% excess of the reagent ensures that the absorbance is constant and larger amounts of ligand can be present without interfering.

Compliance with Beer's law

Beer's law is obeyed up to concentrations of the order of 400 ppm of copper. The calibration curve passes through the origin and the sensitivity is such that 100 ppm of copper gives rise to an absorbance of 0·22. The lower limit of applicability of the method is about 5 ppm of copper, which is a considerable improvement over similar methods.

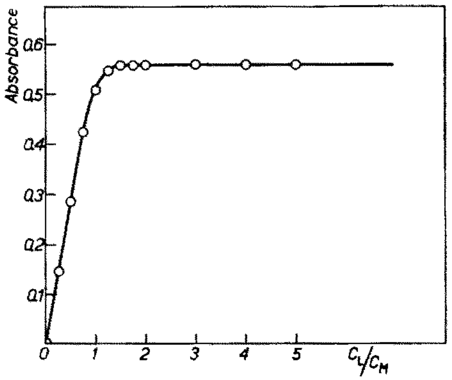


FIG. 3.—Composition of the copper-EDDPA complex (concentration of copper 0·004*M*; pH 6).

Interferences

The effect of foreign cations and anions was studied by adding them to 6 mg of copper and developing the colour with the reagent.

The results obtained showed that sulphates and nitrates do not interfere. Halides may be present up to concentrations 25 times that of copper (chloride and bromide gave errors of +5% when 1 g of NaCl or NaBr was added). Acetate and phosphate can be tolerated in amounts up to about 10 times that of copper; errors of about −4% were obtained when 20 times this amount was used.

Alkali and alkaline-earth ions, manganese, iron, aluminium, zinc, lead, uranium, cadmium, bismuth, chromate, vanadate and molybdate can be considered as non-interfering. Cerium and cobalt can be tolerated in concentrations of the order of, respectively, 10 times and 5 times that of copper. Nickel starts to interfere when present in amounts of the same order of magnitude as that of copper. This metal is practically the only interference which needs to be considered in routine analysis and must be separated when its concentration exceeds that of copper.

RESULTS

We have applied this method to several copper alloys of different compositions, previously analysed by electrolytic deposition in official laboratories. The results obtained are summarised in Table III.

The agreement can be considered as excellent, and deviations may be expected to be less than −0·3% depending on the percentage of copper.

TABLE III.—RESULTS OF ANALYSES OF COPPER ALLOYS[a]

Sample ref.	Copper found, %		Error, %
	Electrolysis	Present method	
L.A. 387	92·14	92·04	−0·11
L.A. 543	67·67	67·50	−0·25
L.A. 544	13·17	13·13	−0·30
L.A. 549	67·68	67·50	−0·25
L.A. 584	99·98	99·90	−0·08
B.C.S. *Bronze* A	85·50	85·45	−0·06

[a] L. A. Laboratório de Análises do Instituto Superior Técnico, Lisbon.
B.C.S. British Chemical Standard.

This makes the present method a very attractive alternative to electrolytic depositions, which are time consuming and have their own difficulties. The spectrophotometric determination of copper using ethylenediamine-N,N′-di-α-propionic acid should be considered when a rapid, easy and considerably accurate method is required for routine determination of this element.

Zusammenfassung—Eine neue Methode zur kolorimetrischen Kupferbestimmung mit Komplexonen wird angegeban. Als Ligand wurde Athylendiamin-N,N′-di-α-propionsäure (EDDPA) ausgewählt; dieser bietet Vorteile vor allen bisher vorgeschlagenen Komplexonen hinsichtlich Empfindlichkeit und Selektivität. Der Kupferkomplex EDDPA absorbiert bei $\lambda_{max} = 670$ mμ mit $\varepsilon_{max} = 140$ bei allen pH-Werten zwischen 3 und 8. Das Beersche Gesetz gilt bei 0–400 μg Cu^{2+}/ml, und Temperatur oder Ionenstärke tun der Methode keinen Abtrag. Nickel stört, wenn es in der gleichen oder größeren Menge als Kupfer vorhanden ist.

Résumé—On décrit une nouvelle méthode spectrophotométrique de dosage du cuivre avec l'acide ethylènediamine-NN′-di-α-propionique (EDDPA). Le complexe de cuivre présente un maximum d'absorption à $\lambda = 670$ mμ et un coefficient d'extinction molaire $\varepsilon = 140$ dans une zone de pH entre 3 et 8. La loi de Beer est vérifiée pour les concentrations de 0–400 μg Cu^{2+}/ml, la méthode étant plus sensible que les autres méthodes utilisant des complexones proposées jusqu'à présent. La temperature et la force ionique ne gênent pas. Seule l'onterférence du nickel est importante quand ce cation est présent dans des quantités supérieures à celle du cuivre.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XIX*

DETERMINATION OF ZINC AND CADMIUM: β-MERCAPTOPROPIONIC ACID AS A MASKING REAGENT FOR CADMIUM

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Summary—A new method for the successive determination of zinc and cadmium (in the presence of copper) is described. It is based on the masking of cadmium (copper) with β-mercaptopropionic acid (MPA) and followed by direct titration of zinc with triethylenetetraminehexa-acetic acid (TTHA). After the addition of DCTA cadmium is determined indirectly by back-titration with zinc nitrate solution. All titrations are carried out with Xylenol Orange as indicator in a slightly acid medium, where alkaline earth metals are without effect on the results.

RECENTLY Yamaguchi and Ueno[1] published some observations on the masking properties of β-mercaptopropionic acid (MPA). In an alkaline medium MPA satisfactorily masks iron, bismuth, cobalt, copper and mercury as colourless or slightly coloured complexes. This masking effect has been used in the complexometric determination of manganese, nickel, calcium, and magnesium in the presence of the above-mentioned metals. MPA has also been used by Hara[2] for masking lead in the EDTA titration of zinc with dithizone as indicator. In an acid medium, however, other complexes are not stable enough to prevent reaction with EDTA.[1] We have confirmed this statement and we have found some interesting reactions of zinc and cadmium, which can be summarised as follows:

(*a*) Cadmium, at pH 5 (urotropine), is masked with MPA against Xylenol Orange. At higher concentrations of cadmium, a white precipitate appears. Zinc does not appear to react with MPA; the zinc colouration with Xylenol Orange still remains even in the presence of excessive MPA.

(*b*) The titration of zinc with EDTA after previous masking of cadmium always gives high results, because the cadmium-MPA complex is not stable enough to mask the cadmium completely. The end-point is, therefore, indistinct.

(*c*) The masking is effective if triethylenetetraminehexa-acetic acid (TTHA)[3] is used as a titrant. Good results for zinc are obtained if the zinc:cadmium ratio does not exceed 1:40.

(*d*) The cadmium-MPA complex (even if it is present as a precipitate) reacts quantitatively with an excess of EDTA. If the excess EDTA is back-titrated with zinc solution, cadmium is displaced to its MPA complex, but the end-point is sluggish and indistinct. ($\log K_{CdY} = 16{\cdot}46$ and $\log K_{ZnY} = 16{\cdot}50$).

(*e*) DCTA also reacts quantitatively with the cadmium-MPA complex, but the

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* Part XVIII: *Talanta*, 1965, **12**, 385.

cadmium is not displaced by back-titration with zinc (log $K_{CdY} = 19{\cdot}23$, and log $K_{ZnY} = 18{\cdot}67$). The end-point of the titration can be located easily. For these reasons DCTA has been used for the determination of cadmium.

(*f*) The colourless copper(I)-MPA complex does not react with either EDTA or DCTA under the same conditions. Therefore, MPA has also been used for the masking of copper in the determination of zinc and cadmium.

TABLE I.—DETERMINATION OF CADMIUM AND ZINC IN THE PRESENCE OF COPPER

Taken, *ml of 0·05M*			MPA, *drops*	0·05*M* TTHA, *ml*	0·05*M* DCTA, *ml*	0·05*M* Zn, *ml*	Found, *ml of 0·05M*	
Cd	Zn	Cu					Cd	Zn
0·50	10·00	—	25	5·00	1·96	1·58	0·38	10·00
3·01	3·00	—	25	1·48	4·90	1·93	2·97	2·96
5·01	0·50	—	30	0·22	9·81	4·85	4·96	0·44
10·03	0·50	—	30	0·24	11·76	1·87	9·89	0·48
0·50	20·00	—	30	9·92	1·96	1·50	0·46	19·84
0·50	20·00	—	15[a]	10·08	1·96	1·70	0·26	20·16
5·01	10·00	10	25	4·99	9·81	4·85	4·96	9·98
0·50	10·00	10	25	5·01	2·94	2·52	0·42	10·02
5·01	0·50	10	25	0·23	9·81	4·83	4·98	0·46

[a] because of high concentration of zinc the used amount of MPA was not sufficient.

EXPERIMENTAL

Reagents

Triethylenetetraminehexa-acetic acid. 0·05*M* solution of TTHA was prepared by dissolving 24·723 g of the free acid (J. R. Geigy, Basel, Switzerland) in 100–120 ml of 1*M* sodium hydroxide with slight warming and diluting to 1 litre. The factor was checked by complexometric titration with standard 0·05*M* zinc solution with Xylenol Orange as indicator.

β-Mercaptopropionic acid. A commercially available sample (Dojindo, Pharmaceutical Laboratories Kumamoto, Japan) was used without purification and dilution.

Other reagents include 0·05*M* DCTA, and the nitrates of copper, zinc and cadmium, concentrated nitric acid, 1*M* nitric acid, solid urotropine and a 0·2% solution of Xylenol Orange.

Procedures

Successive determination of zinc and cadmium. To the acid solution, containing not more than 40 mg of cadmium and 60 mg of zinc, add 10–40 drops of concentrated MPA, adjust the pH to 5–5·5 with solid urotropine, add Xylenol Orange and titrate slowly with 0·05*M* TTHA to a red-yellow colour. Because TTHA forms a 2:1 complex with zinc,[3] 1 ml of 0·05*M* TTHA corresponds to 6·537 mg of zinc.

To the same solution add an excess of 0·05*M* DCTA and titrate with 0·05*M* zinc nitrate to the red colour of the indicator. One ml of 0·05*M* DCTA corresponds to 5·6205 mg of cadmium.

*Determination of zinc and cadmium in the presence of copper.** To the acid solution, containing up to 40 mg of copper, in addition to the cadmium and zinc, add dropwise MPA to discolouration (a slight turbidity always appears if cadmium is present), and some drops of MPA in excess (1·5 ml of concentrated MPA is the maximum) and determine zinc and cadmium as described above. Some results are given in Table I.

Although thiourea is well known as a very active and selective masking agent for copper, it cannot be used. The addition of MPA to a solution containing the copper-thiourea complex and zinc and cadmium causes a white precipitate which reacts slowly with TTHA and so the results are not good.

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* After we had finished this study, Makada, Yamaguchi and Ueno[4] published a note on dimercaptosuccinic acid, which can also be used as a masking agent for cadmium (copper) in the titration of zinc with EDTA, but only for a ratio of zinc:cadmium of less than 1:1.

DISCUSSION

Although the described method is very simple and gives good results under proper conditions, the reaction mechanism during the second titration is rather complicated. At the first end-point (determination of zinc) $Zn_2(TTHA)$ and Cd(MPA) complexes exist. After the addition of DCTA cadmium is complexed and $Zn_2(TTHA)$ can react partly with DCTA:

$$Zn_2(TTHA) + 2DCTA \rightarrow 2Zn(DCTA) + TTHA \qquad (1)$$

It is impossible to calculate the extent of this reaction by back-titration with zinc, because the consumption of zinc is always the same:

$$2DCTA + 2Zn \rightarrow 2Zn(DCTA) \qquad (2)$$

$$TTHA + 2Zn \rightarrow Zn_2(TTHA) \qquad (3)$$

Reaction (1) can, however, be easily followed by back-titration with lanthanum, which forms only 1:1 complexes with both titrants. Two examples illustrate the solution of this problem.

(*a*) 10 ml of $0{\cdot}05M$ zinc solution were determined by titration with 5·11 ml of $0{\cdot}05M$ TTHA. After the addition of 10 ml of $0{\cdot}05M$ DCTA the solution was titrated again with $0{\cdot}05M$ lanthanum solution; the consumption was 8·43 ml (instead of 10 ml).

(*b*) The first experiment was repeated and after the addition of DCTA the solution was titrated in the same way after standing for 1 hr. The consumption of $0{\cdot}05M$ lanthanum solution was only 5·7 ml.

Because reaction (1) is incomplete and x ml of DCTA replace $\frac{x}{2}$ ml of TTHA, the total consumption of lanthanum (A) is given by the following equation:

$$A = 10 - x + \frac{x}{2}.$$

When $A = 8{\cdot}43, x = 3{\cdot}14$ and when $A = 5{\cdot}7, x = 8{\cdot}6$; then the free DCTA $= 10 - x$ ml and liberated TTHA $= \frac{x}{2}$ ml.

In the first experiment the solution contains 6·86 ml of DCTA and 1·57 ml of TTHA; in the second one 1·4 ml of DCTA and 4·3 ml of TTHA. These experiments show that reaction (1) proceeds slowly and is not quantitative even after 1 hr.

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Zusammenfassung—Eine neue Methode zur Bestimmung von Zink und Cadmium nacheinander (auch in Gegenwart von Kupfer) wurde beschrieben. Sie beruht auf der Maskierung von Cadmium (Kupfer) mit β-Mercaptopropionsäure (MPA) und nachfolgende direkte Titration von Zink mit TTHA. Nach Zugabe von DCTA wird Cadmium indirekt durch Rücktitration mit Zinknitrat bestimmt. Alle Titrationen werden mit Xylenolorange als Indikator in schwach saurem Medium ausgeführt, wo Erdalkalien ohne Einfluß auf die Ergebnisse bleiben.

Résumé—On décrit une nouvelle méthode permettant les dosages successifs du zinc et du cadmium (également en présence de cuivre). Elle est basée sur la dissimulation du cadmium (cuivre) au moyen d'acide β mercaptopropionique (MPA), suivie du dosage direct du zinc au TTHA. Après addition de DCTA, le cadmium est dosé indirectement par titrage en retour au moyen d'une solution de nitrate

de zinc. Tous les dosages sont menés en présence de Xylénol Orangé comme indicateur, en milieu légèrement acide, où les alcalino-terreux sont sans influence sur les résultats.

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BEHAVIOUR OF SILVER(II) IN PHOSPHORIC ACID MEDIA AND A GENERAL MECHANISM FOR SOLVENT OXIDATION

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Summary—A spectrophotometric investigation of silver(II) in phosphoric acid solution has revealed the presence of two predominant silver(II) phosphate complexes, which undergo reduction by water according to a rate law second order in silver(II), inverse first order in silver(I) and complex in solvent anion and hydrogen ion concentrations. A comparison of trends in molar absorptivities and pseudo-first order rate constants indicates that the reduction step is preceded by rapid equilibria involving silver(II) complexes. A single oxidation-reduction mechanism seems to be common to the three acidic media studied to date.

BECAUSE silver(II) is a strong oxidising agent in aqueous solution and promises to be useful as a selective oxidant in several stoichiometric reactions of analytical interest, we have previously reported on the nature and stability of this reagent in acidic sulphate[1] and perchlorate[2] media. In our earlier papers we emphasised the importance of silver(II)-solvent ligand complexes and the role of kinetic factors in determining the lifetime of silver(II) with regard to its reduction by water.

In the meantime, Lloyd and Pickering have reported[3] their observations on the use of silver(II) in aqueous solution for the analytical oxidation of manganese(II) and chromium(III). These authors also recognised that the silver(II)-water reaction was responsible for the observed deviations from stoichiometry of the desired oxidation-reduction reaction, and pointed out the need for additional kinetic and mechanistic data in these systems.

The present paper describes our findings regarding the behaviour of silver(II) in phosphoric acid solutions, and thus completes the series of studies employing media of mono-, di-, and tri-basic ligands. On the basis of the equilibrium and kinetic evidence obtained, an attempt is made to arrive at a general reaction scheme for the reduction of silver(II) by water in such solvents and some conclusions are drawn about the use of silver(II) as an effective oxidant for analytical purposes.

EXPERIMENTAL

The reagents, apparatus and procedures used were as described previously.[1]

RESULTS AND DISCUSSION

Previous studies[2,4] have amply demonstrated that the rate of reduction of silver(II) by water is second order in silver(II) and inverse first order in silver(I). This point was confirmed in the present study for this reaction in phosphoric acid media; for purposes of comparison, however, all rate constants are reported as pseudo-first order rate constants and were obtained from rates measured during the early portion of the reaction where the inhibiting effect of silver(I) is minimal.

Spectra of silver(II) as a function of phosphoric acid concentration

Ultraviolet and visible spectra recorded from solutions $4{\cdot}04 \times 10^{-2}$ and $9{\cdot}70 \times 10^{-3}M$ in silver(II) suggest, on the basis of the large rise in absorbance in the ultraviolet region of the spectrum with increasing concentration of phosphoric acid, that at least two phosphate complexes of silver(II) are present in important concentrations in the range of 4 to 44·4*N* phosphoric acid. These predominant species have their absorption maxima at approximately 498 (visible complex) and 300 mμ (ultraviolet complex), respectively. Contary to our findings in sulphuric acid solutions,[1] no reproducible isosbestic point could be distinguished. Small shifts in the location of the maxima occur in changing acid concentrations and can probably be attributed to variable decomposition rates. The spectrophotometric data are summarised in Table I.

TABLE I.—SPECTROPHOTOMETRIC DATA FOR SILVER(II) PHOSPHATE COMPLEXES AS A FUNCTION OF PHOSPHORIC ACID CONCENTRATION

H_3PO_4, *N*	Visible complex maximum, mμ	Absorbance	Ultraviolet complex maximum, mμ	Absorbance
44·4	500	0·040	306	0·773
40	498	0·061	301	0·883
38	498	0·067	300	1·063
35	495	0·067	300	1·178
30	495	0·065	300	1·084
25	496	0·031	300	0·331
14	500	0·024	296	0·173
4	500	0·037	280	0·058

Because of the simultaneous disappearance of silver(II) by a reduction process whose rate depends in a complex fashion on both silver and acid concentrations, the data in Table I, while reasonably reproducible, do not give direct information regarding the complexes involved. For this reason, log absorbance *vs.* time curves for each case were constructed and extrapolated to zero time to give the initial molar absorptivities listed in Table II.

TABLE II.—MOLAR ABSORPTIVITY OF SILVER(II) AS A FUNCTION OF SOLUTION COMPOSITION

H_3PO_4 medium, *N*	Wavelength, mμ	Molar absorptivity
40	500	25·1 ± 3
35	496	21·2 ± 3
30	496	24·6 ± 3
20	496	18·4 ± 3

Similar experiments carried out under conditions of varying acidity at constant phosphate concentration and varying phosphate concentrations at constant acidity, respectively, yielded the apparent molar absorptivities of Table III.

While there is considerable uncertainty in the actual numerical values given, it can be seen that the calculated molar absorptivities vary roughly in a manner proportional to the square of the phosphate concentration and the inverse square of the hydrogen ion concentration. Analogous experiments carried out for the ultraviolet complex

TABLE III.—MOLAR ABSORPTIVITIES AS FUNCTION OF ACIDITY AND PHOSPHATE CONCENTRATION

Formal H^+ conc.	$\frac{1}{[H^+]^2} \times 10^3$	Formal PO_4^{3-} conc.	$[PO_4^{3-}]^2$	Wavelength, *mμ*	Molar absorptivity
21·0	22	22·0	—	496	18 ± 3
20·0	25	22·0	—	496	31 ± 3
19·5	26	22·0	—	496	36 ± 3
19·0	28	22·0	—	496	41 ± 3
20·0	—	23·0	530	496	34 ± 3
20·0	—	22·5	505	496	32 ± 3
20·0	—	22·0	485	496	31 ± 3

(at 300 mμ) are less clear-cut, because of the poor reproducibility and optical interference of silver(I) species, but seem to indicate a decrease in the apparent molar absorptivity with increasing phosphate concentration.

Reduction kinetics of silver(II) phosphate complexes

The decomposition of silver(II) phosphate complexes obtained by dissolution of $4{\cdot}04 \times 10^{-2}$ and $8{\cdot}07 \times 10^{-2}M$ silver oxide (AgO) in 40, 35, 30 and 20*N* phosphoric acid was studied at 496 and 300 mμ. The resulting pseudo-first order rate constants (for experiments carried out in triplicate at 25·0 ± 0·15°) are reported in Table IV as a function of phosphoric acid concentration.

TABLE IV.—RATE CONSTANTS FOR SILVER(II) REDUCTION IN PHOSPHORIC ACID

H_3PO_4, *N*	Wavelength, *mμ*	k, *min*$^{-1}$	Wavelength, *mμ*	k, *min*$^{-1}$
40	496	0·097	300	0·092
	496	0·101	300	0·098
	496	0·099	300	0·091
35	496	0·110	300	0·111
	496	0·108	300	0·115
30	496	0·120	300	0·129
	496	0·119	300	0·132
	496	0·120	300	0·125
20	496	0·161	300	0·185
	496	0·188	300	0·185

An important observation immediately becomes apparent: while the specific rate constants show a small increase with decreasing phosphoric acid concentration, the average rate constants obtained for the decomposition of the "visible" and "ultraviolet" complexes are equal at any given phosphoric acid concentration. In fact, the ratio of rate constants obtained in 16 separate experiments was 0·996 ± 0·018.

In view of this rather remarkable finding, our experiments were extended to the entire accessible range of phosphoric acid concentrations (4 to 44·4*N*). Again, the absolute numerical values of the rate constants were constant within about ±15% (relative), and the ratio of the "visible" to the "ultraviolet" rate constant averages 1·036 ± 0·026 for 35 experiments. From experiments carried out over the temperature range 10–40°, an Arrhenius activation energy of approximately 11·5 kcal/mole was calculated.

Finally, the individual effects of hydrogen ion and phosphate concentrations on the rate constant were evaluated in a manner similar to that used above for the measurement of the molar absorptivities. The results of this study are summarised in Table V.

While it was not possible to hold the ionic strength constant in all experiments, the results of Table V clearly show a second order dependence of the rate constant on hydrogen ion concentration and an inverse second order dependence on phosphate concentration. It is particularly noteworthy that this variation is exactly opposite to that noted for the dependence of the molar absorptivity of silver(II) upon these same variables.

Table V.—Variation in pseudo-first order rate constant with hydrogen ion and phosphate concentrations (496 *mμ*)

Formal H^+ conc.	Formal PO_4^{3-} conc.	k, *min*$^{-1}$
19·0	22·0	0·103
21·0	22·0	0·128
22·0	22·0	0·138
20·0	21·0	0·157
20·0	22·0	0·145
20·0	22·5	0·136
20·0	23·0	0·127

General mechanism for silver(II) reduction in mineral acid media

Four rather striking similarities stand out in the observed kinetics of silver(II) decomposition in all three (perchloric, sulphuric and phosphoric) acid media:

(1) The rate law shows second order dependence on silver(II) and inverse first order dependence on silver(I) concentration.

(2) Arrhenius activation energies are identical (about 11 kcal/mole) in the three media within experimental accuracy.

(3) The rate constants for the decomposition of individual silver(II) complexes in each medium are in a constant 1 : 1 ratio over very wide ranges of solution composition.

(4) Measured rate constants taken under similar conditions of temperature and ionic strength are comparable from one medium to another.

These four observations are consistent with the view that a critical reaction step prevails, which is independent of the nature and charge of the solvent ligand and has general validity for the decomposition of silver(II) in strong acid media. This step is believed to be the disproportionation of silver(II), *i.e.*,

$$2Ag(II) \rightleftharpoons Ag(III) + Ag(I) \qquad (1)$$

followed by the reaction of silver(III) with the solvent to yield oxygen and silver(I) as final products.

Nevertheless, the solvent anion has a very definite effect on the over-all sequence of processes in each medium. Most probably, these anions serve as ligands to form a series of silver(II) complexes which are in rapid equilibrium to furnish reactive silver(II) for step (1). That these equilibria must be rapidly established is shown by the absence of rate constant differences when the kinetics of the oxidation-reduction reaction are followed by monitoring the concentration of the individual complexes. It seems likely that considerable analytical advantage is to be gained by proper choice of ligands both for the purpose of stabilising silver(II) in solution and for improving detection limits [*e.g.*, the molar absorptivity of silver(II) is about 1000 times greater in sulphuric acid than in perchloric or phosphoric acid media].

Acknowledgement—This study was supported in part by the Laboratory for Research on the Structure of Matter, University of Pennsylvania, U.S.A.

Zusammenfassung—Eine spektralphotometrische Untersuchung von Silber(II) in phosphorsaurer Lösung ergab die vorherrschende Gegenwart zweier Silber(II)-phosphatkomplexe, die durch Wasser nach einem Geschwindigkeitsgesetz zweiter Ordnung bezüglich Silber(II) und reziproker erster Ordnung bezüglich Silber(I) reduziert werden; die Anionen- und Wasserstoffionenkonzentration tritt in komplizierter Form auf. Ein Vergleich der Änderungen der molaren Extinktionskoeffizienten und der Geschwindigkeitskonstanten pseudo-erster Ordnung zeigt, daß dem Reduktionsschritt rasche Gleichgewichtsreaktionen der Silber(II)-Komplexe vorgelagert sind. In den bisher untersuchten sauren Medien scheint ein und derselbe Oxydations-Reduktionsmechanismus abzulaufen.

Résumé—Une étude spectrophotométrique de l'argent(II) en solution dans l'acide phosphorique a révélé la présence essentielle de deux complexes de phosphate d'argent(II), qui subissent la réduction par l'eau selon une loi de vitesse de second ordre par rapport à l'argent(II), inversement d'ordre un par rapport à l'argent(I), et complexe par rapport aux concentrations du solvant en anion et ion hydrogène. Une comparaison des tendances dans les absorptions molaires et les constantes de vitesse d'ordre pseudo-un indique que le stade de réduction est précédé par des équilibres rapides mettant en jeu des complexes de l'argent(II). Un seul mécanisme d'oxydo-réduction semble commun aux trois milieux acides étudiés jusqu'à présent.

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POTENTIOMETRIC DETERMINATION OF *N*-SUBSTITUTED DITHIOCARBAMATES

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Summary—A simple and general method for the determination of *N*-substituted dithiocarbamates is described. The sample, dissolved in water, is decomposed with a known amount of acid and the solution is back-titrated with standard base. The number of equivalents of dithiocarbamate (as CS_2^- groups) is easily found from the titration curves.

In the course of our studies on properties and analytical application of different amino-*N*-carbodithioates[1–5] (*N*-substituted dithiocarbamates, $R_2N\text{-}CS_2^-$) we have stated the lack of a simple and general method of assaying amino-*N*-carbodithioates. Several methods of determination of amino-N-carbodithioates[6] have been recommended. A commonly used procedure is based on acid digestion of the sample, followed by colorimetric,[7] iodometric[8,9] or other titrimetric[10] determination of the carbon disulphide formed. This seems to be a general method, but it is neither simple nor rapid. A modification of these methods was described by Shankaranarayana and Patel,[11] who add a known amount of standard acid to the carefully neutralised sample and, after decomposition of diethylamine-*N*-carbodithioate, back-titrate the excess of acid with standard sodium hydroxide. Direct iodometric titration of amino-*N*-carbodithioate[12] may be promising, but for some derivatives the end-point is not distinct. Physico-chemical methods have been also used for determination of amino-*N*-carbodithioates, *e.g.*, polarography,[13–15] ultraviolet[16] and infrared[17] spectrophotometry. Their chief disadvantage is connected with the need of standardisation with samples of known composition. Papers employing the formation of coloured chelates of amino-*N*-carbodithioates are of little value until their properties have been thoroughly investigated.

In this study we present a potentiometric procedure in which the sample is hydrolysed with acid. The excess acid and the protonated base, formed by the hydrolysis, is titrated with sodium hydroxide and the titration curve used to interpret the results.

EXPERIMENTAL

Apparatus

Direct reading pH-meter. Radiometer pHM 22, equipped with glass and calomel electrodes.

Reagents

Perchloric acid. $0{\cdot}1M$ Standard solution.

Potassium hydroxide. $0{\cdot}1M$ Standard solution, free from carbonate.

Amino-N-carbodithioates. Sodium diethylamino-*N*-carbodithioate, sodium morpholine-*N*-carbodithioate, sodium pyrrolidine-*N*-carbodithioate, sodium piperazine-bis-*N,N′*-carbodithioate and sodium piperidine-*N*-carbodithioate were prepared according to the procedure given by Gleu and Schwab.[18]

Ammonium diethanolamino-*N*-carbodithioate and ammonium bis-(carboxymethyl)-amino-*N*-carbodithioate were prepared according to a procedure similar to that of Hass and Schwarz.[10]

Procedure. Titrate the aqueous solution (20 ml) of the amino-*N*-carbodithioate, containing not less than 0·25 mequiv (corresponding to the mmole of carbon disulphide) with standard 0·1*M*, perchloric acid until the pH is reduced to 1·5–2·0 and record the titration curve. Heat the solution and evaporate to one third of the volume. Cool and slightly dilute the solution, then titrate with standard 0·1*M* alkali solution up to about pH 11. The content of the amino-*N*-carbodithioate is calculated from the plot of the titration curves, the amount of the amino-*N*-carbodithioate corresponds to the amount of hydrogen ions used for acid decomposition of the sample.

DISCUSSION AND RESULTS

Titration curves

The decomposition of all amino-*N*-carbodithioates in an acid medium proceeds according to the general equation:

$$R_2N—CS_2^- + 2H^+ \rightleftharpoons R_2NH_2^+ + CS_2.$$

This reaction is relatively rapid, but the reverse reaction also proceeds easily. Significant differences in the rate of reaction and the optimum are found for different aminoderivatives. In general, without an excess of acid this reaction is not rapid enough for direct titration, although in some cases the end-point break may be noted.

When the acid-decomposed solution of amino-*N*-carbodithioate is titrated with standard alkali, the neutralisation proceeds stepwise. At first the excess of strong acid is titrated, a further step is concerned with neutralisation of the protonised amine, the last pH change corresponds to addition of excess of base. When amino-*N*-carbodithioate salts of weak bases are titrated an additional neutralization takes place.

The position of the titration curves on the pH-axis depends on the stability of the N—C bond towards acids and on the dissociation constants of the amines formed (Table I). The former factor influences the position of the acid titration curve (Figs. 1 and 2), the latter the position of the base titration curve. The shape of the curves and the magnitude of the pH break at the respective equivalence points determine the possibility of their use as the basis for quantitative analysis. In the case of pyrrolidine derivative the situation is especially favourable. Pyrrolidine-*N*-carbodithioate is decomposed only in hot acidic solutions and pyrrolidine is a rather strong base. Therefore, both pH breaks extend to at least four pH units, making possible titration even with visual indicators. Diethylamine and piperidine derivatives react similarly; the former has been determined with phenolphthalein as an indicator.[11] In the case of the morpholine derivative, visual titration is possible but is not recommended. The piperazine derivative causes an extra break in the base-titration curve, a result of two

TABLE I.—DISSOCIATION CONSTANTS OF AMINES FORMED IN AMINO-*N*-CARBODITHIOATE DECOMPOSITION

Amine	pK_1	pK_2
Diethylamine	11·0	
Pyrrolidine	11·2	
Morpholine	8·7	
Piperidine	11·0	
Piperazine	9·8	5·8
Diethanolamine	9·0	
Iminodiacetic acid	9·5	2·7
Ammonia	9·2	

nitrogen atoms of different basicity. A similar badly developed break may be seen in the curve of the iminodiacetic acid derivative at low pH values. For the ammonium salts the initial potential break is small, because the pH value of the initial solution is relatively low (<9). In these cases the base-titration curve may include titration of the ammonium ion.

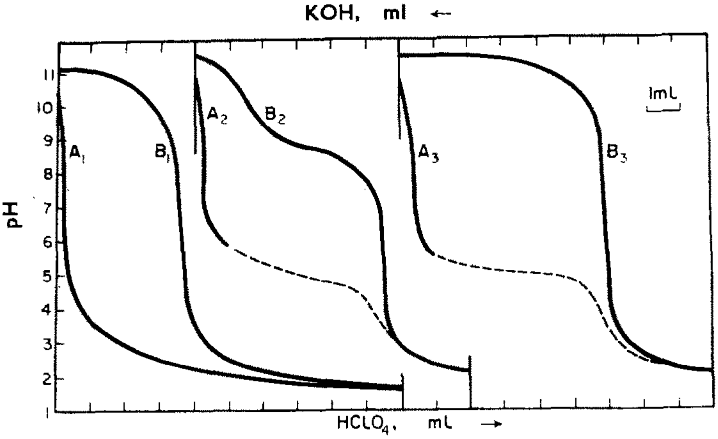

FIG. 1.—Curves of acid, A, and base, B, titration of carbodithioates:
A_1, B_1—sodium pyrrolidine-*N*-carbodithioate
A_2, B_2—sodium morpholine-*N*-carbodithioate
A_3, B_3—sodium diethylamine-*N*-carbodithioate.

Calculations

In quantitative analysis the evaluation of the amino-*N*-carbodithioate assay is based on the potential breaks in both curves. If V_A represents the volume of acid added to the first potential break in the acid titration, corresponding to neutralisation of a small amount of alkali hydroxide added to inhibit the decomposition of the amino-*N*-carbodithioate,[7] V_{AT} the total volume of added acid of concentration C_A,

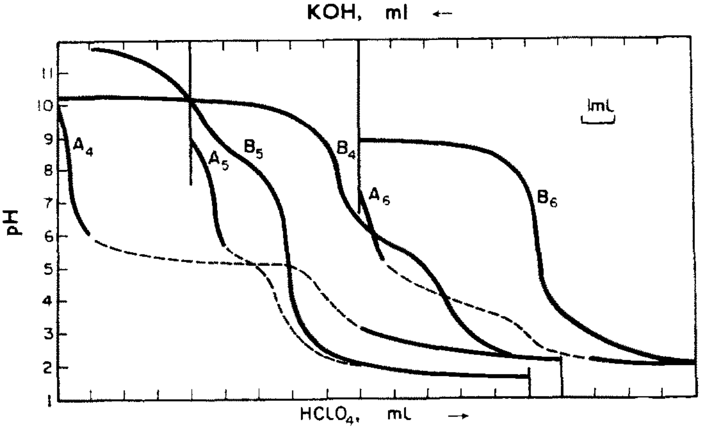

FIG. 2.—Curves of acid, A, and base, B, titration of carbodithioates:
A_4, B_4—disodium piperazine-bis-*N*-carbodithioate)
A_5, B_5—ammonium diethanolamine-*N*-carbodithioate
A_6, B_6—triammonium bis-(carboxymethyl)-amino-*N*-carbodithioate.

and V_B the volume of base of concentration C_B added till the first break in the base titration, then

$$(V_{AT} - V_A) \times C_A - V_B \times C_B$$

represents the amount of equivalents of hydrogen ions used for the decomposition of the sample. Thus, the equivalent of amino-*N*-carbodithioate (1 equivalent corresponds to 1 carbon disulphide group) equals

$$X = \frac{(V_{AT} - V_A) \times C_A - V_B \times C_B}{2}.$$

In the case of piperazine-bis-(*N*-carbodithioate) the calculation may be slightly different, when the point between the two breaks is considered. So the equivalents of hydrogen ions should be divided by 1·5. To improve the accuracy both end-points may be determined and an average result is taken as the basis of the final analysis (Table II). For a very weak amine (pK < 6), the end-point may be taken after the protonised amine has been neutralised. Therefore, the net reaction occurs

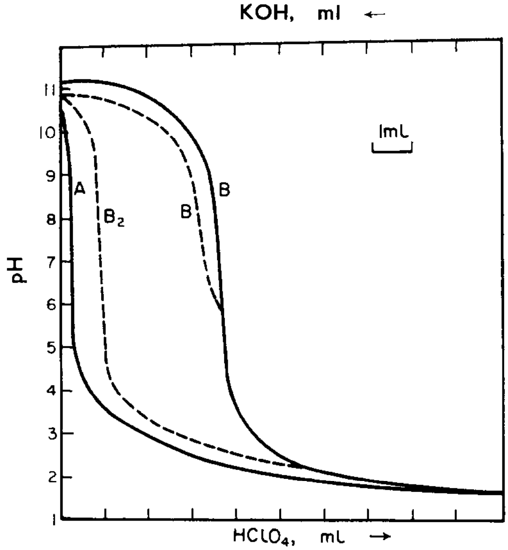

FIG. 3.—Base-titration of various samples of pyrrolidine-*N*-carbodithioate after acid titration, A:

B—sample evaporated to 0·33 volume
B_1—sample heated to boiling
B_2—sample titrated with alkali immediately after addition of acid.

$$R_2N{-}CS_2^- + H^+ \rightleftharpoons R_2NH + CS_2$$

and the number of hydrogen equivalents equals the number of amino-*N*-carbodithioate equivalents.

Effect of heating

Prolonged heating of the acidic solution may be necessary for complete decomposition of the sample. Three equal samples of pyrrolidine-*N*-carbodithioate were titrated with acid (Fig. 3). One of them was immediately back-titrated with alkali, the second was heated to boiling and then titrated, the last one was heated and evaporated to 0·33 volume remained before titration was performed. In the first two

TABLE II.—REPRODUCIBILITY OF RESULTS OF DISUBSTITUTED AMINO-*N*-CARBODITHIOATE DETERMINATION

Compound	Mequiv	Av. mequiv
Sodium diethylamine-*N*-carbodithioate	2·91	
	2·95	
	2·96	
	2·96	
	2·98	
	2·93	
	2·93	2·95
Sodium pyrrolidine-*N*-carbodithioate	2·82	
	2·79	
	2·79	
	2·81	2·80
Sodium morpholine-*N*-carbodithioate	2·82	
	2·86	
	2·86	2·84
Sodium piperidine-*N*-carbodithioate	2·24	
	2·25	
	2·31	2·27
Disodium piperazine-bis-(*N*-carbodithioate)*		
I 2·83 II 2·90	2·87	
2·88 2·94	2·91	
2·91 2·93	2·92	2·90
Ammonium diethanolamine-*N*-carbodithioate	2·22	
	2·18	
	2·27	2·22
Triammonium bis-(carboxymethyl)amino-*N*-carbodithioate	2·46	
	2·44	
	2·51	
	2·47	
	2·40	2·46

* Results given for both end-points and finally the mean for both.

TABLE III.—RESULTS OF DETERMINATION OF DIETHYLAMINE-*N*-CARBODITHIOATE FOR SAMPLES OF VARIOUS SIZE

Taken, *mg*	22·3	66·8	111·3
Found, *mg*	22·6	65·5	110·4
	22·1	66·6	112·0
	21·9	66·7	111·1
	23·1	66·7	110·6
	21·2	67·2	111·5
		66·0	
		66·0	
Average	22·2	66·4	111·1
Standard deviation	0·72	0·57	0·66
Coefficient of variation	3·25	0·88	0·59

solutions the results were lower (only about 30% of the taken amount of the first sample was accounted for) and even an additional break was observed, which was significant for samples of various derivatives. The complete decomposition of the sample may be tested by adding copper solution to the final solution. A yellowish or brown colour should not be observed. Correct and reproducible results have been obtained for different carbodithioates (Table II).

Accuracy and precision

The final result of determination is calculated as a difference of two volumes (or number of equivalents). Care is needed to take for the determination a proper amount of the sample, otherwise the small difference of two quantities results in a relatively large error (Table III). A reasonable precision may be attained when about 3 mequiv of carbodithioate, corresponding to 60–70 mg of the sample, is taken for determination.

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Zusammenfassung—Eine einfache und allgemein anwendbare Methode zur Bestimmung N-substituierter Dithiocarbamate wird beschrieben. Die in Wasser gelöste Probe wird mit einer bekannten Menge Säure gespalten und die Lösung mit eingestellter Lauge zurücktitriert. Die Anzahl der Dithiocarbamat-Äquivalente (als CS_2^--Gruppen) läßt sich aus den Titrationskurven leicht ermitteln.

Résumé—On décrit une méthode simple et générale de dosage des dithiocarbamates N-substitués. La prise d'essai, dissoute dans l'eau, est décomposée par une quantité connue d'acide, et la solution est dosée en retour par une base titrée. Le nombre d'équivalents de dithiocarbamate (à l'état de groupes CS_2^-) se determine aisément à partir des courbes de titrage.

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A SIMPLE COMPUTER CIRCUIT FOR AUTOMATIC SPECTROPHOTOMETRIC ANALYSIS OF BINARY MIXTURES BY DIFFERENTIAL REACTION RATES

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Summary—A simple analogue computer circuit, for application with a continuous reading spectrophotometer to give automatic analysis of binary mixtures of closely related substances using a differential reaction rate technique, is described. The circuit solves the simultaneous equations of the Method of Proportional Equations for the concentrations of the components in the mixture. The method is useful for first- or pseudo-first order competitive reactions. A timing circuit automatically supplies the absorbance (converted as described from the transmittance) of the reacting solution at two chosen times during the reaction, to the computer. The output voltages are adjusted within the circuit to read directly in units of concentration.

INTRODUCTION

IN recent years several analytical techniques based on differential reaction rates have been devised for the *in situ* simultaneous quantitative determination of mixtures of closely related substances.[1–11] All the techniques devised require a rather laborious graphical[5] or mathematical[1] treatment of the data in order to arrive at the concentrations of the unknowns of interest. This paper describes the circuit of an automatic read-out system for the *Method of Proportional Equations*. It can be attached to virtually any continuous reading spectrophotometer that gives an electrical output signal proportional to the transmittance of the sample solution. The simultaneous equations are solved by a simple analogue computer circuit.

PRINCIPLES OF AUTOMATIC READ-OUT CIRCUIT

The *Method of Proportional Equations* can be used for the simultaneous analysis of mixtures of closely related substances if a reagent R can be made to react under pseudo first order conditions with each of the n components $A, B, \ldots, N$ of the mixture at different rates, $K_A, K_B, \ldots, K_N$ to form a common product, O, or different products yielding a similar instrument response.

The circuit described in this paper was designed for the analysis of a two component mixture. However, by following the principles given below it can easily be extended to mixtures of more than two components. The reaction product(s) that are formed are assumed to absorb light at the same wavelength (if two products result, the fact that they might have different extinction coefficients at the wavelength used does not effect the validity of the method[1,6]) and to follow Beer's law. The proportional

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* Participant in University of Michigan Undergraduate Honours Research Programme.

equations for two unknowns have the form:

$$P_1 = K_{A_1}[A]_0 + K_{B_1}[B]_0 \tag{1}$$

$$P_2 = K_{A_2}[A]_0 + K_{B_2}[B]_0 \tag{2}$$

where P_1 and P_2 are the experimentally measured parameters which are proportional to the absorbance of the reaction mixture at times t_1 and t_2 during the reaction, K_{A_1}, K_{B_1}, K_{A_2}, and K_{B_2} are the proportionality constants, and $[A]_0$ and $[B]_0$ are the initial concentrations of the species to be analysed [see references 1 and 6 for the derivation of equations (1) and (2)].

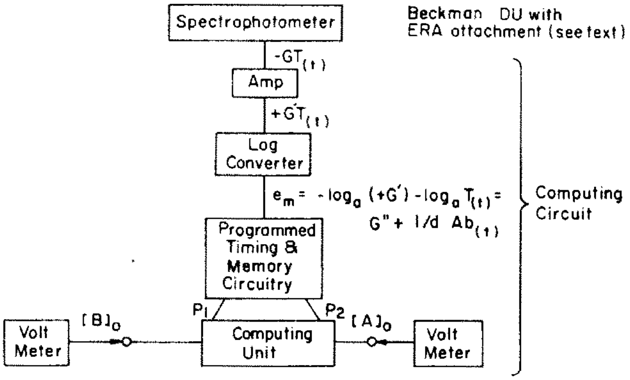

FIG. 1.—Block diagram of automatic read-out apparatus.

A block diagram of the complete analytical system is shown in Fig. 1. The spectrophotometer used in this work was a Beckman DU equipped with a Beckman Energy Recording Adapter (ERA). The ERA converts the phototube current to a voltage suitable for the input of a recorder. [Any recording spectrophotometer can be used with the read-out circuit described, provided that the instrument can be operated at a fixed wavelength. The instrument's output (the input to the spectrophotometer's recorder) is fed directly into the read-out circuit.] The output of the ERA unit, $-GT(t)$, is proportional to the transmission, $T(t)$, of the sample solution at the selected wavelength at any time during the reaction. The proportionality constant is G. Voltages proportional to the absorbance are needed for computation: the logarithm of the output of the ERA must be taken. First, however, the voltage, $-GT(t)$, is fed into a high input impedence amplifier which serves a dual purpose: its high input impedence prevents loading of the ERA output, and it amplifies the original signal $-GT(t)$ to a new signal $+G'T(t)$ which is in the range (1–10 V) for proper operation of the log circuit. By its nature, the amplifier inverts the sign of the input.[12] The device used to perform the logarithmic operation on the input signal was a slightly modified version of the circuit described by Savant and Howard.[13] The response of the circuit was directly logarithmic for the above input voltage range with a 1-V input corresponding to a 0-V output. The output of the log circuit is thus:

$$e_m = -\log_a [G'T(t)] = -\log_a G' - \log_a T(t). = +G'' - \log_a T(t) \tag{3}$$

where G'' is the constant $-\log_a G'$.

The absorbance, $Ab(t)$, of a system is defined in terms of transmission

$$Ab(t) \equiv -\log_{10} T(t) = d \log_a T(t) \tag{4}$$

Substituting equation (4) into (3) gives the output of the log circuit in terms of the absorbance and the constants G'' and $1/d$

$$e_m = +G'' + 1/d\, Ab(t) \tag{5}$$

At two preselected times, t_1 and t_2, during the reaction, a programmed timer feeds the signal e_m into memory units. In the memory units, the sign of e_m is inverted; thus, two voltages $-P_1 - \alpha G''$ and $-P_2 - \alpha G''$ (α is a constant introduced by the memory unit) are available for computation of $[A]_0$ and $[B]_0$ by a simple computer circuit at any time after t_2. For detailed descriptions of the memory and computer circuits see below.

Two operational amplifiers employed as conventional integrating circuits[12,14] were used as the memory units (see Fig. 2). The voltage e_m entering the integrator circuit is of the form in equation (5). At time t_1, the switching circuit applies $e_m(t_1)$ to the integrator for a time Δt_1 that is short in comparison to the reaction time, t_1. The output of the integrator is then:

$$e_{m_1} \text{ out} = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1} e_m(t)\, dt = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1} \left[G'' + \frac{1}{d} Ab(t)\right] dt \tag{6}$$

Because Δt_1 is short, $e_m(t_1)$ can be considered constant during the interval and to have a value $e_m(t_1)$. (R is the value of the resistance and C the capacitance of the elements of the integrator circuit and e_{m_1} is the output of the memory circuit.) Thus,

$$e_{m_1} \text{ out} = -\frac{1}{RC}\int_{t_1}^{t_1+\Delta t_1} e_m(t)\, dt = -\frac{1}{RC}[G'' + \frac{1}{d} Ab(t_1)]\Delta t_1 \tag{7}$$

$$= -\frac{\Delta t_1}{RC} G'' - \frac{\Delta t_1}{RC}\frac{Ab}{d}(t_1)$$

$$= -\alpha G'' - \frac{\alpha}{d} Ab(t_1) \tag{8}$$

where α = a constant = $\Delta t_1/RC$. Note that the sign of the voltage of equation (5) has been inverted.[12] At time t_2 the programmed timer feeds the signal $e_m(t_2)$ into the second integrator. By the same arguments as above the signal output of the second memory unit is:

$$e_{m_2} \text{ out} = -\alpha' G'' - \frac{\alpha'}{d} Ab(t_2) \tag{9}$$

The two integrators hold (as a memory) e_{m_1} out and e_{m_2} out, respectively, after the input signals are applied.[12] If $\Delta t_1 = \Delta t_2$ and the RC constants of the integrators are identical, $\alpha = \alpha'$. The two signals in the memory are:

$$\left.\begin{aligned} e_{m_1} \text{ out} &= -\alpha G'' - \frac{\alpha}{d} Ab(t_1) = -\alpha G'' - P_1 \\ e_{m_2} \text{ out} &= -\alpha G'' - \frac{\alpha}{d} Ab(t_2) = -\alpha G'' - P_2 \end{aligned}\right\} \tag{10}$$

The use of integrator circuits for the memories allows a small but finite current to be drawn from them for computing without effecting the values e_{m_1} out and e_{m_2} out.[12]

The voltages in the memory are proportional to the absorbance at t_1 and t_2 [equations (10)] but contain the additive constant potential $-\alpha G''$. At a finite time, 1 min after t_2, the programmed timer then applies e_{m_1} out and e_{m_2} out to the two operational amplifiers of the computing circuit. (See below for a detailed discussion of the timer.) The computing circuit (see Fig. 2) used is a standard analogue circuit for solving a system of simultaneous equations.[11] Simultaneously, the timing circuit applies a voltage equal to $+\alpha G''$ to each amplifier. The circuit is designed so that the $+\alpha G''$ voltage is added to both signals, e_{m_1} out and e_{m_2} out. The result is an effective input to the computer of $-P_1 = \left[-\frac{\alpha}{d}Ab(t_1)\right]$ and $-P_2 = \left[-\frac{\alpha}{d}Ab(t_2)\right]$. These voltages are thus directly proportional to the concentrations of products of the reactions at the times t_1 and t_2, and are exactly the voltages necessary to solve equations (1) and (2) for $[A]_0$ and $[B]_0$. The input and feedback impedences of the computer network are chosen to make the output of the computer read directly in terms of the concentrations of $[A]_0$ and $[B]_0$. No further calculation is necessary. (For a detailed discussion of the computing circuit, see below.) It is a simple matter to connect two voltmeters to read $[A]_0$ and $[B]_0$. Digital voltmeters, such as the Electro Instruments (San Diego, California, U.S.A.) Model 4000 Digital Voltmeter, are recommended to give numerical display of the read-out.

It should be noted that although the above circuit is constructed for a spectrophotometric method of following the reaction, any method that gives an output signal directly proportional to the concentration of product(s) can also be used. In such a case, the logarithmic circuit is omitted and the amplified signal applied directly to the timer-memory circuit.

EXPERIMENTAL

Construction and operation details of each circuit in the automatic read-out system are given below.

Amplifier circuit

This circuit consists of two parts, (i) a standard type high input impedance ($\sim 10^{13}\ \Omega$) voltage follower F which prevents loading of the spectrophotometer output,[12] and (ii) a variable gain amplifier (gain of $-$G) which is capable of amplifying the signal by a factor of -1, -10, -10^2 and -10^3. (The sign inversion is inherent in analogue circuits of this type.[14]) These circuits are standard and the details of their operation and associated equipment (power supply, bias, *etc.*) are found in references 12 and 14.

Logarithmic circuit

The logarithmic circuit is essentially the same as that described by Savant and Howard.[13] The 350 Ω and 3·5 K potentiometer are used to bias the tube so that it operates on the logarithmic portion of its characteristic curve for the 1–10 V input range. The 10 K and 250 K potentiometer are then adjusted to make the output read 0 V with a 1-V input. It was found that the rise-time response of this circuit on a 1-V instantaneous change input was about 10 sec. This is well within the time required to follow most reactions for which this technique would be employed,[1,15] but must be considered when the unit is used with fast reactions. Considerable current is drawn from the -6 V bias supply because there is only 350 Ω to ground at this point. If a standard type "C" battery is used, there is a noticeable change in the circuits' characteristics after continuous operation for 6 hr. This can be reduced by using an automobile battery or a commercial transistorised low voltage power supply instead. The ±300 V d.c. operating voltage of the circuit is supplied by the same power supply that runs the operational amplifiers (a Philbrick R-100 B ± 300 V d.c. power supply was used[14]). The adjustable base resistor of this circuit[13] is used to adjust the logarithmic base to a convenient value to give a slope of about 1 on a semi-log plot of output *vs.* input. A value of 10 Meg was used in this work. Other satisfactory logarithmic circuits based on the logarithmic characteristics of certain transistors are described in the literature.[16]

Programmed sequence timing and memory circuit

As stated before, the memory circuits are simply two conventional analogue computer operational amplifiers (Philbrick K2-W, K2-P stabilised units were used[14]) connected as integrators[12,14] (Fig. 2). The two variable resistors R_6 in the integrator circuits are used to equalise the *RC* time constants of the integrators [see equations (7)–(9)]. The two identical bridge circuits (R_8, R_9, R_{10} and R_{11}) are connected to the summing points[14] of the two integrators. They supply a small current (adjustable by R_{10}) to compensate for leakage in the system (amplifier grid current, capacitor leakage, *etc.*).[12]

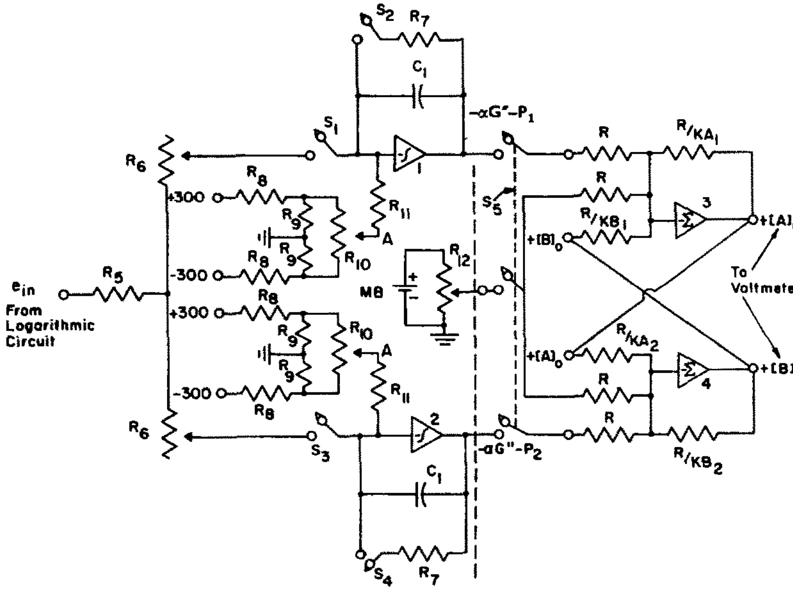

FIG. 2.—Memory and computing circuits:

R = 100 k to 10 Meg (see text)
R_5 = 7 M 1%
R_6 = 1M—Used to equalise RC time constants of integrators
R_7 = 500 Ω
C_1 = 1·0 Mfd
R_8 = 1 M 1%
R_9 = 39 Ω
R_{10} = 500Ω
R_{11} = 10 M
R_{12} = 1K, 2W
MB = Mercury battery of necessary magnitude.

The timing circuit, shown in Figs. 2 and 3, operates as follows: Switches S_8, S_9 and S_{10} are microswitches that are activated by a synchronous timer. S_8 can also be activated by a latching relay (Fig. 3), *R* built into the timer and controlled by S_6 (this timer is an Industrial Timer Corporation Model RC-8 unit). Closing switch S_6 starts the timer motor by activating S_8. [Note. Fig. 3 shows the circuit just after the cycle has been started and before any signal has been applied to the memory]. S_8 then stays in the position shown in Fig. 3 until the end of the cycle when it automatically opens and stops the motor. At a time t_1 during the reaction, S_9 is closed by the timer cam for a time Δt_1 that is *small* (less than 1 %) compared to the over-all reaction time. This accomplishes two operations: (i) It opens the latching relay S_2 so that the short circuit (discharge path) though R_7 around capacitor C_1 (see Fig. 2) is opened, which permits C_1 to then store a potential [S_2 remains latched in this position for the rest of the cycle until manually reset by closing S_7 momentarily (described later)]. (ii) Simultaneously, S_1, which applies the output of the logarithmic circuit at t_1 into the integrator is closed. It opens again after a time Δt_1 when S_9 opens again (timer activated). Thus $G'' + \frac{1}{d} Ab\,(t_1)$ is applied to, and its integral is stored on, integrator 1. At time t_2, the timer closes S_{10} for a time $\Delta t_2 = \Delta t_1$. Relays S_3 and S_4 operate similarly to S_1 and S_2 in controlling the sequence of events in the second integrator circuit. Then, at any time $t > t_2$, the output of integrator 1 is $-\alpha G'' - P_1$ and the output of integrator 2 is $-\alpha G'' - P_2$. At a time $t > t_2$, dependent on the duration of the timer cycle, the timer automatically turns itself off. Switch S_8 goes to the upper position [position (1)] in Fig. 3. This activates relay S_5. This relay then applies $-\alpha G'' - P_1$, $-\alpha G'' - P_2$ and $+\alpha G''$ into the inputs of the computing circuit [see Fig. 2 and equation (10)]. The computer then develops $[A_0]$ and $[B_0]$ as output voltages and will hold these "answers." (The computing process is described below). To reset the latching relays, S_2, S_4 and S_5, and thus erase the memory in preparation for another run, S_7 is closed momentarily. However, it will be noticed that if S_8 is in the upper position [position (1) in Fig. 3], S_5 will get a signal to activate again. Thus, the proper reset sequence is the following: close S_6 momentarily to activate relay R and thus S_8. The timer motor is now running [S_8 in position (2)]. Immediately close S_7 momentarily to reset S_2, S_4 and S_5. (If it is desired to erase the memories without reactivating the cycle, just close S_7, but recall that S_5 will *not* be reset.)

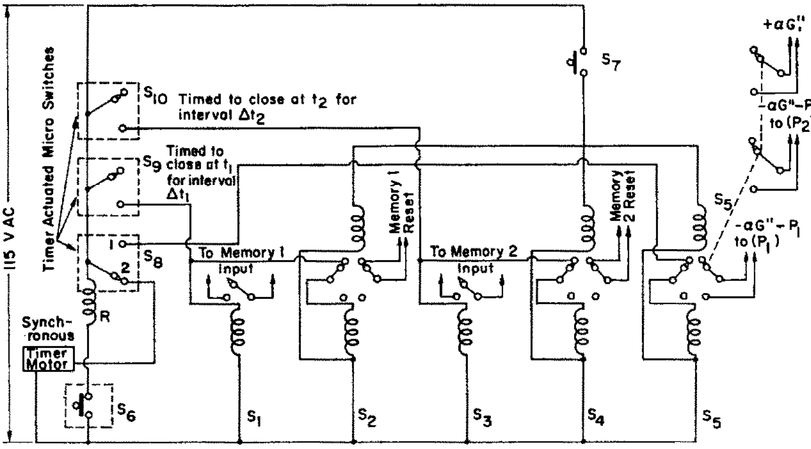

FIG. 3.—Programmed Timing Circuit (controls the sequence of the activation of the switches in the memory and computing circuits; switch numbers are the same as in Fig. 2):

Timer—Industrial Timer Corp., Model RC-8;
S_1 and S_3—Potter-Brumfield Relay—Model #KA11AY 115 V a.c.;
S_2, S_4 + S_5—Potter-Brumfield Latching Relay—Model #KB17AY 115 V a.c., 4PDT.

Switches S_8, S_9 and S_{10} are cam operated and t_1, Δt_1, t_2 and Δt_2 are easily preset to any desired value. The desired duration of the full cycle will depend on the speed of the reaction that is being followed. The length of the timer cycle can be adjusted by simply changing the synchronous motor gear ratios. Different sets of gears are commercially available that can vary the cycle from 10 sec to several hours.

Computing circuit

The computing circuit consists of two summing operational amplifiers[12,14] (Fig. 2). The principles governing the application of summing amplifiers in solving simultaneous equations can be easily shown by rearranging the proportional equations (1) and (2) in the form

$$[A]_0 = \frac{P_1}{K_{A_1}} - \frac{K_{B_1}}{K_{A_1}}[B]_0 \qquad (11)$$

$$[B]_0 = \frac{P_2}{K_{B_2}} - \frac{K_{A_2}}{K_{B_2}}[A]_0 \qquad (12)$$

The memory circuits have stored the voltages $-\alpha G'' - P_1$ and $-\alpha G'' - P_2$, which can be substituted as input voltages (e_{in_1} and e_{in_2}) along with the voltage $+\alpha G''$ (e_{in_3}) in the expression describing the operation of a summing amplifier[14] (the value of the feedback resistor, R_f, is any convenient value such that all the resistance values fall between 10 K and 20 M). One obtains:

$$\begin{aligned} e_{\mathrm{out}} &= -(-\alpha G'' - P_1)\frac{1}{K_{A_1}} - \alpha G''\frac{1}{K_{A_1}} - (+[B]_0)\frac{K_{B_1}}{K_{A_1}} \\ &= +\frac{P_1}{K_{A_1}} - [B]_0\frac{K_{B_1}}{K_{A_1}} \qquad (13) \end{aligned}$$

This is the expression for $+[A]_0$ of equation (11). A similar circuit can be used to calculate $+[B]_0$. [The voltage $+\alpha G''$ is supplied by means of a mercury battery MB which can be varied from 0 to about 20 V and it is adjusted precisely by the potentiometer (10 turn Helipot) R_{12}.] Of course, the values, $+[B]_0$ and $+[A]_0$, which are the solutions sought, are not available as such for substitution into the right hand side of equations (11) and (12). However, if the output of amplifier 3 is fed back into the $+[A]_0$ input of amplifier 4 and the output of 4 fed into the $+[B]_0$ input of amplifier 3, when the potentials $-\alpha G'' - P_1$, $-\alpha G'' - P_2$ and $+\alpha G''$ are applied to the respective inputs (see Fig. 2), the circuit will rapidly come to steady state condition with $+[A]_0$ and $+[B]_0$ reading at the outputs,[1,17] This type of *solution feedback* is the basic principle of all analogue computation.[1,12,14,17]

The values of K_{A_1}, K_{B_1}, K_{A_2} and K_{B_2} are experimentally determined by reacting a solution of pure A and then pure B and measuring P_1 and P_2 for each at times t_1 and t_2. The values of K_{A_1}, *etc.*, are then calculated simply from:

$$
\begin{aligned}
K_{A_1} &= P_{A_1}/[A]_0 \\
K_{B_1} &= P_{B_1}/[B]_0 \qquad (14) \\
&\vdots \\
&\textit{etc.}
\end{aligned}
$$

In order to determine the accuracy and precision of the automatic read-out unit, a large number of simulated reaction rate curves were applied to this unit by means of an electronic function generator. These simulated rate curves were constructed from theory using several different cases. (Different rate constants and ratios of $[A]_0/[B]_0$) were used, rather than actual experimental rate curve responses from the spectrophotometer in the evaluation of the automatic unit in order to eliminate all source of variation of parameters not directly introduced by the read-out unit. Thus, no error resulting from spectrophotometer drift, temperature change of the reacting solution, *etc.*, complicated the comparison of the hand calculated and automatic read-out results, and the accuracy and precision of the automatic read-out unit is obtained exactly.) It was found that the results obtained by the automatic read-out unit had an accuracy of better than ±2% when compared with the hand calculated (theoretical) results and a precision (standard deviation) of less than ±2%, when care is taken in measuring the proportionality constants, K's, and in adjusting the instrument.

The increased speed over hand calculation of determining the values of the experimental proportionality constants of the system as well as the analysis result make this unit very useful when large numbers of analyses are being made with this kinetic method. The computing unit would be even more useful when the mixtures contained three or four components because the calculation becomes very tedious in these cases.

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Zusammenfassung—Eine einfache Analogrechnerschaltung wird beschrieben, die mit Hilfe eines kontinuierlich anzeigenden Spektralphotometers eine automatische Analyse binärer Mischungen nahe verwandter Substanzen liefert, wobei eine Technik verwendet wird, die sich auf Reaktionsgeschwindigkeitsunterschiede gründet. Die Schaltung löst die simultanen Gleichungen der Methode der proportionalen Gleichungen für die Konzentrationen der Bestandteile in der Mischung. Die Methode ist von Nutzen bei Konkurrenzreaktionen erster oder pseudoerster Ordnung. Eine Zeitgeberschaltung gibt die Extinktion (die auf bekannte Weise aus der Durchlässigkeit erhalten wird) der reagierenden Lösung zu zwei wählbaren Zeiten während der Reaktion automatisch in den Rechner. Die Ausgangsspannungen werden in der Schaltung so justiert, daß sie direkt Konzentrationseinheiten angeben.

Résumé—On décrit un circuit calculateur analogique simple, en liaison avec un spectrophotomètre à lecture continue, pour l'analyse automatique de mélanges binaires de substances étroitement apparentées, par l'emploi d'une technique de vitesses de réaction différentielles. Le circuit résout les équations simultanées de la méthode des équations proportionnelles, pour les concentrations des composants du mélange. La méthode est utile pour les réactions concurrentes d'ordre un ou

pseudo-un. Un circuit chronométreur fournit automatiquement au calculateur l'absorption (à partir, ainsi qu'il est décrit, de la transmission) de la solution réagissante à deux instants choisis durant la réaction. Les voltages à la sortie sont ajustés dans le circuit de façon à permettre la lecture directement en unités de concentration.

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DETERMINATION OF AMINOALKYLTHIOPHOSPHORUS COMPOUNDS AND THIOLS WITH PALLADIUM(II) IONS AS THE REAGENT

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Summary—Two methods of determination based on the reactions of the palladium(II) ion with thiol compounds, thiocholine esters and thiophosphorus compounds are described. One of the methods is photometric, and the substance measured is the palladium-thiol complex formed when palladium chloride is added to a solution of a thiocholine ester or a thiophosphorus compound. The second method, used for the determination of thiol compounds, is titrimetric, with a palladium chloride solution as the titrant.

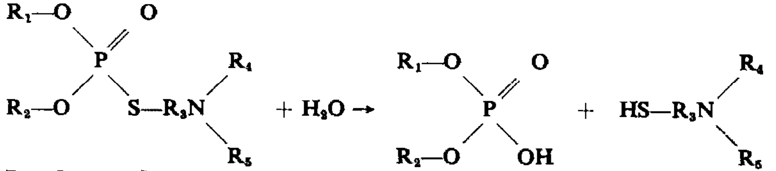
INTRODUCTION

The many methods available for the determination of thiols, organic sulphides, thiophosphorus compounds and thiocholine esters have been reviewed in detail by Cecil and McPhee[1] and by MacDougall.[2] The latter has used fluorimetric measurements for the determination of pesticide residues. Mercurimetric methods for the determination of thiols, aryltriethyl sulphides and disulphides have been described by Gregg, Bouffard and Barton.[3] Fritz and Palmer[4] have also made mercurimetric determinations of thiols. At this laboratory we were in need of methods for determining the main components and decomposition products of thiocholine esters and aminoalkylthiophosphorus compounds, *e.g.*, dimethylaminoethylthiodiethoxyphosphine oxide and dimethylaminoethanethiol.

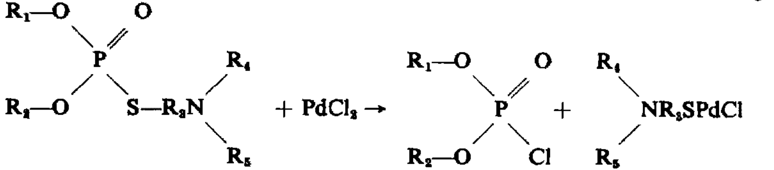
PRINCIPLES

Thio compounds of the type shown in equation (1) are almost invariably contaminated by the corresponding thiol compounds formed by hydrolysis. To determine the extent of this contamination two methods have been worked out, both of them based on the reaction of the palladium ion with the two types of compound.

The reactions involved are the following:



(1)



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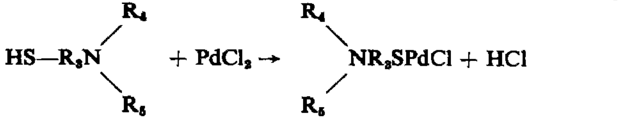

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With thiol compounds the palladium ion instantaneously forms stable complexes, which can be written as $PdSR^+$ and $Pd(SR)_2$.

The effect of palladium ions on some thio compounds, *e.g.*, thiocholine esters or aminoalkylthiophosphorus compounds, which can be transformed by hydrolysis to thiol residues, is to increase the rate of decomposition in ethanol or aqueous solutions. After distillation of the reaction products of equation (2), the presence of the phosphoryl chloride may be demonstrated by applying Schönemann's reaction[5] to the distillate. In aqueous solution the phosphoryl chloride is rapidly hydrolysed. The palladium-mercapto chloride formed is a very stable complex, which absorbs radiation in the ultraviolet range.

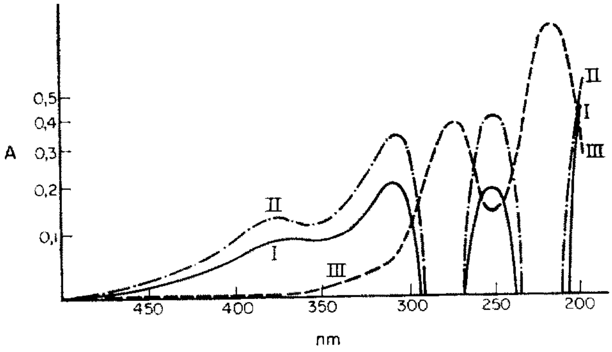

FIG. 1.—Absorbance curves (the substances are dissolved in 0·3*M* hydrochloric acid):

I. Dimethylaminoethylthiodiethoxyphosphine oxide + palladium chloride, measured against a palladium chloride solution.
II. The corresponding dimethylaminoethanethiol + palladium chloride, measured against a palladium chloride solution.
III. Palladium chloride solution measured against 0·3*M* hydrochloric acid.

The palladium–thiol complex can be assayed by photometry in the ultraviolet range and a direct titration of the thiol compound with a palladium chloride solution is possible. At the equivalence point excess palladium is indicated by a colour reagent.

The photometric method has recently been applied in work described by Åkerfeldt and Lövgren.[6]

EXPERIMENTAL

Photometric Method

The absorbance curve from 220 to 500 nm for dimethylaminoethylthiodiethoxyphosphine oxide + palladium chloride in 0·3*M* hydrochloric acid, measured against a reference solution of palladium chloride in 0·3*M* hydrochloric acid, and the corresponding absorbance curve for dimethylaminoethanethiol + palladium chloride are identical (Fig. 1). This confirms the reaction represented by equation (2). The reaction times may vary from minutes to hours, depending on which substances are used.

The absorbance curves have two maxima, at 250 and 310 nm. They also have two minima, at 280 and 225 nm; both are "negative". The absorbance curve for the reference solution, palladium chloride in 0·3*M* hydrochloric acid, measured against 0·3*M* hydrochloric acid, also has two maxima at 280 and 225 nm—the same wavelengths as for the minima for the palladium–thiol complex. The formation of the complex on mixing a thiol compound with the palladium reagent results in a decrease in the palladium ion concentration. For the reagent solution in the reference cell, however, the palladium ion concentration is unchanged, and because it is higher than for the sample, the absorbance is higher at 280 and 225 nm than for the sample solution. This is the reason for the "negative" absorbance at the two minima.

The measurements are carried out in acid solutions with a pH of less than 3. At higher pH the absorbance curve for a palladium chloride solution no longer has well defined peaks at 280 and 225 nm, but two broad maxima at 250 and 225 nm, which merge (Fig. 2). If measured at a pH of more than 3 the maximum of the palladium-thiol complex at 250 nm is disturbed, so that at this wavelength, too, a "negative" absorbance may appear.

Beer's law is obeyed for both absorbance maxima. For 10^{-5}–$10^{-3}M$ solutions the absorptivity at 250 nm is 5×10^3 and at 310 nm it is 4×10^3 litre. mole^{-1}. cm^{-1}. The standard deviation for a single value at 250 nm is $4{\cdot}0 \times 10^{-7}$ mole/litre (measured on $7{\cdot}4 \times 10^{-6}$ molar solutions) and at 310 nm it is $10{\cdot}0 \times 10^{-7}$ mole/litre.

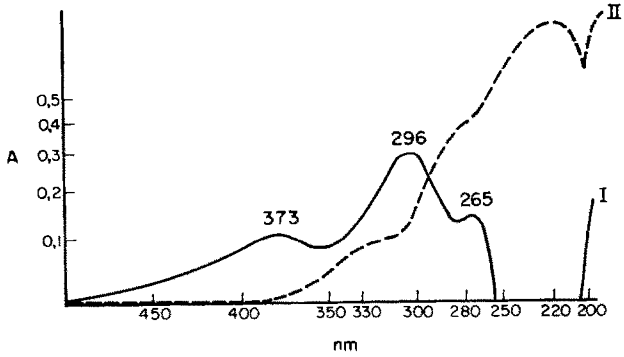

FIG. 2.—Absorbance curves (the substances are dissolved in distilled water);

I. Dimethylaminoethanethiol + palladium chloride, measured against a palladium chloride solution.

II. Palladium chloride solution measured against distilled water.

The method is applicable to aminoalkylthiophosphorus compounds, thio esters and the corresponding thiol compounds, provided that the palladium complexes are soluble in water.

Apparatus

Zeiss spectrophotometer PMQ II

Quartz cells, 1 *cm*

Wavelength, 250 or 315 nm; in most cases 250 nm is preferable.

Reagents

Palladium chloride solution. 0·05M (ammonium chloropalladite, Specpure, Johnson, Matthey & Co. Ltd., London), in 0·3M hydrochloric acid.

Hydrochloric acid. 0·3M

Standard solution for the calibration curve. The thiol compound to be measured, *e.g.*, dimethylaminoethylthiodiethoxyphosphine oxide dissolved in isopropanol.

Reference solution. 0·5 Ml of the palladium chloride solution diluted to 50 ml with 0·3M hydrochloric acid.

Calibration curve

Measure 0·5 ml of the palladium chloride solution into each of five 50-ml volumetric flasks. Add known amounts of the standard solution to cover a concentration range between 2×10^{-6} and $2 \times 10^{-4}M$. Make up to the mark with 0·3M hydrochloric acid. Measure the absorbance at 250 and 310 nm against the reference solution and plot the calibration curve.

Procedure

Dissolve the sample in any solvent that is soluble in water and has zero absorbance in the wavelength range to be used. Measure 0·5 ml of the palladium solution into a 50-ml volumetric flask, add a known amount of the sample solution and make up to the mark with 0·3M hydrochloric acid. Measure the absorbance at 250 or 310 nm against the reference solution and calculate the result from the calibration curve.

Titrimetric Method

For a direct titration an instantaneous reaction is necessary. Because palladium ions react instantaneously with thiols but not with most other sulphur compounds, thiols may, therefore, be titrated in the presence of organic sulphides; the palladium ion concentration will be too low during the titration to decompose other organic sulphur compounds (*e.g.*, aminoalkylthiophosphine oxides, thiocholine esters, *etc.*). The equivalence point is indicated by the reaction of *p*-nitrosodimethylaniline[7] with excess palladium ions. A bright red complex is formed which is visible at a palladium ion concentration of $10^{-6}M$.

To be titratable the palladium complex of a thiol must have a solubility in $0{\cdot}3M$ hydrochloric acid of at least 2×10^{-3} mole/litre. The titration should preferably be performed in a recording photometric titrator, but can also be carried out manually. The apparatus used was an EEL titrimeter, modified to enable a recorder to be connected.[8] A typical titration curve is shown in Fig. 3; it is preferable to choose the equivalence point in the middle of the slope of the curve. The standard deviation is $0{\cdot}02 \times 10^{-5}$ mole when a total of $1{\cdot}5 \times 10^{-5}$ mole of thiol are titrated. For titration of aminoethanethiols, for instance, the burette speed was $2{\cdot}966 \times 10^{-3}$ ml/min and the paper speed on the recorder 1·055 cm/min.

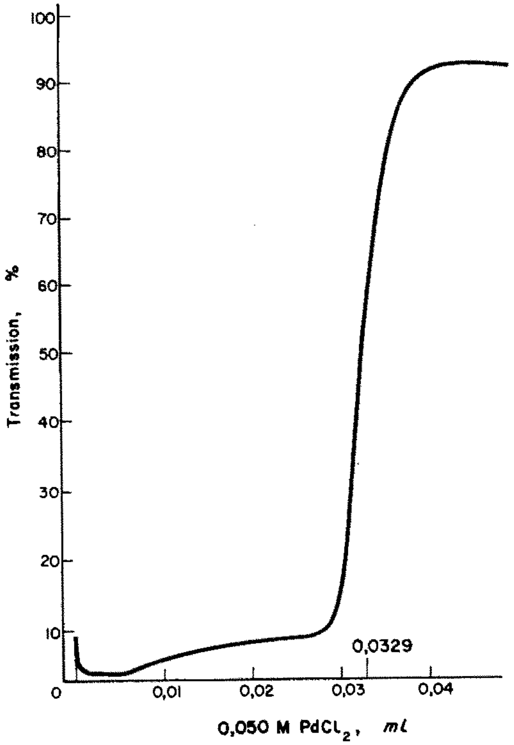

FIG. 3—Titration of 0·50 ml of a $3{\cdot}26 \times 10^{-2}M$ dimethylaminoethanethiol solution with $0{\cdot}050M$ palladium chloride solution.

Apparatus

EEL titrimeter with filter No. 603 (absorption maximum 490 nm). The apparatus is equipped with an amplifier[9] and is connected to a recorder (Honeywell Brown) and an Agla syringe supplied with a motor-driven gear-box.[9]

Reagents

Palladium chloride solution. $0{\cdot}0500M$ (ammonium chloropalladite, Specpure) in $0{\cdot}3M$ hydrochloric acid; standardise the solution against cysteine hydrochloride.

Cysteine hydrochloride. $0{\cdot}0100M$ (Roche, pro. anal.) dissolved in $0{\cdot}3M$ hydrochloric acid.

Indicator solution I. Dissolve 0·5 g of *p*-nitrosodimethylaniline in 100 ml of ethanol. The solution should be used within 10 days.

Indicator solution II. Dilute indicator solution I with ethanol 1:10 (stable for 1–2 days).

Procedure

Add to the cylindrical cell of the apparatus 0·15 ml of indicator solution II, 1 ml of 0·3*M* hydrochloric acid and 15 ml of ethanol in that order. To avoid oxidation of the thiol during the titration pass nitrogen through the solution; the bubbles serve at the same time to agitate the solution. Turn on the nitrogen and about 5 min later add 0·01–1·00 ml of the sample solution containing 10^{-6}–3×10^{-5} mole. Set the gear-box of the burette at a suitable speed and the recorder at a suitable paper speed. The complex constants defining the equivalence point have not been determined. We have, however, for empirical reasons, chosen the equivalence point in the middle of the slope. The error will be of minor importance because the slope is very steep. One mole of palladium chloride corresponds to one mole of thiol.

DISCUSSION

By means of the two methods described it is possible to determine organic sulphur compounds that can be decomposed by palladium ions to palladium–thiol complexes. With the photometric method the sum of the original thiol contamination of the organic sulphur compound and the thiol formed during the reaction with the palladium ion can be determined, whereas the titrimetric method gives only the original thiol contamination. For the methods to be applicable, the palladium complexes formed must be soluble in the solvent used. All thiols meeting this requirement and sulphur compounds that can be converted to thiols can be determined by the methods. Parathion and Systox can be determined photometrically if enough time is allowed for complete reaction. Cysteamine, cysteine and certain aminoalkanethiols have been assayed titrimetrically by the method. On the other hand, dodecanethiol has presented difficulties, because of its low solubility.

Disulphides and sulphides present in the sample solution disturb the titrimetric determination only to a negligible extent, provided that their concentrations are low. In some experiments a concentration of 30 mole-% of disulphide which was present gave values which were 2% too high.

Whether the photometric method can be of use for organic sulphur compounds will depend on the velocity of their reaction with the palladium ion. This is easily found by adding the palladium reagent to the sample and measuring the absorbance at regular intervals.

Zusammenfassung—Zwei Analysenvorschriften werden angegeben, die auf der Reaktion von Palladium(II) mit Mercaptanen, Thiocholinestern und Thiophosphorverbindungen beruhen. Die eine Methode ist eine photometrische; gemessen wird die Extinktion des Palladium-Mercaptan-Komplexes, der sich bei Zusatz von Palladiumchlorid zu einer Lösung eines Thiocholinesters oder einer Thiophosphorverbindung bildet. Die zweite Methode, die zur Bestimmung von Thiolen verwendet wird, besteht in einer Titration mit Palladiumchloridlösung als Titriermittel.

Résumé—Deux méthodes sont décrites, basées sur les réactions du ion de palladium(II) aux composés de thiol, aux esters de thiocholine et aux composés de thiophosphore. L'une de ces méthodes est photométrique, et la substance mesurée se compose du complexe de palladium-thiol qui se produit quand on ajoute du chlorure de palladium à une solution d'un ester de thiocholine ou d'un composé de thiophosphore. L'autre méthode, employée pour déterminer les composés de thiol, est titrimétrique, avec une solution de chlorure de palladium comme solution titrante.

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LIQUID–LIQUID, DISCONTINUOUS, COUNTER-CURRENT SOLVENT EXTRACTION FOR DETERMINATION OF TRACE CONSTITUENTS IN GEOLOGICAL MATERIALS—I

EXTRACTION WITH SOLVENTS LIGHTER THAN WATER

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Summary—A new analytical technique for the determination of trace constituents in silicate rocks has been developed. This consists of the use of liquid–liquid, discontinuous, counter-current, solvent extraction in which the chloro-complexes of a number of elements are extracted into a ketonic solvent. Extraction into methyl isobutyl ketone is followed by spectrographic analysis of the contents of the individual extraction tubes, from which a series of extraction curves is plotted. These curves show that trace constituents of a silicate rock can be separated from the main constituents and can be fractionated from eachother. By the use of a solution of a granite-gneiss in 3*M* hydrochloric acid and varying concentrations of this ligand as the aqueous phase in the extraction train, it is shown that a number of trace constituents can be isolated and hence enriched from the rock solution. The method appears to have the advantages of speed, flexibility, relative freedom from contamination and the fact that even weakly-extracted elements may be determined quantitatively. It is suggested that the technique may be suitable not only for the analysis of trace constituents in silicate rocks, but also as a separation method in radioactivation analysis. A further application may be the separation of different oxidation states of the same element, *e.g.*, antimony(III) from antimony(V).

INTRODUCTION

In recent years there has been an increasing interest in the determination of trace elements in geological materials. This is due in the main to the development of more sensitive methods of analysis, *e.g.*, radioactivation, X-ray fluorescence, isotope dilution, *etc.*

Another approach to the problem has been the development of ion-exchange enrichment of the trace constituents, followed by spectrochemical analysis.[1–2] Solvent extraction enrichment methods have also received attention[3–4] and are likely to increase in the future in view of their simplicity and relative freedom from contamination.

Craig and Post[5] have developed a suitable apparatus for discontinuous, counter-current, solvent extraction but the potentialities of this technique for inorganic systems have been largely overlooked. Such systems as have been investigated appear to be largely confined to separation of the rare earths.[6–9]

Werning *et al.*[10] have used the technique for the separation of tantalum from niobium. Recently, Ishimori[11] has used counter-current solvent extraction for the separation of ^{233}U and ^{233}Pu from thoria. To date, there appears to be no literature concerning possible geochemical applications of the technique.

In the work which is now described, a preliminary study has been made of the application of counter-current solvent extraction of the chloro-complexes of certain elements into methyl isobutyl ketone (MIBK). MIBK was chosen for these investigations because of its cheapness, ready availability and known property of being able to extract the chloro-complexes of certain metals.[12]

By analogy with the absorption of chloro-complexes onto an anion-exchange resin,[13] it was to be expected that a number of elements present normally in low concentrations in rocks and minerals would extract into the organic solvent; whereas, of the major constituents, only iron would be likely to extract.

EXPERIMENTAL

Apparatus

Solvent-extraction operations were carried out with a fully-automatic, discontinuous, counter-current extraction apparatus comprising 120 tubes.[5] The individual extraction tubes were mounted on a shaking rack whose axis was attached to an automatic control unit which automatically effected the operations of shaking, settling and decantation. Individual tubes had a capacity of 20 ml for the stationary lower phase and the upper moving phase was fed into the system at the end of each shaking and decantation cycle by means of a 20-ml dispenser attached to a 10-litre reservoir. After each shaking operation, the rack was tilted through 90° and the upper phase decanted into the next extraction tube. The cycle was then repeated. In all cases the contents of individual tubes or sets of tubes were taken to dryness, sodium chloride was added as carrier and the residues were examined spectrographically in the d.c. arc using anode excitation.

Procedures

Initial experiments were carried out with stock solutions containing the following elements: copper, silver, gold, cadmium, gallium, indium, thallium, tin, lead, bismuth, iron, molybdenum, platinum, iridium, palladium (1000 ppm); antimony, vanadium, rhenium, osmium, ruthenium, rhodium (5000 ppm); zinc, arsenic (10,000 ppm); mercury (20,000 ppm). The stock solutions were treated with chlorine gas to ensure that all elements were in their highest oxidation states.

A solution of the elements in 20 ml of $2M$ hydrochloric acid was placed in the first extraction tube and 20 ml of pure hydrochloric acid in each of the following 49 units. The acid solutions were, in all cases, pre-equilibrated with MIBK before use. The solvent, which had also been pre-equilibrated with $2M$ acid, was fed into the system from the reservoir and counter-current extraction was carried out for 50 transfers. The total contents of each tube were then examined spectrographically. The experiment was repeated with $3M$ hydrochloric acid as the aqueous phase. In a further experiment, a solution of the metals in $3M$ hydrochloric acid was placed in the first tube and pure acid of the same strength was added to the next 9 tubes. The subsequent 4 sets of 10 tubes contained $2M$, $1M$ and $0{\cdot}5M$ hydrochloric acid and pure water, respectively.

Although redistilled analytical reagent grade hydrochloric acid was used in the experiments, faint traces of lead, silver and tin were detected in all tubes but were taken into account when plotting distribution curves. A blank run with pure water in place of the hydrochloric acid showed very faint traces of lead in the tubes.

The distribution curves of a number of elements for each experiment were plotted from the spectrographic data and are shown as curves A, B and C in Fig. 1. To avoid confusion in the plot, not all extracted elements are shown.

In a later experiment, 60 ml of a solution of a granite-gneiss (from Charleston, Westland, New Zealand), was prepared in $3M$ hydrochloric acid and placed in the first three extraction tubes. This represented 6% of the total number of tubes and is the maximum permissible for 50 transfers without undue disturbance of the theoretical distribution pattern.[14] The following 7 tubes contained pure $3M$ hydrochloric acid and the arrangement of the aqueous phases in the remaining tubes was exactly as in the previous experiment.

After counter-current extraction with 50 transfers, the tubes were divided into 4 fractions as follows:—

Fraction 1:	Tubes 1–5;
Fraction 2:	Tubes 6–20;
Fraction 3:	Tubes 21–26;
Fraction 4:	Tubes 27–50.

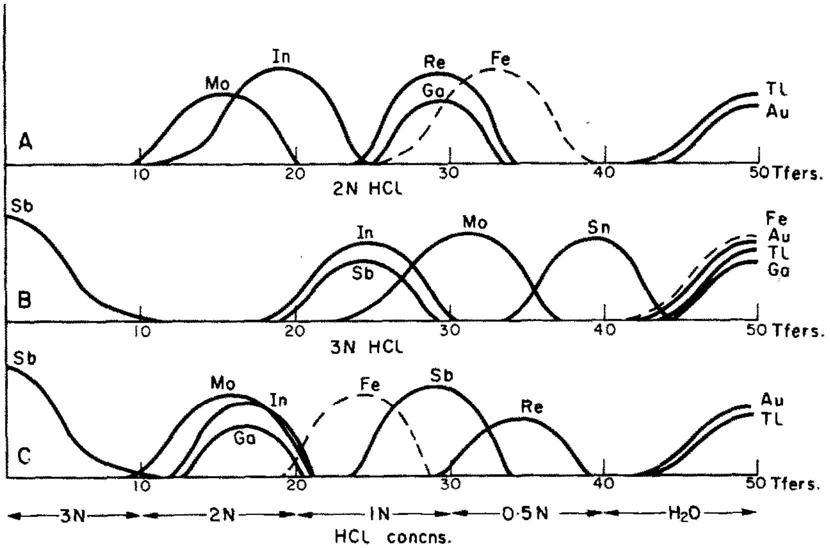

Fig. 1—Distribution curves for a number of elements after counter-current extraction from hydrochloric acid solutions.

The samples were taken to dryness, collected in a matrix of 20 mg of sodium chloride and examined spectrographically. Fraction 1 contained the bulk of the unextracted material. The distribution of the elements is shown in Table I.

TABLE I.—DISTRIBUTION OF ELEMENTS IN EXTRACTS OF A GRANITE-GNEISS SOLUTION AFTER 50 TRANSFERS WITH COUNTER-CURRENT SOLVENT EXTRACTION

Fraction	Tube no.	Cations detected
1	1–5	Ca, Al, Mg, Na, K, Ti
2	6–20	Zn, Ga, In, Mo
3	21–26	Ga, Sn, In, Mo, Fe
4	27–50	Sn, Ni

DISCUSSION

The experiments have clearly demonstrated that separation of trace constituents from the major elements in a rock and from each other is readily feasible with the aid of counter-current solvent extraction.

This form of extraction has a number of advantages over certain other enrichment techniques such as ion-exchange.

(a) The difficulty of completely removing absorbed ions, so commonly encountered in ion exchange, does not arise.

(b) The method is significantly free from contamination dangers because the operations are simple and involve only two reagents, both of which can be readily purified by distillation.

(c) It is now possible to separate quantitatively, ions which are only weakly extracted, provided that the extraction is sufficiently great for them to be removed from the tube or tubes initially containing the sample. This separation can always be achieved by increasing the number of transfers.

(d) The method is extremely flexible in that not only is there a wide choice of ligands and solvents, but also it is a simple matter to alter the nature or concentration of the ligand during the extraction sequence as has been shown above.

A disadvantage of the method lies in the fact that a fully-automatic Craig unit is required for the experimental procedure. However, such units, if obtained, may also be used for separations in organic chemistry for which they were originally designed and hence a certain economy may be achieved.

It would seem that counter-current solvent extraction should have wide applications in geochemical trace analysis. In the experiments with MIBK, the only major element extracted simultaneously with the trace constituents appears to be iron. The presence of this element would normally cause difficulties in the later stages of the analytical procedure. It can be seen from Fig. 1, however, that iron may be separated from other constituents merely by varying the concentration of the ligand. Thus, where iron was originally associated with gold, gallium and thallium (curve B), it now becomes effectively separated from two of these elements (curve C).

Counter-current extraction may also prove to be a useful technique in radioactivation analysis. Even after 50 transfers, it is clear that gold and thallium are effectively separated from all other constituents. This should afford a speedy and reliable method of separating either or both these elements from an irradiated sample without the need for a carrier.

It is interesting to note in Fig. 1, that different oxidation states of the same element may apparently be separated from each other. This can be done where the two separate extraction curves presumably represent antimony(III) and antimony(V).

Because preliminary work on a granite-gneiss has shown the geochemical application of the method, futher investigations are being undertaken with a view to the quantitative determination of a number of trace elements in a suite of silicate rocks.

In a later paper, the geochemical applications of counter-current solvent extraction with solvents heavier than water will be discussed.

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Zusammenfassung—Ein neues analytisches Verfahren zur Bestimmung von Spurenbestandteilen in Silikatgesteinen wurde entwickelt. Es besteht in einer diskontinuierlichen Gegenstrom-flüssig-flüssig-Extraktion, bei der die Chlorokomplexe einiger Elemente in ein Keton extrahiert werden. Nach der Extraktion in Methylisobutylketon wurden die Inhalte der einzelnen Extraktionsgefäße spektrochemisch analysiert; daraus wurde eine Reihe von Extraktionskurven konstruiert. Diese Kurven zeigten, daß Spurenbestandteile in Silikatgesteinen von den Hauptbestandteilen getrennt sowie untereinander fraktioniert werden können. An Hand einer Lösung eines Granit-Gneises in 3n HCl und wechselnden Konzentrationen von Chlorid in der wäßrigen Phase der Extraktionsbatterie wurde gezeigt, daß eine Anzahl von Spurenbestandteilen isoliert und aus der Gesteinslösung angereichert werden können. Die Methode zeigt die Vorteile, daß sie schnell, anpassungsfähig und relativ frei von Möglichkeiten zur Verunreinigung ist, sowie die Tatsache, daß auch nur schwach extrahierbare Elemente quantitativ bestimmt werden können. Es wird die Ansicht vorgetragen, daß das Verfahren nicht nur für die Analyse von Spurenbestandteilen in Silikatgesteinen, sondern auch als Abtrennmethode bei der Radioaktivierungsanalyse geeignet sein könnte. Eine weitere Anwendung kann die Trennung verschiedener Oxydations-stufen des selben Elements sein, wie z.B. Sb^{3+} von Sb^{5+}.

Résumé—On a élaboré une nouvelle technique analytique pour le dosage de constituants à l'état de traces dans les roches aux silicates. Elle consiste en l'emploi d'une extraction par solvant en milieu liquide, discontinue et à contre-courant, au cours de laquelle les chloro complexes d'un certain nombre d'éléments sont extraits dans un solvant cétonique. L'extraction en méthyl-isobutylcétone est suivie d'une analyse spectrochimique du contenu de chaque tube d'extraction, permettant le tracé d'une série de courbes d'extraction. Ces courbes, montrent que les constituants à l'état de traces d'une roche aux silicates peuvant être séparés des constituants principaux, et fractionnés. En utilisant une solution de granit-gneiss en HCl 3N, et en variant les concentrations de ce complexe en phase aqueuse dans l'ensemble d'extraction, on a montré qu'on peut isoler un certain nombre de constituants à l'état de traces à partir de la solution de roche, puis procéder à leur enrichissement. La méthode présente les avantages suivants: rapidité, souplesse, elle est relativement exempte de contamination, et même des éléments faiblement extractibles peuvent être déterminés quantitativement. On suggère que la technique peut convenir, non seulement à l'analyse de constituants à l'état de traces dans les roches aux silicates, mais comme méthode de séparation en analyse par radioactivation. On peut en outre l'appliquer à la séparation d'un même élément à divers degrés d'oxydation, par exemple Sb^{3+} et Sb^{5+}.

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LIQUID–LIQUID, DISCONTINUOUS, COUNTER-CURRENT SOLVENT EXTRACTION FOR DETERMINATION OF TRACE CONSTITUENTS IN GEOLOGICAL MATERIALS—II*

EXTRACTION WITH SOLVENTS HEAVIER THAN WATER

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Summary—A new analytical technique has been developed for the determination of trace elements in sea water and other natural waters. The method consists of the use of liquid-liquid, counter-current, solvent extraction with solvents heavier than water. Relatively large volumes of sea water form the moving aqueous layer in the extraction procedure, whereas the lower stationary layer comprises the chelating agents dithizone or 8-hydroxyquinoline dissolved in carbon tetrachloride and chloroform, respectively. Elements are progressively absorbed from the sea water as the aqueous layer passes along the extraction train. Trial experiments with sea water containing additives shows that solutions of 8-hydroxyquinoline and to a lesser extent dithizone are capable of quantitatively retaining a number or elements in a small number of extraction tubes. An experiment has been carried out with a sample of pure sea water from which Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn and La were quantitatively extracted into a solution of 8-hydroxyquinoline in chloroform; the elements were all determined spectrographically. It is considered that the method should have wide applications in the analysis of trace elements in sea water because enrichment factors of 400,000 are obtained for the concentrations of these elements. The technique is simple and comparatively free from contamination dangers.

INTRODUCTION

In an earlier paper,[1] the use of liquid–liquid, discontinuous, counter-current solvent extraction enrichment techniques has been proposed as a new technique for trace analysis in geochemistry. This work has hitherto been confined to extraction of solutions of silicate rocks with solvents lighter than water.

Further investigations have been undertaken with a view to extending the scope of the technique to the enrichment and separation of trace constituents from sea water and other natural waters.

The analysis of trace constituents in sea water has been stimulated by the development of new sensitive analytical tools, such as radiochemical and radioactivation analysis,[2–4] atomic absorption or flame photometry[5–6] and isotope dilution. However, despite these new methods, the analysis of many trace elements in sea water has not proceeded much beyond their detection.[7] Lal *et al.*[8] have employed a method involving *in situ* extraction of certain elements onto a hydrated iron(III) oxide gel, but most existing methods depend on some technique of concentration from a

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* Part I: see reference 1.

relatively large volume of sea water coupled with a suitably sensitive analytical procedure.[9–11] For the analysis of trace elements in many natural waters, a high degree of enrichment can be obtained merely by evaporation of the sample to dryness.[12] However, the high salinity of sea water renders this procedure impracticable and clearly, in such cases, there is scope for new and improved methods of extraction.

In the investigations which are now to be described, it has been shown that counter-current solvent extraction can be used for the enrichment of trace constituents from sea water by the use of solvents heavier than water as the lower stationary phase. The basis of the procedure is a reversal of the normal arrangement of counter-current extraction in that the solvent is placed in the extraction tubes and the aqueous sample forms the upper moving layer. In this way, if the aqueous phase were to consist of a large volume of sea water (8 litres) it should be possible for trace constituents to be progressively absorbed from the aqueous phase as it passes through the extraction tubes. The procedure is rendered possible by the fact that none of the major constituents of sea water is extracted strongly into the organic phase.

EXPERIMENTAL

Apparatus

This was as described previously.[1]

Procedures

Initial experiments were carried out with a 0·05% solution of dithizone in carbon tetrachloride. The aqueous phase consisted of 8 litres of sea water at a pH of 7·5 to which had been added small amounts of the following elements: copper, gold, silver, cadmium, gallium, indium, thallium, tin, lead, bismuth, iron, molybdenum, platinum, iridium, palladium (2 mg each); antimony, vanadium, rhenium, rhodium, osmium (10 mg each); zinc, arsenic (20 mg each); mercury (40 mg). To each of 30 extraction tubes was added 20 ml of the organic mixture. In order to avoid loss of carbon tetrachloride because of its very slight solubility in water, the aqueous phase was pre-equilibrated with this solvent. No precautions were necessary for dithizone because it is virtually insoluble in water.

Counter-current solvent extraction was carried out for a total of 400 transfers and the effluent was collected in a suitable container. Visual observation of the dithizone colour showed a conversion from green to red in the first tubes of the extraction train. This coloured front gradually moved along until after 400 transfers it had reached the 20th tube. At the same time, a brown colour developed in the earlier tubes and had replaced the red colour in the first set of three or four tubes by the end of the experiment. The contents of each tube were examined spectrographically after removal of the aqueous layer. The observations indicated quantitative retention of gold, platinum, palladium, copper, thallium and cobalt in the first few tubes of the extraction train. These results are shown in Fig. 1. Cobalt shows displacement along the extraction train and this indicates probable displacement by stronger complexes of other elements.

The experiment was repeated using sea water containing sufficient hydrochloric acid to make the solution 0·1*M* and containing the usual added elements. In this case, because of the lower stabilities of the chelate complexes at low pH,[14] only platinum, gold and palladium were retained quantitatively.

Because dithizone suffers from the disadvantage of being only slightly soluble in carbon tetrachloride so that very little of it can be employed, a search was made for a more suitable chelating agent. The reagent selected for further experiments was 8-hydroxyquinoline (oxine), because this complexes with a large number of ions[15] and is quite soluble in chloroform. An experiment analogous to those carried out previously, was performed with 1% oxine in chloroform as the organic phase and sea water containing the usual additions as the lighter moving phase. Sea water pre-equilibrated with chloroform was treated with 100 ml of saturated chlorine water, because oxine forms complexes only with the higher oxidation states of most elements. This altered the pH to 7·2. Pre-equilibration of the water was effected by the addition of 100 ml of chloroform to the reservoir, which was in constant movement during the extraction. Counter-current extraction was carried out for 400 transfers (8 litres of aqueous phase) with individual shaking times of 2 min, settling times of 0·5 min and decantation times of 0·5 min. Hence, the operation was completed in 20 hr. The tubes were analysed as before and the results, which are shown in Fig. 1, indicated that at least 16 elements had been quantitatively retained in the first 24 tubes. After passage of 8 litres of water, exactly 50% of the oxine had dissolved

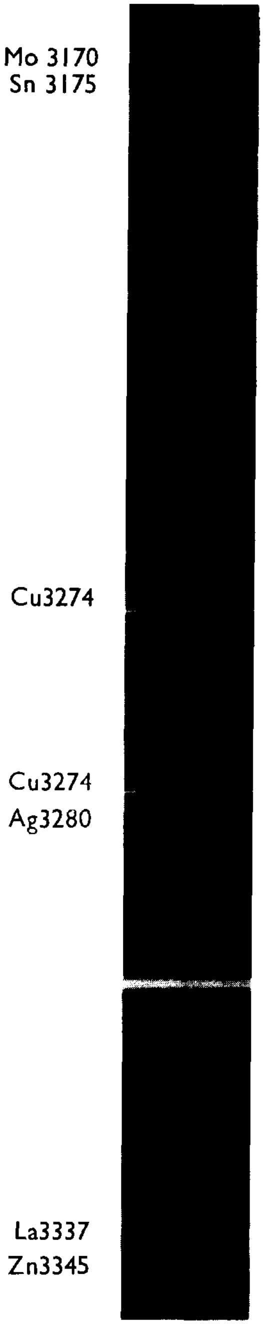

FIG. 2.—Emission spectrum of 8-hydroxyquinoline concentrate from sea water.

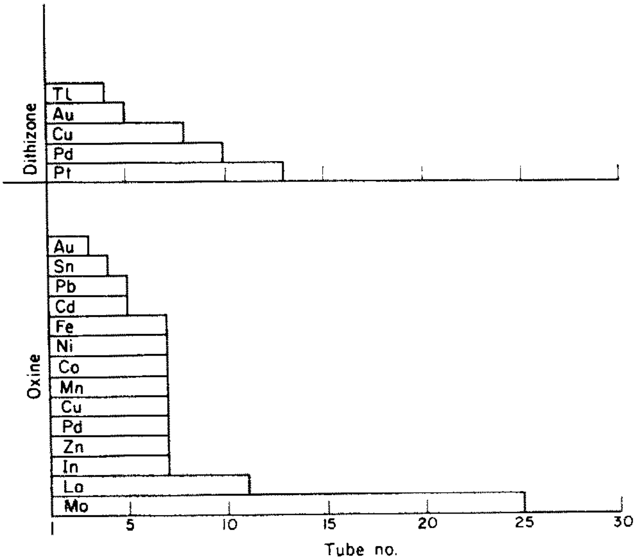

FIG. 1.—Relative retention of elements in extraction tubes containing dithizone or 8-hydroxyquinoline.

out from the organic layer and clearly this will have to be considered in future experiments in relation to the volume of aqueous phase used.

A further experiment was carried out in which pure sea water was used. The conditions were exactly as in the previous trial except that in this instance the organic layers from all the 25 tubes were combined together, taken to dryness and examined spectrographically. The results are shown in Table I.

TABLE I.—ELEMENTS EXTRACTED FROM SEA WATER WITH 8-HYDROXYQUINOLINE IN CHLOROFORM

Element	Pb	Mn	Mo	Sn	Ni	Al	V	Ag	Zn	La
Spectral lines detected, Å	2614 2833	2605 2798	2816 3170	2839 3175	3003 3050	3082 3092	3183 3184	3280 3382	3282 3345	3337 3949

The elements found in the extract were: manganese, lead, molybdenum, tin, nickel, aluminium, vanadium, silver, zinc and lanthanum. Fig. 2 shows an emission spectrum of the sea water extract.

DISCUSSION

The experiments have demonstrated that it is possible to remove selectively trace elements from sea water by use of counter-current solvent extraction with organic phases heavier than water. The total weight of extract from 8 litres of sea water was approximately 20 mg, representing an enrichment factor of 400,000. If this technique were applicable to all trace elements normally found in sea water it should be possible to detect and estimate most of them provided that the extraction technique were coupled with some suitably sensitive analytical system. This is illustrated by consideration of Table II which shows estimated abundances of trace elements in sea water,[7] final concentrations in extract representing an enrichment factor of 400,000 and the spectrographic detection limits of the elements concerned.[16]

If a factor of 10 is allowed to account for variations from expected spectral sensitivities and to allow for sufficient intensities for quantitative determinations, it should be possible to analyse the elements marked with an asterisk in the table by a combination of counter-current extraction and emission spectroscopy. Such calculations are based on a volume of 8 litres of sample and, obviously, greater or lesser volumes may be employed either to increase the sensitivity of the method or to take advantage of a more sensitive system of final analysis.

TABLE II.—EXTRACTION OF TRACE ELEMENTS FROM SEA WATER
(Asterisks indicate elements which should be readily determinable by a combination of the enrichment technique with spectrographic analysis)

	Estimated concn. in sea water (ppm) (Goldberg, 1961)	Concn. if enriched by factor of 400,000, *ppm*	Spectrographic detection limit (ppm) (Ahrens & Taylor, 1960)
Al*	0·01	4000	2
Sc	0·00004	1·6	2
Ti*	0·001	400	10
V*	0·002	800	5
Cr	0·00005	2	1
Mn*	0·002	800	10
Fe*	0·01	4000	5
Co	0·0005	20	10
Ni*	0·002	800	5
Cu*	0·003	1200	0·5
Zn*	0·01	4000	3
Ga	0·00003	1·2	3
Ge	0·00007	28	5
As*	0·003	1200	100
Rb*	0·12	4800	1
Sr*	8	800,000	5
Y	0·0003	12	10
Nb	0·00001	0·4	30
Mo*	0·01	4000	5
Ag*	0·0003	12	0·5
Cd	0·0001	4	10
In	0·02	8000	1
Sn*	0·003	120	10
Sb	0·0005	20	20
Cs*	0·0005	20	2
Ba*	0·03	12,000	5
La	0·0003	12	10
Ce	0·0004	16	500
W	0·0001	4	20
Au	0·000004	0·2	10
Hg	0·00003	1·2	100
Tl	0·00001	0·4	1
Pb	0·0001	4	5
Bi	0·0002	8	20
Th	0·0037	28	100
U	0·003	120	100

Some of the advantages of counter-current extraction enrichment techniques are enumerated below.

(a) Very high enrichments of the order of 400,000 can be obtained from a volume of approximately 8 litres of sea water.

(b) There is little risk of serious contamination because only two reagents are used, both of which can be easily purified.

(c) The versatility of the method is apparently high. For example, it should be possible to incorporate several chelating agents in the extraction train, either together or in separate tubes in order to increase the number of elements extracted. Greater selectivity can be obtained by varying the pH (as in the case of the dithizone experiments) or alteration of the nature of the chelating agent.

Against these advantages must be set the fact that a fully-automatic counter-current extraction apparatus is necessary for the technique. Such units are relatively expensive but have many other uses, such as in organic separations for which they were originally designed. They can also be used for separation and enrichment of trace elements in silicate rocks using solvents lighter than water.[1]

Although an operating time of 20 hr is comparatively long for one determination, this makes little imposition on the operator's time because the apparatus is fully automatic.

In spite of the fact that only two reagents are used, the sensitivity of the method is likely to be limited by the reagent and container blanks. Blanks carried out on the purified reagents* showed only slight traces of lead among those elements under study. In cases where impurities often extracted from laboratory glassware (*e.g.*, iron, lead, *etc.*) are themselves present in very low concentrations in sea water, the sensitivity of the method will be lowered. In most cases, however, very high enrichments should be capable of achievement. The magnitude of the blank for a particular element could be determined by re-extraction of a once-extracted sample of sea water.

Work is at present being carried out on the application of the method to the quantitative determination of a number of trace elements in specimens of sea water from the oceans around New Zealand.

Acknowledgements—The author is indebted to the New Zealand University Research Committee and the Nuffield Foundation for grants towards the establishment of a spectrographic laboratory at Massey University. He is also indebted to Chemistry Division D.S.I.R., New Zealand for the loan of a 120-tube fully-automatic counter-current extraction apparatus.

Zusammenfassung—Ein neues analytisches Verfahren zur Bestimmung von Spurenelementen in Meerwasser und anderen natürlichen Wässern wurde entwickelt. Es besteht in einer diskontinuierlichen Gegenstrom-flüssig-flüssig-Extraktion mit schwereren Lösungsmitteln als Wasser. Relativ große Meerwasser-Volumina bildeten die bewegte wäßrige Schicht beim Extraktionsvorgang; die stationäre Unterphase bildeten die Chelatbildner Dithizon oder Oxin in Tetrachlorkohlenstoff bzw. Chloroform. Im Verlauf der Wanderung der wäßrigen Phase durch die Extraktionsbatterie wurden einige Elemente immer mehr aus dem Wasser extrahiert. Tests mit Zusätze enthaltendem Meerwasser zeigten, daß Lösungen von Oxin und, in geringerem Ausmaß, von Dithizon eine Anzahl von Elementen in wenigen Extraktionsstufen quantitativ zurückhalten können. Ein Versuch wurde ausgeführt mit einer Probe von reinem Meerwasser; aus diesem wurden Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn und La quantitativ in eine Lösung von 8-Hydroxychinolin in Chloroform extrahiert. Alle Elemente wurden spektrochemisch bestimmt. Es wird erörtert, daß die Methode bei der Analyse von Spurenelementen in Meerwasser zahlreiche Anwendungsmöglichkeiten haben wird, da Anreicherungsfaktoren bis 400,000 für diese Elemente gefunden wurden. Das Verfahren ist einfach und relativ frei von Gefahren der Verunreinigung.

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* All chemicals except oxine were purified by distillation. Oxine was purified by vacuum distillation.

Résumé—On a élaboré une nouvelle technique analytique pour le dosage d'éléments à l'état de traces dans l'eau de mer et autres eaux naturelles. La méthode consiste en l'emploi d'une extraction par solvant en milieu liquide, à contre-courant, avec des solvants plus denses que l'eau. Des volumes relativement importantes d'eau de mer forment, dans le procédé d'extraction, la couche aqueuse mobile, cependant que la couche stationaire inférieure est constituée par les agents chélatants dithizone ou oxine, en solution respectivement dans le tétrachlorure de carbone et le chloroforme. Les éléments sont progressivement absorbés de l'eau de mer, tandis que la couche aqueuse traverse l'ensemble d'extraction. Des essais de sondage avec l'eau de mer contenant des additifs ont montré que les solutions d'oxine et, à un degré moindre, de dithizone, sont capables de retenir quantitativement un certain nombre d'éléments dans un petit nombre de tubes d'extraction. Une expérience a été menée avec un échantillon d'eau de mer pure, de laquelle on a extrait quantitativement Mn, Pb, Mo, Sn, Ni, Al, V, Ag, Zn et La dans une solution de 8-hydroxyquinoléine en chloroforme. Les éléments ont tous été dosés spectrochimiquement. On considère que la méthode devrait avoir de larges applications dans l'analyse d'éléments à l'état de traces dans l'eau de mer, des facteurs d'enrichissement de 400,000 ayant été obtenus pour les concentrations de ces éléments. La technique est simple et comparativement exempte de dangers de contamination.

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SPECTROFLUORIMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF THALLIUM

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Summary—Thallium(I) in a concentrated hydrochloric acid-potassium chloride medium shows a violet fluorescence with an excitation maximum at 250 mμ and a fluorescence emission maximum at 430 mμ. This has been applied for the spectrofluorimetric determination of thallium down to the range 0·01 to 0·08 ppm. The interference of 53 ions has been examined at the 100-fold molar excess level. Hydrogen peroxide oxidation to thallium(III) and extraction from 1·5*M* hydrochloric acid into diethyl ether, followed by sulphur dioxide reduction, separates microgram amounts of thallium quantitatively from all interfering cations investigated except antimony(V), bismuth, gold and platinum(IV). Large amounts ($\times 10^6$) of sulphate do not interfere.

SEVERAL colorimetric methods are available for the determination of small amounts of thallium in solution; these utilise the reagents Methyl Violet,[1] Rhodamine B,[2] iodine,[3] dithizone,[4] thionalide[5] and 8-hydroxyquinoline.[6] Onishi[7] has proposed a fluorimetric method for the determination of 2-20 μg of thallium in which the fluorescence of Rhodamine B chlorothallate in benzene solution is measured at 560 mμ. In this method the thallium(III) is extracted into chloroform as thallium dithizonate and then into benzene as Rhodamine B chlorothallate.

The present paper describes the determination of microgram amounts of thallium using the violet fluorescence of the thallium(I) ion in the presence of excess chloride ion in concentrated hydrochloric acid. This fluorescence was first reported by Pringsheim and Vogels[8] and subsequently applied to the detection of thallium in ores and other minerals by Sill and Peterson.[9]* The violet fluorescence was attributed to the existence of the complex anionic $TlCl_3^{2-}$ species, with neither H_2TlCl_3 (formed in the presence of considerable acid) nor thallium ion showing any fluorescence. The fluorescence can only be obtained in a medium containing a vast excess of both alkali chloride and hydrochloric acid. It is, therefore, not possible to employ the mole-ratio, slope-ratio and continuous variations procedures to elucidate the nature of the fluorescent species. The fluorescence emission is measured at 430 mμ with an excitation wavelength of 250 mμ in a concentrated hydrochloric acid-potassium chloride medium. Optimum conditions have been established for the determination and the effect of numerous ions has been investigated. An extraction system has been devised which readily separates thallium from the more important interfering ions. Cupferron, 8-hydroxyquinoline and acetylacetone extraction procedures were examined before it was decided that the most efficient and selective separation could be obtained by oxidation of thallium(I) to thallium(III) with hydrogen peroxide

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* After preparation of this manuscript we noted a recent paper by R. Bock and E. Zimmer (*Z. analyt. Chem.*, 1963, **198**, 170) describing the spectrofluorimetry of thallium(I) in strong sodium chloride solution in the absence of hydrochloric acid. Their note contains no interference data and does not describe an analytical procedure.

followed by extraction into diethyl ether from the optimum concentration of hydrochloric acid; thallium(I) cannot be extracted quantitatively from hydrochloric acid into diethyl ether. In the other extraction procedures examined it is difficult to remove the thallium from its cupferron, oxine or acetylacetone complex before the determination. Extraction from 1·5*M* hydrochloric acid separates thallium(III) almost quantitatively from all foreign ions investigated except gold, bismuth, platinum(IV) and antimony(V), which co-extract to varying extents. The efficiency of the separation is further improved by washing the ether extract with an aliquot of 1·5*M* hydrochloric acid which back-extracts traces of, for example, iron(III), which extract with the thallium(III) to an extent of <1%. The ether phase is then evaporated to dryness and the thallium(III) reduced to the univalent state by gaseous sulphur dioxide before the determination. Although the extraction of thallium(III) chloride into diethyl ether has been applied on a macro scale,[10] the present investigation shows that it can be used successfully for microgram amounts of thallium, with an extraction efficiency of *ca.* 98% in the range of 1 to 8 μg of thallium.

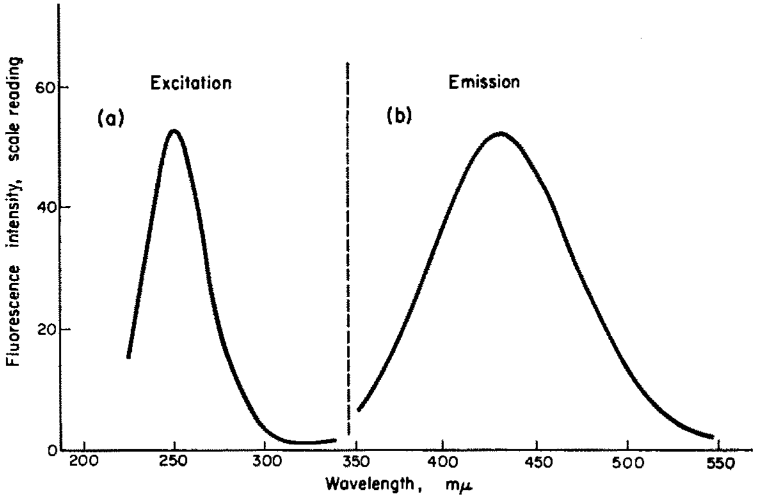

Fig. 1.—Excitation and emission spectra (uncorrected) of thallium(I) complex in HCl-KCl solution [Tl(I) concentration: 2·5 × $10^{-4}M$; sensitivity scale: × 10]:

(A) Emission measured at 430 mμ.

(B) Exciting wavelength set at 250 mμ.

Spectral characteristics

Fig. 1 shows the excitation and emission spectra for the thallium(I) ion in hydrochloric acid-potassium chloride solution. These spectra are uncorrected for variations in the emission characteristics of the lamp and the response characteristics of the photomultiplier. The relevant correction curves are given in Fig. 2. Correction methods are dealt with fully elsewhere by Parker and Rees[11] and their paper may be consulted for guidance. The excitation maximum occurs at 250 mμ and the fluorescent emission maximum at 430 mμ. Fig. 3. shows the emission spectra of more dilute

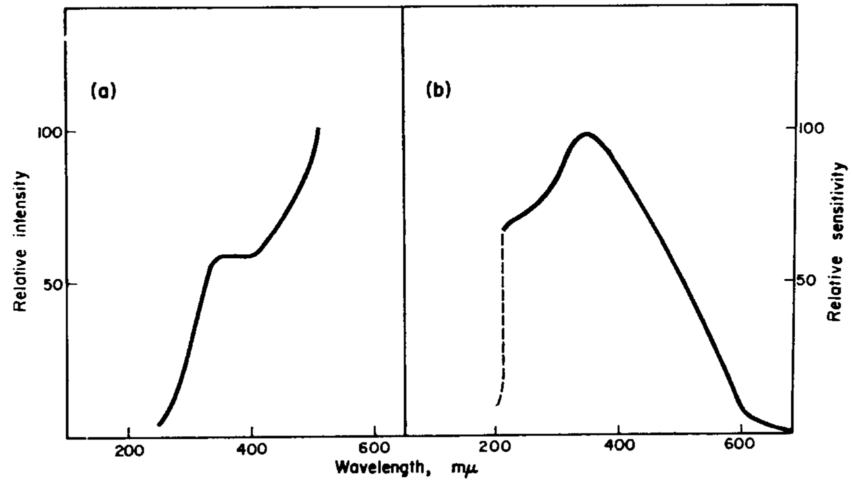

FIG. 2.—Correction curves for variations of lamp intensity and photomultiplier sensitivity with wavelength:

(A) Spectral characteristics of lamp + excitation monochromator (relative intensity against wavelength).

(B) Photomultipler characteristics (relative sensitivity against wavelength).

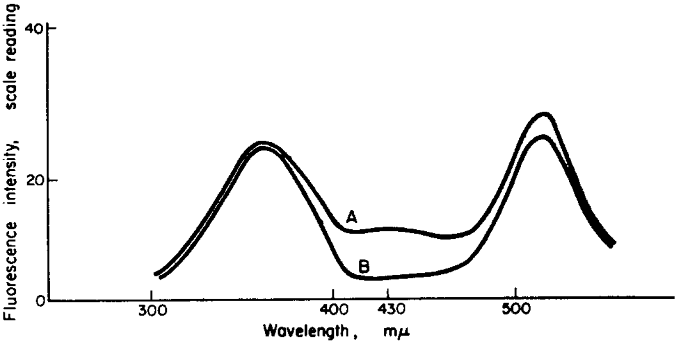

FIG. 3.—Emission spectra (uncorrected) in HCl-KCl solution (exciting wavelength set at 250 mμ; sensitivity scale: × 0·1):

(A) Tl(I) concentration 4 × $10^{-7}M$.

(B) No Tl(I) present.

solutions (uncorrected) at much increased sensitivity with wide (20 mμ) slits and no protective filters. The peaks at approximately 510 mμ and 360 mμ are attributed to second order diffraction from the analysing (grating) monochromator and stray radiation within the monochromators. The *tails* of these peaks make up the blank *fluorescence* at 430 mμ. The signal at this wavelength is then directly proportional to the thallium concentration. Calibration curves prepared at this level of concentration pass above the origin for the reasons discussed.

Effect of hydrochloric acid and potassium chloride concentrations

The optimum amounts of hydrochloric acid and potassium chloride for the determination were established by varying their concentrations dependently. In a solution 3·3*M* in hydrochloric acid, the fluorescence intensity increases with increase of potassium chloride concentration up to 0·8*M*. Above this level, the fluorescence intensity remains constant and potassium chloride tends to precipitate by the common ion effect. It was also shown that in 0·8*M* potassium chloride, a 3·3*M* hydrochloric acid concentration is required to produce maximum fluorescence. Thus, the best solution should be approximately 3·3*M* in hydrochloric acid and 0·8*M* in potassium chloride, *i.e.*, 100 ml of solution contains 30 ml of concentrated hydrochloric acid and 20 ml of saturated potassium chloride.

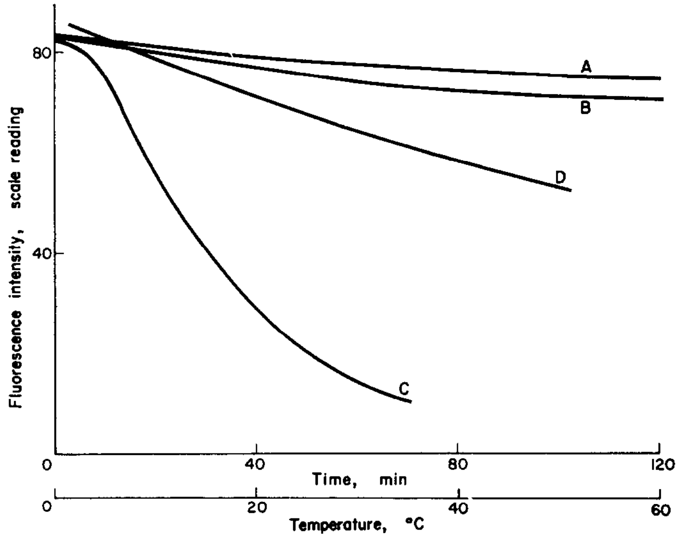

FIG. 4.—Effect of time and temperature on fluorescence intensity:

(A) Variation of fluorescence with time: standing in darkness.
(B) Variation of fluorescence with time: standing in normal laboratory conditions.
(C) Variation of fluorescence with time: continuous irradiation at 250 $m\mu$.
(D) Variation of fluorescence with temperature.

A slight reduction in the fluorescence intensity ($<10\%$) was observed when ammonium chloride or sodium chloride was substituted for potassium chloride in the recommended procedure.

Effect of time

Thallium(I) in a strongly acid medium is oxidised by air to thallium(III) and this process is accelerated by ultraviolet radiation. An $8 \times 10^{-7}M$ solution of thallium(I) prepared by the recommended procedure showed an average reduction in fluorescence intensity of 10% after standing for 2 hr in darkness, and a reduction of 14% after standing for 2 hr under normal laboratory conditions, *i.e.*, under fluorescent tube lighting, while continuous irradiation of the solution at 250 $m\mu$ in the spectrofluorimeter completely destroyed fluorescence within 1 hr (*cf.* Fig. 4).

Effect of temperature

Between the limits of the temperature range investigated, *i.e.*, 3–43°, a decrease of fluorescence intensity with increase in temperature of development was found which corresponds to a temperature coefficient of approximately 1 %/°C (*cf.* Fig. 4). Under normal laboratory conditions, all measurements of the thallium fluorescence were made at 23 ±3°, and the observed fluorescence intensities were compared with standards prepared simultaneously, so that the existence of this temperature coefficient did not alter the validity of the results obtained. However, care should be taken to minimise generation of heat of mixing between concentrated hydrochloric acid and water during the preparation of samples for measurement, by adding the acid to as large a volume of water as possible and thoroughly mixing immediately.

Precision

The precision of the method at its maximum sensitivity is compounded of (a) the chemical precision, and (b) the instrumental precision. These were, therefore estimated separately by multiple determinations, (a) using sufficient thallium (80 μg) to give readings on a less sensitive scale (× 0·1) where instrumental *noise* is negligible; and (b) using 8 μg of thallium and measuring directly on the most sensitive scale (× 0·01) where instrumental *noise* is appreciable, without treating the solution by the extraction procedure.

These experiments indicated a chemical precision of ±1·3% and an instrumental precision of ±1·6%.

Accuracy

The data in Table I were obtained from the results of the analysis of solutions for thallium by the recommended procedure (see *Experimental*).

TABLE I.—ANALYSIS OF THALLIUM(I) SOLUTIONS TREATED AS UNKNOWN SAMPLES

Sample	Thallium, μg		Error		Foreign ions present, μg
	Present	Found	μg	%	
1	4·90	4·57	−0·33	−6·6	Fe(III) (5600)
2	6·92	6·72	−0·20	−2·9	Fe(III) (5600)
3	3·87	3·75	−0·12	−3·1	Fe(III) (5600)
4	3·26	3·26	—	—	Fe(III) (5600)
5	5·91	6·13	+0·22	+3·7	Cu(II) (630), Hg(II) (2000)
6	3·67	3·77	+0·10	+2·8	Cu(II) (630), Hg(II) (2000)
7	3·87	4·04	+0·17	+4·4	Cu(II) (630), Hg(II) (2000)
8	4·08	3·89	−0·19	−4·7	Al (2700), Zn (6500)
9	7·14	6·72	−0·42	−5·9	Al (2700), Zn (6500)
10	5·91	5·87	−0·04	−0·6	Be (900), Mg (2400)
11	7·95	7·78	−0·17	−2·1	Be (900), Mg (2400)
12	3·87	3·75	−0·12	−3·1	Al (2700), Ba (13700)
13	6·31	6·11	−0·20	−3·2	Al (2700), Ba (13700)
14	2·24	2·24	—	—	Be (900), Mg (2400)
15	4·28	4·50	+0·22	+5·2	Be (900), Mg (2400)
16	5·10	4·87	−0·23	−4·5	Co (5900), Fe(III) (5600)
17	7·14	6·68	−0·46	−6·5	Co (5900), Fe(III) (5600)

Effect of foreign ions

The effect of 53 foreign ions on the thallium fluorescence in pure solution was studied. None of the cations investigated produced a fluorescence similar to that of thallium, but several, when present in relatively large concentrations, showed fluorescence at different wavelengths, *e.g.*, lead (excitation maximum 290 mμ/fluorescence maximum 480 mμ), copper(I) (390/460 mμ), tin(II) (270/480 mμ) and cerium(III) (250/350 mμ). The effect of a 100-fold molar excess of each ion on the determination of 8 μg of thallium was investigated. After consideration of the reproducibility of the determination of 8 μg of thallium in pure solution, ions were considered to interfere at this level when they caused a variation of fluorescence intensity of $\geqslant \pm 5\%$. The investigation revealed that the following ions do not interfere under the above conditions: aluminium, ammonium, arsenic(III), arsenic(V), barium, beryllium, calcium, cadmium, cobalt, chromium(III), gallium, indium, lead, lithium, magnesium, manganese(II), nickel, scandium, selenium(IV), silver, sodium strontium, thorium, tin(II), titanium(IV), tungsten(VI), vanadium(IV), zinc, zirconium, bromide, fluoride, thiocyanate, nitrate, sulphate and tartrate. A 100-fold excess of the following ions caused the error in the fluorescence intensity given in parenthesis: antimony(V) (−49%), bismuth (−69%), cerium(III) (+900%), cerium(IV) (+900%), copper(II) (−21%), gold (−100%), iron(II) (−25%), iron(III) (−92%), mercury(II) (−28%), molybdenum(VI) (−100%), platinum(IV) (−92%), tellurium(IV) (−32%), tin(IV) (−59%), uranium(VI) (−18%), vanadium(V) (−20%), iodide (+13%), bromate (−100%) and iodate (−100%).

The interfering cations listed above were then taken, normally in large excesses over 8 μg of thallium, through the recommended extraction procedure. The results are shown in Table II.

TABLE II

Cation	Molar excess	Variation in fluorescence intensity[a]
Au	10	−68%
Bi	500	−20%
Pt(IV)	200	−14%
Sb(V)	2500	−100%
Ce(III)	500	$\leqslant \pm 5\%$
Ce(IV)	500	$\leqslant \pm 5\%$
Cu(II)	2500	$\leqslant \pm 5\%$
Fe(II)	2500	$\leqslant \pm 5\%$
Fe(III)	2500	$\leqslant \pm 5\%$
Hg(II)	250	$\leqslant \pm 5\%$
Sn(IV)	250	$\leqslant \pm 5\%$
Te(IV)	2500	$\leqslant \pm 5\%$
U(VI)	500	$\leqslant \pm 5\%$
V(V)	2500	$\leqslant \pm 5\%$

[a] With respect to thallium(I) standard.

Because this method is likely to find application in the determination of thallium in biological and other materials which require dissolution or destruction before determination, the effect of the presence of a large excess (*ca.* 10^6-fold) of sulphate and nitrate on the extraction and determination was investigated. The presence of sulphate ions has no effect on the method, but nitrate ions interfere at this level by co-extraction into diethyl ether with the thallium(III). Large excesses of nitrate (>100-fold molar excess over thallium) must, therefore, be removed by fuming the solution with hydrochloric acid before the determination.

EXPERIMENTAL

Reagents

$10^{-3}M$ *Thallium(I) solution.* Dissolve 0·2525 g of analytical reagent grade Tl_2SO_4 (Hopkin and Williams, Chadwell Heath, Essex, England) in water and dilute to 1 litre, using water from an all-glass distillation apparatus. This stock solution was diluted to $10^{-5}M$ as required.

Hydrochloric acid. Analytical-reagent grade (Hopkin and Williams) was used. Prepare a $2M$ solution by diluting 45 ml of the concentrated acid to 250 ml with water.

Saturated potassium chloride solution. Dissolve *ca.* 150 g of reagent grade potassium chloride (Hopkin and Williams) in 500 ml of boiling water, filter the solution while warm and allow to crystallise on cooling. The saturated solution is approximately 4·1M in potassium chloride and was standardised by Volhard's method.

Hydrogen peroxide. Prepare 6% (20-vol.) solution from general purpose reagent (Hopkin and Williams).

Diethyl ether. Solvent grade (Hopkin and Williams)

Sulphur dioxide. Liquified (Hopkin and Williams)

Foreign ions. 0·1M, 0·02M or 0·01M Solutions of analytical-reagent grade salts were used.

Apparatus

Fluorescence measurements were made with a Farrand spectrofluorimeter (Farrand Optical Co. Cat. No. 104244) in which grating monochromators are used to isolate both the exciting and fluorescent radiation, and fitted with a 150-W xenon arc lamp (Hanovia Div. Cat. No. 901 C-1), an RCA IP 28 photomultiplier and a Honeywell-Brown recorder. Fused quartz cells (10 × 20 × 50 mm) were used throughout the work. Fluorescence was measured at right angles to the incident light such that the mean solution path-length of the exciting radiation is 5 mm and that of the fluorescent emission is 10 mm. 20-Mμ bandwidth slits were used in both the exciting and analysing monochromators, and no filters were used during these experiments.

Determination of thallium

Calibration curve. To 20 ml of saturated potassium chloride solution, 30 ml of water and 30 ml of concentrated hydrochloric acid in a 100-ml volumetric flask, transfer accurately between 0·5 and 4·0 ml of standard thallium(I) solution ($10^{-5}M \equiv 2{\cdot}04\ \mu g/ml$) and dilute to volume with water. Allow the solutions to stand for 15 min, then measure the intensity of the fluorescence at 430 mμ and an excitation wavelength of 250 mμ. The plot of fluorescence intensity against thallium concentration (0·01–0·08 ppm) is a straight line and passes slightly above the origin. Linearity extends beyond this upper limit to a final concentration of 2 ppm of thallium, *i.e.*, 200 μg in 100 ml of aqueous solution. Prepare and measure two standards with each group of samples, using 0 and 4 ml of the thallium(I) solution (2·04 μg/ml), respectively.

Extraction procedure

Transfer an aliquot of standard thallium(I) solution (0·5–4·0 ml of $10^{-5}M$ solution) to a separating funnel containing 15 ml of 2M hydrochloric acid and 1 ml of 20-volume hydrogen peroxide. Extract once into 25 ml of diethyl ether and discard the aqueous phase. Wash the organic phase with 10 ml of 1·5M hydrochloric acid and again discard the aqueous phase. Transfer the ether phase to a 100-ml beaker, rinse the separating funnel with a further 10 ml of ether, combine the ether extracts and evaporate to dryness on a water-bath. Dissolve the residue in 50 ml of water, pass gaseous sulphur dioxide into the solution for 5 sec, then evaporate the solution to a volume of 10 ml, after the addition of 1 ml of concentrated hydrochloric acid to assist the removal of sulphur dioxide (Note). Cool the solution, transfer to a 100-ml standard flask containing 20 ml of saturated potassium chloride solution, add 30 ml of concentrated hydrochloric acid, dilute to volume with distilled water and measure the fluorescence after 15 min at 250/430 mμ.

Note. It is essential to ensure complete removal of sulphur dioxide because it has a strong quenching action on the $TlCl_3^{2-}$ ion fluorescence.

Acknowledgment—We wish to thank the Department of Scientific and Industrial Research for the provision of a grant to one of us (T. S. W.) for the purchase of the spectrofluorimeter used in this work and also for providing a Research Studentship to another (C. W.).

Résumé—Le thallium (I), en milieu acide chlorhydrique concentré—chlorure de potassium, présente une fluorescence violette, avec maximum d'excitation à 250 mμ et maximum d'émission de fluorescence à 430 mμ. On a appliqué ce fait au dosage spectrofluorimétrique du thallium jusqu'à des teneurs de 0,01 à 0,08 p.p.m. On a étudié les interférences de 53 ions à des concentrations molaires 100 fois plus élevées. L'oxydation par l'eau oxygénée en thallium (III), et l'extraction en éther diéthylique, à partir d'une solution 1,5M en acide chlorhydrique, suivie de réduction au moyen d'anhydride sulfureux, permettent de séparer quantitativement des quantités de thallium de l'ordre du microgramme de tous les cations interférants étudiés, à l'exception de l'antimoine (V), du bismuth, de l'or et du platine (IV). Des quantités importantes de sulfate (× 10^6) n'interfèrent pas.

Zusammenfassung—Thallium (I) gibt in einem Medium aus konzentrierter Salzsäure und Kaliumchlorid eine violette Fluoreszenz mit einem Anregungsmaximum bei 250 mμ und einem Emissionsmaximum bei 430 mμ. Diese Erscheinung wurde zur spektrofluorimetrischen Bestimmung von Thallium bis herunter zum Konzentrationsbereich 0,01–0,08 p.p.m. ausgenutzt. Die Störung von 53 Ionen wurde bei 100-fachem molarem Überschuß untersucht. Oxydation mit Wasserstoffperoxyd und Extraktion aus 1,5 *M* Salzsäure in Diäthyläther mit nachfolgender Reduktion mit Schwefeldioxyd trennt Mikrogrammengen Thallium quantitativ von allen untersuchten störenden Kationen außer Antimon(V), Wismut, Platin(IV) und Gold. 10^6-facher Überschuß von Sulfat stört nicht.

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DÜNNSCHICHT-CHROMATOGRAPHIE—XV*

TRENNUNG VON TERPEN- UND SESQUITERPENALKOHOLEN AUF SILBERNITRAT-KIESELGEL-SCHICHTEN

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Zusammenfassung—Gemische von C_{10}-, C_{15}- und C_{20}- Alkoholen lassen sich auf normalen Kieselgel-Schichten nicht trennen. Auf paraffin-imprägnierten Schichten wurde eine Trennung in Gruppen mit gleicher Kohlenstoffatomzahl möglich. Mit der Gradient-DC konnte nun festgestellt werden, daß mit zunehmender $AgNO_3$-Imprägnierung einer Kieselgel H-Schicht die Trennung derartiger Gemische gelingt. Der optimale und ökonomische $AgNO_3$-Gehalt der Schicht liegt bei 3%. Als Fließmittel dient ein Gemisch von Methylenchlorid-Chloroform-Äthylacetat-n-Propanol (50 + 50 + 5 + 5 V/V). Der Trenneffekt lässt sich durch eine Mehrfachentwicklung noch verbessern.

AUF normalen Kieselgel- oder Aluminiumoxid-Schichten lassen sich Gemische von Mono-, Sesqui- und Diterpenalkoholen nicht oder nur unzureichend trennen. Einen Fortschritt brachte die in unserem Arbeitskreis von Jork hierzu angewendete "reversed phase"-Technik.[1] Hat man die Alkohole aus einem ätherischen Öl abgetrennt, so gelingt es mit dieser Technik schnell, festzustellen, ob C_{10}-, und/oder C_{15}-Alkohole vorliegen. Auch bei der von uns seit Jahren durchgeführten Kombinationsanalyse GLC-TLC ermöglichen die paraffin-imprägnierten Schichten eindeutige Entscheidungen im Ultramikrobereich. Es erschien jedoch wünschenswert, neben der Gasphasenchromatographie (GLC), die sich für die Trennung von Monoterpenalkohol-Gemischen bestens eignet,[2] eine weitere dünnschicht-chromatographische Methode zu haben, mit der man Gemische von Terpen-, insbesondere aber von Sesquiterpenalkoholen zerlegen kann.

Es ist bekannt, daß man in manchen Fällen durch eine Imprägnierung des Adsorbens mit Verbindungen, die Koordinations-, Chelatkomplexe oder Einschlußverbindungen zu bilden vermögen, substanzspezifischere Trennungen erreichen kann. So wird auf dem Lipid-Gebiet seit einigen Jahren bei der Trennung von Fettsäureestern unterschiedlichen Sättigungsgrades von deren Neigung, mit Silberionen labile Koordinationskomplexe zu bilden, Gebrauch gemacht. Das von Winstein und Lucas[3] zur Verteilungstrennung zwischen zwei nicht mischbaren flüssigen Phasen ausgearbeitete Verfahren wurde dann mit gütem Erfolg von de Vries[4] und Morris[5] auf die Kolonnen- und die Dünnschicht-Chromatographie übertragen. Inzwischen liegen hierüber zahlreiche Arbeiten vor.

Nachdem zunächst festgestellt wurde, daß sich bei Verwendung geeigneter Fließmittel auf Kieselgel-Schichten, die mit 20% Silbernitrat imprägniert waren, Ansätze

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* XIV. Mitteilung: *Chem. Ing. Tech.*, 1964, **36**, 941.

zu einer Trennung von Terpenalkoholen ergaben, wurde der Einfluß verschiedenartiger Sorptionsmittel und Fließmittel, sowie der Imprägnierungsgrad untersucht. Über die Einzelergebnisse dieser Untersuchungen wird später berichtet. Hier soll nur über die daraus resultierenden optimalen Versuchsbedingungen berichtet werden. Eine wertvolle Hilfe beim Studium des Einflusses der Silbernitrat-Konzentration auf den Trenneffekt war uns die Gradient-DC.[6] Es wurden zunächst Gradient-Schichten mit einer Silbernitrat-Konzentration von 0 bis 25% hergestellt und quer zum Gradient chromatographiert. Nachdem sich zeigte, daß eine Verbesserung der Trennung bei einer Konzentration von über 3% nicht mehr auftritt, wurden Schichten mit einem $AgNO_3$-Gradient von 0–2,5% verwendet. Wie die Abb. 1 zeigt, beginnt bereits bei einer Konzentration von 1,5% $AgNO_3$ die Abtrennung des Nerolidols vom Geraniol. Sie verbessert sich mit der Zunahme der Silbernitrat-Konzentration bis 2% und bleibt dann nahezu gleich. Auch das kritische Paar Guajol/Borneol zeigt ein ähnliches Verhalten. Bei allen weiteren Versuchen wurde nun auf uniformen Kieselgel H-Schichten, die mit 3% Silbernitrat imprägniert waren, gearbeitet.

Von zahlreichen getesteten Fließmitteln ergaben Gemische von chlorierten Kohlenwasserstoffen, denen ein oder zwei stärker polare Lösungsmittel in kleinen Mengen zugesetzt waren, den besten Trennerfolg. Allerdings ließ sich ein aus 9 Alkoholen bestehendes Gemisch (s. Abb. 2/I) nicht vollständig trennen; Borneol, Daucol und Cuminalkohol liegen hier praktisch zusammen. Erst durch eine Mehrfachentwicklung mit Fließmitteln unterschiedlicher Polarität konnten auch diese 3 Alkohole gut getrennt werden (Abb. 2/III). Für die erste Entwicklung wurde Methylenchlorid-Chloroform-Äthylacetat- n-Propanol (50 + 50 + 5 + 5 V/V) und für die zweite und dritte Entwicklung Methylenchlorid-Chloroform (40 + 60 V/V) verwendet. Es sei jedoch nicht verschwiegen, daß sich unter den bisherigen Versuchsbedingungen eine Reihe der uns zur Verfügung stehenden Terpen- und Sesquiterpenalkohole nicht trennen lassen, so liegen z.B. Cedrol und Maalialkohol, ferner Guajol, Citronellol, Terpineol und Zimtalkohol auf einer Höhe.

Um nun anhand einer größeren Anzahl von Alkoholen unterschiedlichen Sättigungsgrades zu allgemeineren Aussagen zu kommen, wurden zahlreiche, im Handel erhältliche Terpenalkohole und weitere $C_5 - C_{20}$ – Alkohole in die Versuche mit einbezogen. Zunächst wurden sie mit der vorstehend beschriebenen Methode auf ihre Einheitlichkeit geprüft. Hierbei ergab sich, dass zumeist Gemische vorlagen. Zur Zeit laufen Versuche, diese Produkte auf Silbernitrat-Kieselgel-Kolonnen in präparativem Maßstab zu trennen.

Zusammenfassend lässt sich schon beim augenblicklichen Stand der Untersuchungen feststellen, daß die Anwendung von Silbernitrat-Kieselgel-Schichten ein wertvolles Hilfsmittel zur Auftrennung von verschiedenartigen Alkoholen ist. In unserem Arbeitskreis hat sie bei zahlreichen Problemen ihren praktischen Nutzen gegezeigt, so z.B., um den Hydrierungsverlauf von ungesättigten Alkoholen zu verfolgen. Auf die vorteilhafte Verwendung zur Kontrolle der Identität und Reinheit wurde bereits hingewiesen. Darüberhinaus konnten $AgNO_3$-Kieselgel-Schichten mit Erfolg bei anderen Stoffklassen eingesetzt werden und es gelang u.a., Allyl- von Propenylmethoxybenzolen sauber zu trennen.[7]

Die Versuche werden fortgesetzt. Im Rahmen einer späteren Arbeit sollen dann die Ergebnisse anhand eines größeren Materials diskutiert und weitere Anwendungsmöglichkeiten aufgezeigt werden.

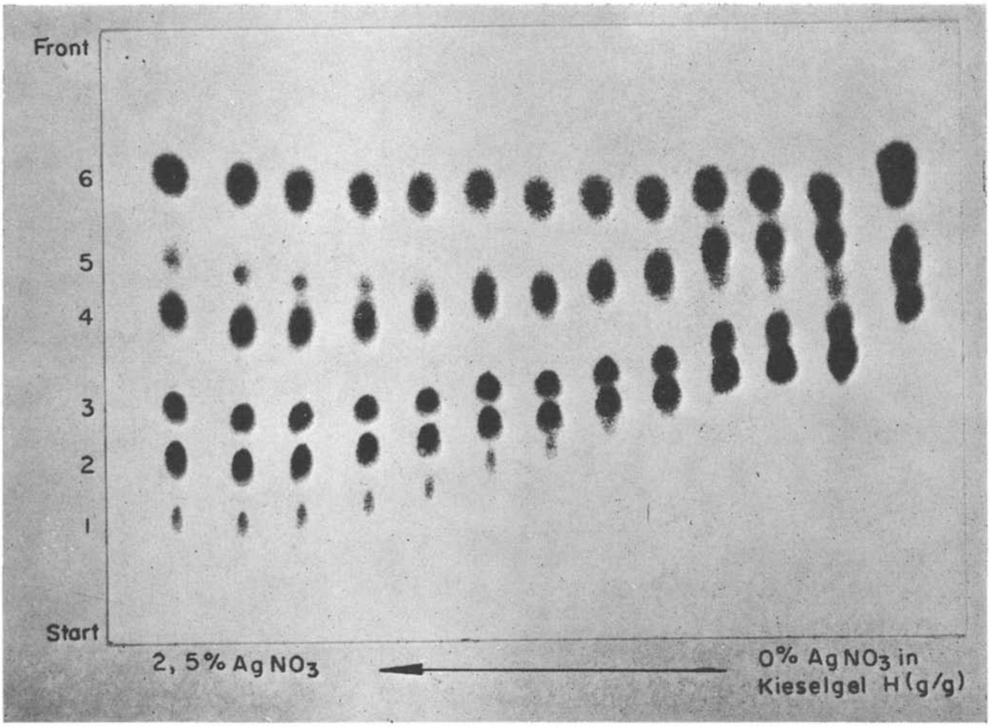

ABB. 1.—Gradient-Schicht-Chromatogramm zur Ermittlung der optimalen $AgNO_3$-Konzentration
(Bezifferung siehe Abb. 2; Einzelheiten im experimentellen Teil).

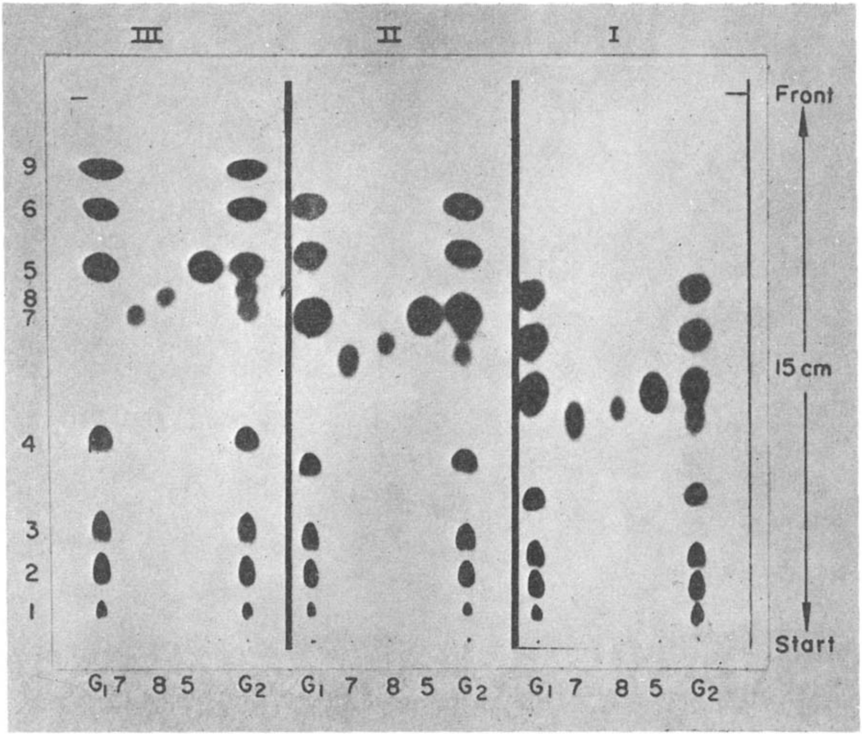

Abb. 2.—Mehrfachentwicklung zur Trennung eines Alkoholgemisches auf einer uniformen $AgNO_3$-Kieselgel-Schicht:

I: Einmalige Entwicklung mit Fließmittel I;
II u. III: Zweite bzw. dritte Entwicklung mit Fließmittel II.

(1	Nerolidol	6	Cedrol
2	Geraniol	7	Cuminalkohol
3	Nerol	8	Daucol
4	Guajol	9	Carotol
5	Borneol	G_2	Gemisch 1–9
		G_1	Gemisch 1–6, 9)

EXPERIMENTELLER TEIL

Herstellung der uniformen Silbernitrat-Kieselgel H-Schichten

Das Beschichten der 20 × 20 cm DC-Platten erfolgte mit der Desaga-Grundausrüstung nach der Standardmethode[1]. 25 g Kieselgel H nach Stahl für die Dünnschicht-Chromatographie der Fa. Merck wurden mit 65 ml Wasser, in dem zuvor 750 mg $AgNO_3$ p.a. "Merck" gelöst waren (= 3% g/g) homogen angerührt. Zum Ausstreichen wurde ein aus V4A-Stahl hergestelltes Streichgerät benutzt.

Herstellung der Gradient-Schichten

Durch Einbau der Mischwelle und Aufsetzen des Teilers wurde das normale Streichgerät in den GM-Streicher verwandelt. In einem Kolben wurden 18 g Kieselgel HF_{254} mit 45 ml Wasser gemischt. In einem zweiten Kolben wurden 18 g Kieselgel H (ohne Fluoreszenzindikator!!) mit 45 ml Wasser, in dem die gewünschte Silbernitratmenge (2,5 bzw. 25% g/g) gelöst ist, gemischt. Darauf wurden die beiden Suspensionen jede in eine der beiden Teilerkammern des GM-Streichers gleich hoch eingefüllt. Nach Herausnehmen der Trennwand wurde die Hülse mittels Kipphebel in Füllstellung gebracht. Das Mischen erfolgte mit einem Antriebsmotor jeweils 30 Sekunden mit und gegen den Uhrzeigersinn. Das Ausstreichen wurde auf einer genau waagerechten Arbeitsschablone vorgenommen.

Prüfung des Gradient-Verlaufs

Die Gradient-Schichten wurden im kurzwelligen UV-Licht betrachtet und es war an der gleichmäßigen Abnahme der Fluoreszenzintensität ein kontinuierlicher Übergang erkennbar.

Trocknung und Chromatographie

Die beschichteten Platten wurden bei 110°C getrocknet, (30 min). Die Aufbewahrung erfolgte unter Lichtabschluß im Exsikkator über Blaugel. Zur Chromatographie wurde die normale Desaga-Trogkammer mit Filtrierpapierauskleidung (Kammersättigung) verwendet. Die Laufstrecke betrug in allen Fällen, auch bei der Mehrfachentwicklung, 15 cm.

Fliessmittel: Zur Herstellung der Fließmittelgemische wurden Lösungsmittel der Firma Merck "zur Chromatographie" oder "zur Analyse" verwandt.

Fließmittel I: Methylenchlorid-Chloroform-Äthylacetat-n-Propanol (50 + 50 + 5 + 5 V/V).

Fließmittel II: Methylenchlorid-Chloroform (40 + 60 V/V). Aufgetragene Mengen: Die Alkohole wurden 1% g/V in Toluol gelöst. Zumeist wurden 0,3 – 1,0 μl (= 3–10 μg) mit der 10 μl Spezialpipette aufgetragen.

Sichtbarmachung: Phosphormolybdänsäure p.a. "Merck" wurde 20% in Methanol gelöst und 10 ml je Platte (20 × 20) cm aufgesprüht. Die besprühten Chromatogramme wurden 5–10 min auf 110°C erwärmt; die Alkohole treten als blaue Flecken auf gelbem Grund hervor.

Summary—Mixtures of C_{10}-, C_{15}- and C_{20}- alcohols cannot be separated on normal silica-gel layers. A separation into groups with the same number of carbon atoms is possible on paraffin-impregnated layers. With gradient thin-layer chromatography it has been established that with increasing silver nitrate impregnation of silica gel, the separation of such mixtures is possible. The optimum and economic silver nitrate content is 3%. As solvent is used a mixture of methylene chloride-chloroform-ethyl acetate-n-propanol (50 + 50 + 5 + 5 v/v). The separation may be improved by multiple development.

Résumé—Des mélanges d'alcools en C_{10}, C_{15} et C_{15} et C_{20} ne peuvenpas être séparés sur des couches de gel de silice normales. Une séparation en groupes à même nombre d'atomes de carbone est possible sur couches imprégnées de paraffine. Par chromatographie sur couche mince à gradient, on a établi qu'avec une imprégnation croissante en nitrate d'argent du gel de silice, la séparation de tels mélanges est possible. La teneur en nitrate d'argent optimale et économique est de 3%. On utilise, comme mélange de solvants, un mélange chlorure de méthylène–chloroforme–acétate d'éthyle–n-propanol (50 + 50 + 5 + 5 v/v). On peut améliorer la séparation par développement multiple.

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TALANTA REVIEW*

APPLICATIONS OF NUCLEAR AND ELECTRON MAGNETIC RESONANCE IN ANALYTICAL CHEMISTRY

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Summary—The principles of nuclear and electron magnetic resonance are briefly described, with reference to the use of these techniques in analytical chemistry. A wide field of analytical applications is reviewed in order that the scope and limitations of the methods may become apparent.

CONTENTS

I. INTRODUCTION

THE widespread interest in nuclear and electron magnetic resonance techniques, which has been such a striking feature of chemical progress in the last decade, has centred

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* For reprints of this review see Publisher's Announcement at the end of this issue.

largely on the important contributions made by these techniques to the solution of structural problems in organic chemistry and, in the case of electron resonance, to the very detailed information which it has provided on the electronic structure of free radical species. The applications of both techniques to problems in analytical chemistry has been much less rapid, although the characteristic nature of the spectra observed left no doubt, from the outset, of the potential importance of both techniques, at least in qualitative analysis. The reason for this comparatively slow growth in analytical applications lies mainly in the stringent requirements in instrumental stability and sensitivity when information of a quantitative nature is required. In the past few years these requirements have been adequately met by commercially available spectrometers, and the way is open for rapid advance.

The present review is designed to cover a wide field of analytical applications in order that the scope and limitations of the methods may become apparent. Only sufficient of the theory is included to permit some understanding of the requirements of the techniques when quantitative information is sought, and to provide, at the same time, a brief introduction to the terminology involved.

II. NUCLEAR MAGNETIC RESONANCE

(*A*) *Principles*

When a sample with nuclei possessing magnetic moments is placed in a strong uniform magnetic field, such that it experiences a field H_0, and is irradiated with energy in the radiofrequency (rf) range, transitions are induced between the possible orientations of the nuclear spins in the magnetic field. A nucleus has a maximum observable component of angular momentum $I(h/2\pi)$ when I, the spin quantum number, is finite. The angular momentum can be resolved into $2I + 1$ components which, because the angular momentum and nuclear moment (μ) behave as parallel vectors, necessitates the latter also having $2I + 1$ values and the nucleus the same number of energy levels. The frequency, ν_0, corresponding to transitions between these orientations is related to the field strength by the equation

$$\nu_0 = \mu H_0/Ih \tag{1}$$

where h is Planck's constant. It is the fact that the field strength observed by a particular nucleus may be different from the applied field, depending upon the chemical and physical environment of the nucleus, which makes nuclear magnetic resonance (n.m.r.) spectroscopy a tool of such immense importance for the study of liquid or gaseous samples in structural chemistry. Because each set of identical nuclei will respond at a slightly different applied magnetic field, each molecular species will give rise to a spectrum which usually permits its ready identification, alone or mixed with other molecular species of a different nature. No problem arises from overlap of the absorption regions of nuclei of different elements, or even from isotopes of the same element, which are well separated in the frequency spectrum.

Because the magnetic field, H_0, at a given nucleus depends upon its environment, the field may be represented by the equation

$$H_0 = H(1 - \sigma) \tag{2}$$

where H is the applied static field, and σ represents the factor by which this field is modified by the environment of the nucleus. The displacement of a resonance signal for different chemical environments caused by variations in the value of σ is referred to as a chemical shift (δ). Because of the way in which it is usually measured, the chemical shift is best expressed in terms of frequency:

$$\delta = (\Delta\nu/\nu_0)10^6 \tag{3}$$

where $\Delta\nu$ is the separation in c/sec between the sample and reference peaks, and ν_0 is the rf oscillator frequency in c/sec. Chemical shifts are usually given relative to a standard substance, and for protons this is often tetramethylsilane (TMS), although other substances have been used. For most protons δ lies in the range 0–15 ppm, which for an oscillator frequency of 100 Mc/sec, corresponds to 1500 c/sec. Much higher values of the chemical shift have, however, been observed in special situations. When TMS is used as a standard, negative values of δ are found for most protons. To avoid this difficulty Tiers has proposed an arbitrary scale,

$$\tau = 10 + \delta \tag{4}$$

which gives positive values in the majority of cases. The Tiers scale has been widely used, although, because the chemical shift is measured by the operator in c/sec, there is an advantage in the more direct δ-scale, in spite of the negative values.

Another important feature of n.m.r. spectra is the fine structure arising from a field-independent interaction which occurs between closely neighbouring nuclear spins. This interaction, known as spin-spin coupling, gives rise to splitting of the resonance line, and leads to spin-spin multiplets. Very detailed information about the environment of the nucleus in question may, in suitable cases, be obtained from a study of the distribution of the lines and of their intensities within the multiplet.

With solid samples the n.m.r. lines are broadened as a result of dipole–dipole[1] and electric quadrupole[2] interactions, and only wide lines devoid of fine structure are obtained. Application of this wide-line spectroscopy to analytical problems will be described later. With gases and liquids these interactions are averaged to zero as a consequence of the rapid tumbling motion of the molecules, and detailed fine structure is observed. It is in this high-resolution spectroscopy that the bulk of the chemical applications are to be found.

The potential of the technique as a qualitative tool for the identification of molecular species is now clear. When quantitative information is sought, other considerations arise. Because an n.m.r. signal will only be observed if there is an excess of nuclei in the lower energy state, the processes by which excited nuclei return to the ground state are of importance for the maintenance of the signal. If these relaxation processes are inefficient, the populations in the two energy states may become equalised, and the absorption signal will then disappear. This phenomenon is known as saturation. Two ways in which the nucleus may relax can be recognised. The energy may be transferred to the molecular system or lattice as translational or rotational energy. This mechanism is referred to as spin–lattice or longitudinal relaxation, and is characterised by a half-life or relaxation time T_1. In liquids and gases T_1 is short ($10^{-2} - 10^2$ sec); in solids T_1 may be measurable in hours or days. In a different relaxation process the spin energy may be exchanged with neighbouring nuclei. This is spin–spin or transverse relaxation, characterised by a half-life T_2. Spin–spin relaxation does not alter the distribution of the nuclei in the two spin states, but it does contribute to the line width of the resonance signal.

The mean life, Δt, of a nucleus in a given energy state determines the mean spread, ΔE_s, of the energy state, and is intimately related to the line width through the Heisenberg uncertainty principle,

$$\Delta E_s \,.\, \Delta t \approx h/2\pi \tag{5}$$

Because $\Delta E_s = h \,.\, \Delta \nu$, this implies that the uncertainty in the frequency of absorption

$$\Delta \nu \approx 1/2\pi\Delta t \tag{6}$$

The commonest broadening of resonance lines is that provided by the relaxation processes mentioned above. Strong interactions give rise to short relaxation times, and thus to wide lines. The magnetic field inhomogeneity can also contribute to the measured line spread.

The signal observed at the receiver coil of an n.m.r. spectrometer consists of two components, one in phase with the applied rf field, H_1, called the dispersion mode (u), and an absorption component (v) which is out of phase, the two components being readily separable by electronic phase-sensitive detection methods. The amplitudes of these signals are given by the expressions:

$$u = \frac{M_0 \gamma H_1 T_2^2(\omega_0 - \omega)}{1 + (\gamma H_1)^2 T_1 T_2 + (\omega_0 - \omega)^2 T_2^2} \tag{7}$$

$$v = -\frac{M_0 \gamma H_1 T_2}{1 + (\gamma H_1)^2 T_1 T_2 + (\omega_0 - \omega)^2 T_2^2} \tag{8}$$

where M_0, the total nuclear magnetic moment, is proportional to the number of magnetic nuclei present, and $\omega_0 - \omega$ is the distance from resonance in angular frequency units. Two features of these relationships are of importance in quantitative analysis. Although at first sight the dispersion mode may seem more useful because of its independence of T_1 and T_2 in certain circumstances, the fact that it falls off with $1/(\omega_0 - \omega)$, as against $1/(\omega_0 - \omega)^2$ for the absorption mode, makes the latter much more suitable for analytical purposes, because the broader dispersion mode signals may overlap in complex spectra. Secondly, the amplitude of these signals is a function of the relaxation times T_1 and T_2. Because these relaxation times may vary from one nucleus to another, even within the same molecule, the maximum amplitudes or peak heights are not necessarily a measure of the number of nuclei present.

A study of the integral of the absorption mode against time, assuming a linear sweep of the magnetic field at a uniform rate, dH/dt, reveals a more interesting situation, as shown by the equation

$$\int v \, \mathrm{d}t = \frac{\text{constant } N H_1}{T(\mathrm{d}H/\mathrm{d}t)[1 + (\gamma H_1)^2 T_1 T_2]^{1/2}} \tag{9}$$

in which N is the number of magnetic nuclei and T is the absolute temperature, the polarisation moment, M_0, being inversely proportional to T. Provided that T_1 and T_2 are short, or that the applied rf field is kept small, so that $(\gamma H_1)^2 T_1 T_2 \ll 1$, the integrated area will be independent of the relaxation times for the slow passage through the resonance signal for which the above equations are valid. It can be shown experimentally that if the rf driving field is kept sufficiently low, the area obtained will approximate closely to the true area, provided that the integrator can follow the rapid oscillations or "wiggles" of the oscillatory signal obtained when the rate of traverse of the field is insufficiently slow. There is no simple way in which the allowable rf level may be decided upon in advance. In practice the operator will wish to use a value of H_1 as high as possible to maximise the signal-to-noise level, particularly with dilute solutions, and it will then be necessary to run the spectrum at several increasing power levels to ensure that the maximum permitted value has not been exceeded. The important point to note is that if the rf power is properly chosen, the integral obtained will be closely proportional (within $\sim 1\%$) to the number of nuclei responsible for the observed signal.

Because, in the majority of cases, quantitative determination of the numbers of nuclei will be made by direct comparison in a single sample, or in a single molecular species, the fact that the integral is dependent upon temperature [equation (9)] will not affect the accuracy of the estimation unless the temperature were to vary rapidly during the course of the measurement. When the temperature is deliberately varied, as in a kinetic study, this dependence upon temperature must, however, be recognised, and allowance must be made for it.

The requirements of quantitative analysis clearly place severe demands on the frequency and magnetic field stability of the n.m.r. spectrometer and on the linearity of the detectors and amplifiers used in the recording and integration of the signal. It will be sufficient to say that commercial instruments are now readily available in which these requirements are satisfactorily met.

A further point should be noted. The signal strength in the receiver coil of the spectrometer theoretically depends upon the square of the magnetic field strength. It is, therefore, essential, where sensitivity is important, to work at the highest possible magnetic field and rf frequency. Much of the published quantitative work in n.m.r. has been carried out at an operating frequency for protons of 40 Mc/sec or 60 Mc/sec. However, commercial spectrometers operating at 100 Mc/sec and capable of meeting the requirements of quantitative analysis are now available, and offer substantial improvements in sensitivity. An additional advantage of a higher operating frequency in the field of analysis lies in the increased resolving power, because chemical shifts are field dependent and therefore proportional to frequency. This increased separation of the absorptions, which may be of critical importance in structural work, is also of considerable significance in quantitative analysis in so far as signals which overlap at a lower operating frequency may be sufficiently resolved to permit separate integration and evaluation.

On the debit side it should be mentioned that spectra obtained with spectrometers operating at around 100 Mc/sec may show fewer lines than are observed in spectra obtained from spectrometers operating at lower frequencies. These additional peaks are attributable to second-order splitting, and arise from electron-coupled spin–spin interaction between nuclei which are not first neighbours. The second-order separation is proportional to J^2/δ, where J, the spin–spin coupling constant, and δ, the appropriate chemical shift, are both expressed in c/sec. Because J is a constant for a given molecule and δ is field-dependent, the second-order separation, easily observable at low field strengths, gradually disappears within the natural line width as the applied field is increased in strength. It has been pointed out,[3] however, that almost all of the chemically valuable information, except relative signs of coupling constants, is available by direct measurement of the chemical shifts and spin–spin splittings in the *first order* spectrum, and the second order structure can be computed, if desired, from these parameters.

(*B*) *Experimental method*

The basic n.m.r. spectrometer consists of a large magnet, providing a stable and very homogeneous magnetic field, an rf oscillator, a single coil or crossed coil system containing the sample and located between the pole pieces, and a sensitive receiver. For analytical purposes the important features required are sensitivity, stability and reproducibility. The most useful recent advances have been in systems designed to maintain the stability of the applied magnetic field and to provide electronic integration of the n.m.r. spectrum. Some commercial spectrometers employ flux-stabilisers in which special windings on the pole pieces develop voltages proportional to the rate of change in magnetic flux intensity. These voltages are used, after amplification, to produce suitable corrections to the applied field. Such stabilisers, in conjunction with carefully regulated power supplies, provide magnetic fields of very high stability. Other spectrometers employ a system in which a nuclear resonance signal is employed to maintain a definite relationship between the applied magnetic field and the oscillator frequency rather than to maintain a specified magnetic field. These systems, employing a field-frequency locking system, are particularly advantageous from the point of view of reproducibility, and may be used for rapid routine measurements with the minimum of attention to the spectrometer controls. N.m.r. spectrometers incorporating facilities for electronic integration of the spectrum have been commercially available for some time. Reproducibility and accuracy in integration are dependent on many factors, including signal-to-noise ratio, line width, and variations in sample temperature. With available circuits and chart recorders, a reproducibility to 1% can be expected under good conditions. This accuracy may be improved by averaging a number of such integrations, and where the maximum accuracy is required the output of the integrator may be applied simultaneously to a digital voltmeter. Jungnickel and Forbes[4] have shown that under optimum conditions of sample concentration, rf power, gain and sweep rate, integrals should be accurate to within a few tenths of 1% of the total hydrogen content. The sensitivity depends upon a number of factors, including, as has been indicated already, the rf oscillator frequency. At 100 Mc/sec, identification may be made with as little as 0·1–0·2 mg of sample in a suitable cell, whilst useful quantitative results may often be obtained with about ten times this quantity of material. At lower frequencies, higher concentrations of solutions are necessary. Much of the published results have been obtained at 60 Mc/sec using solutions of 5–20% concentration and a sample volume of about 0·5 ml.

(*C*) *Applications of high-resolution n.m.r.*

(*i*) *Proton resonances: General.* The proton is by far the most important nucleus for study by high-resolution n.m.r. spectroscopy. It gives a stronger resonance signal than any other nucleus of chemical interest, and the spectra are not complicated by quadrupole relaxation effects present in the spectra of nuclei with spin greater than 1/2. The chief disadvantage in proton spectroscopy is the smallness of the chemical shifts, which are, in general, more than an order of magnitude smaller than in other n.m.r. spectra. Although proton resonance lines are usually sharp except when molecular motion is restricted, the small range of chemical shifts often prevents complete resolution of the lines, especially with spectrometers operating at 60 Mc/sec and under. Accordingly, both the experimental measurements and their interpretation are made more difficult.

High-resolution proton spectra are used most frequently for the determination of the structure of hydrogen-containing molecules. Although the consideration of n.m.r. as a structure-determining tool is outside the scope of this review, it may be noted that the use of high-resolution spectra in solving problems in structural organic chemistry is well advanced. A procedure for extracting the structure information made available by the n.m.r. technique is described by Chamberlain.[5] Useful correlations of proton chemical shifts with chemical structure have been published as charts[6] and as tables.[7,8]

(*ii*) *Qualitative analysis.* The use of high-resolution n.m.r. as a qualitative analytical tool is now firmly established. For each compound the n.m.r. spectrum is probably unique. The number and relative intensities of the resonances, their chemical shifts and multiplicities from spin–spin coupling, and also their relaxation times, allow such a vast number of possibilities that it is most unlikely that two different chemical compounds would have the same n.m.r. spectrum. Although, in general, it is desirable to unravel the n.m.r. spectrum of a complex molecule and express it in terms of chemical shifts and spin–spin coupling parameters before attempting to draw conclusions concerning the molecular structure of the sample, it is frequently possible to identify unknown compounds of considerable complexity by simple inspection of the n.m.r. spectra and comparison with the spectra of known molecules. Consequently, the publication of classified high-resolution spectra, already begun for hydrogen-containing molecules,[9] should eventually make the "fingerprinting" of molecules by their n.m.r. spectra very attractive.

The chemical shift is used analytically as the primary means of identification of functional groups containing the observed isotope. Notwithstanding the small range of proton chemical shifts, it is often possible in mixtures of hydrogen-containing compounds to select a peak as being representative of a given compound in the mixture. Detection of the compound then requires a simple examination of the proton spectrum for this peak. A good example of this type of application is the detection of specific compounds, such as benzene in such a complex mixture as aviation fuel.[10] Where doubt exists as to the identity of signals, it is usual to run the spectrum and then add some of the compound in question, noting whether or not the appropriate peaks increase in amplitude, or whether additional peaks appear in the spectrum. Because the observed resonance signal may arise from a very small percentage of the hydrogen in a given compound, the sensitivity of the n.m.r. method in applications of this kind will not always be large, but in favourable cases high sensitivity can be achieved.[11]

(*iii*) *Proton counting.* The number of hydrogen atoms of each type in a molecule can readily be obtained by high-resolution n.m.r. spectroscopy using integrated spectra. This is illustrated in Fig. 1 which shows both the absorption and integrated spectrum for prodigiosin[12] obtained at 60 Mc/sec. From the value of the chemical shift it seems certain that the peak at −235 c/sec represents the three protons of a methoxyl group. The integral of the remaining protons then gives 22, making a total of 25 for the molecule. For molecular structure determination, proton counting by n.m.r. has the great advantage that it allows the number to be fixed to the nearest proton. Calculations made solely from molecular weight determinations and hydrogen analyses are often accurate only within several hydrogen atoms. The n.m.r. method requires that at least one peak be positively identified. If this is not possible, an approximate molecular weight and percentage of hydrogen will serve to fix the total number of protons, because each step on the integral curve should represent an integral number of protons and often approaches closely to such a value.

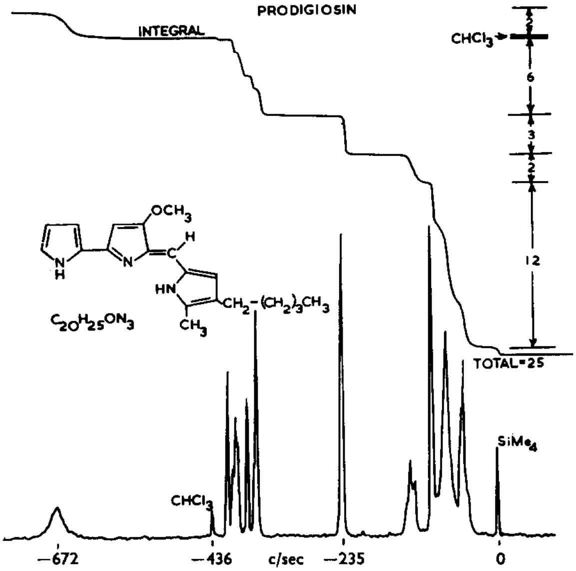


FIG. 1.—Proton counting as demonstrated on the molecule prodigiosin (Varian Associates[12]).

(*iv*) *Total hydrogen analysis.* Another application of integrated n.m.r. intensities lies in the analysis of small samples for total hydrogen. By comparison with compounds of known hydrogen content in sample tubes of identical cross-sectional area, it is possible to determine the percentage of hydrogen by weight in an unknown sample. Table I shows the results obtained for three complex natural products with naphthalene used as a standard.[13] The naphthalene was run in triplicate to establish the precision of the measurement. The percentage of hydrogen by weight agrees in

TABLE I.—TOTAL HYDROGEN ANALYSIS BY N.M.R. FOR COMPLEX ORGANIC MOLECULES[13]

Sample	Wt., *mg*	H, % (by wt.)	H, % (n.m.r.)[a]
$C_{10}H_8$ (A)	25·1	6·29	6·31 ± 0·03[b]
$C_{10}H_8$ (B)	25·3	6·29	6·28 ± 0·01
$C_{10}H_8$ (C)	25·3	6·29	6·28 ± 0·02
$C_{27}H_{44}O_3$	25·1	10·65	10·58 ± 0·05
$C_{15}H_{18}O_6$	25·2	6·26	6·27 ± 0·04
$C_{15}H_{20}O_6$	25·1	6·80	6·81 ± 0·03

[a] Based on average integral of naphthalene solutions
[b] Standard deviation

nearly all cases with calculated values to within the standard deviation of the measurement, which is about 0·5% of the percentage present. This accuracy compares favourably with the standard combustion method. The accuracy, speed and non-destructive nature of the n.m.r. analysis may make the method more attractive than the combustion method when a limited amount of sample is available.

(*v*) *Quantitative analysis of mixtures.* The capability of obtaining accurate integrals has greatly extended the analytical usefulness of the high-resolution n.m.r. spectrometer and permitted its application to many other important problems. Thus, the addition of electronic integrators has made possible the complete quantitative determination of the components in an increasing variety of mixtures. One recent example of this type of analysis has been described by Hollis.[14] Considerable effort has been devoted to the problem of developing suitable methods for the routine quantitative analysis of commercial analgesic preparations containing aspirin, phenacetin and caffeine. Procedures have been published utilising separation by extraction and partition chromatography, and determination by ultraviolet, visible and infrared spectrophotometry. The extraction procedure is not suitable for routine quality control because of the time required to complete the analysis. Of the other procedures the infrared method seems to be most advantageous in terms of accuracy and speed. The accuracy and speed of the n.m.r. method described by Hollis is about the same as that of the infrared procedure, but it has the advantages of being more direct, in that a separate analytical peak of known origin is present for each component and no calibration curves are required. The results obtained by n.m.r. show that the technique can be used to analyse commercial aspirin-phenacetin-caffeine preparations with an accuracy sufficient for quality control purposes.

Chupp and Speziale[15] have used the n.m.r. method to advantage in a study of the *N*-hydroxymethylation of some *N*-methylamides by formaldehyde. Assay of the reaction mixtures by titration of excess formaldehyde is open to criticism because of the possibility that only formaldehyde is titrated and the doubt whether the equilibrium is stable under conditions of varying pH. The authors successfully used 60 Mc/sec spectra with electronic integration to obtain quantitative estimates of the reactants, products and unchanged formaldehyde in a large number of different reaction systems. Conventional chemical analysis by isolation of crystalline derivatives presents serious difficulties in this kind of mixture.

(*vi*) *Characterisation of mixtures.* Many multicomponent systems are so complex that the complete determination of their composition is extremely difficult. In such cases a great deal of valuable information can still be obtained from a knowledge of the functional groups present and their quantitative distribution. This characterisation leads to a knowledge of the compound types present and sometimes permits the deduction of a structure for the "average molecule". Williams[16] [see also ref. (5) p. 1935] has presented analytical schemes for characterising saturated, aromatic and olefinic fractions derived from petroleum, based upon high-resolution n.m.r. measurements giving the hydrogen distribution, total hydrogen content and average molecular weight. These characterisations have proved very helpful in following the processing of petroleum fractions.

(*vii*) *Molecular weight determination.* The determination of molecular weights by n.m.r. again involves comparison of the integrated intensities of an added standard and of a recognisable peak or group of peaks of the unknown in a solution containing known weights of standard and unknown. The molecular weight is given by the formula:

$$M = \frac{I_s n W M_s}{I n_s W_s} \tag{10}$$

where I = intensity, n = number of protons in the peak or peaks, W = weight and M = molecular weight (subscript s = standard). Barcza[17] found that a suitable standard is hexamethylcyclotrisiloxane, removable by sublimation. Other possible standards include iodoform, benzoquinone and, in the absence of complex formation with aromatic unknowns, *p*-dinitrobenzene and 1,3,5-trinitrobenzene. The molecular weight determination can be combined with taking the n.m.r. spectrum of the unknown, the only extra work required being the weighing of sample and standard, and the calculation. Important features of the n.m.r. method are that the molecular weight values obtained in this way are not affected by dissociation and solvent interaction phenomena, and the error resulting from impurities is proportional to their weight. On the assumption that most impurities are smaller molecules than the unknown, this method should, therefore, give smaller errors than methods depending primarily on the number of particles present. Possible sources of error in the measurement, and details of procedure, are discussed by Barcza.[17] As pointed out by this author, the protons of hydroxyl groups exchange with moisture in the solvent, hence absorption peaks attributable to these protons should not be used in the determination.

Both the unsaturation and the average molecular weight of fatty acid triglycerides (natural fats) have been estimated by Johnson and Shoolery[18] using the n.m.r. technique. The proton spectra of these triglycerides in carbon tetrachloride were characterised by the signals from the olefinic protons, the four glyceride methylene protons, methylene groups attached to two doubly-bonded carbon atoms and the protons on saturated carbon atoms. By using the area of the signals from the C_1 and C_3 glyceride protons as an internal standard, the number of olefinic protons and the total number of hydrogen atoms can be determined. From these determinations the average molecular weight can be calculated. An iodine number obtained from the number of olefinic protons and the average molecular weight agrees well with that determined by the Wijs titration method. The total time spent in obtaining the n.m.r. results was about 20 min per sample. The calculation can be simplified by using suitable nomographs.

(*viii*) *Polymer analysis.* Few articles have appeared in the literature on the application of high-resolution n.m.r. to the study of polymers. This situation may have arisen because few polymers have a high enough solubility and at the same time exhibit narrow enough line widths to permit a detailed analysis of their spectra with the spectrometers available until quite recently. With the advent of more sensitive spectrometers, the position is changing rapidly and it seems likely that high-resolution n.m.r. spectroscopy will also prove of increasing importance in this field of study. A general discussion of the application of high-resolution n.m.r. to the study of polymers has been given by Bovey, Tiers and Filipovich.[19] These authors point out that the line widths obtained in n.m.r. spectra of polymer solutions are dependent on the local viscosity in the immediate neighbourhood of the chain segments and not on the macroscopic viscosity of the sample. The local viscosity is independent of molecular weight and is influenced by concentration only when this becomes so high that segmental motion is restricted. These observations are utilised in the determination of stereochemical configurations and functional groups in polymeric systems. An example of the former is the determination of the relative amounts of iso-, syndio- and atactic triads in methyl methacrylate polymers by measurement of proton peak areas in the α-methyl region of the spectrum.[20] Chen[21] has used high-resolution n.m.r. to determine the structural groups in butadiene-isoprene copolymers of varying composition and in the molecular weight range of 100,000 to 200,000. These copolymers gave well-resolved spectra in carbon tetrachloride solution at room temperature. The error in determining the relative concentrations of the various structural groups in a typical 1:1 butadiene-isoprene copolymer was estimated to be within 2–3%.

Infrared procedures have been widely used for the determination of the microstructure of polyisoprene. The method is satisfactory for the determination of the 1,2- and 3,4- repeating units, but is unsatisfactory for the determination of the *cis*- and *trans*-1,4- unit contents of polyisoprenes.[22] It has now been shown[22] that the areas of the *cis*- and *trans*-methyl n.m.r. peaks in solutions of 1,4-polyisoprene are satisfactory measures (estimated error ±0·5%) of the *cis- trans* content of the polymer. In combination with the n.m.r. method previously described by Chen,[21] this analysis can be extended to polyisoprenes containing *cis*- and *trans*-1,4-, 1,2- and 3,4-recurring units with an over-all error of 2–3%.

Senn[23] has developed a method for the analysis of styrene-butadiene copolymers using the n.m.r. absorption bands derived from the aromatic and olefinic protons incorporated into the copolymer. The composition of the copolymer is determined in terms of the mole per cent styrene, 1,2-butadiene addition and 1,4-butadiene addition, and no calibration is required. The major time-consuming step in the method, which has been used routinely for determining styrene-butadiaene copolymer composition, is the dissolution of the sample. The time required for analysis after dissolution is approximately 20 min.

The detection and estimation of branching in polymers has always been a difficult problem because of the absence of a convenient physical method of analysis. It has now been shown that n.m.r. spectroscopy can be used not only to detect branching in dextran, but also to make a reasonably good estimate of the extent of branching.[24] The proton spectrum of branched dextran contains a peak, not found in the spectrum of linear dextran, which is assigned to C-1 protons at non-1,6-linkages, linkages which in most branched dextrans form the branch points. A quantitative measure of the extent of branching, the ratio of 1,6-linkages to non-1,6-linkages, is thus obtained by taking the ratio of the areas of the peaks associated with these two types of linkage. The ratio so obtained (71:29) agrees well with that obtained by periodate analysis (70:30). This method of detecting and estimating branching can obviously be extended to other polysaccharides in which the non-1,6-linkages are known to be at branch points. In principle the method should be applicable to polymers other than polysaccharides.

(*ix*) *Analysis of surfactants.* Previous methods of characterisation of non-ionic surfactants containing a polyoxyethylene chain have been slow and rather inaccurate. Quantitative measurement of the proton signal intensity in high-resolution n.m.r. spectra offers a simple and relatively rapid method (a complete determination can be made in about 30 min) for determining the composition and structure of such materials.[25] Relative amounts of protons are determined to characterise the hydrophobe and to find the ratio of the hydrophilic to hydrophobic portions of the molecule. When applied to alkyl phenol-ethylene oxide condensates, the method allows the average molecular weight of each portion of the molecule to be determined directly. The authors discuss the applicability of the method to the characterisation of other common commercial non-ionic surfactants. All represent cases where standards, other than a known portion of the molecule, are unnecessary for quantitative measurements.

(*x*) *Isotope analysis.* Isotope-abundance ratios are readily obtained by the n.m.r. method. Thus, proton resonance has been used to measure the water content of H_2O–D_2O mixtures with an accuracy of $\pm 0{\cdot}2\%$, the analysis being completed in a few minutes by comparison with standards of known concentration.[26] Mitchell and Phillips[27] have applied the proton n.m.r. technique to the measurement of H_2O in D_2O in a flowing sample, using a special sample tube arrangement. When only small amounts of H_2O are to be detected, a dilution technique gives increased sensitivity.[28] Known amounts of H_2O are added to accurately measured aliquots of the H_2O–D_2O sample. The amplitude of the proton signal is measured and plotted against the amount of H_2O added. Extrapolation of the plot to zero signal amplitude enables the concentration of H_2O in the original sample to be obtained from the intercept on the concentration axis.

Whether or not deuterium enters an organic compound (by exchange with protons) and where it has been substituted for hydrogen are analytical problems which can be rapidly solved by high-resolution n.m.r. spectroscopy. Organic applications involving deuterium so far reported have all been in terms of the influence of deuterium substitution upon the proton spectrum. Thus, proton n.m.r. has been used to establish the deuteration sites and to determine the degree of deuteration in

$$C_6H_5\,CD\,(CHD_2)\,CHD\,CHD\,CO_2H.$$[29]

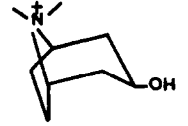
Similarly, proton spectroscopy has been used to measure the amount of ^{13}C enrichment in a methyl group with an accuracy of $\pm 0{\cdot}1\%$.[30]

(*xi*) *Estimation of hydration numbers.* Nuclear resonance studies have provided information on ion hydration. Zhernovoi and Yakovlev[31] have measured the proton relaxation time, T_1, in water and in the dihydrogen phosphate ion, using aqueous solutions of sodium dihydrogen phosphate and of potassium dihydrogen phosphate. Their results can be explained by assuming positive hydration for ions like sodium and negative hydration for ions like potassium. A study of the ^{17}O resonance in water enriched in ^{17}O (abundance $0{\cdot}096\%$) has indicated that solvent water can be distinguished from water in the hydration sphere of certain cations. Jackson, Lemons and Taube[32] found that for aquo-cations with a slow rate of water exchange (half-life $> 10^{-4}$ sec) it is possible to display the hydration water as a separate n.m.r. peak when the solvent peak is shifted by addition of a paramagnetic ion. The actual ^{17}O shift observed will depend on the number of water molecules involved in the aquo-cation, and thus not available to interact with the paramagnetic ion. The authors suggest either the measurement of the relative areas under the absorption curves of solvent water and bound water or a method based on the effective molal shift of solvent water for the estimation of hydration numbers. Unfortunately, the enrichment level of the ^{17}O at present available does not permit precise determination of these numbers.

(*xii*) *Determination of sample purity.* An important use for high-resolution n.m.r. spectroscopy is the determination of the purity of a given sample. As the example[33] given below illustrates, the n.m.r. method compares favourably with more conventional methods or criteria for determining the homogeneity or otherwise of a sample. Supposedly pure 5,16-pregnadiene-3β,20α-diol, obtained by lithium aluminium hydride reduction of 16-dehydropregnenolone acetate, resisted separation into two components by thin-layer, paper, gas-phase and conventional column chromatographic techniques. Inspection of the n.m.r. spectrum showed that in the region of the spectrum where one would expect a singlet associated with the absorption produced by the C-28 methyl protons there occurred two peaks separated by 3 c/sec, each with one half the intensity of the single C-19 methyl resonance. Furthermore, the doublet associated with the C-21 methyl group appeared as a discrete pair of doublets. The author concluded that the supposedly pure 20α-hydroxy compound was, in fact, a molecular complex of the epimeric 20α- and 20β-diols.

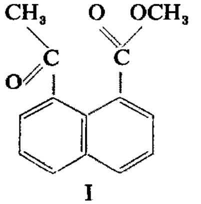
(*xiii*) *Applications to the study of equilibria and kinetics.* The non-destructive nature of the n.m.r. method, and the selective character of high-resolution spectra, make the technique particularly valuable for the study of equilibria and of rate processes in solution. In these situations the n.m.r. method may have marked advantages over other physical or chemical analytical techniques, although some problems remain. Because of the requirement of a spinning sample to obtain the necessary field homogeneity in high-resolution studies, temperature control is less simple than in some other techniques. Grunwald, Loewenstein and Meiboom,[34] in an early rate study, relied on temperature control of the room, which remained within $\pm 2°$ over a period of days. The problem of temperature control of the sample has now largely been solved, and devices using a rapid flow of preheated or precooled nitrogen, and capable of maintaining any temperature within the range $-60°$ to $+200°$, are commercially available. Again, in some equilibrium studies, the $\pm 1\%$ accuracy obtainable in ordinary circumstances may be insufficient. Solubility limitations may also operate.

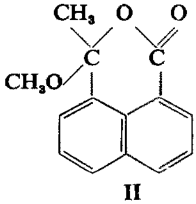
The advantages of the technique are illustrated by studies of the keto-enol tautomerism of acetylacetone (2,4-pentanedione).[35] At 40 Mc/sec the signals from the tautomers are well separated, and the relative areas under the $-CH_2-$ and $=CH-$ peaks have been used to obtain the relative concentrations of the keto and enol forms. An earlier investigation,[36] in which bromine titrations were used in the analysis, gave a considerably higher proportion of the keto tautomer, but there is no reason to doubt the accuracy of the n.m.r. results. The effect of temperature on this equilibrium has been examined.[37] Closs[38] has studied the equilibrium, in acid solution, between the isomeric forms of pseudo-tropine hydrochloride which arise



from the two possible configurations of the *N*-methyl group. The CH_3 resonance appears as a doublet in each case, consequent on splitting produced by the adjacent hydrogen nucleus, and the relative amounts of each isomer were estimated by measuring the areas under the respective doublets by cutting out from the chart the peak areas and weighing. Using a series of ten estimations the error in the area estimation was believed by these investigators to be ±10%. Much higher accuracy could doubtless have been obtained by electronic integration. In D_2O the CH_3 doublets collapse to a singlet as the hydrogen nucleus is replaced by deuterium, and better estimation of the areas is possible. Although of limited accuracy, this study is an excellent example of the ease with which the separate determination of molecular species differing in structure only in a most subtle way may be effected by the n.m.r. method.

Lansbury and Bieron[39] have used the n.m.r. technique to investigate the keto acid–pseudo acid tautomerism in the normal- (I) and Ψ-methyl esters (II) of 8-acetyl-1-naphthoic acid


I


II

One of the methyl signals in I is typical of a methyl aryl ketone, whereas in the Ψ-ester it is typical of a methyl ether. Quantitative analysis of the mixture was effected by electronic integration of the 60-Mc/sec spectrum with an estimated accuracy of ±1%. This analytical procedure was checked by a study of synthetic compositions.

Rearrangement of 3,3-dichloro-*exo*-tricyclo [3.2.1.0] octane (III) to *exo*-3,4-dichlorobicyclo [3.2.1] oct-2-ene (IV) was easily followed by De Selms and Combs[40] by observing the disappearance of the absorption of III at 9·24τ from one of the protons on carbon-8 and the simultaneous appearance of the absorptions of IV at 3·92τ and 5·89τ because of the protons on carbon-2 and carbon-4. The rearrangement exhibited first-order kinetics at 22° in carbon tetrachloride and a number of other solvents.

Clearly, therefore, there is a wide field of application in which n.m.r can be used as an analytical technique of unrivalled discriminating power for measuring the relative amounts of reacting species, either in equilibrium systems or in the course of slow reactions, that is to say, reactions which are slow relative to the time required to obtain a high resolution spectrum, which is usually of the order of several minutes. Faster reactions may be studied by an entirely different n.m.r. method which permits the measurement of rate processes with half-lives in the approximate range 0·002–0·2 sec. Where exchange of a nucleus between two separate species occurs in a molecular system, the nature of the spectrum obtained depends on the magnitude of the rate of exchange of the nuclei. If exchange is slow, the spectrum will consist of two separate but superimposed spectra corresponding to the two individual species. With sufficiently fast exchange a time averaged spectrum will be observed. In intermediate cases predictable line shapes are observed, and from a study of the detailed line shape information may be obtained about the rate of exchange. Similarly, multiplets caused by coupling with a nucleus which is exchanging rapidly will merge to a single line if the frequency of exchange is large compared with the spin–spin coupling. In general, therefore, information may be obtained by this method in cases where the frequency of exchange is comparable with the frequency separation in the spectrum.

The theory of this averaging effect has been discussed by Gutowsky and his coworkers.[41] The effect has been demonstrated for the hydroxyl protons of ethanol by Arnold.[42] Grunwald, Loewenstein and Meiboom have used it with advantage to study the protolysis of methylammonium ions in aqueous solution.[34] The exchange rate is nearly proportional to $[CH_3NH_3^+][CH_3NH_2]$, the second-order rate constant being $6 \times 10^8\ M^{-1}.\ \text{sec}^{-1}$ at 19°. Two separate reactions appear to contribute to this rate constant, one being the direct transfer of a proton from $CH_3NH_3^+$ to CH_3NH_2. The other, it is clear from the broadening of the water line and from the merging of the H_2O and NH_3^+ resonances into a single line at higher pH values, involves a solvent molecule. This investigation is an example of the large amount of quantitative information obtainable from the n.m.r. spectra. Similar studies of the dimethyl- and trimethylammonium ions have been described by Loewenstein and Meiboom.[43] From an examination of line-broadening, information has been obtained about the proton exchange rate between t-butanol and some alkynes, $R{-}C{\equiv}CH$, in aqueous solution.[44] The exchange is catalysed by hydroxyl ions, and the rate-determining step is believed to be the removal of the terminal acetylenic protons by the hydroxyl ion.

In the method just described a limit is imposed by the resolution of the spectrometer, there being a finite contribution to the measured line width from the inhomogeneity of the applied magnetic field. Forsen and Hoffman[45] have described a different method which does not depend on the line widths and separations in a single resonance spectrum. Consider a simple two-component system in which a nucleus is rapidly transferred back and forth between two non-equivalent sites A and B. In a double resonance experiment, when the signal from the nucleus at site B is saturated by a strong rf field, and the signal from site A is simultaneously observed by a weak field, its decay to zero may be followed as a function of time (t). It can be shown that M_z^A, the z-axis magnetisation at site A, is given by

$$M_z^A = M_0^A \left[\frac{\tau_{1A}}{\tau_A} . \exp.\left(-\frac{t}{\tau_{1A}}\right) + \frac{\tau_{1A}}{T_{1A}}\right] \tag{11}$$

where M_0^A is the initial z-magnetisation at site A, τ_A is the lifetime of the nucleus in site A, T_{1A} is the spin-lattice relaxation time in site A, and τ_{1A}, the time constant obtainable from a logarithmic plot of the decay curve, is defined by

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A} \tag{12}$$

From the value of τ_{1A} and the quotient τ_{1A}/T_{1A}, τ_A and T_{1A} may be obtained. From a second double-resonance experiment in which B is observed while A is saturated, τ_B and T_{1B} may also be evaluated. Thus, the lifetimes in the two states are separately obtained, as are the two spin-lattice relaxation times. The method has been applied to the exchange of the hydroxyl protons in an equimolar mixture of t-butanol and 2-hydroxyacetophenone. It clearly provides interesting information relevant to the exchange mechanism, as well as quantitative information on the rate process.

Where two rapidly exchanging kinds of proton contribute to the same n.m.r.

absorption line the observed chemical shift may be a linear function of the concentration ratio of the two species,[46–48] if the change in composition is not accompanied by gross changes in the solvent medium. This observation has been utilised by Grunwald Loewenstein and Meiboom[49] to study acid-base equilibria in systems containing trimethylammonium ions. The chemical shift follows the typical S-shaped titration curve when plotted against pH. Bhar and Forsling[50] have made use of the same phenomenon in a study of the kinetics of the hydrolysis of acetic anhydride to acetic acid. Similarly, the dimerisation constant for acetic acid in carbon tetrachloride has been obtained from a study of the chemical shift of the OH proton on dilution caused by the rupture of the hydrogen bonds in the dimer.[51]

(*xiv*) *Other nuclei.* References in the literature to analytical applications with nuclei other than ^{1}H and ^{19}F are severely limited. Several factors contribute to this situation, notably the much lower signal strength obtained with some nuclei which would otherwise be of considerable chemical and analytical interest. In others, with $I \geqslant 1$, the presence of an electric quadrupole moment leads to short relaxation times and excessive line broadening. Again, spin-lattice relaxation times may be unfavourably long. There is a compensating advantage, however, in that, because the chemical shifts are frequently much larger than in proton spectra, and the requirements in homogeneity therefore less stringent, much larger samples may be employed.

For a given magnetic field and a fixed number of magnetic nuclei the intensity of the n.m.r. absorption signal is proportional to

$$\frac{I+1}{I^2}\,\mu^3 H_0^2 \tag{13}$$

Values of the spin I in multiples of $h/2\pi$, magnetic moment μ in multiples of the nuclear magneton, and the relative sensitivity for a fixed number of nuclei are shown in Table II for a number of magnetic nuclei of interest from the analytical standpoint. ^{12}C and ^{16}O are non-magnetic. Of the nuclei with spin 1/2, other than the proton, ^{19}F in particular, and ^{31}P are clearly promising from the viewpoint of quantitative analysis. The low natural abundance (4·70%) of ^{29}Si, which also has a spin of 1/2, contributes to the difficulties in making full use of this isotope. Nuclei with $I \geqslant 1$, *i.e.*, ^{11}B, ^{14}N and ^{35}Cl, present difficulties because of the quadrupole relaxation effect, although in some cases, notably ^{11}B and ^{14}N, this has not prevented much useful structural information being obtained. In practice, quantitative analytical applications appear to have been confined to ^{1}H, ^{19}F and ^{31}P.

Muller and Goldenson,[52] in an early paper, described the application of ^{31}P measurements to the analysis of mixtures of phosphorus compounds. The spectra were obtained at 17 Mc/sec in a field of 9850 gauss, and areas rather than peak heights were used because of probable differences in relaxation times. Integration measurements made by a weighing technique on a series of six recordings led to an estimated accuracy in the analysis of 1–2%. In a later study Ames *et al.*[53] investigated the system H_2O–HF–P_2O_5 by ^{31}P resonance, and succeeded in estimating quantitatively the nine separate structural entities possible in this system. Proton spectra are of no value in this case because the rapid interchange of the acidic hydrogens of HF, the protons in water and in the various phosphoric acids leads to a single proton resonance line useless for analysis. Both ^{31}P and ^{19}F spectra were obtained with the same magnet at about 9000 gauss. The samples were contained in 15-mm o.d.

polyethylene tubes with a reference material (85% phosphoric acid for the ^{31}P spectra or 100% trifluoracetic acid for the ^{19}F spectra) contained in a small concentric tube. Spectra were obtained using the absorption mode, and the areas of the resulting resonance peaks were measured by weighing traces on a paper of uniform weight. Replicate ^{19}F area measurements showed a standard deviation of 2·4% of the peak area on peaks exhibiting areas in the range of 15–30% of the total fluorine, whereas replicate ^{31}P area measurements showed a standard deviation of 5·0% in the same range. The increased accuracy in the fluorine measurements arises partly from the improved signal-to-noise ratio at the higher fluorine resonance frequency and partly to the greater multiplicity of the spin–spin multiplets in the phosphorus spectra. Groenweghe and Payne[54] used a similar technique to investigate the mixed halide systems $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$ using the ^{31}P resonances. Because of the large chemical shifts in these systems (~140 ppm), which meant that resonance peaks were observed at fields relatively far apart, the authors found it necessary to correct the results obtained by the weighing technique for deviations from linearity of the magnetic field sweep. Corrections up to 13% of the measured areas were applied. Van Wazer and Fluck,[55] in a subsequent paper from the same laboratory in which a study of the system H_3PO_4–$POCl_3$ was described, omitted the sweep non-linearity correction. A study of the system phosphorus trichloride, tribromide and triphenyl phosphite by the n.m.r. method has also been reported.[56] A detailed study of the application of ^{31}P resonances to the analysis of polyphosphoric acids has been described by Guffy and Miller.[57] Absorption mode spectra were used and area measurements were made with a planimeter. The total time required for an analysis was estimated to be 15 min, including setting up of probe balance (5–8 min), area measurements (4–6 min) and calculations (1–2 min). These authors found comparison of peak heights less satisfactory, and claimed an accuracy in the area measurements of ±2%. The area measurements gave the ratio of end-phosphorus groups to ortho-phosphorus groups from which the acid concentration could be calculated with an estimated accuracy of ±0·2%, checked by magnesium pyrophosphate determinations. Guffy and Miller claimed the method to be as accurate as the best wet methods available, and the sensitivity for showing slight differences in composition even better. It should be noted, however, that the method is not suitable for low

Table II.—Nuclear properties*

Isotope	I	μ	Resonance frequency at 10 kgauss, *Mc*	Relative sensitivity at constant field
^{1}H	1/2	2·79268	42·576	1·000
^{2}H	1	0·85738	6·536	$9·64 \times 10^{-3}$
^{7}Li	3/2	3·2560	16·547	0·294
^{11}B	3/2	2·6880	13·660	0·165
^{13}C	1/2	0·70220	10·705	$1·59 \times 10^{-2}$
^{14}N	1	0·40358	3·076	$1·01 \times 10^{-3}$
^{17}O	5/2	−1·8930	5·772	$2·91 \times 10^{-2}$
^{19}F	1/2	2·6273	40·055	0·834
^{29}Si	1/2	−0·55477	8·458	$7·85 \times 10^{-2}$
^{31}P	1/2	1·1305	17·236	$6·64 \times 10^{-2}$
^{35}Cl	3/2	0·82091	4·172	$4·71 \times 10^{-3}$

* Reproduced by permission of Varian Associates.

concentrations because of the unfavourable intensity of the resonance signals compared with proton or fluorine spectra. Fluorine resonance has been used in quantitative analysis of mixtures of uranium hexafluoride and bromine pentafluoride.[58]

(D) *Applications of wide-line n.m.r.*

Wide-line n.m.r. stands on the same theoretical foundation as the high-resolution technique, but the spectra obtained by the respective methods differ considerably. In wide-line measurements fine spectral details are not obtained; line widths and shapes, particularly as a function of temperature, are the features from which intelligence usually is derived. For this reason, the instrumentation in this type of spectroscopy is simpler than in the high-resolution method.

Wide-line n.m.r. provides a simple, rapid method for the quantitative measurement of isotope concentration in liquid samples. Of particular interest are the determination of light water in D_2O,[59] of residual hydrogen in highly fluorinated or deuterated compounds,[59] and of fluorine in fluorocarbon liquids.[60] Because of the relative size of the chemical shifts, differences exist between hydrogen and fluorine analysis by the wide-line technique. In proton resonance from liquids the shifts are too small to be detected with the magnet used in a broad-line instrument. In fluorine resonance the chemical shifts are larger by an order of magnitude, and can be observed with magnets of such homogeneity. Quantitative analysis of fluorine-containing organic molecules from integrated intensities can, therefore, lead to the determination of both the total fluorine content and fluorine present in different groups.[59] Other nuclei which have been examined in the liquid state by wide-line n.m.r. for quantitative analytical purposes[59] are ^{11}B and ^{27}Al.

One of the most important current applications of the wide-line technique involving quantitative analysis is the accurate and rapid determination of the water content in a wide variety of agricultural and food products.[61] The principle underlying this application is that the n.m.r. absorption is broadest in "rigid lattice" solids and that molecular motions result in line narrowing. Consequently, the proton resonance spectrum of the above systems consists of a narrow line arising from the moisture, superimposed on a broad line from the less mobile protons in the host material. Two procedures have been used for determining the moisture content. In one method, the peak-to-peak amplitude of the derivative of the absorption signal from the moisture is measured. This is then compared with a calibration curve for the material to be analysed, obtained under standardised conditions using samples of known moisture content. Materials varying in water content from a few to 100% can be analysed. The precision of the analysis is of the order of $\pm 0{\cdot}1\%$. In the other method, the width of the narrow central line from the moisture is measured. As the percentage of moisture present increases, the line width decreases and may become as narrow as 10^{-2} gauss. An empirical calibration curve is constructed as before. Although the latter method is limited to relatively low moisture contents (it becomes too insensitive at high moisture levels) it has the advantage that variations in the packing of the test sample are less critical.

Other analytical applications of wide-line n.m.r., of a similar nature to that described in the preceding paragraph, are the determination of the liquid content of fats[62] and the determination of the liquid content of liquid-solid slurries.[5]

The wide-line technique can be applied directly to solids. Because the possibilities of movement in solid systems are more restricted, the shape of the resonance absorption obtained from many solids is characteristic of the arrangement of the nuclei in the lattice. A study of the broad-line proton magnetic resonance spectrum of crystalline potassium trisoxalatorhodium hydrate obtained at a number of temperatures[63] has indicated that some of the protons in the crystal are present other than as water of crystallisation, and that the water of crystallisation can be grouped into at least three sets, the water molecules in different sets having different degrees of mobility. Wide-line n.m.r. has also been used for determining the degree of crystallinity of polymers[64] and, from observation of the changes in line width and shape with changes in temperature, for investigating order-disorder transitions in polymers.[65] A good example of such an application is seen in Fig. 2, which shows two superimposed lines, one narrow and one broad, presumed to be associated with the ^{19}F nuclei in the amorphous and crystalline regions, respectively, of polytetrafluorethylene (Teflon). With rising temperature the motional effects in the amorphous regions are more pronounced and more rapid, so that this signal narrows first. The broad component narrows abruptly at 293°K (not shown) and this abrupt narrowing appears to be associated with the first-order thermodynamic-transition point in Teflon.

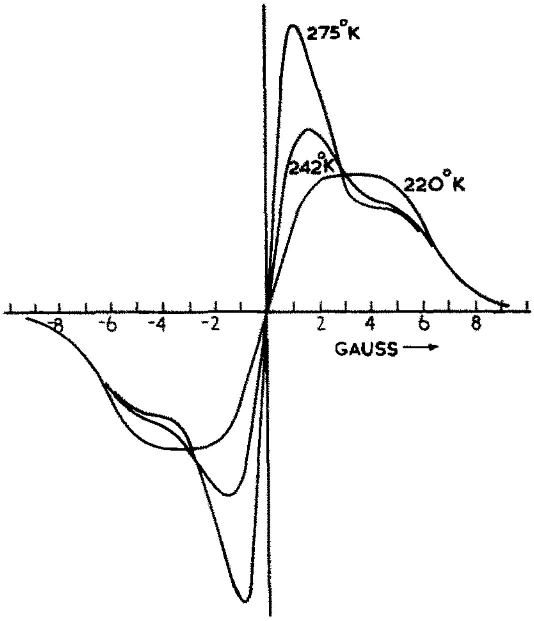


FIG. 2.—Absorption derivatives for the ^{19}F resonance in Teflon at 30 Mc/sec and the indicated temperatures (Wilson and Pake[64]).

Examples of the determination of hydrogen in solids by wide-line n.m.r. are the analysis of cerium hydride and zirconium hydroxide compounds by comparing the peak area of the signals with those obtained from standards.[59] An example of a direct fluorine determination on a solid is the analysis of fluorspar which contains more or less of one fluorine-containing species, calcium fluoride.[60] This sample was analysed by comparing the peak-to-peak amplitude of the signal with the linear calibration plot obtained for a series of fluorspar ores in which the fluorine content ranged from 34 to 46% fluorine by weight.

III. ELECTRON SPIN RESONANCE (ELECTRON PARAMAGNETIC RESONANCE)

(*A*) *Principles*

Whereas nuclear magnetic resonance utilises the energy levels of nuclei, electron spin resonance (e.s.r.) utilises those of electrons. The e.s.r. method is restricted, however, to systems possessing electrons whose spins are not paired, and whose magnetic moments are, therefore, not cancelled. The quantisation of the spatial orientation of the electron spins with respect to a static magnetic field results in discrete energy levels, just as with atomic nuclei possessing magnetic moments. Magnetic dipolar transitions may be induced between these energy levels by an alternating rf field whose frequency fulfills the resonance condition:

$$h\nu_0 = g\beta H_0 \tag{14}$$

where β is the Bohr magneton and g is the Landé or spectroscopic splitting factor, commonly referred to as the g value. For a static magnetic field of a few kilogauss the frequency of the radiation needed to include electron resonance lies in the microwave region of the spectrum.

The g value determines the position of the centre of the resonance, and has a value of 2·0023 for a completely free spin. Deviations from this value occur if there is an appreciable electronic orbital magnetic moment, and resonance will then occur either at higher or lower fields than that required for the free electron. To a good first approximation, orbital motion is completely quenched in nearly all organic free radicals, leaving the g values very close to that of a free spin. In transition metal compounds, however, the orbital contribution to the magnetic moment is often high, and g values differing widely from 2·0023 are found.

An e.s.r. spectrum may exhibit both fine and hyperfine structure. Where an atom or molecule has two unpaired electrons which interact strongly, a splitting of the electronic levels may result in fine structure being observed in the magnetic resonance spectrum. Apart from the case of biradicals no electronic splitting is possible in free radical spectra, but it is an important parameter in the e.s.r. study of many transition-metal ions. The hyperfine structure in a resonance spectrum arises from the interaction between the electron spin and the nuclear moments. This field may come from the nucleus of a paramagnetic ion itself or, in the case of a free radical, from a nucleus which is embraced in the molecular orbit of the electron. Because a nucleus of spin I may set itself in any of $2I + 1$ orientations, the vector sum of the external field and the nuclear field will have $2I + 1$ possible values, and the e.s.r. absorption line will be split into $2I + 1$ components. The splitting between the lines is termed a hyperfine splitting. This example illustrates hyperfine interaction in its simplest form. When more than one atomic nucleus in a given molecule can affect the resonance absorption, the final spectrum may be complicated. Fig. 3 shows the e.s.r. response of naphthacene positive ion, formed by dissolving naphthacene in concentrated sulphuric acid.[66] This molecule has three different kinds of proton positions with four protons in each class, and a spectrum of 125 lines might, therefore, be expected. One of the splittings, however, is within 1% of being three times another, and this results in 85 lines, 81 of which could be counted in the original spectrum. Although the detailed interpretation of an e.s.r. spectrum is not always possible, it is the occurrence and analysis of the hyperfine splitting which frequently makes high-resolution e.s.r. such an important tool for analytical purposes.

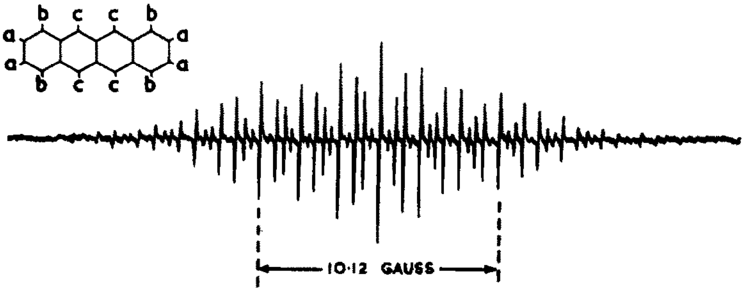


FIG. 3.—Hyperfine pattern (derivative tracing) of naphthacene positive ion (Hyde and Brown[66]).

Whilst in high-resolution n.m.r. the line widths are primarily determined by instrumental effects, in particular the homogeneity and stability of the magnetic field, the widths of the hyperfine components in an e.s.r. spectrum are governed by physical events within the sample itself, *i.e.*, by the relaxation phenomena. Three mechanisms by which relaxation occurs are: (1) spin–lattice interaction, (2) spin–spin interaction, (3) exchange interaction. Exchange interaction occurs when electrons are exchanged between the orbitals of different atoms or molecules. The effect is usually to average out the internal magnetic fields acting on the electrons, and thus narrow the line width. Exchange narrowing occurs only at high concentrations. The line widths observed in e.s.r. spectra vary from as little as 17 mgauss for free radicals in solution[67] to as much as 800 gauss for a paramagnetic ion in the solid state, even at 12°K.[68]

(*B*) *Experimental method*

The apparatus commonly used in e.s.r. studies differs from that used in n.m.r. studies chiefly in that microwave components replace conventional radiofrequency equipment. Although the choice of microwave frequency for optimum sensitivity depends among other factors on the nature of the sample, the most generally used frequency band is that centred on 10,000 Mc/sec (X-band). To achieve a higher sensitivity and to improve the resolution of the e.s.r. method, an a.c. modulation of the steady magnetic field, followed by phase-sensitive detection, is normally used in conjunction with a pen recorder to display the signal. The absorption line appears on the recorder as its first derivative, with respect to time. E.s.r. spectrometers which use a.c. modulation and phase-sensitive detection can now be obtained commercially.

For an introduction to the experimental techniques of e.s.r. the reader is referred to the literature (see *Bibliography*). Two recent advances in measurement technique will be mentioned here. A method by which an important gain in signal-to-noise ratio may be obtained has been described by Piette.[69] The output from an e.s.r. spectrometer is applied to a computer of average transients (CAT) with the result that the resonance signal is reinforced, because all additions of a positive signal are in phase. Noise signals, being random, are not in phase and thus average out. A signal-to-noise improvement factor of $\sqrt{n}$ is obtained where n is the number of times the spectrum is run. It should be noted that this technique is equally applicable to n.m.r., where it may be of special value when only small quantities of sample material are available.

With the methods commonly used for quantitative analysis by e.s.r., the unknown samples are compared with standards containing known concentrations of paramagnetic molecules, by measuring them successively and independently. The main experimental difficulty encountered is that different samples may perturb the measuring system in different ways. Thus, the intensity of absorption of a paramagnetic species depends, among other things, on the strength of the microwave magnetic field. Therefore, if the number of unpaired spins is to be determined, the strength of the microwave field must be kept rigidly constant when the comparisons of standards and unknowns are made. A recent device for comparative measurements of concentrations which avoids this and other sources of error is the double cavity.[70] In the double cavity two different samples can be placed at different maxima of the polarising magnetic field in the same microwave field. By arranging that the samples are in different polarising fields, overlap of their spectra is avoided. Using the double cavity it is possible to make exact determinations of the free-spin concentrations of samples with significant non-resonance absorption, especially of those containing water.

(C) *Applications of e.s.r.*

Because e.s.r. spectroscopy is only applicable to systems containing unpaired electrons its analytical capabilities are strictly limited, and the method will never rival n.m.r. in its importance to the analyst. Within its range, however, it is unexcelled both for sensitivity and speed. It is still a relatively young technique, which has undergone much slower instrumental development than that which has taken place with n.m.r. The full potential of e.s.r. as an analytical tool has certainly not been reached nor can it be truly evaluated at this early date.

Ingram,[71] Feher[72] and Fraenkel[73] have discussed in detail the factors that affect the sensitivity of the e.s.r. method. The theoretical limit of sensitivity approaches 10^9 unpaired spins. Realisable sensitivities at room temperature, with currently available commercial instruments, approach 10^{11} spins, or less than 10^{-12} mole, for an absorption line width of $\sim$2 gauss. This sensitivity is beyond that of other physical and chemical methods of quantitative analysis, and it can be improved by cooling the sample to low temperatures; severe cooling may, however, destroy the typical characteristics of the system under investigation. The highest sensitivities may be achieved only with samples of low dielectric loss. When aqueous or other samples showing high dielectric loss are used, it is necessary to use smaller volumes, *e.g.*, specimen tubes of 1 mm diameter instead of the more usual 5–6 mm diameter, to avoid excessive damping of the cavity and consequent reduction of sensitivity. Optimum e.s.r. signals with aqueous samples may be obtained by the use of flat quartz cells suitably oriented at the node of the electric field in the cavity.

Although the sensitivity of the e.s.r. method is high, the accuracy of quantitative measurements is often low. The inaccuracy arises, at least in part, because the recorded spectrum is usually a derivative trace and this must be integrated twice to obtain the signal intensity, and then compared with some standard, similarly treated. In these determinations of concentration the error may reach ±20%. If the line shape remains unchanged in a series of measurements and only relative concentrations of unpaired spins are required, integration may be dispensed with and measurements of peak-to-peak height on the derivative presentation used for comparison purposes. The error in such determinations of concentration should not exceed ±5% in favourable cases.

The analytical applications of e.s.r. will be surveyed here under three headings.

(*i*) *Free radicals.* A considerable amount of work utilising the e.s.r. technique simply as a method of detecting free radicals has been reported (*e.g.*, see references 74–78). Because the widths of the absorption lines observed for free radicals are usually quite small, strong signals are observed from small amounts. Radiation damage, however caused, commonly involves the rupture of bonds and the formation of free radicals, which may remain trapped in a solid structure. Many reports on e.s.r. studies in this field will be found in a collection of papers from a symposium on free radicals in biological systems.[79]

The e.s.r. technique has been used in many cases not only to detect, but also to identify free radicals. Analysis of the hyperfine structure of the resonance spectrum can be particularly useful in this respect.[71,80] The presence of the perinaphthenyl radical in the pyrolysis products of petroleum hydrocarbons has been inferred from the hyperfine pattern of the observed e.s.r. spectrum.[81] With free radicals of biological importance the resolution of hyperfine structure frequently fails because of molecular complexity. Even in this case, however, some general features can often be recognised, and identified with the same spectrum in simpler compounds.[82]

Although not nearly as useful as the hyperfine splitting for distinguishing radical spectra, the g value can be used for the purpose of identification. If the hyperfine structure is poorly resolved, it may, in fact, be the only determinable quantity which can be used to identify the radical. Because the g values of nearly all free radicals are within 0·5% of the free-spin value, precision measurements are required. An extensive study of the g values of semiquinone free radicals and hydrocarbon ions has been made.[83] The g values of a particular homologous series were found to vary in an apparently systematic manner. Observed shifts caused by changes in temperature, solvent and radical concentration were small compared to shifts caused by changes in molecular structure. An investigation of the nature of free radicals in petroleum asphaltenes has shown that the g values differ from those of the semiquinoid system, but are close to those of aromatic systems.[84] Peroxy radicals, $RO_2\cdot$, have no hyperfine structure detectable by present methods except that attributable to ^{17}O. Because of the difficulty of ^{17}O labelling, a method of identification based on the ^{17}O hyperfine splittings of free radicals is not yet broadly applicable. It has recently been shown[85] that the g values of peroxy radicals may distinguish them from free radicals of the type $R\cdot$ or $RO\cdot$.

Because the total intensity of the spectral lines is directly proportional to the number of unpaired spins present, the e.s.r. spectrum serves not only for identification purposes but also gives a direct measure of the concentration of free radicals. An example of such an application is the measurement of free radical concentration in low-temperature carbons.[86] Other examples are the estimation of the number of free radicals trapped during polymerisation,[87] and the number of radiation-induced free radicals in alanine and some related amino acids.[88] Hydroperoxides are usually determined by iodometry, but this method does not determine different types of hydroperoxide separately from their mixture. Electron resonance has now been used as an analytical technique for the determination of hydroperoxides in a solution, and can estimate a particular type of hydroperoxide in a mixture of several different hydroperoxides.[89] The e.s.r. method is based on the reaction between 1,1-diphenyl-2-picrylhydrazyl and hydroperoxides.

The ability to obtain free radical concentrations directly from the e.s.r. spectra makes the technique particularly useful for measuring the concentration of radical intermediates as a function of time. Free radicals which disappear at a slow rate are easily measured by merely following the decay of the e.s.r. signal with time. On the other hand, radicals with short lifetimes may be stabilised by freezing them at liquid nitrogen or liquid helium temperatures, and the actual concentration thus caught at any desired time interval. In this way rate constants of different chemical reactions and polymerisation processes have been determined (*e.g.*, see ref. 90). The e.s.r. spectrometer can also be used to study short-lived radical intermediates in chemical reactions under steady-state conditions by means of a flowing-sample technique.[91] The reactants are vigorously mixed at the entrance of the sample cell, and by varying the flow rate radicals can be observed within mseconds after mixing. A paper by Yamazaki, Mason and Piette[92] describes a typical kinetic application of the e.s.r. spectrometer to rapid free-radical reactions. Using a flow system, these workers were able to detect and identify free radicals from substrates, and to follow the kinetics of their formation and their subsequent decay during the oxidation of ascorbic acid and hydroquinone by peroxidase-hydrogen peroxide solutions.

It has been established that some aromatic hydrocarbons are oxidised to the corresponding cations at the surface of well-dried silica-alumina, and that the resulting species are stable in the adsorbed state.[93] These results have led to the development of an analytical method for the estimation of certain polynuclear hydrocarbons by e.s.r..[94] The e.s.r. method can detect less than 10^{-10} mole of hydrocarbon and its accuracy compares favourably with other spectroscopic methods of analysis at low concentrations. The resonance method depends for its success on the quantitative nature of radical formation on the catalyst surface. For each of the hydrocarbons studied (anthracene, perylene, dimethylanthracene and naphthacene) conversion into the radical form was found to be complete, within the limit of experimental error, over a wide range of concentration. The radical concentration in an unknown solution is determined by direct comparison of the signal amplitude (peak-to-peak height on the first derivative curve) for the unknown with that for a standard solution of the same radical. Using two such standards, the time required for a complete determination on a solution of unknown concentration is about 30 min. The method is accurate to about 5%.

(*ii*) *Transition-element ions.* The transition group elements are characterised by having unpaired electrons in the *d* and *f* orbitals, and their e.s.r. spectra usually differ from that given by free radicals. The *g* values of most free radicals remain close to the free-spin value of 2·0023 because there is very little coupling between the spin motion and any orbital motion. With paramagnetic atoms or ions the *g* value may vary over a wide range from 1 to 6 or more. This is because the electron is still bound to the paramagnetic atom, and thus has some interaction with the orbital motion *via* the spin-orbit coupling. In such cases the *g*-value variation can be very useful for distinguishing different spectra. Where the spin-orbit coupling is appreciable, the contribution from the orbital angular momentum is dependent on the relative orientation of the external magnetic field with respect to the paramagnetic ion and the resultant splitting of the energy levels is, therefore, anisotropic. In such cases a resolved spectrum can usually be obtained only by studying single crystals; in powders or solutions the anisotropic splitting gives rise to broad lines. If the ion has strong spin-lattice interaction, it will also be necessary to cool the specimen until the line width produced by this effect is less than that of the spin–spin interaction. With most of the ions in the rare-earth group, liquid helium temperatures are required to reduce the spin lattice interaction sufficiently for fine structure to be observed. The requirements for the iron group are less severe but, for many of the members, liquid hydrogen temperatures are necessary. Spin–spin interaction can be reduced by diluting with an isomorphous diamagnetic salt.

Typical spectra of transition-element ions extend over several hundreds of gauss and rarely contain resolved components as narrow as a few gauss. Fig. 4 shows the hyperfine structure of the e.s.r. spectrum of $^{55}Mn^{2+}$ (which possesses an isotropic g value) in water at room temperature. Other ions with isotropic g values include tervalent iron and tervalent gadolinium. The Mn^{2+} spectrum extends over ~700 gauss. The six-line pattern results from the six $(2I + 1)$ possible magnetic orientations of the ^{55}Mn nucleus $(I = 5/2)$ with respect to the applied magnetic field. Such a spectrum may be used to identify the Mn^{2+} ion, and its concentration may be estimated from comparative peak height measurements using a suitable standard. The method is a sensitive one. Spectra with a 10:1 signal-to-noise ratio may be obtained from aqueous solutions of 10^{-6} molarity using a flat quartz cell.[95] The technique has been used to detect trace paramagnetic elements, such as manganese or copper, as they occur in natural tissue,[96] and to investigate the concentration of manganese in certain micro-organisms.[97]

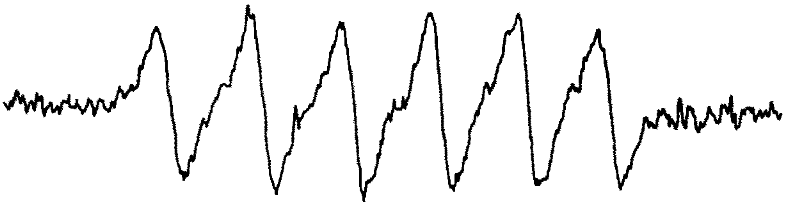


FIG. 4.—E.s.r. spectrum (first derivative) obtained from a $10^{-6}M$ aqueous solution of manganous ion (Varian Associates[95]).

The conversion of normally diamagnetic impurities into paramagnetic ones by excitation or by the attachment or removal of an electron has opened up another field of qualitative analysis. Various sources of irradiation may be used to bring about the conversion. For example, if quartz containing aluminium impurity is X-irradiated, the e.s.r. spectrum consists of six groups of lines each with six hyperfine lines.[98] This hyperfine structure may be accounted for by the unpaired electron being close to the aluminium impurity ion, which has a nuclear spin quantum number of 5/2.

Electron resonance has been used for the estimation of vanadium ion in petroleum distillates and residues.[99] In these investigations the most intense line of the vanadium absorption spectrum (first derivative curve) was used for quantitative analysis by directly comparing its height with that of a standard. Vanadium was detected down to at least 0·1 ppm, which makes e.s.r. spectroscopy applicable to vanadium analysis in practically all distillates. The time required for an estimation is only a few minutes.

(*iii*) *Atoms*. One of the intrinsic properties of atoms, with the exception of the rare gases, is that they all possess one or more unpaired electrons. Application of the e.s.r. technique to the gaseous phase is a recent development and it is likely that its use will be extended in the near future. Methods for using both diffusion and flow systems for detecting and estimating atoms in the gaseous phase have been described.[100]

The e.s.r. technique has been used to study the effect of water vapour on the dissociation of hydrogen in an electrical discharge.[101] The yield of hydrogen atoms was determined from the integrated intensity of the hydrogen hyperfine doublet. Both relative and absolute concentrations of oxygen atoms have been determined by e.s.r. spectroscopy in a study of the recombination process.[100] The maximum of the derivative of the absorption was used for making relative concentration measurements. Absolute concentrations were determined by comparing the atomic oxygen absorption with absorption by a known concentration of oxygen molecules, integrated intensities being employed for the comparison. The general theory relating the measured integrated intensities of e.s.r. absorption lines to the concentrations of odd-electron species in the gas phase has recently been reviewed and discussed in some detail by Westenberg and de Haas.[102] These authors then applied the theory in the form required for determining the absolute concentrations of oxygen, nitrogen and hydrogen atoms using molecular oxygen as the calibration gas. The determination of absolute oxygen and nitrogen atom concentrations by e.s.r. was shown to be a reliable experimental technique by comparison with the independent results of titration with nitrogen dioxide and nitric oxide, respectively.

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M. C. R. Symons, "The Identification of Organic Free Radicals by Electron Spin Resonance", in V. Gold (ed.), *Advances in Physical Organic Chemistry*. Academic Press, London and New York, 1963. Vol. I.

Résumé—On décrit brièvement les principes des résonances magnétiques nucléaire et électronique, en relation avec l'emploi de ces techniques en chimie analytique. On passe en revue un large champ d'applications analytiques afin de mettre en évidence le domaine et les limitations de ces méthodes.

Zusammenfassung—Die Grundlagen der magnetischen Kern- und Elektronenresonanz werden unter Berücksichtigung ihres Gebrauchs in der analytischen Chemie kurz beschrieben. Es wird eine Übersicht über ein breites Spektrum analytischer Anwendungen gegeben, um den Einsatzbereich dieser Methoden und dessen Grenzen zu zeigen.

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Talanta, 1965, Vol. 12, pp. 559 to 566. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

A thermogravimetric pyrolysis study of the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines

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THIS paper arises from a study of the products obtained through the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines.[1] In earlier papers information was presented on the interaction of certain organic amines with 1,2,3-benzotriazole derivatives of cyano complexes of the platinum group elements.[2,3] Pyrolytic results obtained for the amine derivatives gave support to the proposed formulae of the products formed in the interaction of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV).

EXPERIMENTAL

Apparatus and material

The thermobalance and its calibration, operation, and use have been reported previously.[4] The temperature of the combustion chamber was increased at an average of 3°/min over a temperature interval from room temperature to 750°. A Beckman IR-5-Spectrophotometer was used for obtaining infrared spectra of various decomposition products, using a standard potassium bromide-pellet technique and sodium chloride cells.

All precipitates were prepared according to the procedure of Wilson and Merchant.[1] The precipitates were filtered using fine-porosity, sintered-glass crucibles. The compounds were dried for 10 hr in a vacuum desiccator, using magnesium perchlorate as the desiccant.

RESULTS

Pyrolysis curves of the compounds with respective formulae:

(1) $(C_2H_5NH_3)_2Ru(CN)_6$; (2) $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$;
(3) $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$; (4) $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$;
(5) $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$; (6) $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$;
(7) $[CH(CHCH)_2NH]_2Ru(CN)_6$; (8) $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$;
(9) $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

are presented graphically in Figs. 1–3 and the analysis of the curves is given in Table I. The plateau at C_2 which persists up to the 750° limit of this study corresponds to indefinite mixtures of ruthenium

TABLE I

Compounds	Initial weight, *mg*	C_1 Weight corrected for moisture, *mg*	C_1 Temp. range, °*C*	C_2 Weight of ruthenium residue obtained, *mg*	C_2 Temp. range, °*C*
1. $(C_2H_5NH_3)_2Ru(CN)_6$	21·1	20·0	<110	4·2	>257
2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$	22·3	21·7	<53	5·6	>337
3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$	26·2	25·8	<65	6·3	>466
4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$	19·9	19·8	<61	3·6	>586
5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$	24·4	24·0	<159	6·3	>532
6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$	26·5	26·1	<151	5·2	>641
7. $[CH(CHCH)_2NH]_2Ru(CN)_6$	25·1	25·1	<30	5·4	>210
8. $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$	26·2	25·9	<65	5·7	>391
9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$	26·7	26·4	<128	6·2	>607

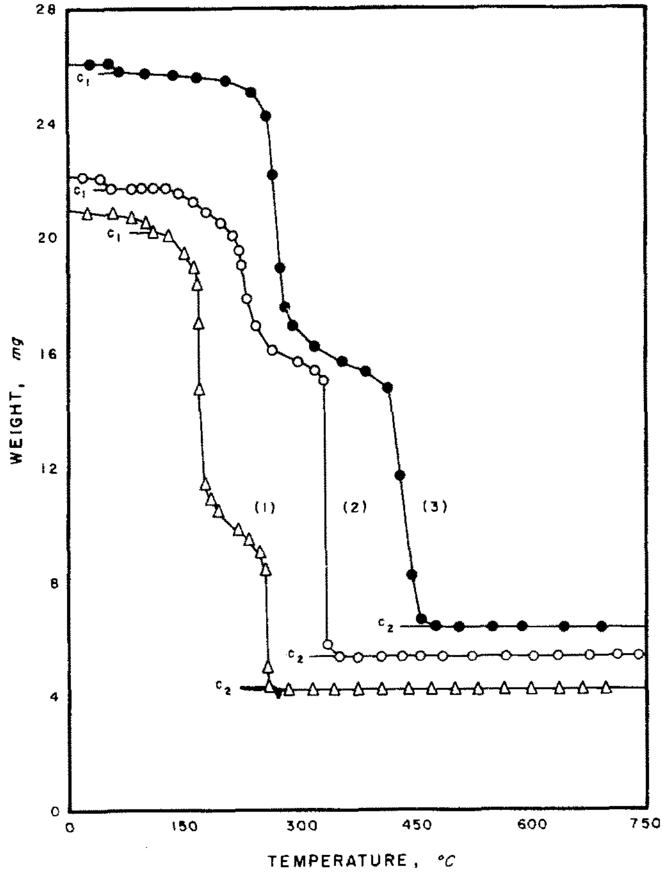

FIG. 1.—Thermogravimetric analysis of compounds 1-3:

1. $(C_2H_5NH_3)_2Ru(CN)_6$ —△—
2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$ —○—
3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$ —●—

and/or ruthenium oxides. The thermal decomposition of the amine derivatives is probably best explained by the following reactions:

1. $(C_2H_5NH_3)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{110°\text{–}257°} 2(C_2H_5)NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

2. $(C_6H_5NH_3)_2(C_6H_5NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{53°\text{–}337°} 4C_6H_5NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

3. $(CH_3NH_3)_2(CH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{65°\text{–}466°} 4CH_3NH_2\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{61°\text{–}586°} 4(C_2H_5)_2NH\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

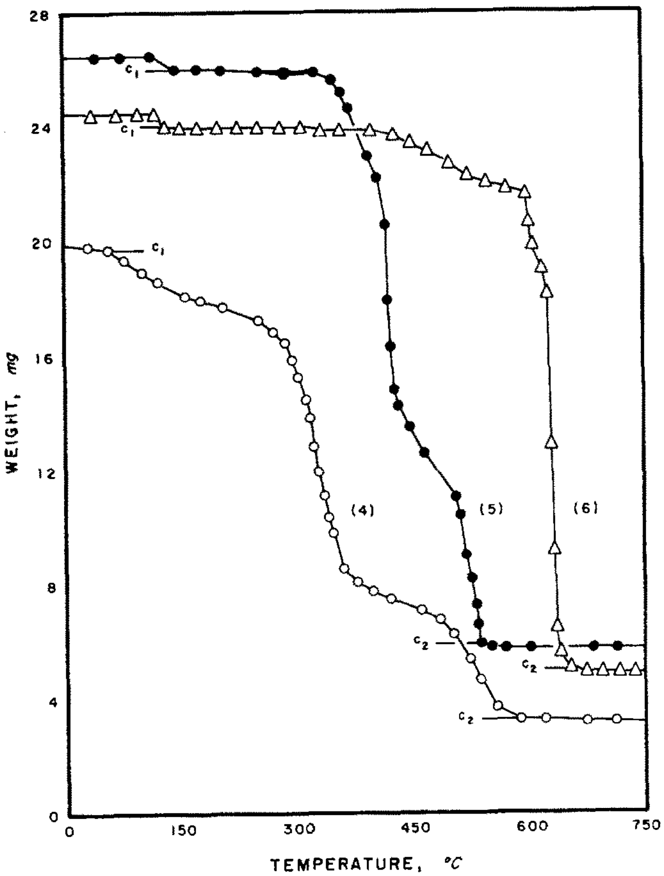

FIG. 2.—Thermogravimetric analysis of compounds 4-6:

4. $[(C_2H_5)_2NH_2]_2[(C_2H_5)_2NH]_2Ru(CN)_6$ —○—
5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$ —●—
6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$ —△—

5. $[(CH_3)_2NH_2]_2[(CH_3)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{159°\text{–}532°} 4(CH_3)_2NH\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

6. $(p\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{151°\text{–}641°} 2(p\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

7. $[CH(CHCH)_2NH]_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{30°\text{–}210°} 2CH(CHCH)_2N\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

8. $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$

$$\xrightarrow[\text{Air}]{65°\text{–}391°} (CH_3)_4NCN\uparrow + C_6H_4N_2NH\uparrow + HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$

$$\xrightarrow[\text{Air}]{128°\text{–}607°} 2(m\text{-}C_6H_4NH_2NH_2)\uparrow + 2HCN\uparrow + 2(CN)_2\uparrow + \text{ruthenium residue}$$

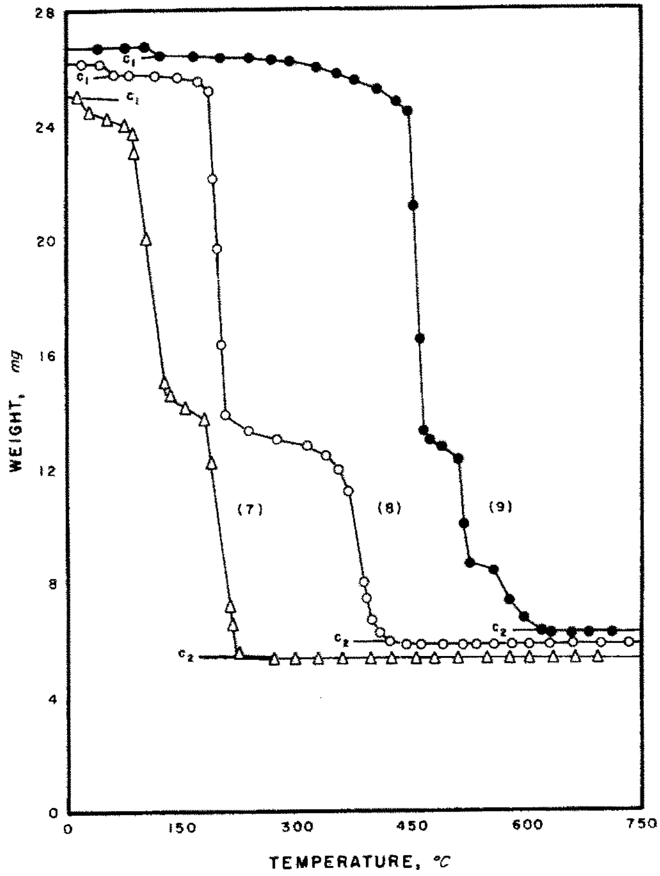

Fig. 3.—Thermogravimetric analysis of compounds 7-9:

7. $[CH(CHCH)_2NH]_2Ru(CN)_6$ —△—
8. $(CH_3)_4N(C_6H_4N_2NH_2)Ru(CN)_6$ —○—
9. $(m\text{-}C_6H_4NH_3NH_2)_2Ru(CN)_6$ —●—

Isolation of pyrolytic products

The pyrolysis results presented for the thermogravimetric determinations of the amine derivatives obtained through the interactions of di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV) with certain organic amines suggest the presence of several decomposition products. To further verify the presence of certain decomposition products, 1-g samples of the respective amine derivatives were separately decomposed in a special decomposition apparatus as described by Wilson and James.[5] The coolant (CO_2) was sufficient to condense *m*-phenylenediamine and *p*-phenylenediamine from their respective amine derivatives, and 1,2,3-benzotriazole from the tetramethylammonium chloride derivative. The presence of aniline was verified by decomposing a 1-g sample of the amine derivative and allowing the resulting vapours to dissolve in water. On the addition of hydrogen chloride to the solution, aniline hydrochloride was obtained. The vapours resulting from the diethylamine, ethylamine, methylamine, dimethylamine and pyridine derivatives were each dissolved in separate carbon tetrachloride solutions. In all cases the infrared spectra obtained from the aniline hydrochloride and the respective amine samples contained all of the principal absorbance bands corresponding to the infrared spectra of the respective pure samples. The presence of hydrogen cyanide and/or cyanogen was verified by decomposing 1-g samples of the respective amine derivatives and allowing the vapours to dissolve in aqueous silver nitrate solution. In each case a white precipitate of silver cyanide was obtained.

DISCUSSION

In this study the thermobalance was employed to follow the pyrolysis reactions taking place in certain complex interaction products obtained through the interaction of several organic amines and tetramethylammonium chloride with di(1,2,3-benzotriazolatium)hexacyanoruthenate(IV). Decomposition of the amine derivatives gave hydrogen cyanide and/or cyanogen, the respective amine, a ruthenium residue and in one case 1,2,3-benzotriazole and tetramethylammonium cyanide.

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Zusammenfassung—Es wird über die thermogravimetrische Pyrolyse der Reaktionsprodukte einiger organischer Amine und Tetramethylammoniumchlorid mit Di(1,2,3-benztriazolatium)hexacyanoruthenat (IV) berichtet.

Résumé—On décrit la pyrolyse thermogravimétrique des produits d'interaction de certaines amines organiques et du chlorure de tétraméthylammonium avec l'hexacyanoruthénate(IV) de di (1,2,3-benzotriazolatium).

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(*Received* 12 *February* 1965. *Accepted* 1 *March* 1965)

In a previous paper[1] a study was presented of the coprecipitation of tracer quantities of radioactive scandium, yttrium, cerium(III) and indium with milligram quantities of aluminium precipitated as the tris-(8-hydroxyquinolate) by slow isothermal evaporation of aqueous acetone solutions. For these systems it was concluded that coprecipitation of the tracer (M) remained small over almost the complete range of precipitation of the carrier unless the tracer took the form $M(C_9H_6ON)_3$. This conclusion has now been examined in relation to the behaviour of iron(III) and zinc as tracers.

EXPERIMENTAL

The reagents, apparatus and procedure were those used in the earlier investigation with the following additions or modifications.

Tracers. Iron-59 (containing some inactive iron) and carrier-free zinc-65 were obtained (in 0·1*M* and 1*M* hydrochloric acid, respectively) from the Radiochemical Centre, Amersham, England. Dilute solutions of each isotope were prepared in 0·1*M* hydrochloric acid as required.

Counting. Counting was performed by means of a well-type sodium iodide (thallium activated) scintillation counter.

Procedure. In experiments 9, 10 and 11 of Table I, the final measurements were made on aliquots of solutions prepared by diluting the filtrates with acetone to the volumes they occupied before evaporation.

Infrared spectra. The infrared spectra were obtained from Nujol mulls in the 2·5 to 25 μ region using a Grubb-Parsons double-beam grating spectrophotometer.

RESULTS AND DISCUSSION

Milligram amounts of iron and zinc are precipitated quantitatively from acetic acid-acetate solution.[2] The former is obtained[2,3] as $Fe(C_9H_6ON)_3$ on drying at 120°, the latter as $Zn(C_9H_6ON)_2 \cdot xH_2O$ where x is variable and depends on the drying temperature.[2,4] If the pattern of behaviour previously observed is followed, iron(III) would be expected to show similarities to indium, and zinc to the rare-earth ions.

The results recorded in Table I for the coprecipitation of tracer quantities of iron with aluminium tris-(8-hydroxyquinolate) are in agreement with the predicted behaviour. Values of D and λ show that the distribution of tracer follows the logarithmic law of Doerner and Hoskins.[5] The results may be compared with those obtained with indium as tracer when the fractional precipitation of tracer and carrier so nearly coincided over the whole range of precipitation that a distinction between the two limiting types of distribution could not be made. It has been reported[2] that iron(III) salts yield the tris-(8-hydroxyquinolate) from solutions containing as much as 25% acetic acid-sodium acetate. Acetate is, therefore, not expected to influence the tracer iron distribution appreciably; this conclusion finds support from the few measurements (Table I, experiments 12, 13, 14 and 15) made at lower acetate concentrations and from the observation that iron precipitated from aqueous acetone in the same molar quantity and under the same conditions as aluminium when used as carrier, gave the product $Fe(C_9H_6ON)_3$ on drying at 130°. The solubility of the iron compound, which is granular, appears to be quite low relative to that of aluminium in aqueous acetone.

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No.	Al pptd., %	Fe copptd., %	D	λ
1	7·90	10·7	1·40	1·36
2	29·5	38·9	1·52	1·41
3	30·3	42·9	1·73	1·55
4	39·4	51·5	1·63	1·44
5	50·9	65·3	1·81	1·48
6	58·3	74·1	2·05	1·55
7	61·1	73·5	1·77	1·41
8	68·2	80·8	1·96	1·44
9	78·8	89·8	2·37	1·47
10	78·2	90·5	2·66	1·55
11	84·7	94·1	2·88	1·51
12	12·8	17·1	1·41	1·37
13	21·7	30·8	1·61	1·51
14	48·6	63·1	1·81	1·50
15	61·6	77·6	2·16	1·56

* About 1×10^{-8} mole of iron was present in the system during each precipitation. Using the general procedure outlined previously[1] 40 ml of 2·0*M* ammonium acetate were used in experiments 1–11 and 40 ml of 0·20*M* in the remainder.

TABLE II.—THE COPRECIPITATION OF ZINC-65 FROM SOLUTIONS TO WHICH WERE ADDED 40 ml OF 2·0*M* AMMONIUM ACETATE

Al pptd., %	21·49	31·98	40·15	48·95	61·52	81·40	83·45
Zn copptd., %	0·421	0·526	0·547	0·874	1·14	1·06	0·925
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TABLE III.—COPRECIPITATION OF ZINC WITH ALUMINIUM IN DILUTE ACETATE SOLUTION AND IN THE ABSENCE OF ACETATE

No.	Al pptd., %	Zn copptd., %	$D \times 10^2$	$\lambda \times 10^2$
1	23·5	0·621	2·03	2·23
2	28·7	0·841	2·10	2·50
3	51·5	2·16	2·08	3·03
4	55·6	1·81	1·47	2·26
5	63·0	2·75	1·66	2·80
6	66·3	3·03	1·59	2·82
7	77·8	3·45	1·02	2·33
8	83·4	3·57	0·739	2·03
9	7·78	0·262	3·11	3·24
10	14·3	0·364	2·20	2·36
11	25·2	0·430	1·29	1·48
12	25·3	0·588	1·75	2·02
13	49·6	0·896	0·919	1·31
14	66·4	1·91	0·984	1·77
15	76·6	2·14	0·670	1·49
16	77·0	2·26	0·692	1·56
17	80·8	3·01	0·739	1·85
18	87·1	2·75	0·420	1·36

* Nos. 1–8 were carried out using 40 ml of 0·20*M* ammonium acetate and Nos. 9–18 had 15 ml of 0·100*M* sodium hydroxide + 25 ml of water replacing the ammonium acetate in the general procedure.[1]

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The explanation for the observed dependence of zinc coprecipitation on the medium is not clear. A thermogravimetric study of picolates and dipicolates of certain rare-earths[6] shows that solvates obtained directly on precipitation may depend on the pH of the medium from which precipitation occurs and it is possible that a similar dependence exists in the zinc coprecipitation. However, although conditions are not strictly comparable to those pertaining to the tracer experiments, when zinc replaces the same molar quantity of aluminium an identical product, as determined by its infrared spectrum, is isolated from solutions of the three compositions discussed. Some portions of the products examined were air dried at 130° and others for about 1 week at the laboratory temperature (20 ± 2°). Analysis of part of the precipitate obtained from the strong acetate medium and dried at 130° gave Zn, 18·4%; C, 61·1%; H, 3·43% [$Zn(C_9H_6ON)_2$ requires Zn, 18·5%; C, 61·1%; H, 3·42%]. The same precipitate dried at 20° gave Zn, 16·9%; C, 55·8%; H, 4·37%; H_2O, 9·01% [$Zn(C_9H_6ON)_2.2H_2O$ requires Zn, 16·8%; C, 55·5%; H, 4·14%; H_2O, 9·25%]. The precipitate, like that obtained previously with yttrium, has a low solubility relative to aluminium in aqueous acetone and is flocculent, suggesting extensive hydrogen bonding.

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Résumé—On a étudié, par radiochimie, la coprécipitation du fer (III) et du zinc, en très petites quantités, à l'état de traceurs, avec l'aluminium, précipité à l'étet de 8-hydroxyquinoléinate, par évaporation isotherme de la solution hydroacétonique. La coprécipitation du fer (III) suit la loi de répartition logarithmique, avec $\lambda = 1{,}47 \pm 0{,}07$, dans un large domaine de concentrations en acétate. Le zinc présente des analogies avec l'yttrium et d'autres ions de terres rares, par le fait qu'il ne coprécipite que pour une faible partie, sauf en cas de précipitation totale de l'entraîneur. Les résultats obtenus à partir de différents milieux ont montré des différences petites mais nettes, en particulier lors de la précipitation fractionnée croissante de l'entraîneur.

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LETTER TO THE EDITOR

Interlingua

SENIOR,

ESSEVA facilissimo de leger quel littera de Dr. Rieman[1] e credo que le majoria del chemistas pote leger alsi iste littera scribite sensa dictionarios o grammaticas de interlingua. Ora non esiste un metodo por scribire sistematicamente le chimicas in iste lingua ma non esserea multo difficile de far lo. Io provava cum nulla instructione in interlingua de traducer in "pidgin-interlingua" le articulos anglese in le littera de Professor Wilson: "... un novo analitico metodo esse introdotto pro (le analisso de) molecùli fluorescenti—analisso estingue—fluorescentia. Iste campo de ricerca avera applicationi grandi in analisso organico por traccias. Uso analitico esse fatto del effetto de estinguere in spectrofoto-fluorometria. Sostantias come antracene, fenantrene pyrene, benz(a)antracene, benzo(a)pyrene, perylene etc. esse stati trovati a esser non-fluorescenti in solutione de nitrometane, ma idrocarbonas contenenti il cercolo fluorantene esse fluorescenti".

However, I do not see how Interlingua, which is obviously based on Latin roots, could be any more understandable to readers (*e.g.*, Slavs or Orientals) knowing no Romance language than naturally existing members of this language group such as French, Italian and Spanish.

I feel, sir, that it would be far more useful for *Talanta* to publish papers in English, French, German or Russian and to give longer, more detailed abstracts in whichever three of these languages was not used by the author.

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AMPEROMETRISCHE BESTIMMUNGSMETHODE DES THIOACETAMID

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(*Eingegangen am* 30. *Oktober* 1964. *Angenommen am* 7. *Marz* 1965)

Zusammenfassung—Ein Verfahren zur amperometrischen Bestimmung von Thioacetamid wird angegeben. Die Bestimmung wird bei konstanter Temperatur (25°C) bei ungefähr konstantem pH (ca. 9,5; Ammoniak-Ammoniumnitrat-Puffer) und bei konstantem Potential (—0,4 Volt gegen eine gesättigte Kalomelelektrode) durch Zusatz von $AgNO_3$ durchgeführt. Als Kathode wird eine Quecksilber-Tropfelektrode verwendet, als Anode eine gesättigte Kalomelelektrode. Der Verlauf der Reaktion der komplexen Silberammine mit Thioacetamid wird an Hand des Reduktionsstromes verfolgt. Die Bestimmung geht schnell und einfach; die Ergebnisse sind ziemlich gut reproduzierbar. Der Fehler liegt im allgemeinen unter 1% bei Thioacetamidkonzentrationen von $1{,}0 \,.\, 10^{-2}$ bis $2{,}5 \,.\, 10^{-2}$ m und unter 2% von $5{,}2 \,.\, 10^{-4}$ bis $1 \,.\, 10^{-3}$ m.

EINLEITUNG

DIE in der quantitativen Analyse immer steigende Anwendung des Thioacetamid (TAA) bildet die Anregung, neue Bestimmungsmethoden für diesen Reagent aufzusuchen. Die bisher bekannten Methoden gehören meistens zu den jodometrischen und argentometrischen.

Zu den jodometrischen gehört z.B. die von Ray und Dey[1] so wie die unlängst von Anson[2] und von Waugh[3] angegebene Bestimmungmethode. Kurze Beschreibung beider letzten Methoden geben Swift und Anson[4] an.

Bush, Zuehlke und Ballard haben eine direkte, argentometrische Bestimmungsmethode ausarbeitet.[5] Bovalini und Piazzi melden auch von einer potentiometrischen und zugleich argentometrischen, direkkten Bestimmungsmethode des TAA an.[6]

Petri und Lipiec haben eine indirekte potentiometrische TAA-Bestimmungsmethode ausarbeitet.[7] Eine komplexometrische, indirekte Bestimmungsmethode des TAA wurde von Lesz, Wieczorkiewicz und Lipiec angewandt.[8]

Die von uns angegebene amperometrische TAA Bestimmungsmethode, gehört auch zu den argentometrischen.

Die Reaktion zwischen TAA und Ag^+-Ionen in ammoniakalischer Lösung bildet den Grund dieser Methode. Wegen der grossen Geschwindigkeit dieser Reaktion, die schon von Flaschka beobachtet wurde,[9] eignet sie sich speziell zur amperometrischen Bestimmung des TAA.

DER EXPERIMENTALE TEIL

Apparatur

Polarograph "Radiometer" PO 3m (Dänemark) und Polarograph LP 55 (CSR) (Tropfende Quecksilberelektrode als Kathode und gesättigte Kalomelelektrode als Anode); pH-Meter "Piezoelektronika" (Polen) Spektrophotometer "Unicam" SP 500 (England); Termostat nach Wobser (DDR); Generator zur elektrolytischen Gewinnung des Wasserstoffs; Automatische Büretten und Mikrobüretten.

Lösungen

Zur Vorbereitung der AgNO$_3$-Standardlösung wurde "spektral reines" metalisches Silber angewandt.* Thioacetamidlösung wurde aus dem "reinen" Handelspräparat nach mehrmaliger Kristallisation vorbereitet.

Die TAA-Lösungen wurden kühl (in der Temperatur 2°–6°) aufbewahrt.

In diesen Bedingungen sind sie im Zeitintervall von 3—4 Wochen stabil. KNO$_3$ und NH$_4$NO$_3$ wurden aus "analytisch reinen" Handelspräparaten nach zweimaliger Kristallisation angewandt.

Der pH-Wert der Lösungen wurde mittels Ammoniakpuffer (NH$_3$H$_2$O + NH$_4$NO$_3$/stabilisiert.

Prozedur

Die direkte Bestimmung. In ein elektrolytisches Gefässchen mit abgemessenem Volumen der AgNO$_3$-Standardlösung, mit KNO$_3$ als Grundelektrolit (1 g kristallinisches KNO$_3$ auf 12 ml/Lsg.) und mit der ammoniakalischen Pufferlösung führt man in sukzessiven Dosen die untersuchte TAA-Lösung aus einer automatischen Mikrobürette ein und jedesmal-nach der Stabilisierung des Gleichgewichtes -rejestriert man den Grenzstromwert.

Die indirekte Bestimmung. Abgemessenes Volumen der untersuchten TAA-Lösung führt man in ein elektrolytisches Gefässchen, welches schon die AgNO$_3$-Standardlösung in entsprechendem Überschuss, die ammoniakalische Pufferlösung und den Grundelektrolit enthält. Ohne den Ag$_2$S Niederschlag abzutrennen, der sich infolge der Reaktion zwischen TAA und Ag(NH$_3$)$_2^+$-Ionen bildet, titriert man-nach dem diese Reaktion zu Ende ist, den Überschuss der Ag$^+$-Ionen, mittels einer anderen, vorher, bestimmten TAA-Lösung, welche man aus einer Mikrobürette sukzessiv in die untersuchte Lösung einführt. Weitere Prozedur wie vorher im Laufe der direkten Bestimmung.

Die amperometrische Bestimmung wurde in beiden Varianten bei konstanter Temperatur (25,0° – 0,1°) annähernd konstantem pH-Wert (*ca.* 9,5°) und bei konstantem Potential (–0,4 V) durchgeführt. Bei diesem Potential werden nur Ag(NH$_3$)$_2^+$-Ionen an der Quecksilberelektrode reduziert. Die Luft wurde aus jeder Lösung durch Wasserstoffstrom entfernt. Der Verlauf jeder Titrationskurve war geradlinig, was schon früher[10] festgestellt wurde.

Die Konzentration der untersuchten TAA-Lösungen war im Intervall 5,2 . 10^{-4} Mol/L bis 2,5 . 10^{-2} Mol/L enthalten.

Die in der Tabelle I und II zusammengestellten Ergebnisse der direkten Bestimmung einer Serie der Lösungen (Tab. I) und der indirekten Bestimmung einer anderen Serie (Tab. II) illustrieren annähernd die Genauigkeit der angewandten Bestimmungsmethode.

TABELLE I—AMPEROMETRISCHE DIREKTE BESTIMMUNG DER TAA-LSG. UNTER DER ANWEDUNNG DER AgNO$_3$-STANDARDLÖSUNG

Nr.	TAA, *mg*		Δ mg	Δ %
	berechnet	gefunden		
1.	0,751	0,757	+0,006	0,74
2.	0,939	0,948	+0,009	0,96
3.	1,127	1,119	–0,008	0,71
4.	1,503	1,503	—	—
5.	1,653	1,649	–0,004	0,24
6.	1,878	1,897	+0,019	1,00

Potential = –0,4 V; [AgNO$_3$] = 1,00 . 10^{-2} Mol/L;
Temp = 25,0°; [CH$_3$CSNH$_2$] = 1,25 . 10^{-2}Mol/L; pH = *ca.* 9,5.

Der Wert der Fehler der ziemlich grossen Anzahl der Bestimmungen ist im allgemeinen für TAA-Konzentrationswerte von 1,0 . 10^{-2} Mol/L bis 2,5 . 10^{-2} Mol/L nicht grösser als 1,0% und für geringere TAA-Konzentrationen/von 5,2 . 10^{-4} Mol/L bis 1,0 . 10^{-3} Mol/L nicht grösser als 2,0%.

ERGEBNISSE UND DISKUSSION

Die erste Variante der angegebenen Methode (d.h. die direkte Bestimmung) ist nur damals anwendbar, wenn die Menge der untersuchten TAA-Lösung nicht zu gering ist. Die zweite Variante dagegen eignet sich zur Anwendung sogar bei sehr kleinen Mengen der TAA-Lösung.

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* Dieselbe AgNO$_3$-Standardlösung, ist auch zu den spektrophotometrischen Untersuchungen gebraucht worden.

TABELLE II.—AMPEROMETRISCHE INDIREKTE BESTIMMUNG DER TAA-LÖSUNGEN UNTER ANWENDUNG DER $AgNO_3$-STANDARDLÖSUNG (TAA-KONZENTRATIONSWERTE DER UNTERSUCHTEN LÖSUNGEN: 5,2 . 10^{-4} Mol/L bis 1,25 . 10^{-3} Mol/L).

Nr.	TAA, *mg* eingeführt	TAA, *mg* gefunden	Δ mg	Δ %
1.	0,470	0,466	0,004	0,85
2.	0,563	0,572	0,009	1,60
3.	0,677	0,674	0,003	0,44
4.	0,939	0,924	0,015	1,58
5.	1,033	1,017	0,016	1,54
6.	1,127	1,118	0,009	0,80

Potential = −0,4 V; $[AgNO_3] = 1{,}00 . 10^{-2}$ Mol/L;
Temp = 25,0°; $[CH_3CSNH_2] = 2{,}50 . 10^{-2}$ Mol/L; pH = *ca.* 9,5

Sowohl im ersten als auch im zweiten Fall der dargestellten Methode der TAA-Bestimmung, sind die Ag^+-Ionen in der Lösung hauptsächlich in der Form der ziemlich stabilen $Ag(NH_3)_2^+$-Komplexionen anwesend, da Ammoniak, der hier auch als Komplexbildner wirkt, immer in grossem Überschuss anwesend ist.

Das Sinken der Ag^+-Ionenkonzentration infolge der Bildung der $Ag(NH_3)_2^+$-Komplexionen bedingt starke Erniedrigung des Redoxpotentials des Silbers (der normale Redoxpotential sinkt vom Wert 0,799 V bis 0,370 V,[11] was eben die Anwendung der tropfenden Quecksilberelektrode ermöglicht, ohne Gefahr irgendwelcher unerwünschten Reaktion zwischen dem Quecksilber und den $Ag(NH_3)_2^+$-Ionen. Kalvoda und Zyka haben davon auch schon Gebrauch gemacht, indem sie zur amperometrischen Bestimmung des Silbers in der Form der $Ag(NH_3)_2^+$-Ionen die Quecksilberelektrode angewandt haben.[12]

Es ist charakteristisch für beide Varianten der dargestellten Methode, dass im Laufe der TAA-Bestimmung die $Ag(NH_3)_2^+$-Ionen im Überschuss gegenüber dem TAA sind, was die Möglichkeit der Bildung der $Ag(TAA)_n^+$-Komplexionen, wenn nicht gänzlich liquidiert, so doch stark vermindert.

Die komplexbildenden Eigenschaften des TAA wurden bereits mehrmals festgestellt. Swift und Anson[13] signalisieren über den hemmenden Einfluss des Überschusses des TAA auf die Ag_2S-Bildung in der Reaktion zwischen TAA und Ag^+-Ionen infolge der Komplexbildung.

Nach Smith und Owen[13] reagiert TAA als Komplexbildner mit Hg^{2+}-Ionen und nach Booth[13] mit Cu^+-Ionen. Nardelli und Chierici[14] melden von TAA-Komplexverbindungen mit manchen zweiwertigen Metallen wie z.B. Fe^{2+}, Co^{2+}, Zn^{2+}u. anderen.

Die komplexbildenden Eigenschaften des TAA bilden den Gegenstand der Untersuchungen auch in unserem Institut.

Aus unseren spektrophotometrisch durchgeführten Untersuchungen folgt, dass in ammoniakalischen Ag^+-Ionenlösungen, im Falle der gleichen Konzentration des TAA und Ag^+-Ionen so wie im Falle der überwiegenden Konzentration der Ag^+-Ionen keine Syptome der Komplexbildung zwischen TAA und Ag^+-Ionen auftreten. Das heisst, dass in Konzentrationsverhältnissen, die im Laufe der amperometrischen Bestimmung des TAA nach der dargestellten Methode stattfinden, TAA mit $Ag(NH_3)_2^+$-Ionen nicht als Komplexbildner reagiert und die Reaktion ausschliesslich in der Richtung der Ag_2S-Bildung verläuft. Dafür spricht auch die Tatsache, dass im Laufe der amperometrischen Bestimmung nach der Einführung jeder sukzessiven Dose des TAA in die $Ag(NH_3)_2^+$-Ionenlösung, das Gleichgewicht sich fast sofort einstellt. Die reichlich durchgeführten Proben, der direkten amperometrischen Bestimmung der TAA-Lösung, die in ein elektrolytisches Gefässchen eingeführt wurde, mittels $AgNO_3$-Lösung, welche man sukzessiv, aus der Mikrobürette dosierte, waren erfolglos.

Die so erhaltenen Ergebnisse waren nämlich immer zu gering, indem der Prozentfehler grösstenteils $> 3{,}0$ war.

Der Mechanismus der Reaktion zwischen TAA und $Ag(NH_3)_2^+$-Ionen ist also vermutlich nicht derselbe im Fall, wenn im Gang der Titration-die Konzentration der TAA-Lösung die der Ag^+-Ionen überwiegt (wie es in den eben genannten Proben war), als wenn die Ag^+-Ionenkonzentration im Laufe der Bestimmung überwiegt.

An dieser Stelle sage ich Frau E. Malkiewicz meinen Dank für ihren Anteil im experimentalen Teil der vorliegenden Arbeit.

Summary—A method is given for the amperometric determination of thioacetamide. The determination is carried out at constant temperature (25°) at approximately constant pH (*ca.* 9·5 ammonia-ammonium nitrate buffer) and at constant potential ($-0{\cdot}4$ V *vs.* a saturated calomel electrode) by the addition of silver nitrate, using a dropping mercury electrode as cathode and a saturated calomel electrode as anode. As the $Ag(NH_3)^+$ ions react with the thioacetamide, the reduction current of the ions is registered. The determinations are rapid and easily carried out, and the results are fairly reproducible. The error is generally $<1{\cdot}0\%$ for concentrations of thioacetamide in the range $1{\cdot}0 \times 10^{-2}$ to $2{\cdot}5 \times 10^{-2}$ M and $<2{\cdot}0\%$ in the range $5{\cdot}2 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-3}$ M.

Résumé—On décrit une méthode de dosage ampérométrique du thioacétamide. Le dosage est mené à température constante (25°), à pH approximativement constant (environ 9,5; tampon ammoniaque-nitrate d'ammonium) et à potentiel constant ($-0{,}4$ V par rapport à l'électrode au calomel saturée), par addition de nitrate d'argent, en utilisant une électrode à goutte de mercure pour cathode et une électrode au calomel saturée pour anode. Les ions $Ag(NH_3)^+$ réagissant avec le thioacétamide, le courant de réduction des ions est enregistré. Les dosages sont rapides et aisés à mener, et les résultats assez bien reproductibles. L'erreur est en général $< 1{,}0\%$ pour des concentrations en thioacétamide comprises entre $1{,}0 \times 10^{-2}$ et $2{,}5 \times 10^{-2}$ M, et $< 2{,}0\%$ entre $5{,}2 \times 10^{-4}$ et $1{,}0 \times 10^{-3}$ M.

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SEPARATIONS OF PROTACTINIUM FROM NIOBIUM, TANTALUM AND OTHER ELEMENTS BY SOLVENT EXTRACTION USING *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

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Summary—The extraction of niobium, tantalum and protactinium from hydrochloric acid solutions containing fluoride into chloroform solutions of *N*-benzoyl-*N*-phenylhydroxylamine has been studied. From such aqueous systems it is possible to separate pairs or all three of these elements efficiently and in a reasonably quantitative manner. In addition, protactinium may be easily separated from zirconium (and presumably also hafnium), aluminium, titanium, manganese(II), iron(III), rare earths and thorium by extracting it from concentrated hydrochloric acid solutions. The back-extraction of niobium, tantalum and protactinium into aqueous phases of various compositions and additional separations thus revealed are also discussed. Phase distribution measurements and separations have been performed using suitable radioactive isotopes of the elements concerned.

THE separation of protactinium-231 from uranium ores and ore residues and protactinium-233 from thorium and uranium necessitates the removal of this element from a large number of other elements.[1–3] Preliminary separations are frequently achieved by coprecipitation of the protactinium with zirconium (and hafnium), tantalum, niobium, titanium, thorium (when they are hydrolysed from solution at high pH or precipitated with certain elements as phosphates or occasionally as oxalates or iodates) or with manganese (precipitated as manganese dioxide).[4,5] The separation of protactinium from several of these elements, notably the first three, presents difficulties.[4] A separation from zirconium, niobium and tantalum from hydrochloric-hydrofluoric acid solutions using an anion exchanger has been described by Kraus and Moore.[6] Maddock and Pugh[7] separated zirconium from protactinium by preferential elution of the former with 6–7M hydrochloric acid. Such methods, while giving highly satisfactory separations, are slower than solvent-extraction procedures. However, few systematic studies of the separation of protactinium from zirconium, niobium and tantalum by solvent extraction exist; methods only exist at present for the separation of pairs of the elements, frequently from aqueous media of widely differing compositions. Thus Moore[8] has described an efficient extraction of niobium from protactinium in dilute hydrofluoric-sulphuric acid solutions using di-isobutyl carbinol, but in the course of the present work it was found that under the same conditions only about 30% of tantalum is removed in a single extraction. The same solvent has been used[9] to extract protactinium from thorium and fission products; the solutions were $4M$ in nitric acid and $0{\cdot}6M$ in aluminium nitrate. The decontamination factor from niobium-zirconium was $2{\cdot}5 \times 10^2$ employing four successive extractions and five scrub stages using $2M$ nitric acid, and $0{\cdot}6M$ aluminium nitrate scrub solutions. To minimise emulsification, a problem with this solvent, the extractions were performed at 50°.

N-Nitroso-*N*-phenylhydroxylamine, ammonium salt (cupferron), reacts with protactinium in quite strong mineral acid solution; the product from $2M$ sulphuric acid is extracted into amyl acetate. Maddock and Miles[10] and more recently Spitsyn and Golutvina[11] used this substance to separate protactinium from manganese. The first mentioned authors observed that decomposition of the cupferron in solution can lead to serious loss of protactinium unless reagent solutions are stabilised (quinol was recommended) and frequently prepared fresh. They also state that fluoride must be absent and that tantalum is separated from protactinium by extracting the latter into amyl acetate from an aqueous tartrate solution $3M$ in hydrochloric or nitric acid and containing cupferron. Satisfactory conditions for a separation from zirconium (or hafnium) using cupferron were not obtained.

N-Benzoyl-*N*-phenylhydroxylamine (NBPHA), a substance which behaves in many of its reactions with metal ions in a similar manner to cupferron,[12] has been applied to a study of the extraction of protactinium in $3{\cdot}5M$ sulphuric acid solution and separations from iron, niobium, rare earths, thorium and uranium were thus obtained.[13] This reagent possesses greater chemical stability than cupferron, particularly in strong acid solutions in which the latter is readily decomposed. In the work to be described a study has been made of the behaviour of tracer amounts of protactinium and up to mg amounts/ml of niobium and tantalum in hydrochloric-hydrofluoric acid systems upon equilibration with a chloroform solution of NBPHA. The presence of fluoride helps to ensure maintenance of the protactinium in true solution, particularly at lower acid concentrations. Back-extraction of these elements from the chloroform phase into aqueous phases has been examined. On the basis of this work convenient separations of protactinium from niobium and tantalum have been devised by liquid–liquid extractions. The behaviour of zirconium in hydrochloric-hydrofluoric acid solutions has already been described[14] and the separation of protactinium from elements like titanium, manganese, iron and aluminium is also taken into account using NBPHA solutions in chloroform. Partition coefficients were measured and separations tested using radioactive isotopes of the appropriate elements.

EXPERIMENTAL

Radioisotopes

Protactinium-233. Obtained by irradiating thorium oxide with thermal neutrons in BEPO, Harwell. The protactinium was separated in the carrier-free form by the ion-exchange method described by Hill.[15]

Tantalum-182. Obtained from The Radiochemical Centre, Amersham, England, as tantalum pentoxide (activity 1 mc/1·1 mg of tantalum) dissolved in potassium hydroxide.

Zirconium-95 *and niobium*-95. Carrier-free zirconium-95/niobium-95 in 0·5% oxalic acid, was obtained from The Radiochemical Centre, Amersham, England. From this mixture niobium was separated using NBPHA.[14] Zirconium-95 was freed from traces of niobium daughter, when required, by the same method.

Reagents

All reagents used were of analytical-reagent grade unless otherwise stated.

Niobium carrier solution. Niobium pentoxide [B.D.H. laboratory reagent grade] was weighed out accurately and fused with twice its weight of potassium hydrogen sulphate. The melt was extracted into boiling $1M$ tartaric acid solution, cooled and diluted to give a solution containing 10 mg of niobium/ml.[16]

Tantalum carrier solution. An accurately weighed quantity of tantalum metal was dissolved in a mixture of nitric and hydrofluoric acids by warming to 65°. The solution was cooled and diluted to give 10 mg of tantalum/ml.[16]

N-*Benzoyl*-N-*phenyldroxylamine.* Obtained from B.D.H. or L. Light and Co., Colnbrook, England. Samples having melting points of 120°–121° were used directly while those with lower melting points were recrystallised from hot water.

Chloroform. B.D.H. laboratory reagent grade (contains 2% ethanol as preservative).

Apparatus

Counters. Niobium, tantalum, and protactinium samples in the liquid form (2 ml) were counted in a well-type γ-scintillation counter having a sodium iodide (thallium activated) scintillator. Use was made of the 776 keV γ-ray from niobium, the 100 keV γ-ray from tantalum and 107 keV γ-ray from protactinium in the distribution measurements.[17]

γ-Ray spectra were obtained for each nuclide separately and for mixtures of pairs of these nuclides using a Hutchinson-Scarrat pulse-height analyser (100 channels) of type 1363 D made by Clifford and Snell, Sutton, Surrey, England. This instrument was used in conjunction with a flat (cylindrical) sodium iodide (thallium activated) crystal, 3″ in diameter and 3″ deep, and a non-overloading linear amplifier (Nuclear Enterprises, Edinburgh, Scotland,, type NE 5202).

Shaker. Equilibrations of the phases were performed in polyethylene bottles using a mechanical shaker of the vibrator type and the phases separated afterwards in a glass separatory funnel.

Outline of procedure

In the distribution measurements 10-ml samples of each aqueous phase were equilibrated with equal volumes of the chloroform phase containing NBPHA. The effect of fluoride-ion concentration on the extraction was first determined by shaking the two phases together for a time (usually 15 min) known to be longer than that required for equilibrium to be established. A 1% solution of NBPHA in chloroform was used with the hydrochloric acid concentration being maintained at $1M$ for niobium, $2M$ for tantalum and $11M$ for protactinium. (Appropriate fluoride concentrations were obtained by adding weighed quantities of potassium fluoride.) When the maximum fluoride ion concentrations consistent with maximum efficiency of extraction of each metal had been determined, the effect of varying the hydrochloric acid concentration on the metal extraction was investigated at this fluoride ion concentration. Next, experiments were performed to investigate the effect of reagent concentration in the chloroform phase and minimum time for the equilibrium to be established on the efficiency of metal ion extractant (see Table I for conditions). Back-extractant systems of various compositions and concentrations and equilibrations of various times were examined in order to establish conditions for quantitative back-extraction and to improve the efficiency of separations.

In the experiments referred to above, after equilibration and separation of the phases the aqueous phase was always washed twice with equal volumes of chloroform before withdrawing the sample for counting. A check on the material balance was frequently performed by measuring the activity transferred to the organic phase as well as that in the aqueous phase.

Separation Procedures

Separation of tantalum from protactinium

1. The mixture, containing tantalum and protactinium, is adjusted to $1M$ in hydrochloric acid and not more than $0{\cdot}4M$ in fluoride-ion concentration.
2. Transfer to a polyethylene bottle and equilibrate with an equal volume of a 0·5% solution of NBPHA in chloroform by shaking for 9 min.
3. Separate the phases in a separatory funnel and repeat step 2 on the aqueous phase.
4. Wash each of the separated phases twice with 10-ml portions of wash liquid: chloroform for the aqueous phase and $1M$ hydrochloric acid made $0{\cdot}2M$ in fluoride ion for the chloroform phase.
5. Transfer the washings to the appropriate fractions.

Note: Tantalum may be back-extracted into an aqueous phase of the composition and under the conditions given in Table IV.

Separation of niobium from protactinium. The same steps used in the above procedure are applicable, but the aqueous phase is adjusted to $0{\cdot}05M$ in fluoride and $1M$ in hydrochloric acid and a 0·2% NBPHA solution in chloroform is employed. The optimum equilibration time is 12 min. The back-extraction of niobium has been dealt with in a previous paper;[14] conditions are summarised above.

Separation of niobium, tantalum and protactinium. While the conditions given above provide a means of separating niobium from tantalum or niobium from protactinium, further separations are possible by making use of selective back-extraction steps for protactinium and niobium.

1. Extract niobium and tantalum from an aqueous phase 1*M* in hydrochloric acid and 0·05*M* in fluoride into a 0·5% solution of NBPHA in chloroform. Protactinium remains in the aqueous phase.

2a. Back-extract niobium into *aqua regia* by shaking the phases together for 15 min, or 2b. Back-extract the niobium and tantalum into 6*M* aqueous ammonia and adjust the acidity of the extract to 0·01*M* with hydrochloric acid, make 0·05*M* in fluoride and partition the niobium into a 0·2% NBPHA solution in chloroform (this gives a more efficient separation of niobium from tantalum than 2a).

3. Protactinium is separated from niobium and tantalum by extracting all three elements into NBPHA in chloroform followed by a selective back-extraction of protactinium into oxalic, tartaric or hydrofluoric acid under the conditions set out in Tables III and IV.

Measurements of the material balance of the different systems by accounting for the radioactivity showed that all the metal ions were in solution and that between 92 and 100% could be extracted in one pass.

RESULTS AND DISCUSSION

Fig. 1 summarises collected data on the effect of fluoride ion on the extraction of niobium, tantalum and protactinium, each in hydrochloric acid of such concentration that the percentage extraction is independent of increasing concentration of this acid. The results show that the efficiency of the extraction of niobium, tantalum and protactinium is not impaired by fluoride concentrations up to 0·05*M*, 0·4*M* and 0·025*M* in that order and that above these concentrations the percentage extraction of both niobium and protactinium is considerably more sensitive to fluoride ions than is tantalum.

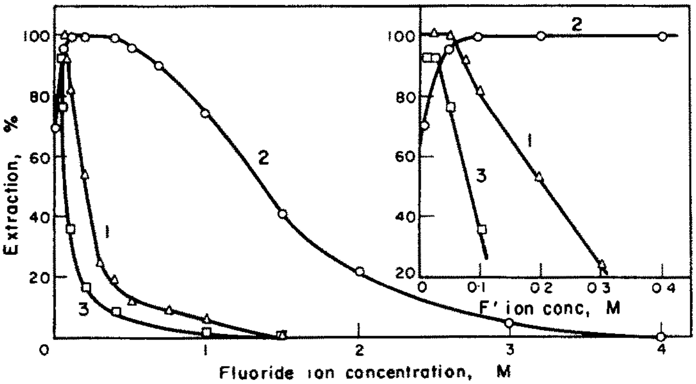

FIG. 1.—Extraction of niobium (△), tantalum (○) and protactinium (□) as a function of fluoride-ion concentration. For conditions see footnotes to Tables I and II. The inset shows curves 1, 2 and 3 drawn to a larger scale at low fluoride-ion concentrations. Curve 1 is largely based on data from ref. 14.

The effect of hydrochloric acid on the extraction of the same three elements is recorded in Fig. 2 at fluoride-ion concentrations permitting maximum efficiency of extraction. The extraction of protactinium is markedly dependent on acid concentration, the maximum only being attained above 10·5*M*; tantalum shows a strong dependence below 1*M* and niobium appears to be independent of it. At low acidities, partial hydrolysis of protactinium species in addition to or rather than complex formation with fluoride may account for the low or negligible extraction into the chloroform phase; at high hydrochloric acid concentrations, chloride displacement of fluoride in some way as yet unknown is probably responsible for the improved extraction. In experiments performed even in 1*M* acid (in which 0·025*M* fluoride is present), however, hydrolysis is either limited or slow because losses of protactinium from the liquid phases were not observed. In the experiments just described the NBPHA concentration in the organic phase was kept high (1 % solutions were used); Table I shows the effect of reagent concentration on the percentage extraction. For maximum extraction niobium requires a 0·2%, tantalum a 0·5% and protactinium a 1% reagent solution. Table II shows that with optimum fluoride ion, hydrochloric acid and reagent concentrations maximum extraction is obtained in 12 min for niobium, 9 min for tantalum, and 6 min for protactinium. Solutions containing from radiotracer quantities up to at least 1 mg/ml of tantalum and 0·5 mg/ml of niobium are extracted efficiently under these conditions. It would seem, therefore, reasonable to expect that the same extraction efficiency and behaviour observed for tracer protactinium-233 would apply to solutions containing up to at least a few tenths of a mg of protactinium-231/ml.

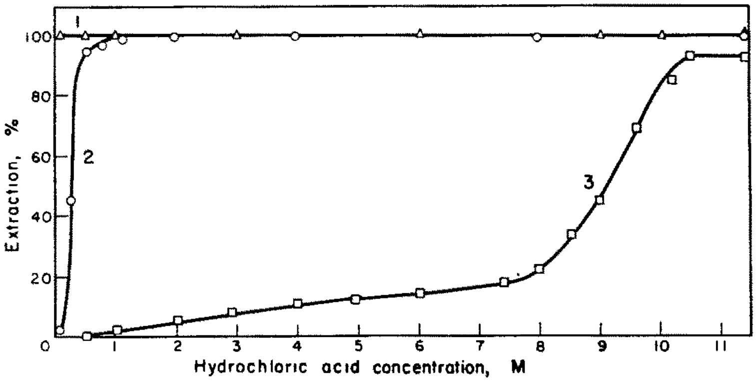

FIG. 2. Extraction of niobium (△), tantalum (○) and protactinium (□) as a function of hydrochloric acid concentration. For conditions see footnotes to Tables I and II.

The results obtained on the back-extraction of tantalum and protactinium into aqueous phases of varying compositions are recorded in Table III. The behaviour of niobium in back-extraction into hydrogen peroxide at pH 10 to 11 is the same as that of protactinium. Aqueous ammonia extracts niobium a little less efficiently than it does tantalum; maximum extraction of the former is attained at about 6*M*.[14] Aqueous ammonia is, however, an unsuitable medium into which to extract protactinium because hydrolysis results in losses of this element to the walls of the container and also because extraction even with 5–6*M* aqueous ammonia leaves some 15% of the element in the chloroform phase. While *aqua regia* has proved to be an efficient back-extractant for niobium, it does not extract protactinium and only removes about 1% of the tantalum from the chloroform phase after equilibrating the phases for 15 min. Chloroform solutions of NBPHA containing niobium and tantalum behave similarly when shaken up with aqueous hydrofluoric, oxalic or tartaric acid solutions; extraction does not occur at readily attainable concentrations of these substances which proved, however, efficient for the removal of protactinium (Table III). A summary of the optimum composition of the aqueous phases, time of equilibrations for back-extraction of niobium, tantalum and protactinium and the percentage of each transferred in a single extraction is given in Table IV.

The data of Figs. 1 and 2 suggest that a separation of protactinium and tantalum or of protactinium and niobium may be achieved by control of the fluoride ion and

TABLE I.—EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM AS A FUNCTION OF NBPHA CONCENTRATION

No.	NBPHA, % *w/v*.	Extraction, %		
		Niobium	Tantalum	Protactinium
1.	0·01	9·0	37·1	3·1
2.	0·02	19·0	44·0	—
3.	0·025	30·4	49·7	—
4.	0·04	46·2	56·8	—
5.	0·05	62·6	62·1	7·2
6.	0·06	71·0	66·8	10·3
7.	0·075	88·3	71·8	12·4
8.	0·10	90·3	73·1	15·9
9.	0·15	95·6	79·0	21·3
10·	0·20	100·0	85·8	27·6
11.	0·40	100·0	95·3	53·9
12.	0·5	—	99·4	62·8
13.	0·8	—	99·4	86·3
14.	1·0	—	99·4	92·2
15.	2·0	—	99·4	92·2

The composition of the aqueous phases were: $1M$ HCl, $0{\cdot}05M$ F^- for Nb; $2M$ HCl, $0{\cdot}4M$ F^- for Ta; $10{\cdot}5M$ HCl, $0{\cdot}025M$ F^- for Pa.

Equal volumes of the two phases were equilibrated for 15 min.

Extraction values refer to single extractions. All three elements were present at radiotracer concentration levels.

TABLE II.—EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM AS A FUNCTION OF TIME

No.	Time, *min*	Extraction, %		
		Niobium	Tantalum	Protactinium
1.	1	—	31·8	23·1
2.	1.5	50·3	—	—
3.	3·0	81·6	67·1	80·3
4.	4·5	88·0	—	—
5.	5·0	—	82·7	84·4
6.	6·0	93·0	89·4	92·5
7.	9·0	96·0	99·45	92·5
8.	12·0	100·0	99·45	92·5

NBPHA concentration in chloroform is 0·2% for niobium, 0·5% for tantalum and 1% for protactinium. The aqueous phases were maintained the same as those described in the footnote to Table I.

hydrochloric acid concentrations. A solution made $0{\cdot}4M$ in fluoride ion and $1M$ in hydrochloric acid should give a separation of protactinium and tantalum, while a separation of protactinium from niobium would be expected with a solution $0{\cdot}05M$ in fluoride and $1M$ in hydrochloric acid. It is also clear that at low hydrochloric acid (say $0{\cdot}01M$) and fluoride ion ($0{\cdot}05M$), niobium may be separated by extraction from a mixture containing tantalum as has been reported previously.[18]

The results and observations just discussed provide the basis for the procedures for the separation of pairs or all three elements if present together.

The efficiency of the separations were examined by obtaining the γ-ray spectra of

TABLE III.—BACK-EXTRACTION OF TANTALUM AND PROTACTINIUM FROM THE CHLOROFORM PHASE INTO VARIOUS AQUEOUS PHASES

Tantalum						
Ammonia	0·31	0·62	1·25	2·1	2·5	3·0
% Back-extracted	28·7	59·1	85·5	96·2	99·7	99·7
Hydrogen peroxide*	0·25	0·5	1·0	1·5	2·0	3·0
% Back-extracted	8·1	47·8	83·3	92·0	100·0	100·0
Protactinium						
Oxalic acid	0·1	0·3	0·5	0·8	1·0	1·5
% Back-extracted	38·3	66·0	87·1	94·1	100·0	100·0
Tartaric acid	0·1	0·5	1·0	1·5	2·0	2·5
% Back-extracted	10·2	55·1	77·3	84·2	95·7	95·2
Hydrogen peroxide*	0·5	1·0	2·0	4·0	6·0	7·0
% Back-extracted	55·1	79·9	90·6	93·9	96·8	100·0
Hydrofluoric acid	0·1	0·2	0·3	0·4	0·6	0·7
% Back-extracted	17·8	43·1	68·7	83·4	100·0	100·0

The concentrations of components of the aqueous phases are given in moles l.$^{-1}$.

* pH adjusted to 10 to 11 with dilute aqueous ammonia. Equal volumes of the two phases were equilibrated for 15 min, data refer to single extractions.

TABLE IV.—OPTIMUM CONDITIONS FOR THE BACK-EXTRACTION OF NIOBIUM, TANTALUM AND PROTACTINIUM

	Element	Aqueous phase	Optimum time, *min*	Extraction, %
1	Niobium	*aqua regia*	15	100·0
2	Niobium	6*M* ammonia	12	100·0
3	Niobium	7*M* hydrogen peroxide*	15	100·0
4	Tantalum	2·5*M* ammonia	8	99·7
5	Tantalum	2·0*M* hydrogen peroxide*	12	99·8
6	Protactinium	1*M* oxalic acid	9	100·0
7	Protactinium	2*M* tartaric acid	6	95·7
8	Protactinium	7*M* hydrogen peroxide*	12	100·0
9	Protactinium	0·6*M* hydrofluoric acid	9	100·0

* In all cases hydrogen peroxide was adjusted to pH 10 to 11 with dilute aqueous ammonia; other conditions as in Table III.

pairs of the isotopes together and of the single isotopes niobium-95, tantalum-182 and protactinium-233, and comparing the spectra with those obtained from the fractions separated from mixtures by the methods outlined. Contamination was not observed in these experiments but the sensitivity is somewhat limited (about 1% contamination is detectable) and further separate experiments were performed by radioactive labelling of one of the elements in the mixture, performing the separation in the prescribed manner and measuring the radioactivity in what should be the inactive fraction. From such experiments separation factors were calculated and the results are recorded in Table V.

Zirconium (and presumably also hafnium) does not extract at high hydrochloric

TABLE V.—SEPARATION FACTORS* FOR PAIRS OF ELEMENTS

	Element A separated from B	System	Method of separation	Separation factor
1.	Ta separated from Pa	^{233}Pa, inactive Ta (1 mg/ml)	A	10^3
2.	Nb separated from Pa	^{233}Pa, inactive Nb (0·5 mg/ml)	B	10^3
3.	Nb separated from Ta	(1) ^{182}Ta, inactive Nb (0·5 mg/ml)	C, 2a	10^2
		(2) ^{182}Ta, inactive Nb (0·5 mg/ml)	C, 2b	10^3

* The ratio of the initial amount of B present in the mixture (A — B) to the final amount of impurity B present in the separated sample of A.

acid concentration (10 to 11*M*) as was found using zirconium-95 and, therefore, separation from protactinium presents no difficulties. Zirconium is separated from niobium and also from tantalum by masking it with fluoride and extracting the niobium and tantalum.[14] Protactinium is readily separated from aluminium, titanium, manganese(II), iron(III), rare earths and thorium by extracting it from concentrated hydrochloric acid solutions because these elements have been shown previously[19–22] or during the course of this work only to react with NBPHA at (relatively) very low acidities.

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Zusammenfassung—Die Extraktion von Niob, Tantal und Protactinium aus fluoridhaltigen salzsauren Lösungen in Chloroformlösungen von N-Benzoyl-N-phenylhydroxylamin wurde untersucht. Aus solchen wäßrigen Systemen lassen sich je zwei oder alle drei der genannten Elemente wirkungsvoll und einigermaßen quantitativ abtrennen. Ferner kann Protactinium auch leicht von Zirkonium (wahrscheinlich auch von Hafnium), Aluminium, Titan, Mangan (II), Eisen (III), seltenen Erden und Thorium durch Extraktion aus konzentrierten salzsauren Lösungen getrennt werden. Die Rückextraktion von Niob, Tantal und Protactinium in wäßrige Phasen verschiedener Zusammensetzung und die dadurch entstehenden weiteren Trennmöglichkeiten werden ebenfalls diskutiert. Die Verteilungsmessungen und Trennungen wurden mit Hilfe geeigneter radioaktiver Isotope der betreffenden Elemente durchgeführt.

Résumé—On a étudié l'extraction de niobium, tantale et protactinium, à partir des solutions en acide chlorhydrique renfermant du fluorure, au moyen de solutions chloroformiques de N-benzoyl-N-phénylhydroxylamine. A partir de tels systèmes aqueux, il est possible de séparer ces trois éléments, soit ensemble, soit par paires, de façon efficace et sensiblement quantitative. En outre, on peut aisément séparer le protactinium de zirconium (et probablement aussi hafnium), aluminium, titane, manganèse (II), fer (III), terres rares et thorium, par extraction à partir de ses solutions en acide chlorhydrique concentré. On discute aussi de l'extraction en retour de niobium, tantale et protactinium dans des phases aqueuses de compositions diverses, et des séparations supplémentaires ainsi révélées. Les mesurés de partage entre les phases et les séparations, ont été réalisées en employant les isotopes radioactifs appropriés des éléments concernés.

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DETERMINATION OF LEAD WITH 4-(2-PYRIDYLAZO)-RESORCINOL—I

SPECTROPHOTOMETRY AND SOLVENT EXTRACTION

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Summary—4-(2-Pyridylazo)-resorcinol forms a 1:1 complex, $\lambda_{max} = 520$ mμ, with lead(II) in an ammonia-ammonium chloride medium at pH 10. Maximum colour is developed immediately and is stable for at least 24 hr. The molar extinction coefficient at 520 mμ is 40,000. Many metal ions interfere, but selectivity is achieved by extracting the lead into isobutyl methyl ketone, from an iodide solution, followed by back-extraction into an ammoniacal solution. Those other metals which would also extract as iodides are removed by a preliminary extraction of their thiocyanates into the same solvent or they are subsequently masked by cyanide. The combined extractive separation-determination is rapid, reproducible, highly selective and sensitive.

THE most widely used spectrophotometric methods for the determination of trace amounts of lead are undoubtedly those based upon reaction with dithizone.[1–7] Although the formation of lead dithizonate provides one of the most sensitive methods for determining lead ($\varepsilon_{520\,m\mu} = 65{,}000$),[8] the method suffers many disadvantages arising from non-selectivity, photodecomposition of the dithizone and insolubility of the complex in aqueous media.

In the present examination a search for a more reliable method led to a preliminary investigation of 25 metallochromes as spectrophotometric reagents for lead. Eight of the 25 reagents worthy of further examination, including Alizarin Complexan, Xylenol Orange, 4-(2-pyridylazo)-resorcinol and Bromopyrogallol Red, were investigated with respect to a number of masking agents, and absorption spectra were plotted for each reagent and its lead complex. 4-(2-Pyridylazo)-resorcinol (PAR) appeared to be the most suitable reagent for lead.

The use of PAR as a possible analytical reagent for the photometric determination of lead has been described independently by Pollard and coworkers[9–11] and by Kristiansen and Langmyhr,[12] but they disagree about the nature of the complex, and the method they described would not be directly applicable to solutions containing other metal ions in addition to lead. The present paper seeks to resolve the disagreement and extend the scope of the procedure by use of selective separations and masking agents.

EXPERIMENTAL

Reagents

Hydrochloric acid. 5% v/v aqueous solution

Ammonium thiocyanate. Saturated aqueous solution

Potassium iodide. Saturated aqueous solution

Potassium cyanide. 10% w/v in water

10^{-3} *M lead nitrate solution.* Dissolve 0·3312 g of lead nitrate in water and dilute to 1 l.

10^{-2} *M PAR solution.* Dissolve 0·273 g of PAR (monosodium salt, Hopkin and Williams Ltd., Chadwell Heath, Essex, England) in water and dilute to 100 ml.

Buffer (pH 10). Ammonia-ammonium chloride buffer containing 26 g of ammonium chloride plus sufficient ammonia (*ca.* 85 ml) to give a pH of 10 in 1 l. of solution.

iso-Butyl methyl ketone (*GPR*)

Unless stated otherwise, analytical reagent grade chemicals and distilled water were used throughout.

Apparatus

Spectrophotometer. Beckman D.B. spectrophotometer, with 1-cm cuvettes.

pH Meter. E.I.L. Vibron pH Meter (model 39A).

Procedure

Into a series of 250-ml separatory funnels pipette 0·1- to 1·0-ml aliquots of 10^{-3} *M* lead nitrate solution and dilute each to 20 ml with 5% hydrochloric acid. Add 1 ml of saturated ammonium thiocyanate solution to each funnel and extract with 20 ml of isobutyl methyl ketone by shaking for 1 min. Run the lower (aqueous) solutions into a second series of 250-ml funnels and add 2·5 ml of saturated potassium iodide solution to each one. Extract the solutions with 20 ml of isobutyl methyl ketone by shaking the funnels for 1 min. Discard the lower (extracted) phases and wash the organic extracts with a combined solution of 10 ml of 5% hydrochloric acid and 1·25 ml of saturated potassium iodide solution; discard the washings. To the organic extracts add 15 ml of buffer (pH 10) and 1 ml of 10% potassium cyanide. Shake the funnels to back-extract the lead into the aqueous phase. Pipette 1 ml of 10^{-2} *M* PAR solution into each funnel and shake the funnels for 30 sec. Run the lower phases, containing the PAR-lead complex, into 50-ml volumetric flasks. Wash each of the organic phases with 10 ml of water, add these washings to the volumetric flasks and dilute to volume. Measure the absorbance of the solutions at 520 mμ in 1-cm cuvettes against a reagent blank taken through the procedure.

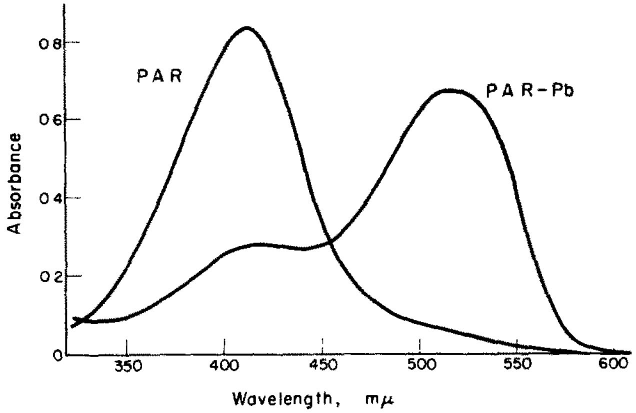

FIG. 1.—Absorption spectra of PAR and its lead complex at pH 10 (measured against water in 1-cm cuvettes):—

PAR: 1 ml of 10^{-3} *M* PAR + 15 ml buffer diluted to 50 ml. PAR-Pb: 1 ml of 10^{-3} *M* PAR + 1 ml of 10^{-3} *M* Pb^{2+} + 15 of buffer diluted to 50 ml.

A graph of the absorbance plotted against the amount of standard lead nitrate solution (from 10-200 μg of lead) is a straight line passing through the origin. The molar extinction coefficient of the PAR-lead complex following the extraction procedure and other operations corresponds to 30,000.

RESULTS AND DISCUSSION

Spectral characteristics

Fig. 1 shows the absorption spectra of PAR and its lead complex. It will be noted that the absorbance of the reagent alone, $\lambda_{max} = 412$ mμ, is very small at the wavelength of maximum absorption, 520 mμ, of its lead complex.

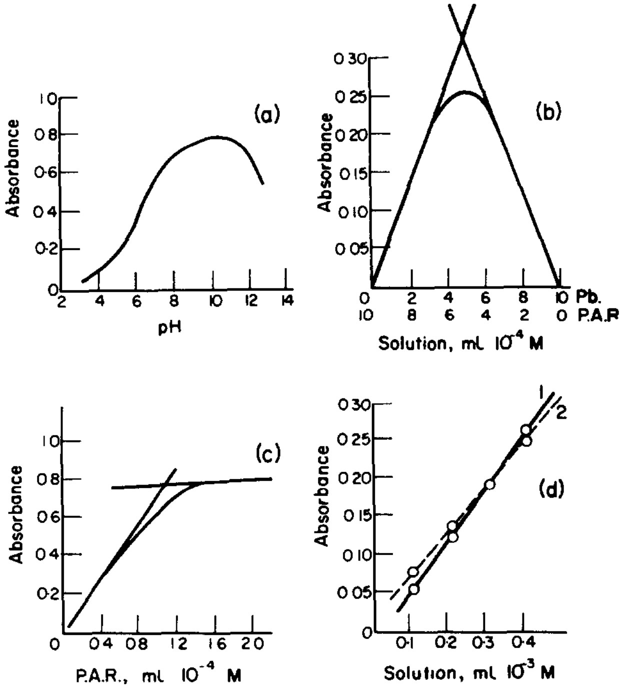

FIG. 2.—Structural and stability data

(*a*) Difference in absorbance between lead complex and PAR blank at various pH (1 ml of 10^{-3} *M* Pb^{2+} + 1 ml of 10^{-3} *M* PAR, 1-cm cuvettes, 520 mμ).

(*b*) Corrected continuous variation curve for lead-PAR (pH 10, 1-cm cuvettes, 520 mμ).

(*c*) Yoe and Jones plot for lead-PAR (1 ml of 10^{-4} *M* Pb^{2+} + 15 ml of buffer + x ml of 10^{-4} *M* PAR diluted to 50 ml, measured against x ml of PAR + 15 ml of buffer diluted to 50 ml, pH 10, 1-cm cuvettes, 520 mμ).

(*d*) Harvey-Manning plot for lead-PAR:
1.—1 ml of 10^{-3} *M* Pb^{2+} + x ml of 10^{-3} *M* PAR;
2.—1 ml of 10^{-3} *M* PAR + x ml of 10^{-3} *M* Pb^{2+};
(pH 10, 1-cm cuvettes, 520 mμ).

Optimum conditions for colour development

pH. Standard amounts of lead and PAR solutions were buffered at varying pH values. The final pH of each solution was measured with a pH meter and the absorbance measured at 520 mμ. From a plot of absorbance against pH (Fig. 2a), maximum absorbance was obtained at pH 10. This is in agreement with the value given by Pollard, Hanson and Geary.[9] Subsequent determinations were, therefore, carried out at this pH.

Reagent excess. The absorbances of a series of solutions containing standard amounts of lead and a 2 to 100-fold molar excess of PAR buffered at pH 10 were measured and plotted against excess of PAR. Maximum absorbance was obtained at about an 8-fold molar excess of PAR with respect to lead and it remained constant up to *ca.* a 50-fold excess.

Development time. The maximum colour of the PAR-lead complex was found to develop immediately and to be stable for at least 24 hr thereafter.

Lambert-Beer law

With the optimum conditions now established, a calibration cure was prepared. Beer's Law was obeyed between 10 and 200 μg of lead, and gave a molar extinction coefficient of 40,000 at 520 mμ for the complex.

Nature of complex

A continuous variation plot measured at three different wavelengths (500, 520 and 540 mμ), exhibits clear indication of a 1:1, PAR to lead, complex (*cf.* Fig. 2b).

Figs. 2c and 2d show, respectively, a Yoe and Jones[13] mole ratio plot and a Harving-Manning[14] slope-ratio plot; both indicate a 1:1, PAR to lead, complex. Potentiometric titrations also confirmed a 1:1, PAR to lead, complex. This value of 1:1 differs from the 2:1, PAR to lead, reported by Pollard and coworkers,[10] but is in agreement with that found by Kristiansen and Langmyhr.[12] The purity of the PAR sample was checked independently by potentiometric titration with sodium hydroxide and by organic elemental analysis.

Effect of foreign ions on colour system

Most of the 25 common metal ions examined showed interference, of which only 7 could be successfully masked with cyanide, *viz.* Ag(I), Cd(II), Co(II), Cu(II), Hg(II), Ni(II) and Zn(II). A number of the interfering metal ions investigated gave high results, but a large number gave low results by coprecipitating lead on their hydroxides, thus giving low recoveries. Consequently, it is necessary to separate lead from most metal ions.

Separation. The solvent extraction of lead iodide by isopropyl methyl ketone from dilute hydrochloric acid solution has been described by West and Carlton.[15] Initial experiments were carried out under their recommended conditions. The isopropyl methyl ketone extract was evaporated to dryness and the residue redissolved in a minimum of nitric acid, buffered to pH 10 and the PAR complex developed. Poor recoveries and high blank values were thought to be caused by the presence of the isopropyl methyl ketone.

Substitution of isobutyl methyl ketone gave more promising results. Optimum conditions for extraction of the lead iodide into this solvent were then determined. Extractions were carried out from varying acid concentrations; maximum extraction was obtained from 5% hydrochloric acid. Lead iodide was then extracted from 5% hydrochloric acid in the presence of varying amounts of iodide; maximum extraction was obtained from *ca.* 7% potassium iodide medium (Fig. 3a).

According to West and Carlton[15] a number of metal ions are wholly or partially extracted with lead as their iodides, but all except cadmium and ruthenium may be removed from 5% hydrochloric acid solution as their thiocyanates by a prior extraction with isobutyl methyl ketone. When this expedient was employed in this study, a successful separation of lead from the interfering ions was obtained, but low results were encountered. It was thought that excess thiocyanate remaining in the aqueous solution might affect the optimum iodide concentration, but experiments showed that it did not (Fig. 3b). It was, therefore, concluded that *if* a preliminary thiocyanate extraction for the removal of interferences was to be employed, a 20% loss of lead would have to be tolerated at this stage. West and Carlton[15] observe that lead is not affected by the thiocyanate extraction, but we have consistently and reproducibly

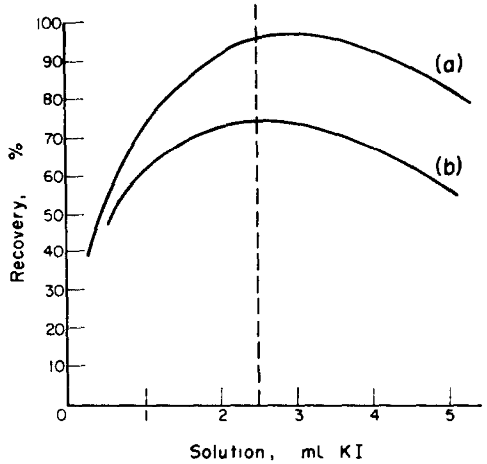

FIG. 3.—Extraction data

(*a*) Extraction of 0·5 ml 10^{-3} *M* Pb^{2+} from 20 ml 5% HCl in the presence of x ml of saturated KI solution with isobutyl methyl ketone.

(*b*) As (a) following an extraction in the presence of 1 ml of saturated NH_4 CNS solution with isobutyl methyl ketone.

observed the above loss. This we presume to be due to extraction of lead thiocyanate which is known to be insoluble in more concentrated media.

The possibility of back-extraction into a pH 10 ammoniacal buffer solution was investigated and satisfactory results were obtained. Thus, the necessity for evaporation of the organic extract to dryness was eliminated. Potassium cyanide was added to the back-extracted solution to mask any cadmium which might pass through the procedure along with the lead. Standard PAR solution was finally added and the absorbance of the PAR-lead complex was measured at 520 mμ.

Acknowledgement—We are grateful to the British Welding Research Association for the provision of a research studentship for one of us (P. Y.).

Zusammenfassung—4-(2-Pyridylazo)-resorcin bildet mit Blei (II) in einem Ammoniak-Ammonchlorid-Medium bei pH 10 einen 1:1-Komplex mit λ_{max} = 520 mμ. Die maximale Farbtiefe wird sofort erreicht und ist mindestens 24 Stunden beständig. Der molare Extinktionskoeffizient bei 520 mμ ist 40,000. Viele Metallionen stören, aber das Verfahren läßt sich selektiv gestalten durch Extraktion von Blei aus jodidhaltiger Lösung in Isobutylmethylketon und Rückextraktion in ammoniakalische Lösung. Die anderen ebenfalls als Jodide extrahierbaren Metalle werden durch vorheriges Extrahieren ihrer Rhodanide in dasselbe Lösungsmittel entfernt oder anschließend durch Cyanid maskiert. Die kombinierte extraktive Abtrennung und Bestimmung geht schnell und ist reproduzierbar, hochselektiv und empfindlich.

Résumé—Le 4-(2-pyridylazo)-résorcinol forme un complexe 1:1, maximum à 520 mμ, avec le plomb (II) en milieu ammoniaque-chlorure d'ammonium, à pH 10. La coloration atteint immédiatement son maximum, et est stable pendant 24 h au moins. Le coefficient d'extinction moléculaire est de 40,000 à 520 mμ. De nombreux ions métalliques interfèrent, mais on peut obtenir la sélectivité par une extraction du plomb, à partir d'une solution d'iodure, au moyen d'isobutylméthylcétone, suivie d'extraction en retour en solution ammoniacale. Ceux des autres métaux qui seraient aussi extraits à

l'état d'iodures sont éliminés par une extraction préliminaire de leurs sulfocyanures dans le même solvent, ou sont ultérieurement dissimulés au moyen de cyanure. La technique associée, séparation-dosage par extraction est rapide, reproductible, hautement sélective et sensible.

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DETERMINATION OF LEAD WITH 4-(2-PYRIDYLAZO)-RESORCINOL—II*

APPLICATION TO STEEL, BRASS AND BRONZE

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Summary—A simple and rapid method is described for the spectrophotometric determination of lead in steel, brass and bronze alloys down to 0.001%. After solution of the sample, lead is separated from the major component, in steel by iso-amyl acetate extraction of the iron, and in brass or bronze alloys by coprecipitation of the lead with calcium carbonate in ammoniacal solution. It is then determined by the procedure described in Part I of this series.

NUMEROUS methods have been described for the spectrophotometric determination of lead in steel.[1-6] These methods are based on reaction with dithizone, the disadvantages of which are mentioned in Part I of this series.

The object of this study was to adapt the previously described spectrophotometric method for lead in pure solution with 4-(2-pyridylazo)-resorcinol (PAR)[7] to the determination of lead in steel, brass and bronze alloys. In the following procedures the initial stages differ according to the type of sample under investigation, *i.e.*, in the separation of lead from the bulk of the major component.

In the analysis of steel samples the bulk of iron present is removed by extraction with iso-amyl acetate from a hydrochloric acid solution of the sample, whereas with brass and bronze samples lead is separated from copper by coprecipitation with calcium carbonate in ammoniacal solution. Interfering metals are removed subsequently from a 5% hydrochloric acid solution as their thiocyanates by extraction with iso-butyl methyl ketone, and the lead is then extracted as dihydrogentetra-iodolead(II) into iso-butyl methyl ketone. After washing this extract, the lead is back-extracted into an ammoniacal cyanide solution, the lead-PAR complex formed and measured at 520 mμ in the aqueous phase against a reagent blank carried through the same procedure. The amount of lead present is determined from a calibration curve prepared by taking standard amounts of lead through the procedure.

EXPERIMENTAL

Reagents

All the reagents are of AR grade except for the organic solvents which were of reagent (G.P.) grade, and distilled water is used throughout.

Hydrochloric acid (sp.gr. 1·18)
Nitric acid (sp.gr. 1·42)
Ammonia solution (sp.gr. 0·88)
iso-Amyl acetate
iso-Butyl methyl ketone
Calcium chloride solution. 5% w/v $CaCl_2$ in water

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* Part I: see reference 7.

Sodium carbonate solution. 10% w/v Na_2CO_3 in water

Ammonium thiocyanate solution. Aqueous saturated solution

Potassium iodide solution. Aqueous saturated solution

Potassium cyanide solution. 10% w/v in water

10^{-3} *M Lead nitrate solution.* Dissolve 0·3312 g of lead nitrate in water and dilute to 1 l.

10^{-2} *M PAR solution.* Dissolve 0·273 g PAR (mono sodium salt) in water and dilute to 100 ml.

Buffer solution (pH 10). Dissolve 26 g of ammonium chloride in about 900 ml of water and add concentrated ammonia solution (about 85 ml) until pH 10 is obtained.

Apparatus

Spectrophotometer. Beckman D.B. spectrophotometer, with 1-cm cuvettes.

pH meter. E.I.L. Vibron pH Meter (model 39A).

Procedure

Removal of major component

Determination of lead in steel. Dissolve a suitable weight of sample [containing 10 to 200 μg of lead (Note 1)] in 10 ml of concentrated hydrochloric acid in a 100-ml beaker, warming to assist solution. Oxidise the iron present to iron(III) by dropwise addition of concentrated nitric acid. After cooling, transfer the solution to a 250-ml separatory funnel with the aid of a further 15 ml of concentrated hydrochloric acid. Add 25 ml of iso-amyl acetate and extract the bulk of the iron(III) by shaking the funnel for 30 sec. Allow the phases to separate and run the lower (aqueous) phase into a second 250-ml separatory funnel. Repeat the extraction with a further 25 ml of iso-amyl acetate and discard the organic extract. Run the aqueous phase into a 100-ml beaker and evaporate the solution to dryness on a hot-plate (Note 2).

Determination of lead in brass and bronze alloys. Dissolve a suitable weight of sample [containing 10 to 200 μg of lead (Note 1)] in a small quantity of concentrated nitric acid in a 100-ml beaker, warming to assist solution. Add 10 ml of 5% calcium chloride solution and make ammoniacal. Add 10 ml of 10% sodium carbonate solution and stir well to obtain intimate mixing. Allow the solution to stand for 5 min, then filter through a small pulp pad (Note 3). Wash the precipitated carbonates with water and discard the filtrate and washings. Redissolve the carbonates in 25 ml of 20% v/v nitric acid and run the solution back into the original beaker. Make the solution ammoniacal (*ca.* 10 ml of concentrated ammonia solution), and add 1 ml of 10% potassium cyanide solution. Reprecipitate the calcium and lead carbonates by adding 10 ml of 10% sodium carbonate solution. Allow the solution to stand for 5 min, filter on a small pulp pad and wash the residue thoroughly with water. Redissolve the residue in 25 ml of 20% nitric acid solution and run the solution back into the original beaker. Finally, evaporate the solution to dryness on a hot-plate.

Extractive separation and determination

After evaporation to dryness, redissolve the residue (Note 4) in 10 ml of 5% v/v hydrochloric acid and 1 ml of saturated ammonium thiocyanate solution. Transfer the solution to a 250-ml separatory funnel with the aid of a further 10 ml of 5% hydrochloric acid. Extract the solution with 20 ml of iso-butyl methyl ketone and run the aqueous phase into a second 250-ml separatory funnel. From a pipette add 2·5 ml of saturated potassium iodide solution and 20 ml of iso-butyl methyl ketone. Shake the funnel for 1 min to extract the lead. Discard the extracted aqueous phase and wash the organic phase with 10 ml of 5% hydrochloric acid plus 1·25 ml of saturated potassium iodide solution; discard the washings. To the organic phase add 15 ml of buffer solution (pH 10) and 1 ml of 10% potassium cyanide solution. Shake the funnel to back-extract the lead into the aqueous phase. Pipette 1 ml of $10^{-2}M$ PAR solution into the funnel and shake for 30 sec to obtain intimate mixing. After phase separation run the lower aqueous phase into a 50-ml volumetric flask. Wash the remaining organic phase with 10 ml of water and add the washings to the volumetric flask. Dilute to the mark with water and measure the absorbance of the solution in a 1-cm cuvette at 520 mμ against a reagent blank taken through the procedure.

A calibration curve should be prepared from 0·1 to 1·0-ml aliquots of a standard $10^{-3}M$ lead nitrate solution taken through the procedure.

Notes on procedure. 1. For steel samples containing greater than 0·04% of lead take 0·5 g of sample, dissolve according to the recommended procedure, dilute to 100 ml with concentrated hydrochloric acid and take a suitable aliquot for further analysis.

2. Baking to a hard dryness should be avoided because this may cause low recoveries.

3. In the presence of large amounts of gelatinous precipitates the use of a centrifuge is much superior with respect to speed and ease of manipulation.

4. Samples containing appreciable amounts of titanium or tungsten cannot be redissolved at this stage. Subsequent extractions are, therefore, made from a suspension of the residue in 5% hydrochloric acid.

Table I.—Analysis of lead in BCS certificated steels

Sample no.	Lead found, %	Average, %	Average certificate value, %	Range in certificate, %
BCS 326	0·013 0·014	0·013$_5$	0·014	0·012–0·017
BCS 327	0·012 0·011	0·011$_5$	0·010	0·009–0·012
BCS 328	0·015 0·016 0·015 0·016 0·014 0·015 0·014 0·016 0·015 0·016 0·016	0·015	0·015	0·012–0·018
BCS 329	0·048 0·049	0·048$_5$	0·05–	0·042–0·053
BCS 330	0·004 0·004	0·004	0·003	0·002–0·004
BCS 271	0·004 0·004	0·004	0·002$_5$	0·001$_5$–0·003
BCS 273*	0·004 0·004	0·004	0·003	—
BCS 275	0·005 0·006 0·007	0·006	0·005	0·003–0·006
BCS 277*	0·008 0·008 0·008	0·008	0·006$_5$	—

* Lead is a non-standardised element in these steels.

Table II.—BCS certificated copper-base alloys

Sample no.	Lead found, %	Average, %	Average certificate value, %	Range in certificate, %
BCS 179/1	0·208 0·216 0·188	0·206	0·19	0·17–0·22
BCS 180/1	0·009 0·009	0·009	0·009	0·003–0·010
BCS 183/1	3·50 3·52	3·51	3·51	3·40–3·63
BCS 207/1	0·073 0·069 0·070	0·071	0·079	0·073–0·084

Table III.—Analysis of some commercial steel samples

Sample no.	Type	Major components, %	Lead found, %	Average, %	Reported,[a] %
1	Stainless steel	Ni Co Mo Ti 18 8 5 0·5	0·007 0·007	0·007	0·008
2	Stainless steel	Cr Ni Mo 18 10 2·5	0·002$_5$ 0·003	0·003	0·002$_5$
3	Stainless steel	Ni Co Mo Ti 18 8 5 0·5	0·010 0·011	0·010$_5$	0·012
4	Sponge iron	—	0·002 0·001	0·001$_5$	0·001
5	Tungsten steel	W 3	0·004 0·003	0·003$_5$	0·002
6	Tungsten steel	W 18	0·004 0·004	0·004	0·002$_5$

[a] Samples supplied by B. Bagshawe.

RESULTS AND DISCUSSION

The results obtained by application of the proposed procedure to the analysis of a variety of certificated British Chemical Standard (BCS) standard steel and copper-base alloys are shown in Tables I and II, respectively, and the reproducibility of the method was verified by repetitive analyses of sample BCS 328 (Table I). The data in these tables show that the method, as operated by us, is capable of yielding results reproducible within ±0·001 %. Furthermore, it will be seen from the data in columns two and five that in all cases, except for BCS 271 and BCS 207/1, the values found by the PAR procedure are within the spread of results reported in the certificate. It is not possible to compare the results on BCS 273 and 277 because the lead in these steels was a non-standardised element and was determined by a polarographic procedure following an extensive separation process.

Table III shows the results obtained by application of the method to a number of commercial stainless and tungsten steel samples. It will be noted that slightly higher results than the reported values were found for the tungsten steels. This was first of all thought to be due to the influence of the tungsten present. However, the results from the analysis of a synthetic mixture of iron, lead and tungsten showed no such influence.

Acknowledgement—We are grateful to Mr. B. Bagshawe of the Brown-Firth Research Laboratories, Sheffield, England, for providing the samples listed in Table III. We also record our grateful thanks to the British Welding Research Association for the provision of a research studentship to one of us (P. Y.).

Zusammenfassung—Eine einfache und schnelle Methode zur spektralphotometrischen Bestimmung von Blei in Stahl, Messing- und Bronzelegierungen bei Konzentrationen bis herunter zu 0,001% wird beschrieben. Nach Lösen der Probe wird Blei vom Hauptbestandteil getrennt: in Stahl durch Extraktion von Eisen mit Isoamylacetat, in Messing- oder Bronzelegierungen durch Trägerfällung mit Calciumcarbonat in ammoniakalischer Lösung. Dann wird das Blei nach der in Teil I dieser Reihe angegebenen Vorschrift quantitativ bestimmt.

Résumé—On décrit une méthode simple et rapide de dosage spectrophotométrique du plomb dans l'acier et les alliages de laiton et de bronze, jusqu'à une teneur de 0,001%. Après mise en solution de l'éhantillon, on sépare le plomb du constituant principal, dans l'acier par extraction du fer à l'acétate d'isoamyle, et dans les alliages de laiton ou de bronze, par coprécipitation avec du carbonate de calcium en solution ammoniacale. On le dose ensuite par la technique décrite dans la partie I de cette série.

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MERCURIMETRIC AND ARGENTOMETRIC TITRATIONS USING *p*-DIMETHYLAMINOBENZYLIDENERHODANINE AS INDICATOR

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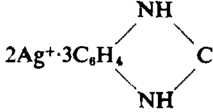
Summary—*o*-Hydroxymercuribenzoic acid (HMB) and silver nitrate, in an ethanol-water mixture containing perchloric or acetic acid, can be used as titrants with *p*-dimethylaminobenzylidenerhodanine as a visual indicator, for the determination of chloride, bromide, iodide, thiocyanate, ferrocyanide, tetraphenylboron, thiourea, thiosemicarbazide, diphenylthiourea, thioacetamide, *o*-phenylenethiourea, ethylenethiourea, *o,o*-diethyldithiophosphoric acid and mercaptans. The consumption of the reagents at the end-point corresponds to the formation of the products AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+\cdot 3NH_2CSNHNH_2$,



$2Ag^+\cdot 3C_6H_4\begin{smallmatrix}NH\\ NH\end{smallmatrix}CS$, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$, $HMB\cdot X$ ($X = Cl^-, Br^-, I^-, CNS^-$), HMB·(–NHCS–), 2HMB·R·SH.

p-DIMETHYLAMINOBENZYLIDENERHODANINE has been suggested as a reagent for silver and mercuric ions,[1,2] and as an indicator for the titration of cyanide[3] and iodide[4] with silver nitrate solution. The author has used this indicator for titration of thiourea and its derivatives with mercurated aniline in the presence of perchloric acid.[5] The use of mercurated aniline has two advantages, a very distinct change of colour at the end-point from yellow to purple and the possibility of titration in aqueous solutions. Titrations in the presence of *p*-dimethylaminobenzylidenerhodanine, with *o*-hydroxymercuribenzoic acid (HMB), silver nitrate or mercuric acetate can be carried out only in organic solvents, such as ethanol and ethanol–water mixture, because in water the colour changes far too soon and the end-point is indeterminable. On the other hand, it is possible to titrate with the above reagents several compounds which cannot be satisfactorily titrated with mercurated aniline, *e.g.*, ferrocyanide and tetraphenylboron with silver nitrate, or chloride and thiocyanate with HMB. The use of *p*-dimethylaminobenzylidenerhodanine as indicator for titrations with mercuric acetate solutions shows no advantages in comparison with diphenylcarbazone; moreover the titration of some sulphur compounds, such as diphenylthiourea or thioacetamide, is not possible because of the formation of mercuric sulphide.

HMB has already been suggested for the titrimetric determination, in alkaline solution, of sulphide,[6] mercaptans[7] and for desulphurating titration;[8] and it has been reviewed.[9,10] The use of the titration with HMB in acid solution extends the field of application of this reagent. On this basis the analysis of some compounds in mixture is possible, using nothing but a solution of HMB for the titration.

EXPERIMENTAL

Reagents

Silver nitrate. 0·0995N aqueous solution

o-Hydroxymercuribenzoic acid (HMB). 0·0504N solution prepared as follows: Dissolve 16 g of *o*-hydroxymercuribenzoic acid anhydride (supplied by FOCh, Poland) in 10 ml of monoethanolamine and 10 ml of water and dilute to 1 l. with 70% v/v ethanol.

Establish the normality of the above solutions on the basis of procedure described in this paper using standard potassium thiocyanate solution.

Perchloric acid.

Indicator. A saturated and filtered solution of *p*-dimethylaminobenzylidenerhodanine in 96% v/v ethanol.

Ethanol. 96% v/v; ethanol containing benzene can be used as well.

The standard solutions of substances for analysis were prepared from known weights of pure reagents supplied by "Apolda" (sodium tetraphenylboron) and "FOCh." The *o,o*-diethyldithiophosphoric acid, in the form of its nickel salt, was a gift from Prof. A. I. Busev (Moscow, USSR). The solutions of mercaptans were standardised with the same solution of HMB, by titration in ammoniacal solution in the presence of thiofluorescein.[7]

Procedure

Add to 2–10 ml of aqueous or alcoholic solution, containing less than 1 mequiv of the test substance, 25 ml of ethanol, 0·5 ml of perchloric acid, 0·5 ml of *p*-dimethylaminobenzylidenerhodanine solution and titrate with HMB or silver nitrate solution until the colour changes from yellow to red or purple. For the titration of tetraphenylboron with silver nitrate add 1 ml of pure acetic acid instead perchloric acid.

Notes. The change of the colour at the end-point depends on the reagent used and on the substance titrated. If the product formed is insoluble the colour changes to purple, if soluble to red. The consumption of reagent for the colour change of the indicator amounts for silver nitrate to 0·001 mequiv and for HMB to 0·003 mequiv. This should be subtracted from the result of the titration.

During argentometric titrations insoluble products are formed with the exception of thiourea, thiosemicarbazide and thioacetamide, whereas all complexes with HMB are soluble. An interesting phenomenon can be observed during the titration of β-mercaptopropionic acid with silver nitrate. The titrated solution remains clear but becomes more and more viscous and if the concentration is *ca.* 1 mequiv/25 ml, at the end-point a gelatinous body is formed, which loses its stickiness slowly and separates into a white precipitate.

Sulphate, phosphate, nitrate, chromate, fluoride, sulphite, selenite, formaldehyde, EDTA, hydrogen peroxide, thallium(I), lead(II), iron(II), iron(III) and copper(II) do not interfere with the above titrations. Chloride and bromide interfere in argentometric titrations.

The titration of tetraphenylboron with silver nitrate in the presence of perchloric acid leads to low results although the end-point is sharp. In the presence of acetic acid the results are satisfactory.

The formation of silver sulphide from thioacetamide and silver nitrate occurs just after the colour change of the indicator; consequently the titration is possible.

The results of the titrations are indicated in Tables I and II.

DISCUSSION

The determination of ferrocyanide, diethyldithiophosphate and tetraphenylboron with silver nitrate in the presence of *p*-dimethylaminobenzylidenerhodanine seems to have real practical significance, although other simple procedures have also been recommended for tetraphenylboron.[11] Potassium can be determined by dissolving a precipitate of potassium tetraphenylboron in dioxan and titrating according to the above procedure. The titration of compounds containing the —NHCS group with silver nitrate opens a new way for identification of these compounds. The argentometric titration of mercaptans cannot be recommended for general use, although the end-point is sharp, because of the great positive errors, increased by the presence of the carboxyl group. The titration of mercaptans in acid solution with HMB has no advantages compared with the titration with HMB in alkaline solution using thiofluorescein

Table I.—The results of titration with silver nitrate solution

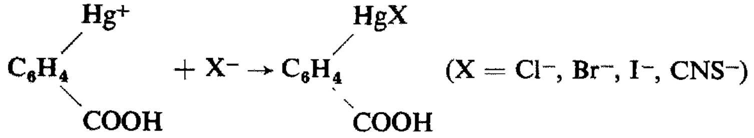
Titrated substance	Taken, *mmole*	Consumption of 0·0995*N* $AgNO_3$, *ml*	Equivalents of Ag^+/mole of substance
Potassium ferrocyanide	0·0880	2·60, 2·58, 2·59	2·93
	0·176	5·16, 5·18, 5·15	2·92
Sodium tetraphenylboron	0·262	2·55, 2·56, 2·54	0·970
	0·524	5·08, 5·08, 5·10	0·968
Potassium thiocyanate	0·395	3·97, 3·98, 3·96	1·00
Potassium iodide	0·370	3·72, 3·70, 3·75	1·00
Thiourea	0·326	2·20, 2·18, 2·20	0·668
Thiosemicarbazide	0·812	5·48, 5·44, 5·50	0·671
Thioacetamide	0·456	2·28, 2·25, 2·28	0·497
o-Phenylenethiourea	0·670	4·50, 4·48, 4·48	0·666
Diphenylthiourea	0·263	1·32, 1·32, 1·30	0·495
Nickel *o,o*-diethyldithiophosphate	0·274	2·80, 2·78, 2·77	1·00
	0·548	5·54, 5·55, 5·56	1·00
Methyl mercaptan	0·464	4·88, 4·92, 4·93	1·05
Iso-amyl mercaptan	0·236	2·50, 2·47, 2·48	1·04
α-Naphthylmethyl mercaptan ($C_{10}H_7CH_2SH$)	0·278	2·88, 2·86, 2·89	1·03
β-Mercaptopropionic acid	0·505	5·60, 5·64, 5·62	1·11
Thiophenol	0·312	3·21, 3·22, 3·22	1·02

Table II.—The results of titration with HMB solution

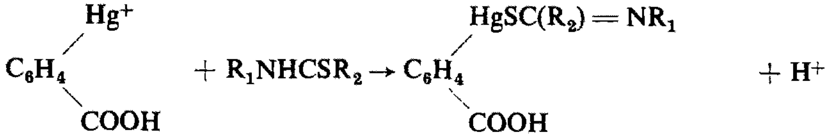
Titrated substance	Taken, *mmole*	Consumption of 0·0504*N* HMB, *ml*	Equivalent of HMB/mole of substance
Chloride	0·200	3·98, 3·98, 3·96	1·00
Chloride	0·400	7·94, 7·92, 7·96	1·00
Thiocyanate	0·198	3·93, 3·96, 3·92	1·00
Thiocyanate	0·395	7·84, 7·86, 7·82	1·00
Bromide	0·208	4·16, 4·10, 4·14	1·00
Iodide	0·185	3·66, 3·66, 3·64	0·995
Thiourea	0·326	6·46, 6·44, 6·45	0·998
Thiosemicarbazide	0·406	8·02, 7·97, 7·94	0·988
Ethylenethiourea	0·470	9·30, 9·24, 9·30	0·993
Diphenylthiourea	0·263	5·20, 5·19, 5·20	0·995
Thioacetamide	0·456	9·12, 9·29, 9·18	1·02
Methyl mercaptan	0·232	9·29, 9·26, 9·25	2·02
Iso-amyl mercaptan	0·188	7·60, 7·59, 7·56	2·02
α-Naphthylmethyl mercaptan	0·222	8·90, 8·87, 8·91	2·02
β-Mercaptopropionic acid	0·253	10·2, 10·1, 10·1	2·02
Thiophenol	0·125	3·00, 3·10, 2·94	1·22

indicator, but has proved valuable for determination of mercaptans in the presence of compounds which are easily decomposed in alkaline solutions, *e.g.*, *S*-alkylthiuronium salts. By titrating with HMB in acid and alkaline solutions and using the desulphurating titration with the same reagent, three components can be determined in the presence of each other, *e.g.*, mercaptan, thiocyanate and thiourea.

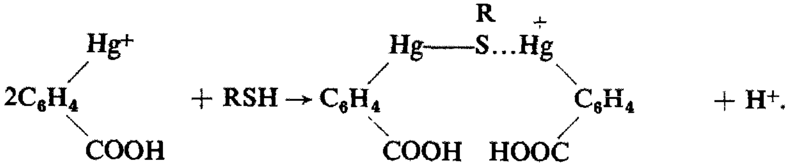
The reactions taking place during the titration with HMB can be represented as follows

(1) 

$$C_6H_4\begin{matrix}Hg^+\\ COOH\end{matrix} + X^- \rightarrow C_6H_4\begin{matrix}HgX\\ COOH\end{matrix} \quad (X = Cl^-, Br^-, I^-, CNS^-)$$

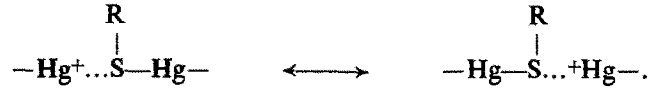
(2) 

$$C_6H_4\begin{matrix}Hg^+\\ COOH\end{matrix} + R_1NHCSR_2 \rightarrow C_6H_4\begin{matrix}HgSC(R_2) = NR_1\\ COOH\end{matrix} + H^+$$

(3) 

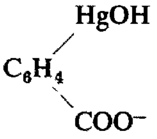
$$2C_6H_4\begin{matrix}Hg^+\\ COOH\end{matrix} + RSH \rightarrow C_6H_4\begin{matrix}Hg\text{---}\overset{R}{S}\ldots\overset{+}{Hg}\\ COOH \quad HOOC\end{matrix}C_6H_4 + H^+.$$

It should be noted that one half of the HMB content in the last complex can be back-titrated in alkaline solutions using thiofluorescein as an indicator. It may be assumed that the sulphur in the HMB-mercaptide is capable, in acid solution, of taking up an additional molecule of HMB, the complex being represented by the resonance structures,



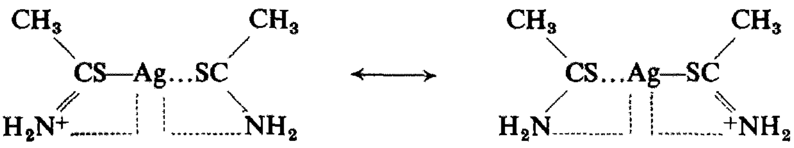
$$-Hg^+\ldots\overset{\overset{R}{|}}{S}\text{---}Hg- \longleftrightarrow -Hg\text{---}\overset{\overset{R}{|}}{S}\ldots{}^+Hg-.$$

In alkaline solution HMB can be represented by the formula



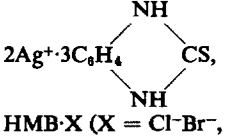
$$C_6H_4\begin{matrix}HgOH\\ COO^-\end{matrix}$$

and a second reagent molecule cannot be taken up. The structure of some complexes with silver can be explained similarly, *e.g.*,



The same tendency can be observed during the titration of aliphatic mercaptans with mercuric acetate in acid solution. The results obtained in the presence of *p*-dimethylaminobenzylidenerhodanine correspond to 1·1–1·2 and in the presence of diphenylcarbazone as indicator to 1·5–2·0 equivalents of bivalent mercury per mole of the mercaptan. For aromatic mercaptans, however, the end-point always corresponds to the formation of the simple complex $Hg(SR)_2$; this is in agreement with the work of Gregg, Bouffard and Borton.[12]

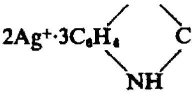
Zusammenfassung—Ortho-hydroxymercuribenzoesäure (HMB) und Silbernitrat in einem Äthanol-Wasser-Gemisch, das Überchlorsäure oder Essigsäure enthält, können als Titrationsmittel zur Bestimmung folgender Substanzen verwendet werden: Chlorid, Bromid, Jodid, Rhodanid, Hexacyanoferrat(II), Tetraphenylborat, Thioharnstoff, Thiosemicarbazid, Diphenylthioharnstoff, Thioacetamid *o*-Phenylenthioharnstoff, Ethylenthioharnstoff, 0,0-Diäthyldithiophosphorsäure und Mercaptane. Dabei wird *p*-Dimethylaminobenzylidenrhodanin als visueller Indikator verwendet. Der Verbrauch der Reagentien am Endpunkt entspricht der Bildung der Produkte: AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+\cdot 3NH_2CSNHNH_2$,



, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$,

$HMB\cdot X$ ($X = Cl^-Br^-, I^-, CNS^-$), HMB(—NHCS—), $2HMB\cdot R\cdot SH$.

Résumé—Pour les dosages de: chlorure, bromure, iodure, sulfocyanure, ferrocyanure, tétraphénylborate, thiourée, thiosemicarbazide, diphénylthiourée, thioacétamide, *o*-phénylenethiourée, éthylenethiourée, acide 0,0-diéthyldithiophosphorique et mercaptans, on peut utiliser, comme solutions de titrage, l'acide *o*-hydroxymercuribenzoïque (HMB) et le nitrate d'argent dans un mélange éthanol-eau contenant de l'acide perchlorique ou de l'acide acétique avec, pour indicateur visuel, la *p*-diméthylaminobenzylidènerhodanine. La consommation des réactifs au point de virage correspond à la formation des produits: AgCNS, AgI, $KAg_3Fe(CN)_6$, $(C_6H_5)_4BAg$, RSAg, $(C_2H_5O)_2PSSAg$, $2Ag^+\cdot 3NH_2CSNH_2$, $2Ag^+.3NH_2CSNHNH_2$,



, $Ag^+\cdot 2CH_3CSNH_2$, $Ag^+\cdot 2C_6H_5NHCSNHC_6H_5$,

$HMB\cdot X$($X = Cl^-,Br^-, I^-, CNS^-$), HMB·(—NHCS—), $2HMB\cdot R\cdot SH$.

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TITRIMETRIC DETERMINATION OF THE IRON(II) OXIDE CONTENT OF SILICATES USING POTASSIUM IODATE

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Summary—A method for determination of the iron(II) oxide content of silicates soluble in hydrofluoric and sulphuric acids is described. The procedure allows the addition of potassium iodate initially during the decomposition, thus minimising error from oxidation of the iron by air. The decomposition of the rock by hydrofluoric and sulphuric acids takes 15 to 20 min at boiling temperatures and can be carried out in a Pyrex flask. Results are given for the analysis of standard rocks G1 and W1.

Available methods for determination of the iron(II) oxide are a very tedious and unsatisfactory part of schemes for the analysis of silicate rocks and minerals. In principle two types of titrimetric method are used for this determination. *1.* The sample is decomposed by acids in a platinum crucible and the mixture is transferred to a beaker; iron(II) is then titrated with a standard oxidant.[1-3] *2.* A measured excess of the standard oxidant is initially added to the decomposition mixture, in which case the iron(II) consumes instantly an equivalent amount of oxidant as it goes into solution; the excess of unreacted oxidant is then determined.[4-7]

In the first or conventional type of procedure great care is required to prevent air oxidation during the initial decomposition and during the subsequent titration. In the second type, the decomposition period must be carried out at room temperatures to minimise reaction of the oxidant and the acid reagents, thus requiring several hours for complete decomposition.

Oxidants suitable for the second type of procedure include potassium dichromate,[5] ammonium metavanadate[4] and iodine monochloride.[7] These procedures all have the advantage over conventional methods of minimising the error from atmospheric oxidation of the iron(II).

It would be desirable to have a procedure which minimises error from air oxidation of the iron(II) and which would also allow the decomposition of the silicate to be carried out in a relatively short period of time at boiling temperatures. The proposed method fulfils these conditions for silicate samples soluble in hydrofluoric and sulphuric acids.

Principle of proposed procedure

Potassium iodate is used as an oxidant for iron(II) in the absence of chlorides. A known excess of this reagent is added, together with hydrofluoric and sulphuric acids, to a silicate rock powder. The iron(II), which is released during the subsequent decomposition at boiling temperature, reacts with iodate to produce iodine by the following reaction

$$10Fe^{+2} + 2IO_3^- + 12H^+ \rightarrow 10Fe^{+3} + I_2 + 6H_2O.$$

The iodine is volatilised from the boiling solution and the iodate remaining is treated in the cooled solution with excess iodide. Standard sodium thiosulphate is used to titrate the liberated iodine. The amount of thiosulphate and hence iodate equivalent to the iron(II) in the sample can then be calculated.

EXPERIMENTAL

Reagents

The chemicals for standard solutions were Baker analysed reagents.

Standard iron(II) *solution.* 24 g of ammonium iron(II) sulphate were dissolved in 20 ml of water containing 10 ml of concentrated sulphuric acid. The solution was filtered through a No. 42 Whatman paper and diluted to 1 l. The concentration of iron was found to be 3·32 mg/ml by both permanganate and ceric sulphate titrations.

Soluble starch indicator solution. A fresh 1% starch solution was prepared each day by mixing 1 g of soluble starch into a slurry with cold water and then dissolving it in 100 ml of boiling water.

Standard 0·1*N potassium iodate and* 0·1*N sodium thiosulphate solutions.* These solutions were prepared as indicated in Kolthoff and Sandell.[8]

Proposed procedure for determination of iron(II) *oxide in silicate rocks*

Weigh 0·5 g of rock sample, crushed to 60 mesh, into a 250-ml Erlenmeyer flask together with 25 ml of standard potassium iodate solution. Swirl the mixture to obtain a thin uniform layer of rock powder over the bottom of the flask. Add 15 ml of 49% hydrofluoric acid and 15 ml of 1:1 sulphuric acid. Heat the mixture to boiling for a period of 12 to 15 min. If any black particles remain, add 10 ml of additional hydrofluoric acid and heat the solution for a further 5 to 10 min. At the end of the decomposition period boil the solution vigorously for 15 sec to ensure complete expulsion of iodine. Cool the resultant mixture in a bath of cold water and add 20 ml of concentrated aqueous ammonia to consume most of the excess acid, and 50 ml of water. Dissolve 2 g of potassium iodide in the solution and titrate the iodine released with sodium thiosulphate solution.

RESULTS AND DISCUSSION

Determination of iron(II) *in a standard solution by proposed procedure*

The following tests were carried out to ascertain whether iron(II) reacts with iodate under the conditions of this experiment to release an equivalent amount of iodine as proposed in the equation above. The procedure for iron(II) determination in silicates was followed except that various aliquots of standard iron(II) solution were added in place of the rock powder to separate 250-ml flasks. The results are given in Table I.

TABLE I.—IRON(II) CONTENT OF SOLUTIONS

Iron(II), *mg*		Error,
Added	Recovered	*mg*
33·2	33·4	+0·2
33·2	33·2	—
33·2	33·1	−0·1
33·2	33·1	−0·1
33·2	33·0	−0·2
33·2	33·1	−0·1
33·2	33·1	−0·1
16·6	16·5	−0·1
16·6	16·3	−0·3
16·6	16·5	−0·1
16·6	16·4	−0·2
16·6	16·4	−0·2
16·6	16·6	—

Because iron was determined quantitatively by the procedure, it can be assumed that under these conditions the reaction between iron(II) and iodate occurs as indicated in the above equation.

Complete volatilisation of iodine from boiling solutions

It is essential that the iodine produced in the reaction between iron(II) and iodate is completely expelled from the solution before the addition of excess potassium iodide. Several silicate rock samples were treated according to the proposed procedure. After the 15-sec boiling period 2 or 3 drops of starch indicator were added to each solution to test for iodine. No blue colour was noticed in any sample and hence the volatilisation of iodine was assumed to be complete.

Reaction of potassium iodate with constituents in Pyrex glass

The consumption of iodate by any constituents dissolved from the Pyrex glass Erlenmeyer flask during the hydrofluoric acid treatment would result in an error. The following experiments were carried out to test for this error.

The proposed procedure was followed except that no material containing iron was introduced into the Erlenmeyer flask. The results are given in Table II, No. 4–7.

TABLE II.—REACTION WITH CONSTITUENTS IN PYREX GLASS

No.	Description	Amount of thiosulphate consumed, *ml*	Deviation from the average value of 21·84 ml, *ml*
1	No HF or H_2SO_4 treatment	21·86	+0·02
2	No HF or H_2SO_4 treatment	21·84	—
3	No HF or H_2SO_4 treatment	21·83	−0·01
4	HF and H_2SO_4 used	21·83	−0·01
5	HF and H_2SO_4 used	21·83	−0·01
6	HF and H_2SO_4 used	21·82	−0·02
7	HF and H_2SO_4 used	21·86	+0·02

These are compared with results No. 1–3 obtained from samples in which excess potassium iodide was added directly to an acidified 25-ml aliquot of potassium iodate without treatment with hydrofluoric and sulphuric acids.

Since there is no significant difference in the amount of thiosulphate consumed in

TABLE III.—DETERMINATION OF IRON(II) OXIDE IN SILICATE ROCKS

Sample	Amount of FeO found, %		Deviation from mean, %	Amount of FeO found by conventional methods, %	Amount of FeO found by Reichen and Fahey,[5] %
WI	9.24	Ave. 9·24	—		
WI	9·24		—		
WI	9·25		+0·01	8·85	9·30
WI	9·24		—		
GI	1·04	Ave. 1·03	+0·01		
GI	1·01		−0·02	0·95	1·11
GI	1·03		—		

each case it was assumed that no interference was occurring from constituents in the glass. However, as a precaution "blank" values obtained in the presence of hydrofluoric and sulphuric acids were used in all calculations.

Reaction of hydrofluoric or sulphuric acids with iodate

Fredenhagen[8] indicated that iodate dissolved without reaction in anhydrous hydrofluoric acid at 0°, whereas it slowly decomposed at boiling temperatures. Under the conditions of these experiments no adverse reaction of the 49% hydrofluoric acid and 1 : 1 sulphuric acid with iodate were recorded as indicated by the results in Table II.

Testing of procedure for determination of iron(II) *oxide in silate rocks*

Samples of U.S. Geological Survey Standards GI and WI were analysed by the proposed procedure. The results are given in Table III.

RESULTS

The results for samples GI and WI obtained by the proposed procedure, although precise, are considerably higher than those recorded using conventional procedures. On the other hand, the results for WI compare favourably with those obtained by Reichen and Fahey.[5] Higher and probably more accurate results are to be expected by a procedure of this nature which eliminates error from air oxidation of the iron(II) before reaction with the standard oxidant.

As was the case with previous procedures, sulphides and vanadium(III) interfere; however, the proposed procedure has the following advantages:—

1. The decomposition can be performed in a vessel open to the air, thus eliminating the need for using inert atmospheres.
2. Platinum crucibles are replaced by Pyrex glass containers, which facilitates visual observation of the completion of the decomposition.
3. The dissolution of the rock powder can be carried out in the presence of the oxidant at boiling temperatures.

Zusammenfassung—Eine Methode zur Bestimmung des Eisen (II)-oxydgehaltes von in Flußsäure und Schwefelsäure löslichen Silikaten wird beschrieben. Dieses Verfahren erlaubt die Zugabe von Kaliumjodat während der Zersetzung; so wird der Fehler durch atmosphärische Oxydation des Eisens sehr klein gehalten. Der Aufschluß des Gesteins mit Flußsäure-Schwefelsäure dauert bei Siedetemperatur 15–20 Minuten und kann in einen Pyrexkolben ausgeführt werden. Ergebnisse der Analyse der Standardgesteine G1 und W1 werden angegeben.

Résumé—On décrit une méthode de détermination de la teneur en oxyde de fer (II) des silicates solubles dans les acides fluorhydrique et sulfurique. La technique permet l'addition d'iodate de potassium au cours même de la décomposition, diminuant ainsi l'erreur provenant de l'oxydation atmosphérique du fer. La décomposition de la roche par les acides fluorhydrique et sulfurique nécessite 15–20 min aux températures d'ébullition, et peut être menée dans un récipient en Pyrex. On donne les résultats d'analyse des roches étalons G1 et W1.

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COLUMN AND THIN-LAYER CHROMATOGRAPHIC SEPARATION OF POLYNUCLEAR RING-CARBONYL COMPOUNDS

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Summary—Methods for the separation of polynuclear ring-carbonyl compounds by alumina column chromatography and alumina and cellulose thin-layer chromatography are described. A method for the thin-layer chromatographic separation of acridones and phenanthridones from other types of polynuclear compound is also described. Compounds on a thin-layer chromatogram are located by fluorescence methods employing trifluoracetic acid fumes and tetra-ethylammonium hydroxide solution. Fluorescence spectra of these compounds on the thin-layer chromatogram and in solution are also reported.

A PREVIOUS paper reported the determination of polynuclear aza heterocyclic compounds, polynuclear aromatic hydrocarbons and long-chain *n*-alkanes in the urban atmosphere.[1] The aromatic hydrocarbons are found in the aromatic fraction, the aza heterocyclic compounds in the basic fraction and the *n*-alkanes in the aliphatic fraction of organic airborne particulates.

Carbonyl compounds would be more difficult to separate as a group. This is because they are a major component of the various fractions of organic airborne particulates, as shown by the infrared spectra of the benzene-soluble fraction and its aromatic, neutral oxygenated, acid, water-soluble and basic subfractions.[2] It should be possible, however, to separate and analyse smaller classes of carbonyl compounds. Because there is a very large variety of carbonyl compounds, it was decided to concentrate our efforts on a study of the aromatic carbonyl compounds and especially the polynuclear ring-carbonyl type.

EXPERIMENTAL

Reagents and apparatus

Carbonyl compounds. The various carbonyl compounds were obtained from commercial sources or synthesised by published procedures. All solid compounds were purified to a constant melting point by recrystallisation.

Spectrophotofluorometry. An Aminco-Bowman spectrophotofluorometer with 0·1-ml and 1-ml cells was used with the following settings: sensitivity 50, slit arrangement No. 2, and phototube RCA type 1P21. The fluorescence spectra of spots on thin-layer chromatograms were obtained by use of an Aminco solid-sample accessory.[3]

An alternative method for preparation of a thin-layer chromatogram for spectrophotofluorometric examination is the following. Spray the developed chromatogram lightly with a chromatogram-preserving medium (Gallard-Schlesinger Chemical Mfg. Corp., Carle Place, N.Y., U.S.A.). When the chromatogram surface feels dry to the touch, cut with a razor blade 0·4-inch wide stripes containing the origin and the sub-spots and peel off the strips. If a strip adheres to the surface, steam the plate for a few minutes so that the strip can be removed easily. Examine each spot on the strip by the slit procedure.[3] Before fluorometric examination, the spot can be immersed in concentrated sulphuric acid or strong alkali.

Spectrophotometer. A Cary Model 11 spectrophotometer was used in the absorption spectral studies.

Column chromatography

Merck acid-washed alumina was washed with ether, dried and heated in an oven at 130° for 4 hr. The treated alumina contained approximately 12% of water (as determined by weighing a sample, heating to a standard red-heat for 10 mins cooling in a desiccator and reweighing). Enough water was then added to give a final concentration of 13·0%. (Less water was added for greater resolution; more water for faster separation.) The alumina was shaken and allowed to stand overnight in a stoppered container before use.

The sample to be analysed was dissolved in a small volume of chloroform and adsorbed onto 1 g of alumina, then the chloroform was evaporated. This alumina was then added to a column (0·5-inch diameter, 15 inches long), which contained a well-packed lower layer of 9 g of the previously prepared alumina and an upper layer of 0·5 g of silica gel, neither containing eluting solvent. The column was eluted with successive 100-ml volumes of pentane solutions containing the following percentages of ether: 8, 16, 24, 32, 40, 48, 56 and 64. Elution required about 3 hr. Fractions of about 15 ml were collected. After evaporation the contents of each tube were dissolved in 3 ml of pentane and the absorption spectrum from 250 to 450 mμ was obtained.

Thin-layer chromatography

Both the cellulose and the aluminum oxide-G plates were prepared by the directions obtained with the adsorbents (Brinkmann Instruments, Inc., Great Neck, N.Y., U.S.A). The R_f values obtained with the cellulose plates were much more reliable and reproducible than those obtained with the alumina plate, which could adsorb enough water on the alumina to affect the R_f values drastically. The laboratory humidity, the type of alumina, the amount of water in the tank and the time of exposure of the plate to the air all contribute to the unreliability of the R_f value. It must be emphasised that in spite of the irreproducibility of the R_f on alumina, this system is very valuable in identification of carbonyl compounds and in the separation of mixtures as long as standards are run alongside the mixture.

DISCUSSION

Column chromatography of ring-carbonyl compounds

The separation of seven ring-carbonyl compounds is shown in Fig. 1. Each compound was present in 1-mg amount. The separation is fairly sharp except for

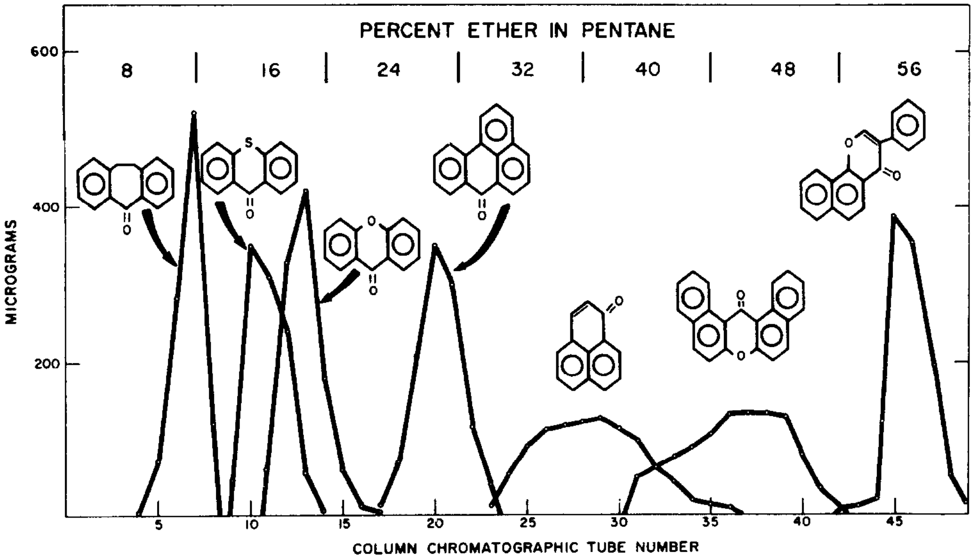

FIG. 1.—Alumina column-chromatographic separation of some polynuclear ring-carbonyl compounds.

phenalen-1-one and 7H-dibenzo(c, h)xanthen-7-one. This pair and the xanthen-9-one and thioxanthen-9-one pair are the only compounds not completely separated. The individual members of each pair can be characterised and estimated through absorption spectrophotometry. Although these compounds ordinarily would be eluted with the aza heterocyclic compounds, the aza compounds can be extracted quantitatively from the carbonyl and other less basic compounds with 20% aqueous sulphuric acid before the separation.

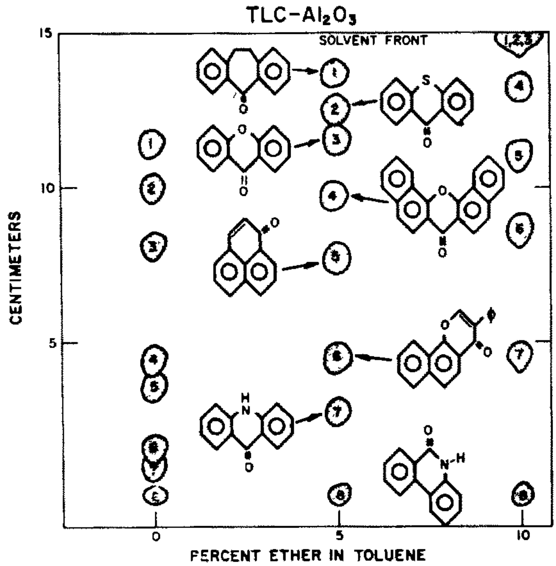

FIG. 2.—The effect of an increasing percentage of ether in toluene on the alumina thin-layer-chromatographic separation of ring-carbonyl compounds.

Thin-layer chromatography

Individual ring-carbonyl compounds can be readily separated on alumina with toluene or toluene-ether solutions (Fig. 2) or with pentane-ether (19:1) (Fig. 3). Thin-layer chromatography on cellulose with dimethylformamide-water (35:65, v/v) separates the compounds in a radically different sequence (Fig. 4).

Freshly made alumina plates that had been activated at 110° for 60 min were spotted within 10 min after activation and immediately run; separations are shown in Fig. 2. The best separation was obtained with toluene-ether (19:1). Compounds 3 and 4 showed superior separation with toluene; compounds 4 and 5, with the 5 and 10% ether solutions; and compounds 6, 7 and 8, with the higher ether concentration.

The separation of various types of polynuclear compound on an alumina plate is shown in Fig. 3. This plate had been previously exposed to wet air long enough that benzo(a)pyrene gave an R_f value of 0·85 with pentane-ether (19:1). Plates of this same activity had been used previously to separate the polynuclear aromatic hydrocarbons[4] and the aza heterocyclic compounds.[5] Of the polynuclear aromatic hydrocarbons found routinely in the air only coronene would be found among the ring-carbonyl compounds. Aza heterocyclic compounds and aromatic amines can

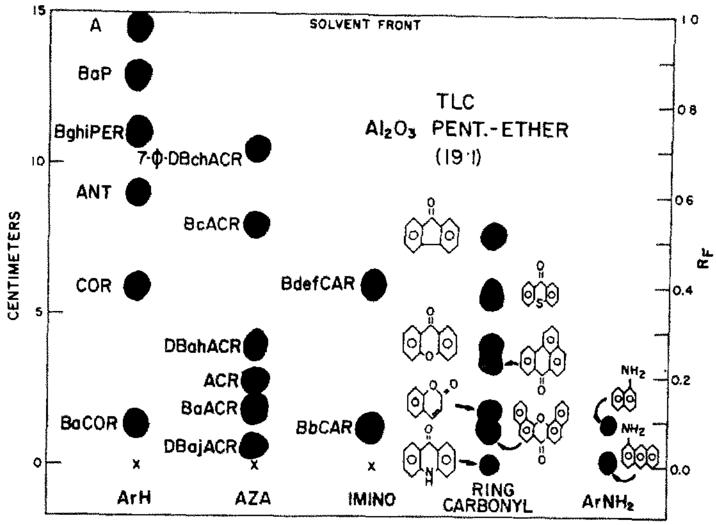

Fig. 3.—A comparison of the alumina thin-layer chromatographic separation of various families of polynuclear compound with pentane-ether as developing solvent [all separations with benzo(a)pyrene (R_f = 0·85) as internal standard].

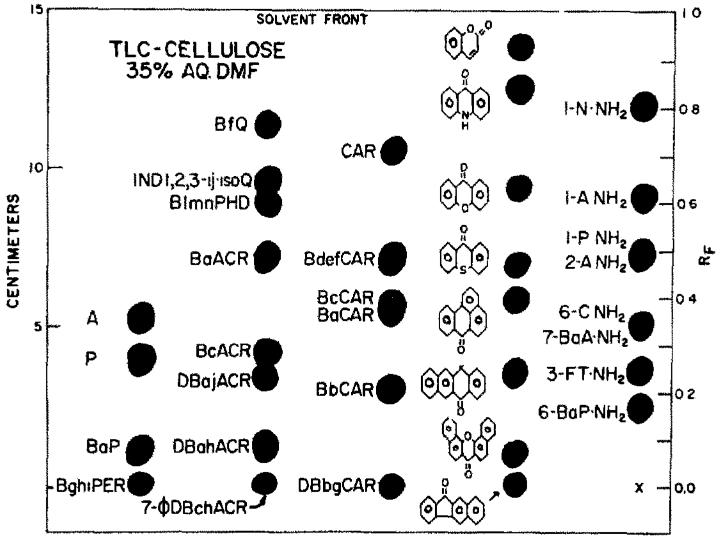

Fig. 4.—A comparison of the cellulose thin-layer chromatographic separation of various families of polynuclear compound with 35% aqueous dimethylformamide as developing solvent.

be readily extracted from a mixture with 20% aqueous sulphuric acid so that their interference could be prevented. The most serious interference could be the carbazole compounds, but this class of compound is readily differentiated from the carbonyl derivatives by fluorescence colour reactions on the plate with tetra-ethylammonium hydroxide and trifluoracetic acid fumes.

Even better separation of the ring-carbonyl compounds is shown in Fig. 4. As in Fig. 3, the main interference is from the carbazole compounds.

The acridone or phenanthridone type of ring-carbonyl compound can be separated readily from the other ring-carbonyl compounds and from the polynuclear aromatic hydrocarbons and aza heterocyclic compounds (Table I). This separation method should also be of value for the larger acridones and phenanthridones, which could be expected to have much lower R_f values than their tricyclic homologues.

The separations of a large number of polynuclear ring-carbonyl compounds and aralkyl ketones are compared in Table II, which lists values for three systems that are useful for the separation of the polynuclear ring-carbonyl compounds and aralkyl ketones.

TABLE I.—SEPARATION OF ACRIDONE AND PHENANTHRIDONE FROM OTHER COMPOUNDS

Polynuclear compounds	R_f
Ring-carbonyl compounds [fluoren-9-one to 7H-dibenzo(c, h)xanthen-7-one]	0·87–1·0
Aromatic hydrocarbons (anthracene to coronene)	0·96–1·0
Aza heterocyclic compounds [benzo(h)quinoline to dibenz(a, h)acridine]	0·93–1·0
6(5H)-Phenanthridinone	~0·60
9-Acridanone	~0·52

Al_2O_3–toluene:methanol (19:1, v/v)

TABLE II.—SEPARATION AND FLUORESCENT LOCATION OF CARBONYL COMPOUNDS

Compound (1 μg of each)	Al_2O_3		Cellulose[a] DMF—H_2O 35:65	Fluor. colour[b]	
	Pentane-ether 19:1	Toluene		Neutral	TFA fumes
10,11-Dihydro-5H-dibenzo(a, d)-cycloheptene-5-one	0·64	0·76	0·67	—	ly
Fluoren-9-one	0·60	0·72	0·11t	d	dR
2-Benzoylpyrene	0·50	0·79	0·08	lY	—
9-Acetylphenanthrene	0·49	0·66	0·64	—	lR
6-Benzoylchrysene	0·48	0·76	0·40	lY	—
Thioxanthen-9-one	0·48	0·66	0·47	B	Y
11H-Benzo(b)fluorene-11-one	0·44	0·64	0·34	lO	—
Anthrone	0·43	0·78	0·63	—	dR
3-Acetylpyrene	0·43	0·64	0·37	B	—
9-Acetylanthracene	0·42	0·74	0·34	—	lB
Xanthen-9-one	0·38	0·53	0·63	—	B
6H-Benzo(c, d)pyrene-6-one	0·31	0·49	0·19t	lYO	RO
5,12-Dihydronaphthacen-5-one	0·30	0·64	0·24	Y	RO
Benzanthrone	0·29	0·58	0·39	GY	O
1-Indanone	0·29	0·55	0·93	—	BG[c]
Coumarin	0·13	0·47	0·92	—	GY[d]
Phenalen-1-one	0·11	0·24	0·81	Y	EmG
7H-Dibenzo(c, h)xanthen-7-one	0·08	0·29	0·07	B	G
7,8-Benzoflavone	0·00	0·10	0·34	B	G
9-Acridanone	0·00	0·08	0·83	lB	B
6(5H)-Phenanthridinone	0·00	0·00	0·79	pB	lB
11,12-Dihydroindeno(2,1-a)-fluorene-11,12-dione	0·00	0·00	0·00	dR	—

[a] t = tails.

[b] On the alumina plate: — = could not see spot, B = blue, d = dull, Em = emerald, G = green, Y = yellow, l = light, O = orange, p = pale, R = red.

[c] H_2SO_4 needed to locate by fluorescence colour.

[d] Drop of 29% methanolic tetra-ethylammonium hydroxide needed to locate by fluorescence colour.

Although the results on alumina are not reproducible from week to week, they are of definite value in separation. Both activated and non-activated plates should be used, because the superiority of either type of plate depends on the compound of interest and the type of mixture in which the compound is present. Except for the acridone type of molecule the relative order of the ring-carbonyl compounds separated with toluene-ether (9:1) on alumina is unaffected by the activity of the alumina. Changes in the R_f values on aluminas of widely varying activities are drastic. With more water in the alumina the carbonyl compounds tend to give higher R_f values. The exception to this rule in the toluene-ether system is acridone. Preliminary results indicate that with more water in the alumina, acridone can give a lower R_f value. Other variables also could have an effect on the R_f value relative to the other ring-carbonyl compounds. This phenomenon should prove useful in the separation and analysis of acridone compounds.

TABLE III.—FLUORESCENCE COLOUR CHANGES AND DETECTION LIMITS FOR RING-CARBONYL COMPOUNDS ON A CELLULOSE THIN-LAYER PLATE

Compound	Dry	TFA[a] fumes	TEA[a] drop	Det. limit,[c] *ng*
9-Acridanone	B	B	lBG	5
Anthrone	—	—	GY	5
Benzanthrone	G	YO	—	5
7,8-Benzoflavone	B	BG	—	1
7H-Dibenzo(c, h)xanthen-7-one	GY	G	—	1
10,11-Dihydro-5H-dibenzo(a, d)cyclohepten-5-one	—	Y	—	100
Phenalen-1-one	lG	EmG	dG → Y[d]	1
6(5H)-Phenanthridinone	lB	lB	B	10
Thioxanthen-9-one	—	G	—	10
Xanthen-9-one	lB	B	—	5

[a] TFA = trifluoroacetic acid; see Table II for key to symbols.

[b] TEA = 29% methanolic tetraethylammonium hydroxide.

[c] All detection limits obtained after treatment with TFA fumes except anthrone, phenalen-1-one and 6(5H)-phenanthridinone, for which treatment with TEA gave the best results.

[d] This change in fluorescence colour took several minutes. At the same time the visible colour changed from light yellow to pink.

Characterisation tests on the plate

Table II lists some of the characteristic fluorescence colours obtained on the alumina plate before and after treatment with trifluoracetic acid fumes. Most of the ring-carbonyl compounds give brilliant fluorescence colours, especially after treatment with trifluoracetic acid fumes. Fluorescence colour changes and detection limits on the alumina plates have been reported for some of the aralkyl derivatives and ring-carbonyl compounds.[6] Trifluoracetic acid fumes were useful in detecting the strongly basic aromatic amines and aza heterocyclic compounds, as well as the weakly basic carbonyl compounds.

Changes in fluorescence colour of ring-carbonyl compounds on the cellulose plate before and after treatment with trifluoracetic acid fumes are shown in Table III, which also gives the fluorescence colour changes with methanolic tetra-ethylammonium hydroxide (TEA). Anthrone, phenalen-1-one and 6(5H)-phenanthridinone give very brilliant colours that should prove useful in their characterisation. Phenalen-1-one shows a green fluorescence after the addition of TEA with a detection limit of 1 ng. After development for 5 min, a yellow fluorescence is obtained which has a detection limit of 50 ng. A visible pink colour is detectable after development for 12 min at a limit of 50 ng. The ring-carbonyl compounds give approximately the same colour changes with TEA on alumina except that the fluorescence of 9-acridanone is a more vivid blue-green.

Fluorometric spectra.

Table IV lists the fluorometric spectra of the ring-carbonyl compounds in solution and on the cellulose plate. The cellulose thin-layer plate was preferred to the alumina plate mainly because we expect the last separation step of a mixture before fluorometry to be by cellulose thin-layer chromatography.

The disadvantage of using trifluoracetic acid fumes to form the salt of a ring-carbonyl compound is that these compounds are so weakly basic that a mixture of salt and neutral compound sometimes forms on the plate. In addition, over a period

TABLE IV.—FLUOROMETRIC SPECTRA AND DETECTION LIMITS OF POLYNUCLEAR RING-CARBONYL COMPOUNDS ON CELLULOSE THIN-LAYER CHROMATOGRAMS AND IN SOLUTION

Compound	C or S[a] solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra[b] emission		Det. limit,[c] *ng*
			λ	MM.T	λ	MM.T	
9-Acridanone	C-dry	0·1	*260*	23	409	23	5
			292	5	*429*	22	
			300s	4	450s	10	
			380s	73	480s	2·4	
			392	75			
	C—DMF	0·01	*257*	0·9	408	1·1	5
			292	0·1	428	1·1	
			382	2·3	*454*s	0·6	
			392	2·6			
	C—TFA	0·1	250	8·1	428	12	5
			290	1·8	*450*	26	
			330	15	473	11	
			372	20	510s	4·5	
			390	24			
			410	18			
9-Acridanone	S—MeOH	(10^{-7})	250	0·11	410	0·12	0·5
			290	0·015	*430*	0·11	
			302	0·01	455s	0·05	
			374	0·15	480s	0·015	
			390	0·16			
	S—H_2SO_4	(10^{-6})	250	1·2	430	0·6	0·8
			292	0·1	*454*	0·77	
			320s	0·4	480s	0·5	
			330	0·7			
			374	0·6			
			390	0·7			
			410	0·5			
Anthrone	C—TEA	0·01	368s	3·3	*530*	5·0	5
			378	3·9			
			400s	2·9			
	S—MeOH	(10^{-5})	*252*	0·13	428s	0·12	100
			364	0·05	*448*	0·14	
			380	0·05			
	S—H_2SO_4	(10^{-6})	250	0·01	*478*	0·1	200
			280	0·02			
			350	0·10			

TABLE IV (*Cont'd*)

Compound	C or S[a] solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra[b] emission		Det. limit,[c] *ng*
			λ	MM.T	λ	MM.T	
Benzanthrone	C—TFA	0·1	*362*	4·0	*550*	4·2	2
			389s	3·0			
			412	4·0			
			442	3·0			
			460	3·6			
			472	3·4			
			482	3·4			
	S—H_2SO_4	(10^{-5})	250	0·24	*570*	1·9	20
			280	0·15			
			370	1·9			
			420	1·0			
			447	0·66			
			462	1·1			
			470	1·1			
			480	1·4			
			487	1·5			
			502s	1·3			
7,8-Benzoflavone	C-dry	0·01	330s	1·1	*468*	0·6	1
			360	1·2			
	C—TFA	0·01	302	3·0	*470*	2·5	1
			345	5·0			
			375s	4·8			
			385	5·0			
	S—MeOH	(10^{-5})	*290*	0·38	412	0·4	250
			310s	0·3			
			342	0·3			
			372	0·1			
			390	0·1			
	S—H_2SO_4	(10^{-6})	240	0·1	*487*	0·64	15
			310	0·48			
			350	0·65			
			380s	0·52			
			390	0·58			
7H-Dibenzo(c, h)xanthen-7-one	C—TFA	0·01	270s	1·6	*490*	6·4	0·3
			300	6·			
			332	6·			
			392s	8·			
			405	8·6			
			411	8·7			
	S—MeOH	(10^{-6})	*290*	0·22	*402*	0·22	5
			342s	0·1			
			358	0·13			
	S—H_2SO_4	(10^{-7})	270	0·015	*490*	0·07	2
			304	0·07			
			334	0·05			
			410	0·07			
10,11-Dihydro-5H-dibenzo-(a, d)cyclohepten-5-one	C—TFA	1	*322*	1·5	*500*	1·5	50
	S—H_2SO_4	(10^{-4})	298	0·15	*516*	0·36	1000
			329	0·23			
			390	0·38			
			400s	0·37			
Phenalen-l-one	C-dry	0·01	374s	0·2	*486*	0·33	10
			390	0·36			
			400s	0·35			
			408s	0·33			

TABLE IV (*Cont'd*)

Compound	C or S[a] solvent	Concentration, μg, or (molarity)	Fluorescence excitation		Spectra[b] emission		Det. limit,[c] ng
			λ	MM.T	λ	MM.T	
Phenalen-l-one (*cont'd*)	C—TFA	0·01	*350*	2·2	*486*	1·9	1
			390	4·2			
	S—H$_2$SO$_4$	(10^{-6})	360	0·56	*500*	0·8	4
			400	0·80			
			450	0·36			
			460	0·44			
			470	0·34			
6(5H)-Phenanthridinone	C-Dry	0·1	240s	0·9	360	1·9	50
			260	1·8	*370s*	1·8	
			320s	6·0			
			330	6·1			
	C—TFA	0·01	*254*	0·1	*370*	0·1	10
	S—MeOH	(10^{-6})	238	0·04	*360*	0·11	20
			258	0·05	370s	0·09	
			320	0·11			
			330	0·1			
	S—H$_2$SO$_4$	(10^{-5})	250s	0·24	*382*	0·43	80
			255	0·25			
			317s	0·23			
			332s	0·36			
			348	0·45			
Thioxanthen-9-one	C—TFA	0·1	268	2·3	*490*	2·3	5
			340	2·0	510s	2·2	
			392	3·7			
			405s	3·5			
	S—MeOH	(10^{-6})	260	0·09	*430*	0·12	5
			282s	0·03			
			378	0·14			
	S—H$_2$SO$_4$	(10^{-6})	*270*	0·7	*500*	0·7	5
			334	0·4	512s	0·68	
			415s	0·2			
			445	0·3			
			460	0·36			
Xanthen-9-one	C—TFA	0·01	240	0·3	*440*	4·0	10
			270s	0·5			
			295s	0·8			
			325	2·3			
			350	2·6			
	S—H$_2$SO$_4$	(10^{-7})	250	0·054	*450*	0·2	1
			268	0·015			
			330	0·2			
			390	0·05			
			400s	0·045			

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[a] C = cellulose thin-layer chromatogram; S = solution in a cell. C-Dry signifies that fluorescence spectra of the dry spot on cellulose obtained. DMF = 0·25 μl of dimethylformamide added to the dry spot before fluorometric examination; all other C—solvents used similarly, except C—TFA, which consists of treatment with trifluoracetic acid fumes. TEA = 29% aqueous tetra-ethylammonium hydroxide solution.

[b] s = shoulder. Italicised values are excitation (emission) wavelength maxima at which emission (excitation) spectra were obtained.

[c] The limits in solution were for a 0·1-ml cell.

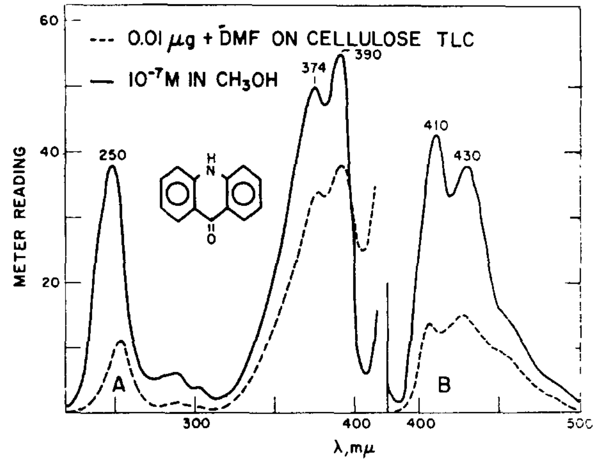

Fig. 5.—Fluorescence excitation (A) and emission (B) spectra of 9-acridanone in the neutral state:— (——) 10^{-7} *M* in methanol at meter multiplier reading (MM) of 0·003; A at emission λ 430 mμ and B at excitation λ 374 mμ. (– – –) 0·01 μg wet with 0·25 μl of dimethylformamide on a cellulose thin-layer plate at MM 0·1; A at emission λ 454 mμ and B at excitation λ 257 mμ.

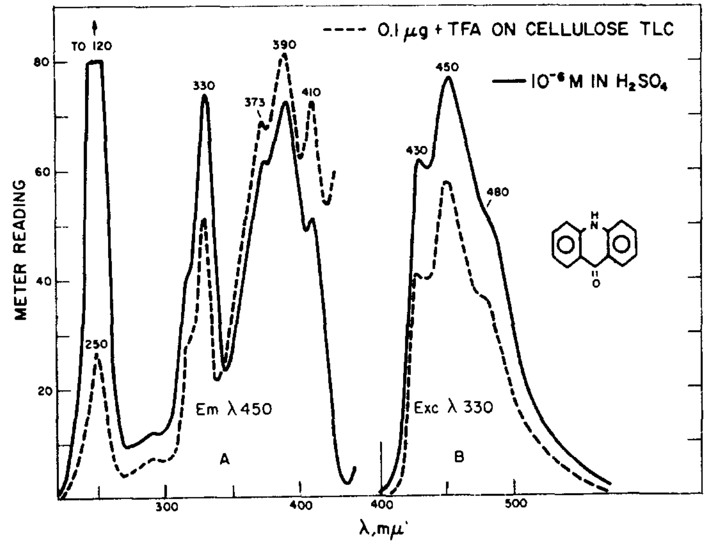

Fig. 6.—Fluorescence excitation (A) and emission (B) spectra of the 9-acridanone cationic salt:— (——) 10^{-6} *M* in concentrated sulphuric acid at MM 0·01. (– – –) 0·1 μg wet with 1 μl of trifluoracetic acid on a cellulose thin-layer plate at MM 0·3. (A at emission λ 450 mμ; B at excitation λ 330 mμ.)

of 5 to 15 min the intensity of the spectral bands of the salt can decrease as the acid evaporates.

Although fluorescence spectra could be obtained from the dry spots of some of the compounds, *e.g.*, 9-acridanone, analogous spectra could not be obtained for other compounds even in 1-μg amounts, *e.g.*, 7H-dibenzo(c, h)xanthen-7-one. Fluorescence spectra could be obtained for phenalen-1-one in the dry state on the cellulose plate, but not when the plate was wet with methanol or dimethylformamide, even at the 1-μg level. Obviously, such phenomena should prove useful analytically and so should be studied more thoroughly.

For some compounds the spectra in solution and on the plate were similar. For example, the spectra of 9-acridanone show this similarity either as the neutral molecule (Fig. 5) or as the cationic salt (Fig. 6). For some compounds the spectra are different on the plate and in solution, especially in the excitation spectra, *e.g.*, thioxanthen-9-one, Fig. 7. In the spectrum on the plate the long-wavelength excitation bands are probably hidden under the scatter peak. The main difference is the 392-mμ band on the plate. The emission spectra on the plate and in solution are almost identical. These differences in spectra should also prove useful in the analysis of these types of compound.

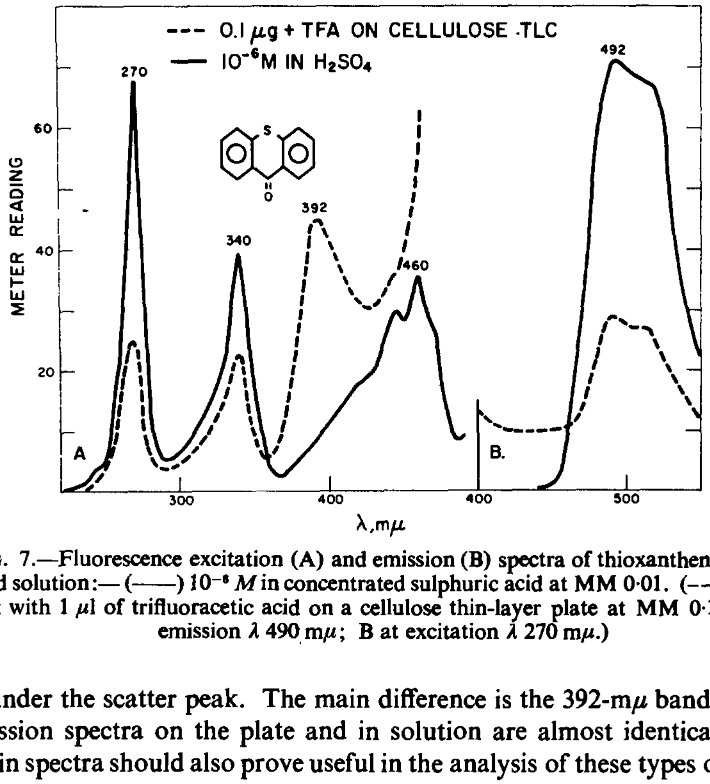

Fig. 7.—Fluorescence excitation (A) and emission (B) spectra of thioxanthen-9-one in acid solution:— (——) 10^{-6} *M* in concentrated sulphuric acid at MM 0·01. (– – –) 0·1 μg wet with 1 μl of trifluoracetic acid on a cellulose thin-layer plate at MM 0·1. (A at emission λ 490 mμ; B at excitation λ 270 mμ.)

CONCLUSION

With the described column and thin-layer chromatographic separation methods, fluorescence location tests and fluorometric analysis on the plate and in solution, it should be possible now to examine complicated mixtures of ring-carbonyl compounds.

The best system for the separation and characterisation for these weakly basic compounds in a mixture seems to be the following sequence: extraction of the basic compounds from the mixture, alumina column chromatography of the non-basic fraction, alumina thin-layer chromatography of the appropriate column chromatographic fractions and cellulose thin-layer chromatography of appropriate alumina thin-layer chromatographic spots, followed by characterisation procedures, such as direct spectrophotofluorometric and spectrophotophosphorimetric examination of the spots.

Zusammenfassung—Methoden zur Trennung mehrkerniger Ring-Carbonylverbindungen durch Säulenchromatographie an Aluminiumoxyd und Dünnschichtchromatographie an Aluminiumoxyd und Cellulose werden beschrieben, desgleichen eine Methode zur dünnschichtchromatographischen Trennung von Acridonen und Phenanthridonen von anderen Typen mehrkerniger Verbindungen. Die Verbindungen auf einem Dünnschichtchromatogramm werden nach Entwicklung mit Trifluoressigsäuredämpfen und Tetraäthylammoniumhydroxydlösung durch Fluoreszenz lokalisiert. Die Fluoreszenzspektren der Verbindungen auf dem Dünnschichtchromatogramm und in Lösung werden ebenfalls angegeben.

Résumé—On décrit des méthodes de séparation de composés polynucléaires à fonction carbonyle sur le noyau, par chromatographie sur colonne d'alumine, et chromatographie en couches minces sur alumine et cellulose. On décrit également une méthode de séparation par chromatographie en couches minces d'acridones et de phénantridones d'autres types de composés polynucléaires. Sur les chromatogrammes en couches minces, on localise les composés par des méthodes de fluorescence, utilisant les vapeurs d'acide trifluoracétique et une solution d'hydroxyde de tétraéthylammonium. On donne aussi les spectres de fluorescence de ces composés sur le chromatogramme en couche mince et en solution.

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THEORETICAL CONSIDERATIONS IN THE ZONE MELTING OF ORGANIC SUBSTANCES*†

ESTABLISHMENT OF IDEAL EQUILIBRIUM CONDITIONS

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Summary—In order to establish in theory the necessary conditions for reaching ideal thermodynamic equilibrium in the zone melting of organic substances, transport of impurity in the melt zone is analysed by:

1. The chemical potential for the case of pure diffusion,
2. Studying complete mixing in the melt by stirring,
3. Deriving the impurity concentration as a function of zone velocity.

These analyses show that for maximum ultrapurity, the factors of zone length and zone velocity are critically defined for equilibrium conditions.

INTRODUCTION

IN the previous article of this series,[1] the significance of ultrapure pharmaceuticals as related to zone refining was described. The underlying principles of zone melting organic compounds under *ideal equilibrium conditions* were also set forth.

To establish *ideal equilibrium conditions* the following factors are involved:

1. Thermodynamic equilibrium,§
2. Length of molten zone,
3. Transport of impurity,
4. Velocity of zone movement.

In order to establish the length of the molten zone a classical thermodynamic analysis of the chemical potential, μ, for the zone-melting process for the case of pure diffusion is discussed. For the special case where complete mixing in the molten zone occurs, such that *mass transport* takes place as distinguished from *molecular diffusion*, a further analysis yields additional information on the length of the molten zone. By collating data from various investigators, equations are suggested which relate the velocity of zone movement and the efficiency of segregation of impurities. From these equations, a zone velocity for *ideal equilibrium conditions* is postulated.

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† This work is abstracted from a dissertation submitted to the Graduate school, University of Connecticut, in partial fulfillment of the requirements for the Ph.D. degree by R. Friedenberg.[4]

‡ Recipient of the Lundsford-Richardson Award—1963.

§ See reference 1.

CHEMICAL POTENTIAL IN THE ZONE-MELTING PROCESS FOR THE CASE OF PURE DIFFUSION

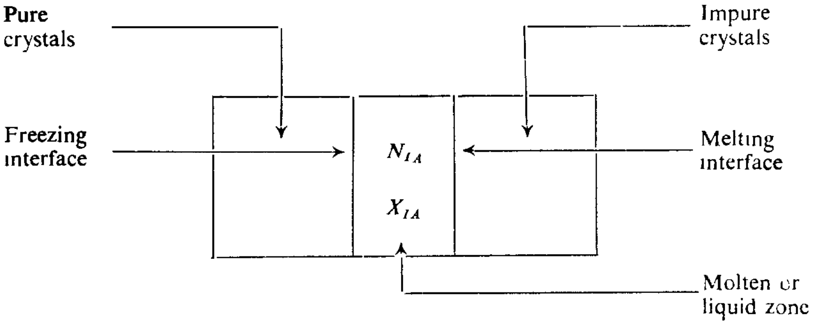
From a thermodynamic point of view, assuming only pure diffusion, a moving zone is analysed for a eutectic type mixture under ideal equilibrium conditions. The partial free energy change, $\mu_i = (\partial F_i/\partial N_i)_{P,T}$ with respect to concentration (N_i = number of moles, F_i = free energy, μ_i = chemical potential. P = pressure, T = temperature) is analysed in two parts:*

$$\Sigma\mu_i dN_i = \mu_I dN_I + \mu_{II} dN_{II} \tag{1}$$

where subscript I indicates the impurity or solute, and subscript II indicates the major component or solvent such that

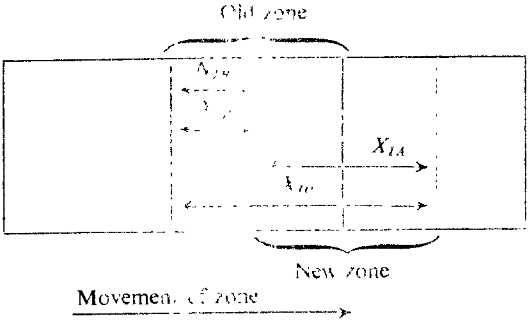
$$\Delta\mu_i = \Delta\mu_I + \Delta\mu_{II} \tag{2}$$

A stationary molten zone that passes through a given distance of a charge may be represented as follows:



where N_{IA} = number of moles of impurity in solvent,
and X_{IA} = mole fraction of impurity in molten zone.

If the zone moves in a horizontal direction, freezing occurs at the interface on the left, freezing out pure component and building up solute concentration in the molten zone at the interface. At the interface on the right, melting occurs and solute and solvent are added to the molten zone.



N_{IB} = number of moles of impurity left in molten zone at interface as pure solvent freezes out.

X_{IB} = mole fraction of impurity at interface as pure solvent freezes out.

X_{IC} = total mole fraction of impurity in molten zone after zone has moved.

$X_{IC} = X_{IB} + X_{IA}$

$N_{IC} = N_{IA} + N_{IB}$

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* The nomenclature used in this paper is taken after I. Klotz, *Chemical Thermodynamics*, Prentice-Hall, New York, 1950. The subscript i is used to indicate an *indicial* definition or equation.

The chemical potential of the solute is given by

$$\mu_I = G(T) + N_{tot}\, RT \ln f_I \tag{3}$$

where μ_I = chemical potential of solute,
$G(T)$ = an arbitrary function of temperature,
N_{tot} = total number of moles of solute,
R = gas constant,
T = temperature,
and f_I = fugacity of solute.

The change in chemical potential is given by

$$d\mu_I = N_{tot}\, RT\, d\ln f_I \tag{4}$$

Integrating between limits and substituting

$$f_I = KX_I \tag{5}$$

where K = Henry's Law constant, yields:

$$\Delta\mu_I = N_{tot}\, RT \ln \frac{f_{I(\text{final})}}{f_{I(\text{initial})}} \tag{6}$$

$$\Delta\mu_I = N_{tot}\, RT \ln \frac{X_{I(\text{final})}}{X_{I(\text{initial})}} \tag{7}$$

Therefore, from the diagram:

$$\Delta\mu_I = \Delta\mu_{IA} + \Delta\mu_{IB} \tag{8}$$

$$\Delta\mu_{IA} = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} \tag{9}$$

$$\Delta\mu_{IB} = N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} \tag{10}$$

$$\Delta\mu_I = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} + N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} \tag{11}$$

In the same manner:

$$\Delta\mu_{II} = N_{tot}\, RT \ln \frac{X_{II(\text{final})}}{X_{II(\text{initial})}} \tag{12}$$

where $\Delta\mu_{II}$ = change in chemical potential of solvent,
N_{tot} = total number of moles of solvent,
and X_{II} = mole fraction of solvent.

Then

$$\Delta\mu_{II} = \Delta\mu_{IIA} + \Delta\mu_{IIB} \tag{13}$$

$$\Delta\mu_{IIA} = N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} \tag{14}$$

$$\Delta\mu_{IIB} = N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{15}$$

$$\Delta\mu_{II} = N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} + N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{16}$$

Thus, the change of chemical potential for this system is given by

$$\Delta\mu_t = \Delta\mu_I + \Delta\mu_{II} \tag{17}$$

$$\Delta\mu_t = N_{IA}\, RT \ln \frac{X_{IC}}{X_{IA}} + N_{IB}\, RT \ln \frac{X_{IC}}{X_{IB}} + N_{IIA}\, RT \ln \frac{X_{IIC}}{X_{IIA}} + N_{IIB}\, RT \ln \frac{X_{IIC}}{X_{IIB}} \tag{18}$$

Although equations (11) and (16) for $\Delta\mu_I$ and $\Delta\mu_{II}$ are by chance similar in form, it is to be noted that differences in the analysis of the role of the solute and the solvent as well as differences of interpretation of the figures are implied in the derivation.

If the impurity is present in ppm, then from the diagram the following relations hold:—

for the solute: $N_{IA} > N_{IB}$
$X_{IB} > X_{IC}$
$X_{IB} > X_{IA}$
$X_{IC} > X_{IA}$
for the solvent: $N_{IIA} > N_{IIB}$
$N_{IIC} > X_{IIB}$
$X_{IIA} > X_{IIB}$
$X_{IIA} > X_{IIC}$
but $N_{IIA} \gg N_{IA}$.

Therefore

$\Delta\mu_{IA} = (+)$ large absolute magnitude,
$\Delta\mu_{IB} = (-)$ very small absolute magnitude,
$\Delta\mu_{IIA} = (-)$ *very* large absolute magnitude,
$\Delta\mu_{IIB} = (+)$ very small absolute magnitude approaching zero.

From this analysis, the following conclusions may be drawn. $\Delta\mu_t$ for the total process will be (—) as expected. The determining factor is $\Delta\mu_{IIA}$; more specifically, the magnitude of N_{IIA}. This means that, depending upon the relative concentration of impurity, the larger the molten zone (*i.e.*, the more solvent in the zone, N_{IIA}) the greater the probability that the sum total of the chemical potential for the whole process will be negative. By increasing the length of the zone, we are also increasing the amount of solute. However, the increase in solute is infinitesimally small compared with the increase in solvent, and the analysis shows that it is this negative quantity which controls the process. Restating the concept in another way, as more solute and solvent are added into the hopper at the melting interface, the concentration gradient in the zone builds up exponentially as the ratio of the solvent to solute increases in the zone.

On close examination of the zone melting process, it is noted that there is a temperature change at the freezing interface as the impurity or component I is rejected into the molten zone. However, if the impurity is present in ppm, the lowering of the freezing point will be so slight in its effect upon the chemical potential compared to concentration effects that, for the purpose of this analysis, it may be assumed to be constant.

COMPLETE MIXING IN THE MELT

During the zone-melting process of a eutectic mixture, if complete mixing in the melt by stirring is assumed, the mathematics describing this process is very simple. Assuming uniform distribution of impurity in the sample initially in ppm,

where C_0 = initial concentration of impurity,

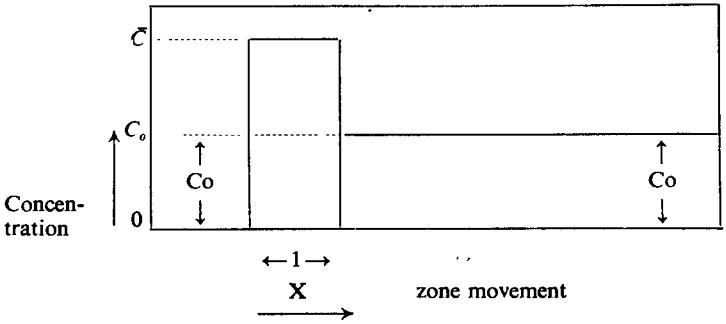
$\bar{C}$ = average concentration of impurity in melt,

and l = length of molten zone,

following the conservation law, an expression for $\bar{C}$ may be derived:

$$C_o\,(x + 1) = \bar{C}l \tag{19}$$

$$\bar{C} = C_o \frac{x + 1}{l} \tag{20}$$



From this analysis, the following conclusions may be drawn:

1. Assuming complete mixing by stirring under ideal equilibrium conditions, $\bar{C}$, the average concentration of impurity in the melt, is a time-independent function. If all the impurity remains in the melt ($K = 0$, where K = partition coefficient), although $\bar{C}$ is dependent upon l, the zone length is at maximum efficiency for all values of l.

2. Because stirring involves convection, which is a mass-transfer process as compared with diffusion which is a very slow molecular process, the length of the zone during the refining procedure may be as large as mechanical features permit. The rapidity of mass transfer makes this highly desirable under ideal equilibrium conditions.

ZONE VELOCITY

Studies by Schwab and Wichers[2] and by Wilcox[3] indicate that zone melting or zone freezing of naphthalene and benzoic acid (with the same length of charge) at different zone velocities, yield the approximate experimental data shown in Table I.

TABLE I

Zone velocity, *cm/hr*	Impurity removed with one pass, %
6·0	45 (40–50)
0·6	90 (88–92)
0·06	95 (92–96)
0·006	99
0·0006	100 (?)

Because these data are only approximate, it is the purpose here to establish a *general* relationship between zone velocity and impurity removal as a first approximation. Fig. 1 illustrates the form of the curve taken by plotting the rate of zone movement against the amount of impurity removed. If one considers a high zone velocity (greater than 6 cm/hr), then the right-hand side of the curve must be considered.

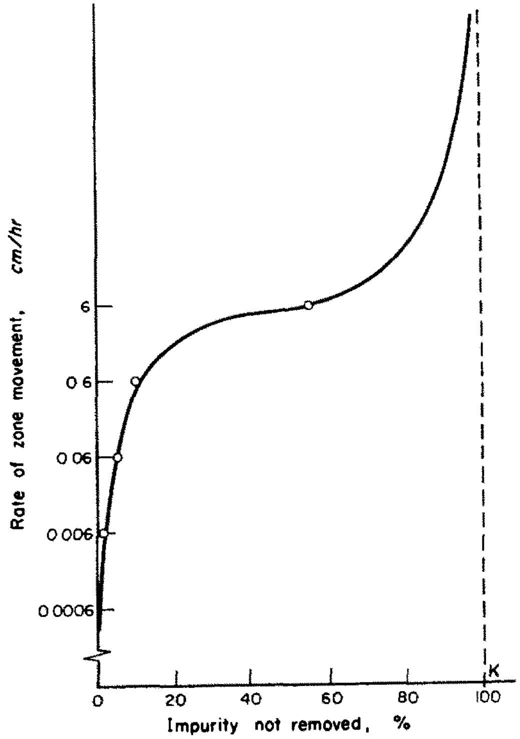


FIG. 1.—Theoretical curve for rate of zone movement (based on data of Schwab and Wicher[2] and of Wilcox[3] for benzoic acid and naphthalene; K = initial amount of impurity).

Although rigorous experimental data for this part of the curve are lacking, studies involving the diffusion gradient show this to be true.* At slower zone rates the curve is exponential and the following equation is suggested to describe this part of the curve:

$$F = I - Ke^{-z}$$

where F = final impurity concentration,

I = initial impurity concentration,

K = empirical constant for the substance dependent upon crystallinity (approach to ideal conditions) and percentage impurity concentration,

and z = zone rate.

An expression describing the entire curve may also be suggested:

$$Z = A + B\tan\left(\frac{F+I}{F}\right)$$

where Z, F and I are as previously defined,

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* See *Theoretical Considerations of Zone Melting of Organic Substances—The Diffusion Gradient* R. Friedenberg, *J. Eng. Sci.*, 1965, January.

A and B = empirical constants for the substance depending on region of impurity concentration,

and
$$\left(\frac{F+I}{F}\right)=\left(\frac{\pi}{2}\right).$$

Substituting in these equations leads to the result of a zone velocity of $6{\cdot}0 \times 10^{-3}$ to 6×10^{-6} cm/hr. One approach to this solution is to substitute known values into the above equation as follows:

$$60 = A + B \tan (3/8\pi)$$
$$6 = A + B \tan (0{\cdot}3\pi)$$
$$0{\cdot}6 = A + B \tan (0{\cdot}1\pi)$$

TABLE II

Zone rate (Z)	Initial impurity (I), %	Impurity removed by zone melting, %	Final impurity left (F), %	$\frac{F+I^*}{F}$
60	100	40	60	8/3
6	100	50	50	3
0·6	100	90	10	11
	100	99	1	101
	100	99+	<1	→ ∞
	100	<1	99+	→ 2

* To convert $\frac{F+I}{F}$ values to radian measure: $\pi \div \frac{F+I}{F} = \theta$ in radians.

It is then necessary to solve for the constants and obtain the zone rate when a final zero concentration of impurity is substituted.

It must be emphasised that these equations represent only a rough first approximation for these data.

CONCLUSIONS

It has long been known that in a eutectic type mixture, if *thermodynamic equilibrium* is reached at the interface of a cooling solid in contact with its melt, the impurities will remain in the melt and the major component will freeze out ultra-pure. Thermodynamic equilibrium means a temperature and velocity differential between the solid and liquid freezing interface.[4] For purposes of this investigation *ideal thermodynamic equilibrium*, referring to the temperature differential, means a temperature gradient ranging from 0·100° to 0·010°C/mm for the solidifying interface. If the boundary of the temperature is not sharp, impurities will be occluded by the advance of this freezing front.[5] The growth rate must be slow enough and the movement of the zone similarly slow such that the impurities have sufficient time to be transported into the bulk of the molten zone by diffusion, convection or with complete mixing by stirring. An analysis of the chemical potential for pure diffusion indicates that the zone should be as large as practicality permits. An analysis of complete mixing in the melt zone indicates a time independent function, such that with complete mixing, the process is independent of its zone length. The zone movement favouring ideal equilibrium conditions was found to have an order of magnitude of 5×10^{-1} to 1×10^{-3} cm/hr. Thus, *ideal equilibrium conditions* are defined here to mean thermodynamic equilibrium at the narrow freezing interface (a temperature gradient of 0·10°C/mm) with a slow moving zone approaching an infinitesimal rate. For each substance, the exact rate before occlusion occurs must be determined experimentally.

In the past, most zone melting of organic compounds has been performed in such a manner that the solid and liquid never reach thermodynamic equilibrium. Under these conditions, of course, an effective distribution coefficient is relevent, but is completely dependent upon the conditions of the system and not upon the nature of the substance (*i.e.*, whether the substance forms a eutectic or solid solution with the impurities).

Zusammenfassung—Die notwendigen Bedingungen für das ideale thermodynamische Gleichgewicht beim Zonenschmelzen organischer Substanzen sollen theoretisch erfaßt werden. Zu diesem Zweck wird der Transport der Verunreinigung in der Schmelzzone analysiert durch (1) das chemische Potential für den reinen Diffusionsfall; (2) völlige Durchmischung der Schmelze durch Rühren; (3) Ableitung der Konzentration an Verunreinigung in Abhängigkeit von der Wanderungsgeschwindigkeit der Zone. Diese Analysen zeigen, daß für höchste Reinheit die Zonenlänge auf die Gleichgewichtsbedingungen kritisch eingestellt werden muß.

Résumé—Afin d'établir théoriquement les conditions nécessaires pour atteindre l'équilibre thermodynamique idéal dans la fusion de zone des substances organiques, on a analysé le transport de l'impureté dans la zone fondue par:

1. Le potientel chimique dans le cas de la diffusion pure.
2. L'étude du mélange complet dans la zone fondue par agitation.
3. L'étude de la concentration en impureté en tant que fonction de la vitesse de la zone.

Ces analyses montrent que, pour atteindre l'ultra-pureté maximale, les facteurs relatifs à la longueur de zone sont fondamentaux pour les conditions d'équilibre.

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PHOTOMETRIC TITRATION OF COBALT WITH HEXACYANOFERRATE(III)

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Summary—An improvement of the oxidimetric determination of cobalt(II) with hexacyanoferrate(III) in ammoniacal solution, by means of a photometric end-point detection, is proposed. Amounts of cobalt down to 20 μg can be determined with fairly good accuracy and precision. Most common elements do not interfere. The interference of manganese(II) can be overcome using glycine or other amino acids as complexing agents instead of ammonia.

INTRODUCTION

THE oxidimetric determination of cobalt(II) in ammoniacal solution with hexacyanoferrate(III), according to the reaction

$$Fe(CN)_6^{3-} + Co^{2+} \rightarrow Co^{3+} + Fe(CN)_6^{4-}$$

was developed by Dickens and Maassen[1] and Tomiček and Freiberger.[2] The reaction proceeds to the right, on the addition of ammonia, because the complexes of cobalt(III) with ammonia are much stronger than the corresponding complexes of cobalt(II). The reaction has proved to be very suitable for the potentiometric determination of cobalt in amounts from 2 to 100 mg, because of its very good accuracy and reproducibility and because of a fairly good selectivity. Two different procedures have been proposed, *viz* a direct titration and a back titration of added excess hexacyanoferrate(III) with a standard cobalt(II) solution. A disadvantage of the direct titration is the oxidation of cobalt(II) in ammoniacal solution by oxygen. Oxygen has, therefore, to be excluded.[3] Most authors[4-8] apply the back titration. Air oxidation does not interfere in the back titration, because the oxidation of cobalt(II) with oxygen is very slow compared with that by hexacyanoferrate(III).

Very recently Lingane[3] thoroughly reinvestigated the qualities of the determination in the absence of other metals. He used a direct titration with the exclusion of oxygen and he found that the error of a single determination of a not too small amount of cobalt (more than 20 mg) is certainly less than 0,1%. This suggests that the method has an extremely good accuracy and reproducibility.

The equilibrium constant of the reaction under the most favourable conditions (pH about 10 and concentration of ammonia not less than 1*M*) is 10^6. Consequently, the increase of the potential of the indicator electrode in the vicinity of the equivalence point is not large, but that does not prevent an accurate determination of the equivalence point.[3]

A large concentration of free ammonia is necessary for a sufficiently large equilibrium constant of the titration reaction. Because of the protonation of ammonia the concentration of free ammonia is dependent upon the pH and the total (analytical) concentration of ammonia. The stability constants of the complexes of cobalt(II) and cobalt(III) with ammonia can be used to show that an analytical concentration of ammonia of 1*M* at pH 10 results in a maximum value of the equilibrium constant. Further increase of pH or analytical concentration of ammonia does not result in a larger value of the equilibrium constant.

The use by Diehl and Butler[9] of ethylenediamine as complexing agent, instead of ammonia, increases the equilibrium constant of the reaction at a given pH and consequently the potential change in the vicinity of the equivalence point, but it leads to a much faster oxidation of cobalt(II) by oxygen than in the case of ammonia. The same holds for the use of triethylenetetramine and tetra-ethylenepentamine as complexing agent.

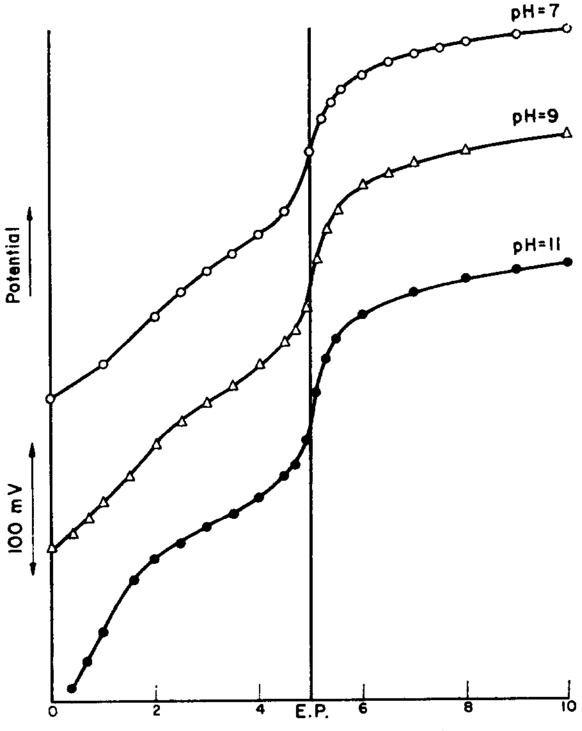

Fig. 1.—Potentiometric titration curve of 3·8 × $10^{-3}M$ cobalt(II) with hexacyanoferrate(III) in a 2·0*M* glycine medium at different pH; the three curves are separated by a shift of about 100 mV in the potential for each new curve.

Recently, the use of amino acids instead of ammonia has been proposed by Kopanica and Doležal,[10] who used glycine in the pH region 9·5–12·0; Agasyan and Khakimova,[11] who used a mixture of alanine or phenylalanine and ammonia; and Chang Yeh Siya, Doležal and Zýka,[12] who used glutamic acid in the pH region 9·8–11·4. In all these cases oxidation by oxygen from the air appeared to be negligible even in the direct titration. The relative stabilities of the complexes of cobalt(II) and cobalt(III) with amino acids give rise to a formal potential of the Co(III)/Co(II) couple larger than in the case of ammonia but still small enough to make possible a titration of cobalt(II) with hexacyanoferrate(III). Consequently, the potential change in the vicinity of the equivalence point and the equilibrium constant of the titration reaction are smaller when amino acids are used instead of ammonia. This is illustrated in Fig. 1. Titration curves of cobalt(II) with hexacyanoferrate(III) in a glycine medium are given for pH values from 7 to 11.

The titration conditions were as follows:
Platinum indicator electrode, area 2 cm^2, calomel electrode as reference electrode, pH meter (Radiometer Copenhagen type 22); glycine concentration 2·0M; cobalt concentration $3{\cdot}8 \times 10^{-3}M$; volume 135 ml; hexacyanoferrate(III) concentration 0·01M; no other metals present; the pH of the solution was adjusted with sodium hydroxide; direct titration.

From Fig. 1 it can be calculated that the equilibrium constant of the titration reaction is about 10^3.

It is obvious that the potential change in the vicinity of the equivalence point is too small to obtain a good reproducibility for the determination of cobalt by this method. No interference by oxygen was observed. An advantage of the titration in the presence of amino acids instead of ammonia is the fact that within the pH range 7–11 no change of the equilibrium constant occurs, and this is very important for the elimination of the interference of manganese(II) (*vide infra*).

DISCUSSION

Whereas Lingane[3] proved the accuracy of this titration in the absence of other metals, our purpose has been the increase of the sensitivity and of the selectivity of the method.

Sensitivity

Potentiometric titration. An increase in sensitivity can be brought about by decreasing the titration volume or the concentration.

Potentiometric titrations are not easily made in a volume of only a few ml. Moreover, a small titration volume is not easy to realise when, as in this case, a back titration is generally carried out and a number of reagents have to be added. In the case of very low concentrations on the other hand, difficulties from the kinetics of the titration reaction or the electrode reaction often occur near the equivalence point.

We compromised, when studying the sensitivity of the potentiometric determination, with a volume of about 60 ml. The electric conditions were the same as in the experiments of Fig. 1. The concentration of ammonia was 4·7M and that of ammonium citrate 1·2M. The lowest cobalt concentration studied by Lingane was $3 \times 10^{-4}M$. Therefore, we investigated titrations in a concentration range down to $10^{-5}M$. The concentration of the hexacyanoferrate(III) solution was six times that of cobalt in every titration, so that 10 ml of hexacyanoferrate(III) solution were needed. Titrations were carried out directly in an oxygen-free atmosphere.

A few results are given in Fig. 2. In one of the titrations a 50-fold amount of iron was added; in the others no foreign elements were present. It can be seen that below a concentration of $10^{-4}M$ an accurate determination of the equivalence point is impossible. Moreover, the reproducibility becomes very bad. The titration in the presence of iron points to the fact that the concentration limit of $10^{-4}M$ is much higher when other elements are present. The presence of ions like iron(III) obviously has an unfavourable influence on the electrode kinetics.

When we assume 25 ml to be the lower limit for the titration volume, we may conclude that 1 to 2 mg of cobalt can be determined potentiometrically with reasonable accuracy (within 1 %) in the presence of other non-interfering elements. This is in agreement with the previously published results.

Photometric titration. It had to be determined whether the bad results of the potentiometric determinations at low cobalt concentrations were caused by a bad electrode response or by anomalies in the titration reaction.

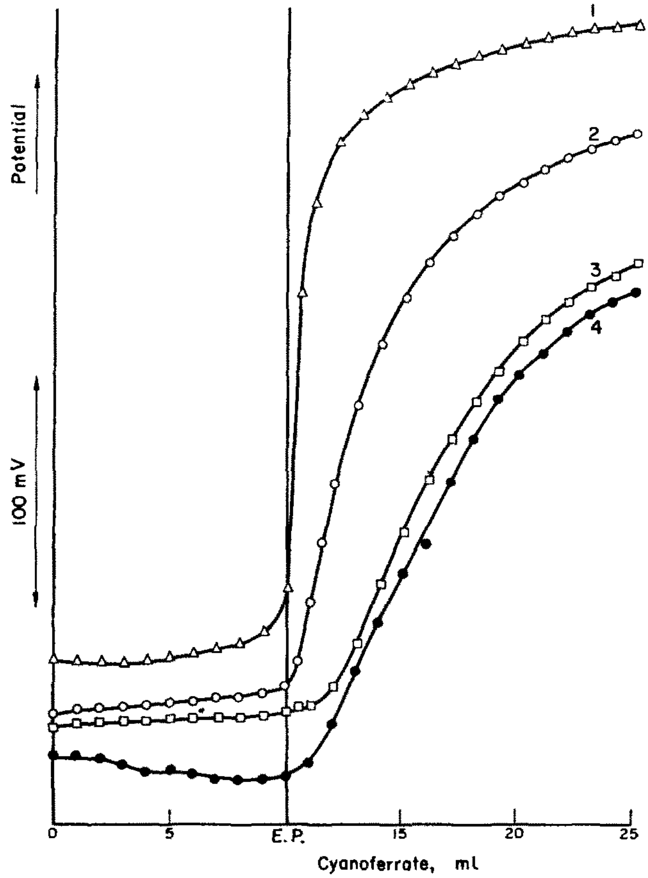

FIG. 2.—Potentiometric titration curve of different concentrations of cobalt(II) with hexacyanoferrate(III) in an ammoniacal medium; the curves are separated by a shift in the potential for each new curve; [Fe(III)] = $2{\cdot}1 \times 10^{-3}M$:—
Curve 1: [Co(II)] = $4{\cdot}2 \times 10^{-4}$; Curve 2: [Co(II)] = $4{\cdot}2 \times 10^{-5}M$;
Curve 3: [Co(II)] = $1{\cdot}7 \times 10^{-5}M$; Curve 4: [Co(II)] = $4{\cdot}2 \times 10^{-5}M$.

Therefore, we investigated another method for the determination of the equivalence point of the reaction. The red-coloured reaction product of the titration reaction makes the reaction suitable for photometric end-point indication.[13] Fig. 3 shows that the absorbance in the 500-mμ region at the equivalence point of the reaction is much larger than can be expected from the absorbances of the two compounds that are supposed to be formed in the reaction. The intense red colour only occurs when cobalt(II) is oxidised by hexacyanoferrate(III), but not when other oxidising agents are used; hydrogen peroxide, lead dioxide, sodium bismuthate or sodium hypochlorite, all result in pale red complexes. The composition of the red-coloured compound formed in this reaction is not clear. It could be a binuclear complex like Co(III) $(NH_3)_5$—N—C—$Fe(CN)_5$, similar to that proposed by Adamson and Gonick[14] for the product formed by cobalt(II), hexacyanoferrate(III) and EDTA.

The molar absorptivity of the product in the 500-mμ region is about 500.

The reproducibility of the formation of the colour is not good enough to base a spectrophotometric determination on this reaction, but the colour is well suited for the photometric end-point detection of a titration based on the reaction.

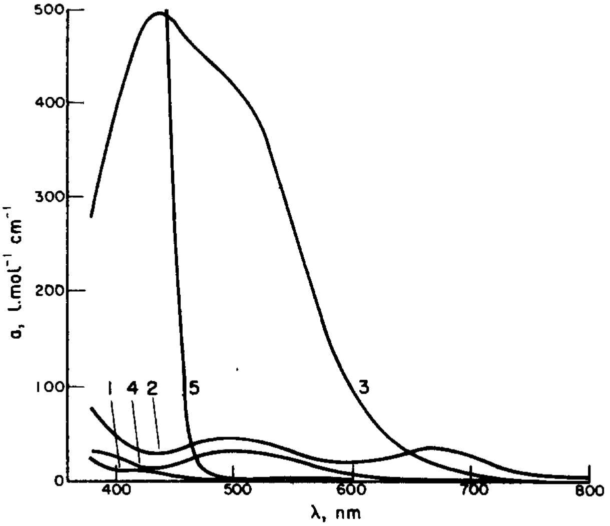

FIG. 3.—Molar absorptivity curves of some products involved in the titration in an ammonical medium:—

Curve 1: hexacyanoferrate(II); Curve 2: cobalt(III), prepared by oxidation with peroxodisulphate; Curve 3: reaction product at the equivalence point; Curve 4: cobalt(II); Curve 5: hexacyanoferrate(III).

Photometric titrations were carried out with an EEL titrator, a Zeiss spectrophotometer PMQ II and a Zeiss ELKO II spectrophotometer.

A typical titration curve is given in Fig. 4. The equivalence point and the end-point of the titration coincide for concentrations down to $5 \times 10^{-5}M$. This proves that the bad results of the potentiometric end-point detection are from a bad electrode response.

When errors of about 1% are tolerated, the lower limit of the concentration of cobalt that can be determined appeared to be 5×10^{-4} for the EEL titrator, corresponding to about 0·6 mg of cobalt, and about $5 \times 10^{-5}M$ for the Zeiss instruments, corresponding to 30 μg of cobalt.

There are other advantages of photometric end-point detection.

The influence of other elements on the end-point detection is, in general, small. It is not necessary to make absorbance measurements in the vicinity of the equivalence point. An equilibrium constant of a titration reaction too small for a potentiometric determination of the equivalence point may still be large enough for accurate photometric end-point detection, because the physical property measured in a photometric titration is directly proportional to the concentration of the indicator compound, whilst there is a logarithmic dependence in the potentiometric titration.

This explains the suitability of the photometric end-point detection of the titrations of cobalt(II) with hexacyanoferrate(III) when amino acids are used instead of ammonia. The molar absorptivity curves of the cobalt(II)- and cobalt(III)-glycine complexes, as well as the corresponding curve for hexacyanoferrate(III), are given in Fig. 5. From these curves it can be concluded that 520 mμ is a suitable wavelength for the photometric titration of cobalt(II) with hexacyanoferrate(III) in a glycine medium.

Selectivity

The selectivity of the potentiometric titration has been investigated extensively.[1,2,4–8,16] The conclusions differ according to the method used (back titration or direct titration), but apart from that there is a good agreement in the results of the various authors.

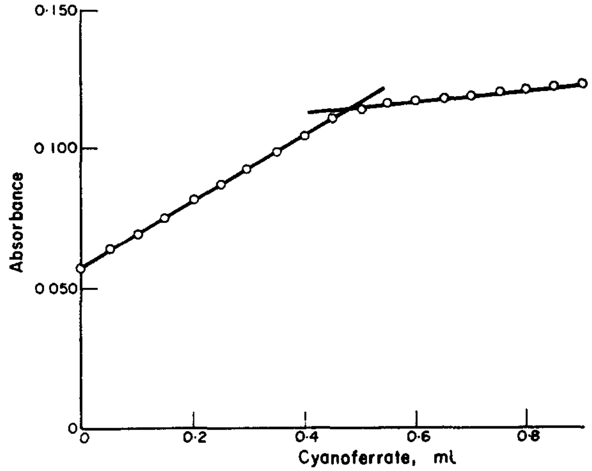

FIG. 4.—Photometric titration curve of $5 \times 10^{-5} M$ cobalt(II) with hexacyanoferrate(III) (Zeiss PMQ spectrophotometer).

All authors recommend the addition of large amounts of ammonium citrate in order to keep a great number of metal ions in solution.

With the conditions pH about 10, a citrate medium and ammonia as complexing agent, the most common elements do not interfere except for manganese(II) and chromium(III).

In the direct titration chromium(III) interferes only when it is present in an amount more than 100 times that of cobalt,[2] because the oxidation of chromium(III) to chromate by hexacyanoferrate(III) is slow. In the case of the back titration small amounts of chromium(III) interfere, because the chromium(III) is in contact with an excess of hexacyanoferrate(III) for some time and oxidation to chromate is appreciable. Prior oxidation of chromium(III) to chromate eliminates this interference, but the reproducibility of the determination is then worse.

Manganese(II) interferes, because it is oxidised by hexacyanoferrate(III). In the presence of citrate the oxidation product is a manganese(III)-citrate complex and no precipitate appears. The reaction takes place in the pH region 7-11, in which the oxidation of cobalt(II) with hexacyanoferrate(III) was investigated. In the absence of citrate manganese(II) is oxidised to manganese dioxide, according to the reaction

$$2\,Fe(CN)_6^{3-} + Mn^{2+} + 4\,OH^- \rightarrow 2\,Fe(CN)_6^{4-} + MnO_2 + 2\,H_2O.$$

This reaction is strongly affected by pH. In the pH range 7–8 or lower, manganese(II) is stable towards hexacyanoferrate(III).

As both oxidation reactions of manganese(II) at pH 10 occur at the same potential as the oxidation of cobalt(II), no simultaneous determination of cobalt(II) and manganese(II) is possible.

The interference of manganese(II) can be overcome in two ways.

First, the use of ethylenediamine[9] instead of ammonia results in a much larger potential change at the equivalence point, because of an extra stabilisation of the tervalent state of cobalt. Moreover, when 5-sulphosalicylic acid is added to complex manganese(III),[9] two potential jumps occur in the titration curve, the first when the oxidation of cobalt(II) is complete, the second after the oxidation of manganese(II). Although in this way cobalt(II) and manganese(II) can be determined simultaneously by a direct titration, the method has the great disadvantage of its sensitivity to oxygen from the air.

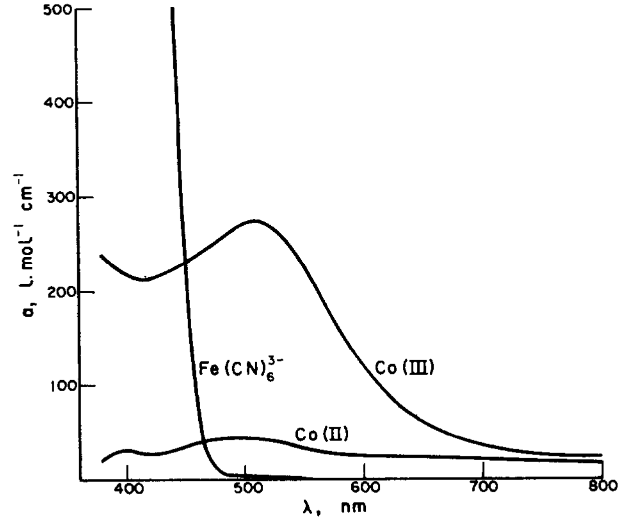

FIG. 5.—Molar absorptivity curves of some products involved in the titration in glycine medium. The curve marked with Co(III) is the curve of the reaction product.

Second, use can be made of the fact that, in the absence of citrate, oxidation of manganese(II) no longer takes place when the pH is 8 or less. In this case ammonia can no longer be used as a complexing agent for cobalt because the actual concentration of ammonia is too small in this medium. As mentioned above, amino acids may be used instead of ammonia at pH 7 to 8. It indeed appeared to be possible to determine cobalt(II) with hexacyanoferrate(III) in the presence of manganese(II) at pH 8 in a medium containing certain amino acids. When other metals like iron(III) are present, auxiliary complexing agents have to be added to avoid the precipitation of hydroxides. Citrate is unsuitable because manganese(II) interferes, but fluoride is suitable. Large amounts of manganese(II), however, cause precipitation of manganous fluoride.

EXPERIMENTAL

Ammonia as Complexing Agent

Reagents

Ammonia. 14*M solution*

Ammonium citrate solution. Dissolve 500 g of citric acid ($C_6H_8O_7.H_2O$) in water, add 180 ml of ammonia solution (14*M*) and dilute to 1 l.

Hexacyanoferrate(III) solution. Recrystallise potassium hexacyanoferrate(III) from water, dry the product for 1 day at 80°, dissolve the desired amount in water and dilute to a known volume. Keep the solution in a brown glass flask.

All chemicals used were of a "pro analysi" quality.

Apparatus

EEL titrator. A sample filter photometer, deflection type with no amplification.

Zeiss spectrophotometer PMQ II. A prism spectrophotometer, deflection type with photomultiplier.

Zeiss spectrophotometer ELKO II. A filter photometer, substitution principle, no amplification; especially suited for the accurate measurement of small absorbances.[15]

Burette. 1-ml Metrohm piston type.

Procedures

For EEL titrator. Place a sample solution, containing 0·4–0·8 mg of cobalt in not more than 10 ml, in the titration vessel (20 ml) of the titrator. Add 5 ml of ammonia and 3 ml of ammonium citrate solution. Dilute, if necessary, to 20 ml. Use filter 601 or 602. Titrate with hexacyanoferrate(III) solution of appropriate concentration from a 1-ml Metrohm burette (type E 374). Add the titrant in equal volumes such that 10–20 additions result in a 100% excess of cyanoferrate(III) (Fig. 4). Wait 30 sec after each addition of titrant before reading the absorbance. The end-point results graphically from the point of intersection of two straight lines (Fig. 4). Points in the neighbourhood of the equivalence point are neglected.

For Zeiss PMQ II spectrophotometer. Use the titration assembly supplied by the manufacturer of the apparatus, which is provided with a titration cell of 2-cm optical path length and a content of 12 ml.

The procedure is the same as in the case of the EEL titrator, but for a few modifications. The sample contains 20–300 μg of cobalt in about 2 ml. The amounts of ammonium citrate and ammonia taken are 4·5 ml and 3·0 ml, respectively. The titration volume in this case is 10 ml. The wavelength at which the absorbance is measured is 510 mμ.

For Zeiss ELKO II photometer. The same titration cell is used as in the case of the Zeiss PMQ spectrophotometer. The procedure is also the same, except for the amounts of ammonium citrate solution and ammonia, which are 2·3 ml and 1·5 ml in this case. The S 51 E filter is used.

Notes to procedures

a. Corrections for volume are only necessary when the absorbance at the beginning of the titration is large. This may be caused by the presence of compounds absorbing in the 500-mμ region [*e.g.*, chromium(III)].

b. Oxygen from the air was neither removed, nor excluded during the titrations. With the concentrations of cobalt used in these titrations air oxidation appears, in general, to be negligible. If the titration solution stands for 1 hr, under the conditions mentioned in the procedure for the EEL titrator an oxidation of about 1% of the cobalt(II) present occurs. Iron catalyses the air oxidation (*vide infra*).

c. The strength of the hexacyanoferrate(III) solution was taken such that 0·2–0·5 ml of the reagent was needed for the equivalence point.

d. Stirring was done magnetically. It is not necessary to stop stirring when absorbances are read.

e. The reproducibility of the determination in the various apparatus was tested for various quantities of cobalt. The standard deviation, in the absence of other metals, calculated from 10 titrations, was: 0·7% for the determination of 0·600 mg of cobalt on the EEL titrator; 1·0% for the determination of 30 μg of cobalt on the Zeiss PMO II spectrophotometer; 0·5% for 300 μg of cobalt, 1·0% for 40 μg of cobalt and 1·6% for 20 μg of cobalt on the Zeiss ELKO II filter photometer.

f. No systematic error was observed for the determination of amounts of cobalt larger than 100 μg. In the 20-μg region a negative systematic error of about 1% occurs. A correction for this error can be applied to the results mentioned in Table I.

g. The determination with the EEL titrator of amounts of cobalt smaller than 0·4 mg is not possible without an appreciable loss of accuracy.

h. The special aspects of photometric titrations on a photometer of the substitution principle (*e.g.*, the Zeiss ELKO II apparatus), such as accuracy, reproducibility and a discussion on the optimum conditions, will be dealt with in a separate paper.[17]

Some results of determinations of cobalt with these three procedures are given in Table I. Only experiments with large amounts of other elements present are included. With amounts of other elements smaller than those mentioned in Table I, the reproducibility and accuracy of the determination generally agrees with the data mentioned above under Note e.

Glycine as Complexing Agent

Reagents

2·8*M Glycine solution.* Dissolve 21 g of glycine in water and adjust to pH 8·0 with potassium hydroxide solution; dilute to 100 ml.

3·4*M Potassium fluoride solution.*

Ammonium citrate solution. Dissolve 50 g of citric acid in water, add aqueous ammonia to bring the pH to 8·0 and dilute to 100 ml.

Hexacyanoferrate(III) solution. As given in the procedure in an ammoniacal medium.

Procedure

Titrations were, in general, carried out with the Zeiss ELKO II photometer.

Place a sample solution, containing 20–300 μg of cobalt in about 5 ml, in the titration vessel. Add, if necessary, 1–10 drops of ammonium citrate solution or fluoride solution. Add glycine solution to a volume of 10 ml. Titrate with hexacyanoferrate(III).

Notes to procedure

a. The glycine concentration should be about 2·0*M* in order to get an equilibrium constant of the titration reaction large enough for accurate photometric indication. When the volume of the sample solution is too large, glycine can be added in the solid state.

b. The buffer capacity of a glycine solution at pH 8 is not large. Therefore, it is necessary to adjust the pH of the citrate solution to the same value. Sample solutions containing many foreign compounds, especially acids or bases, may affect the pH. In that case the pH has to be measured before starting the titration and, if necessary, adjusted.

c. When tervalent or quadrivalent metals are present, an auxiliary complexing agent, fluoride or citrate, has to be added. In general, citrate is better, because fluoride causes precipitation of some metals, but when manganese(II) is present the use of fluoride is obligatory. The amount of fluoride taken should be as small as possible.

d. The standard deviation in the absence of other metals, calculated from 10 determinations, was 1·3% in the region 40–300 μg of cobalt and 2% for 20 μg of cobalt.

RESULTS

Ammoniacal medium

Iron(III) catalyses the air oxidation of cobalt(II). Therefore, large amounts of iron may result in low results. This can be seen in experiments 8, 16 and 28. As mentioned earlier, air oxidation is favoured by increasing the pH or the analytical concentration of ammonia. The experiments with the EEL titrator were carried out at pH 10·2. In order to obtain better results in the presence of iron(III), the pH was decreased in the case of the Zeiss PMQ II spectrophotometer to a value of 10·0. In the procedure for the ELKO photometer the analytical concentration of ammonia was half the value of that in the procedure for the Zeiss PMQ II. The titration conditions resulted in a pH of 9·7 in this case. Indeed, the third procedure turned out to be the best, when large amounts of iron are present. Experiment 27 shows that a 400-fold amount of iron(III) can be tolerated, provided that the titration is started immediately after the preparation of the titration solution.

The presence of large amounts of chromium(III) may lead to two difficulties. Firstly, chromium(III) absorbs strongly in the titration medium in the 500-mμ region. This causes a bad reproducibility for the determination of cobalt on the apparatus without a possibility of amplification of the photocurrent. Therefore, in the presence

Table I.—Determination of cobalt with hexacyanoferrate(III) in the presence of other metals

Number of experiment	Amount of other metals, *mg*				Amount of Co, *μg*		Relative error, %	Remarks
	Cr(III)	Cu(II)	Fe(III)	Ni(II)	Present	Found		
Results with the EEL titrator								
1	20				600	600	0	
2	30				600	591	−1·5	
3		0·6			600	605	+0·9	
4		6·0			600	627	+4·5	
5		120			600	625	+4·2	
6			10		600	597	−0·5	
7			100		600	591	−1·5	
8			240		600	561	−6·5	
9				60	600	590	−1·7	
10				240	600	612	+2·0	
11	15	15	15	15	600	615	+2·5	
Results with the Zeiss PMQII spectrophotometer								
12	3·0				30·0	29·0	−3·3	
13		1·5			30·0	29·3	−2·3	
14		6·0			30·0	30·8	+2·7	
15			3·0		30·0	29·6	−1·3	
16			7·5		30·0	27·2	−9·4	
17				1·2	30·0	29·8	−0·7	
18				15·0	30·0	29·6	−1·3	
19	1·0	1·0	1·0	1·0	30·0	27·8	−7·4	
20	2·0	2·0	2·0	2·0	75·0	73·2	−2·4	
Results with the Zeiss ELKO II spectrophotometer								
21					37·5	37·6	+0·3	
22					37·5	37·3	−0·6	
23	2·2				37·5	35·6	−5·1	
24	3·4				37·5	37·1	−1·1	Waiting for 60 min before titration
25		20			20·0	21·3	+6·5	Absorbance at the start is 1·2
26			4		37·5	37·3	−0·6	
27			15		37·5	37·5	0	
28			30		37·5	33·0	−12	
29				20	20·0	19·8	−1·0	
30	1·1		4		37·5	36·8	−1·9	Waiting for 60 min before titration
31	0·6		7·5		37·5	36·4	−2·9	30 min waiting
32	1·1	4	4	4	37·5	36·0	−4·0	30 min waiting
33	0·4	0·4	4	0·4	37·5	38·6	+2·9	30 min waiting; moreover, 0·4 mg Al(III); 0·4mg Hg(II); 0·4 mg Zn(II); 0·4 mg W(VI) and 0·4 mg V(V) also present

TABLE II.—DETERMINATION OF COBALT IN THE PRESENCE OF OTHER METALS IN GLYCINE MEDIUM

Number of Experiment	Amount of other metals, *mg*					Amount of Co, *μg*		Relative error, %	Complexing agent, *M*	Remarks
	Cr(III)	Cu(II)	Fe(III)	Ni(II)	Mn(II)	Present	Found			
1	4·5					75·0	74·3	−0·9	0·24 citrate	Zeiss PMQ II
2	9·0					75·0	70·5	−6·0	0·24 citrate	Zeiss PMQ II
3	22					75·0	69·7	−7·0	0·24 citrate	Zeiss PMQ II
4		20				20·0	20·4	+20	no	
5			40			40·0	41·5	+3·7	0·24 citrate	
6			20			20·0	19·7	−1·5	0·24 citrate	
7					3·0	37·5	37·9	+1·1	no	
8					3·0	37·5	38·2	+1·9	0·1 fluoride	
9						37·5	37·0	−1·4	0·24 citrate	10 mg Mo(VI) added
10				20		20·0	20·1	+0·4	no	
11				200		20·0	23·4	+17	no	$NiSO_4.7H_2O$ Analar
12				200		20·0	20·7	+3·5	no	Ni specpure
13						37·5	37·3	−0·5	0·24 citrate	0·4 mg V(V) added
14	1·1		3·4		1·1	37·5	37·5	0	0·15 fluoride	
15	0·4	0·4	3·4	0·4		37·5	37·7	+0·4	0·24 citrate	Also present 0·4 mg Al(III); 0·4 mg Hg(II); 0·4 mg W(VI); 0·4 mg Zn(II)

of large amounts of chromium(III), the Zeiss PMQ II spectrophotometer or another equivalent apparatus should be used. Secondly, the absorbance of a titration solution containing chromium(III) is not constant until about 1 hr after its preparation, because of the slow formation of the complexes of chromium(III). This may cause errors when large amounts of chromium(III) are present. Therefore, the titration solution should be allowed to stand for a certain time in this case before starting the titration. This effect is illustrated in experiments 12, 23 and 24. When iron(III) and chromium(III) are both present a middle course has to be steered between the requirements of immediate titration for iron(III) and waiting for chromium(III) (see experiments 19, 20, 30, 31 and 32).

Copper(II), when present in large amounts, strongly absorbs in the 500-mμ region (see experiment 25). In this case also, titration with a spectrophotometer including an amplifier has to be preferred.

Nickel(II) causes no difficulties, even when it is present in a 1000-fold amount (29).

Glycine medium

The combined presence of iron(III) and chromium(II) does not interfere in this procedure.

A 1000-fold amount of iron(III) or copper(II) does not interfere. For nickel(II) even a 10,000-fold amount may be present (experiments 11 and 12). The error in experiment 11 is probably from traces of cobalt in the nickel salt used.

When large amounts of chromium (III) are present it is necessary to allow the formation of chromium(III) complexes with glycine or citrate at pH 5. After the formation of the complexes, which requires about 15 min, adjust the pH to 8·0. If the waiting period is neglected, precipitation of chromium(III) hydroxide may occur.

Manganese(II) does not interfere when the use of citrate is avoided.

Vanadium(V), in general, does not interfere when it is present in an amount less than ten times that of cobalt. The combined presence of vanadium(V) and other elements interferes in some cases. This behaviour is not yet clear.

Other amino acids as complexing agents

Experiments were carried out with aspartic acid and glutamic acid Although good-results were obtained there appeared to be no advantages over glycine. The expected effect, *viz* the possibility of avoiding the addition of auxiliary complexing agents, was not realised.

CONCLUSION

From the experimental results it is obvious that the photometric end-point detection of the titration of cobalt(II) with hexacyanoferrate(III) in a medium of a complexing agent greatly improves the selectivity and sensitivity. The method appears to be practically specific in a glycine medium. Only certain combinations of ions interfere.

Zusammenfassung—Es wird vorgeschlagen die Endpunktsbestimmung der oxidimetrischen Bestimmung von Co(II) mit Hexacyanoferrat(III) in ammoniakalischer Lösung photometrisch durch zu führen. Mengen bis zu 20 μg können bestimmt werden in Anwesenheit von den meisten anderen Metallionen, ausgenommen Mn(II). Die Störung durch Mn-(II) kann durch Anwendung von Glycin statt Ammoniak beseitigt werden. Die Bestimmung ist dann beinahe spezifisch.

Résumé—On propose l'indication photométrique du dosage oxidimétrique du Co(II) avec le hexacyanoferrate(III) dans un milieu ammoniacal. Jusqu'a 20 μg du Co(II) peuvent être dosés en présence de presque tous les autres métaux, avec l'exception du Mn(II). Si l'on remplace l'ammoniac comme agent complexant par le glycine le Mn(II) ne gêne plus et le dosage devient presque spécifique.

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SHORT COMMUNICATIONS

Analytical applications of Solochrome Azurine B.S.: New method for the selective detection of copper

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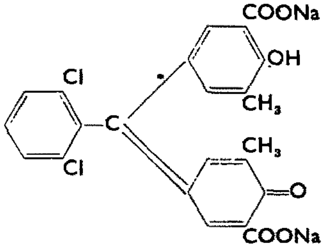
SOLOCHROME dyes have been known to the chemist since the beginning of this century, but only recently have they been used as analytical reagents.[1,2] Solochrome Azurine B.S., which has the following formula



has been shown to be a very sensitive spot reagent for thorium.[3] This dye was also found to give distinct colour reactions with other cations, such as copper(II), uranium(VI), vanadium(IV), iron(III), aluminium(III) and zirconium(IV). The present investigations, which were restricted to the study of the copper complex with the dye, under different conditions, have resulted in the development of a sensitive and selective test for the detection of copper in sub-micro quantities. The following reagents have been used to detect copper by spot tests (the sensitivity for each is given in parenthesis); α-furoinoxime (0·01 μg),[4] rubeanic acid (0·006 μg, but in presence of iron 0·48 μg),[5] dithizone (0·03 μg)[6] and Alizarin Blue (0·05 μg in solution and 0·004 μg as precipitate).[7] Each of these tests is subject to interference from some common cations. The advantage of the proposed detection method is that, whilst maintaining very good identification limits (0·02 μg; 0·01 μg on dye-fluoride paper), it is possible to detect copper(II) in the presence of a number of cations, *e.g.*, uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV), zirconium(IV), cadmium(II), nickel(II) and cobalt(II).

EXPERIMENTAL

Reagents

Standard copper sulphate solution

Solochrome Azurine B.S. *solution.* $10^{-3}M$ and $10^{-4}M$, prepared from a "Gurr" analytical grade reagent. A freshly prepared solution of the dye should be used.

Buffer. A buffer solution having a pH between 3 and 5.

Potassium fluoride solution 1*M*.

Interfering cation solutions. Standard solutions of uranyl acetate, vanadyl sulphate, ferric alum, aluminium chloride, thorium nitrate and zirconium nitrate were used. Analytical-grade reagents were used for the solutions.

RESULTS

Influence of pH *on the dye and its copper complex.*

A neutral aqueous solution of the dye is yellowish-brown, but the colour is dependent upon the pH.[3] The sharpest development of colour between copper and dye was found to be in the pH range 3 to 5.

Effect of dye concentration

The concentration of dye is very important. The studies conducted on a spot plate by using varying concentrations of the dye showed best colour development when 0·01 ml of $10^{-3}M$ dye was used in the presence of 0·2 μg of copper. At concentrations of copper lower than this, $10^{-4}M$ dye was found more suitable because higher concentrations of the dye gave such a prominent colour that it interfered seriously with the test.

Effect of copper concentration

For finding the lowest amount of copper detectable by the test, its quantity was varied from 0·006 μg to 0·6 μg. At concentrations lower than 0·06 μg the colour or precipitate developed with the dye is bluish-green rather than bluish-violet.

Interference by other cations

The dye also gives a blue-violet colour with nickel(II), cobalt(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV) and zirconium(IV) and therefore these cations interfere. All these cations form stable complexes with fluoride ion. Thus, in the presence of fluoride, the dye gives a blue colour only with copper. Cadmium(II) and manganese(II) do not give a colour with low concentrations of the dye. The amounts of interfering ions that can be tolerated are given in Table I.

Procedure for testing on a spot plate

Mix 1 drop of the test solution on a spot plate with 1 drop (0·01 ml) of $1M$ potassium fluoride. Add 1 drop of $10^{-3}M$ dye solution. A positive response is indicated by the appearance of a blue colour or precipitate:—

limit of identification: 0·024 μg of copper;
dilution limit: 1:1,500,000.

The limit of identification is 0·126 μg when the test is conducted in semi-micro tubes.

Note. The optimum pH for the reaction was found to be between 3 and 5. Because the pH of the copper solution in our experiments was approximately of the same order, we did not buffer the solution while carrying out the spot tests. Further, the use of buffer solution increases the dilution and so decreases the intensity of the colour produced. However, if the pH of the test solution is other than this, use of a buffer solution is recommended.

TABLE I.—TOLERANCE OF INTERFERING CATIONS

Cation[a]	Amount tolerated, μg
U(VI)	2·7
V(IV)	0·66
Fe(III)	5·6
Al(III)	2·6
Th(IV)	2·32
Zr(IV)	0·91
Cd(II)	10·2
Mn(II)	10·2
Ni(II)	8·6
Co(II)	9·0

[a] 0·02 μg of copper(II) taken for each test.

Test on paper impregnated with dye and fluoride

In an attempt to attain greater sensitivity, the test was conducted on filter paper (Whatman No. 1) impregnated with dye and potassium fluoride. This paper was prepared by dipping the filter paper first into $1M$ potassium fluoride, then into $10^{-3}M$ dye and finally drying it. However, if the order of treatment is reversed, *i.e.*, first the paper is dipped in dye and then in fluoride solution or if the dipping is carried out simultaneously in a mixture of dye and potassium fluoride, the suppression of the interfering ions is not complete [uranium(VI) and vanadium(IV) are especially difficult to suppress]. The colour of the properly-prepared paper is pinkish-yellow; the colour of paper dipped in dye only is pinkish.

To perform the test, place 1 drop of the test solution on the paper. Copper reacts immediately, producing a blue spot concentrated at the centre. At concentrations of copper lower than 0·063 μg a blank test (by putting 1 drop of water only) should be conducted. At lower concentrations, when a comparison is made with a blank, the main distinction is that in the case of the blank a uniform blue stain is left but with copper the spot is concentrated at the centre. By this method 0·01 μg of copper can be identified.

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Summary—Solochrome Azurine B.S. has been used for the selective detection of copper. The limit of identification is 0·01 μg in the presence of nickel(II), cobalt(II), cadmium(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV), zirconium(IV) and manganese(II).

Zusammenfassung—Solochromazurin B.S. wurde zum selektiven Kupfernachweis verwendet. Die Nachweisgrenze liegt bei 0,01 μg neben anderen Kationen wie Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} und Zr^{4+}.

Résumé—On a utilisé le Solochrome Azurine B.S. pour déceler sélectivement le cuivre. La limite d'identification est de 0,01 μg en présence des cations Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+}, Zr^{4+}.

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Ion-exchange equilibria in the presence of organic solvents—III: Influence of organic solvents on the distribution coefficients of caesium, barium and zinc ions

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IN the last few years, organic solvents have been used more and more, in mixture with a mineral acid, for the elution of cations from ion-exchange resins. This is because the mineral acid produces a dissociation of the resin-cation complex, and the resulting cations form complexes as a result of the dehydrating action of the organic solvent.

In the present paper the results of our study of the influence of some organic solvents on the ion-exchange equilibria of caesium, barium and zinc ions are reported.

Lengyel[1] mentioned that on Dowex 50 W × 8 in alcoholic media, the selectivity for caesium ions increased with the concentration of methyl alcohol, and Materova, Vert and Grinberg[2] showed that, on Wofatit C in alcoholic media, the rate of exchange of barium ions increased more rapidly in the presence of an organic solvent than in its absence.

To perform the test, place 1 drop of the test solution on the paper. Copper reacts immediately, producing a blue spot concentrated at the centre. At concentrations of copper lower than 0·063 μg a blank test (by putting 1 drop of water only) should be conducted. At lower concentrations, when a comparison is made with a blank, the main distinction is that in the case of the blank a uniform blue stain is left but with copper the spot is concentrated at the centre. By this method 0·01 μg of copper can be identified.

Acknowledgements—The authors thank Prof. K. K. Rohatgi for helpful discussions and Prof. C. N. R. Rao for providing the necessary facilities and encouragement during the progress of the work. One of us (U. T.) would also like to thank the Council of Scientific and Industrial Research for the award of a Senior Fellowship.

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Summary—Solochrome Azurine B.S. has been used for the selective detection of copper. The limit of identification is 0·01 μg in the presence of nickel(II), cobalt(II), cadmium(II), uranium(VI), vanadium(IV), iron(III), aluminium(III), thorium(IV), zirconium(IV) and manganese(II).

Zusammenfassung—Solochromazurin B.S. wurde zum selektiven Kupfernachweis verwendet. Die Nachweisgrenze liegt bei 0,01 μg neben anderen Kationen wie Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+} und Zr^{4+}.

Résumé—On a utilisé le Solochrome Azurine B.S. pour déceler sélectivement le cuivre. La limite d'identification est de 0,01 μg en présence des cations Ni^{2+}, Co^{2+}, Cd^{2+}, UO_2^{2+}, VO^{2+}, Fe^{3+}, Al^{3+}, Th^{4+}, Zr^{4+}.

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Ion-exchange equilibria in the presence of organic solvents—III: Influence of organic solvents on the distribution coefficients of caesium, barium and zinc ions

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IN the last few years, organic solvents have been used more and more, in mixture with a mineral acid, for the elution of cations from ion-exchange resins. This is because the mineral acid produces a dissociation of the resin-cation complex, and the resulting cations form complexes as a result of the dehydrating action of the organic solvent.

In the present paper the results of our study of the influence of some organic solvents on the ion-exchange equilibria of caesium, barium and zinc ions are reported.

Lengyel[1] mentioned that on Dowex 50 W × 8 in alcoholic media, the selectivity for caesium ions increased with the concentration of methyl alcohol, and Materova, Vert and Grinberg[2] showed that, on Wofatit C in alcoholic media, the rate of exchange of barium ions increased more rapidly in the presence of an organic solvent than in its absence.

Fritz and Rettig,[8] working in acetone media on Dowex 50 W × 8, concluded that at low acetone concentrations the distribution coefficients of zinc ion increased, but at high solvent concentrations they decreased with increasing solvent content.

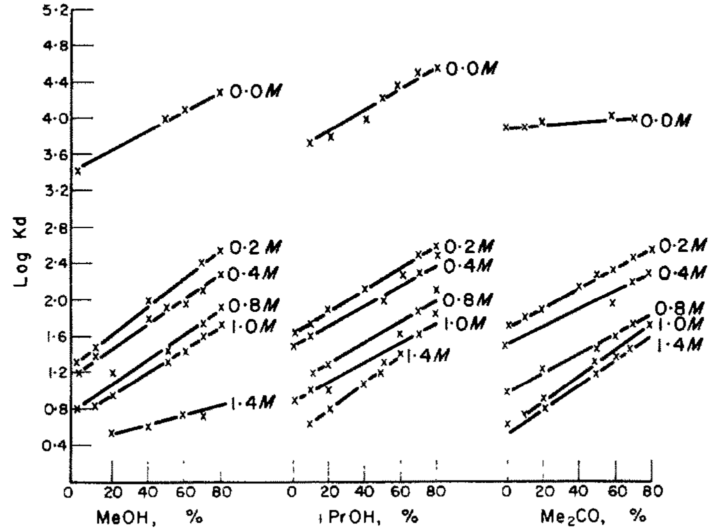

FIG. 1.—Variation of log K_d with the concentration of organic solvent for caesium ions.

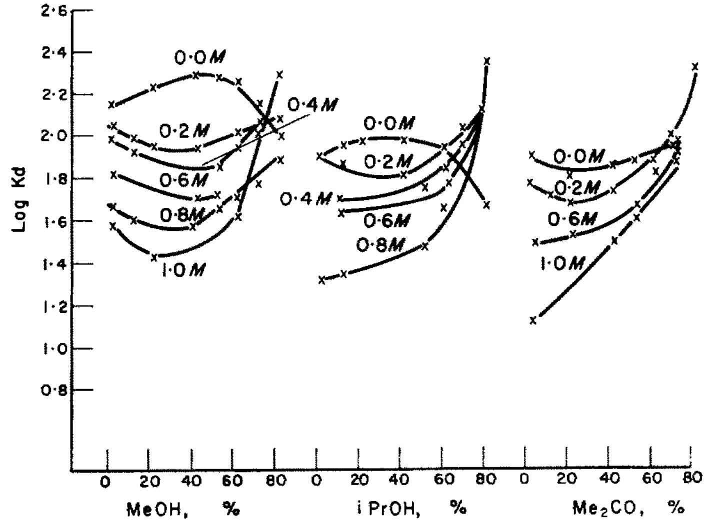

FIG. 2.—Variation of log K_d with the concentration of organic solvent for barium ions.

EXPERIMENTAL

The static distribution coefficient, K_d, of the various cations (concentration: 1.58×10^{-3} equiv/ml) was determined between sulphonated polystyrene resin KU-2 and solutions containing organic solvents (methyl alcohol, isopropyl alcohol and acetone), hydrochloric acid and water.

The cations were identified by using $^{65}_{30}Zn$, $^{140}_{56}Ba$ and $^{134}_{55}Cs$ as radioactive tracers. The concentrations of organic solvent and hydrochloric acid varied between 0 and 80% and 0 and 1.4*M*, respectively.

Results and discussion. The distribution coefficient was calculated from the experimental data using the equation:

$$K_d = \frac{A_i - A_f}{A_f} \cdot \frac{V}{m}$$

where A_i = the initial specific activity of the solution, A_f = the final specific activity, V = the volume of the solution (4 ml) and m = the mass of resin (0·02 g; 0·1 mequiv).

Fig. 1 shows plots of log K_d *vs.* solvent concentration in the case of caesium ions for different concentrations of hydrochloric acid. One can see that the value of K_d increases with increasing organic solvent content.

Fig. 2 shows the same thing for barium ions. In the absence of hydrochloric acid the curves are concave, whereas for acid concentrations between 0·2 and 1·0*M* they are convex with regard to the abscissa with the exception of the cases of 0·0 and 1·0*M* hydrochloric acid with acetone.

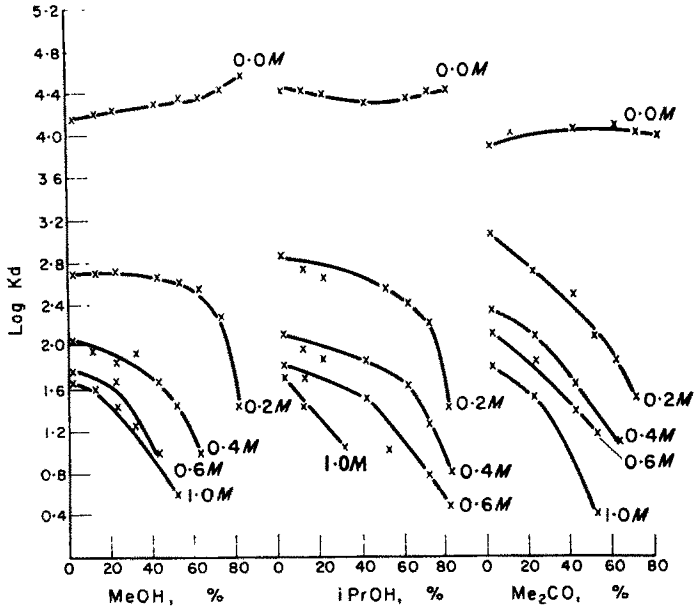

FIG. 3.—Variation of log K_d with the concentration of organic solvent for zinc ions.

In the case of zinc ions (Fig. 3) one observes a decrease in the distribution coefficient, it being more pronounced at higher solvent contents. This could be due to a more strong sorption of zinc ions by the resin at low concentrations of organic solvent and mineral acid but weaker sorption at higher concentrations, because the organic solvent favours the dehydration of zinc ions, which can then form chloro complexes, as proposed by Yoshino and Kurimura:[4]

$$[Zn(H_2O)_4]^{2+} + Cl^- \rightarrow [ZnCl(H_2O)_3]^+ + H_2O$$
$$[ZnCl(H_2O)_3]^+ + Cl^- \rightarrow [ZnCl_2(H_2O)_2]^0 + H_2O$$
$$[ZnCl_2(H_2O)_2]^0 + Cl^- \rightarrow [ZnCl_3(H_2O)]^- + H_2O$$
$$[ZnCl_3(H_2O)]^- + Cl^- \rightarrow [ZnCl_4]^{2-} + H_2O.$$

The maximum of these curves appears at that concentration of hydrochloric acid for which the negatively charged complexes become predominant. Consequently, on a cationic exchanger we have:

$$(C_{Zn})_R = [Zn^{2+}]_R + [ZnCl^+]_R$$

whereas the negatively charged species remain in solution.

Assuming that the law of mass action applies to the reactions

$$RH + Me^+ \rightleftharpoons RMe + H^+ \quad \text{(where Me = Cs)}$$
$$2\,RH + Me^{2+} \rightleftharpoons R_2Me + 2H^+ \quad \text{(where Me = Ba)}$$

we have

$$K_{e_1} = \frac{[\mathrm{R\,Me}]}{[\mathrm{Me}]} \cdot \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} = K_{d_1} \frac{[\mathrm{H}^+]}{[\mathrm{RH}]}$$

$$K_{e_2} = \frac{[\mathrm{R_2\,Me}]}{[\mathrm{Me}^{2+}]} \cdot \frac{[\mathrm{H}^+]^2}{[\mathrm{RH}]} = K_{d_2} \frac{[\mathrm{H}^+]^2}{[\mathrm{RH}]}\,.$$

Zinc ions readily form complexes, so that the reaction takes place in steps:

$$2\,\mathrm{RH} + \mathrm{Zn}^{2+} \rightleftharpoons \mathrm{R_2\,Zn} + 2\,\mathrm{H}^+$$
$$\mathrm{RH} + \mathrm{ZnCl}^+ \rightleftharpoons \mathrm{RClZn} + \mathrm{H}^+\,.$$

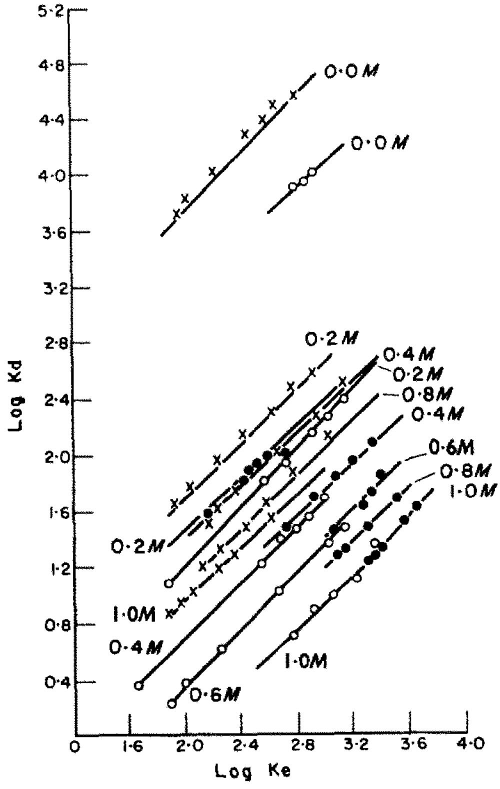

FIG. 4.—Variation of log K_d with log K_e for methyl alcohol:
×—caesium,
●—zinc,
○—barium.

A plot of log K_d *vs.* log K_e (Fig. 4) gives straight parallel lines, corresponding to the equations

$$\log K_e = \log K_d + \log \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} \qquad \text{(for univalent ions)}$$

$$\log K_e = \log K_d + 2 \log \frac{[\mathrm{H}^+]}{[\mathrm{RH}]} \qquad \text{(for bivalent ions).}$$

This shows that the effect of the organic solvent is the same for any concentration of acid, independent of the nature of the solvent.

Considering the quantity of cation sorbed as a function of the acid, a family of curves has been obtained, corresponding to the equations

$$y = -ax^2 + b \quad \text{(for barium)}$$
$$y = -ax + b \quad \text{(for caesium)}$$

where y = the quantity of sorbed ions, b = the maximum quantity sorbed at zero acidity, x = the initial concentration of acid and a = a constant, which is characteristic of the quantity of organic solvent present in the solution. These curves show that the presence of the organic solvent does not change the character of the reaction which takes place, but only increases the sorption of ions.

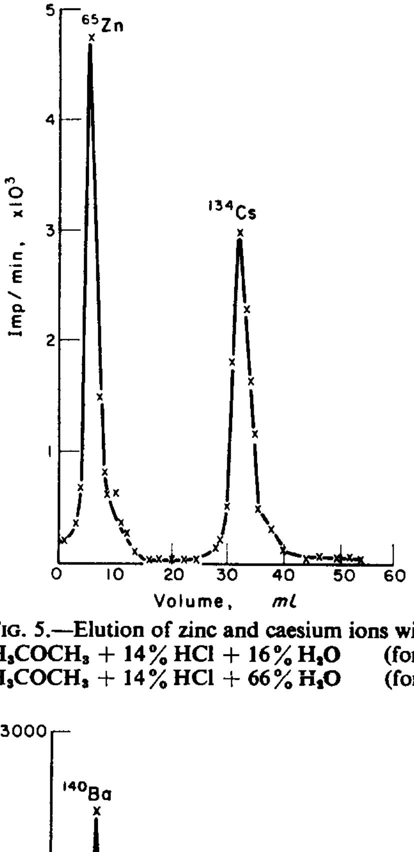

FIG. 5.—Elution of zinc and caesium ions with
70% CH_3COCH_3 + 14% HCl + 16% H_2O (for zinc)
and 20% CH_3COCH_3 + 14% HCl + 66% H_2O (for caesium).

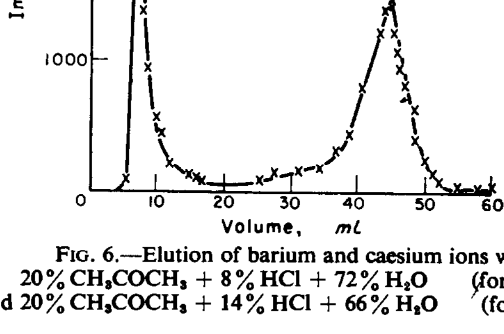

FIG. 6.—Elution of barium and caesium ions with
20% CH_3COCH_3 + 8% HCl + 72% H_2O (for barium)
and 20% CH_3COCH_3 + 14% HCl + 66% H_2O (for caesium).

Finally, the separation of zinc and caesium and of barium and caesium was attempted using a column of KU-2 resin (20 cm × 0·6 cm) and the following eluting agents (Figs. 5 and 6):

$70\% \ CH_3COCH_3 + 14\% \ HCl + 16\% \ H_2O$	for zinc,
$20\% \ CH_3COCH_3 + 14\% \ HCl + 66\% \ H_2O$	for caesium,
$20\% \ CH_3COCH_3 + 8\% \ HCl + 72\% \ H_2O$	for barium.

CONCLUSIONS

(1) The presence of organic solvents in acidic media does not influence the manner in which caesium and barium ions are sorbed on the sulphonated polystyrene resin KU-2.

(2) Zinc ions, because of their complexing capacity, show a decreasing sorption with increase in the concentration of the organic solvent.

(3) The organic solvents increase the values of the distribution coefficients in all cases for caesium, but for barium only in those solutions containing hydrochloric acid and more than 40% of organic solvent.

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Summary—The change in the distribution coefficients of caesium, barium and zinc ions on the sulphonated polystyrene resin KU-2, as a function of organic solvent concentration in hydrochloric acid solution, is studied. The organic solvents investigated are methyl alcohol, isopropyl alcohol and acetone. From the data obtained, it is possible to devise separations of zinc and caesium and of barium and caesium.

Zusammenfassung—Es wird die Änderung der Verteilungskoeffizienten von Caesium-, Barium- und Zinkionen an dem sulfonierten Polystyrolharz KU-2 als Funktion der Konzentration organischen Lösungsmittels in Salzsäure verfolgt. An organischen Lösungsmitteln wurden Methylalkohol, Isopropylalkohol und Aceton untersucht. An Hand der gemessenen Daten ist es möglich, Verfahren zur Trennung von Zink und Caesium sowie von Barium und Caesium anzugeben.

Résumé—On a étudié les changements des coefficients de partage des ions césium, baryum et zinc sur la résine polystyrène sulfonée KU-2 en fonction de la concentration du solvant organique dans l'acide chlorhydrique. Les solvants organiques examinés sont: méthanol, isopropanol et acétone. A partir des données obtenues, il est possible de mettre au point des séparations de zinc et césium et de baryum et césium.

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PRELIMINARY COMMUNICATION

Amperometry with two polarisable electrodes: Chelometric determination of calcium and magnesium

(*Received* 23 *February* 1965. *Accepted* 15 *March* 1965)

BIAMPEROMETRIC indication of the end-point of EDTA titrations has now been found possible even in an alkaline medium. Under similar experimental conditions to those described in our previous papers,[1,2] the following results have been obtained with the use of two graphite or platinum polarisable (stationary) electrodes.

The course of the titration curves corresponding to the titration of calcium with EDTA (in a medium of potassium hydroxide or borate buffer solution) has a quite different nature from that of titrations carried out in an acidic or neutral medium.[1,2] Similar differences have also been observed in the case of titrations in an ammonia/ammonium nitrate buffer solution of the same pH. It is presumed that in the titration of calcium in a strongly alkaline medium, sorption effects play an important role.

On the other hand, similar effects have not been observed in the titration of magnesium in various buffer solutions. The observed differences in titration of calcium and magnesium have been applied as a basis for chelatometric determination of the sum of calcium and magnesium and for the consecutive determination of calcium and magnesium in mixtures. Determination of the sum is carried out in an ammonia/ammonium nitrate medium; the elements can be determined consecutively in mixtures in a boric acid/potassium hydroxide medium.

In potassium hydroxide solution, calcium can be determined even in the presence of a relatively large excess of magnesium. Magnesium is precipitated as its hydroxide and does not interfere. Under identical conditions, strontium and barium can also be determined.

The above observations can be used for determination of the alkaline earth metals in various materials. Chelometric titration of the alkaline earth metals with biamperometric indication of the end-point is now under detailed study and the results will be published in due course.

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Summary—Calcium and magnesium can be determined in an alkaline medium by chelometric titration with biamperometric indication of the end-point using two graphite or platinum stationary electrodes. Under suitable conditions (pH, buffer solution) calcium and magnesium can be determined consecutively and the sum of these elements can also be obtained.

Zusammenfassung—Calcium und Magnesium können in alkalischem Medium chelometrisch titriert werden, wobei der Endpunkt biamperometrisch mit zwei ruhenden Graphit- oder Platinelektroden angezeigt wird. Unter geeigneten Bedingungen (pH, Pufferlösung) können Calcium und Magnesium nacheinander bestimmt werden; auch die Summe beider Elemente ist bestimmbar.

Résumé—On peut doser le calcium et le magnésium en milieu alcalin par titrage chélatométrique, avec indication bi-ampérométrique du point final, en utilisant deux électrodes stationnaires en graphite ou platine. Dans des conditions convenables (pH, solution tampon), on peut doser le calcium et le magnésium successivement, et l'on peut également obtenir la somme de ces éléments.

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Talanta, 1965, Vol. 12, pp. 649 to 650. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Use of iron(III)-1,10-phenanthroline complex in presence of light as an oxidising agent in organic analysis

SIR,

The oxidising properties of the yellow complex of 1,10-phenanthroline with iron(III) have been used for the indirect determination of cobalt[1–4] and of uranyl ions.[5] An indirect determination of oxalic acid using ferron has been described by Burrows[6] and Jablonkowski.[7] The yellow iron (III)-1,10-phenanthroline complex is photosensitive, especially after irradiation with light having a wavelength shorter than 590 nm.[8]

In the presence of organic acids with labile carboxyl groups it is possible to make use of the catalytic influence of light on the reaction:

$$[Fe_2Phen_4\,(OH)_2]^{4+} + 2e + 2\ HPhen^+ \rightarrow 2[FePhen_3]^{2+} + 2\ H_2O.$$

In solutions containing $3{\cdot}7 \times 10^{-5}M$ iron(III) (as chloride), $7 \times 10^{-4}M$ 1,10-phenanthroline, $0{\cdot}6M$ sodium acetate, $0{\cdot}6M$ ammonium chloride and 0·0–1·0 mg of citric, tartaric, malic or oxalic acid in 100 ml, decomposition of the organic acids takes place after irradiation in accordance with the following equations:

$$[Fe_2Phen_4\,(OH)_2]^{4-} + (COO)_2^{2-} + 2\ HPhen^+ \xrightarrow{h\nu} 2[FePhen_3]^{2+} + 2\ CO_2 + 2\ H_2O$$

$$[Fe_2Phen_4\,(OH)_2]^{4-} + 2\ R.CHOH.COO^- + 2\ HPhen^+$$
$$\xrightarrow{h\nu} 2[FePhen_3]^{2+} + 2\ R.CH_2OH + 2\ CO_2 + 2\ H_2O.$$

As a proof of the liberation of carbon dioxide, a stream of argon was first bubbled through the illuminated solutions of the organic acids under the above conditions, then through a solution of barium chloride; a precipitate of barium carbonate was formed in the latter solution.

In samples containing no other substances interfering with the properties of iron-phenanthroline complexes, it is possible to make use of the mentioned oxidising effect for the determination of the stated acids.

The composition of a test sample and of the solution used for plotting the calibration curves must contain a sufficient excess of the yellow iron(III)-1,10-phenanthroline complex (at least 25%). Furthermore, it is necessary to maintain constant conditions of irradiation and temperature.

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Interlingua

SIR,

I have seen Professor Wilson's comment[2] on Dr. Rieman's letter[1] in *Talanta.* The translation challenge included in it is intriguing indeed. I accept it because in doing so I can dramatise the distinctive character of Interlingua. It is not really an artificial language but stands and falls with the axiom that the languages of the West are variants of a traceable common standard. In attempting to translate your challenge passage into Interlingua I do not meet the need to create new terms but to derive them from what I find in French, Spanish, German, English, *etc.* I do run into trouble with 'quencho-', but this is interestingly the same trouble I would have run into, had you asked me for a French or German or Spanish version. My sources tell me that spectrophotofluorometrically 'quench' is German 'abschrecken', French 'tremper', with a blank for Spanish, Italian, *etc.* (The blank is my ignorance and source failure and could be mended.) I boldly assume that the other romance languages use the same root as French, and here we go (I sticking my neck out and you seeing me do so): " .. . un nove procedimento es addite al armamentario del analyse de moleculas fluorescente, i.e., le methodo del analyse "tempero-fluorescentic". [Le termino "tempero-fluorescentic" rende le anglese "*quencho-fluorescence* (*analysis*)".] Iste dominio de recercas va haber extense ramificationes in le analyse oligo-organic. Il se tracta de utilisar, pro le objectivos del analyse, le effecto temperante que existe in le spectrophotofluorometria. Il ha essite trovate que compositos del typo de anthracen, phenanthreno, pyreno, benz(*a*)anthracen, benzo(*a*)pyreno, peryleno, etc es non-fluorescente in solution nitromethanic, sed isto non vale pro hydrocarburos que contine le anulo fluoranthenic. Tal hydrocarburos es fluorescente."

Please note that errors in this translation reflect my ignorance rather than an inadequacy of Interlingua.

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15 *March* 1965

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Talanta, 1965, Vol. 12, pp. 651 to 656. Pergamon Press Ltd. Printed in Northern Ireland

APPLICATION OF ANODIC STRIPPING VOLTAMMETRY TO THE DETERMINATION OF MERCURY IN LITHIUM SULPHATE

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Summary—The technique of anodic stripping voltammetry, using a carbon-paste electrode, has been applied to the determination of mercury in solutions of 1·8 M lithium sulphate. Over the range 0·08–2·5 μg/ml, the relationship between peak current and mercury content is linear. At the higher level, the standard deviation of the results is 0·1 μg/ml, falling to 0·04 μg/ml at the lower level. The interference of other cations has been studied and their effect overcome by the use of a standard addition procedure.

INTRODUCTION

Anodic stripping voltammetry consists of plating a metal onto an electrode surface at a potential sufficiently negative to deposit the metal, but not to electrolyse the solvent. The voltage is then scanned anodically at a set rate and the metal stripped from the electrode;[1–6] the resulting current/voltage trace is recorded automatically and gives a peak current at a potential corresponding to the polarographic half-wave potential of the element, the height or area of this peak being related to the concentration of the metal in the solution. The method is more sensitive than conventional polarography and involves a much larger proportion of the electro-active metal, which is in effect concentrated onto the electrode. An excellent review of anodic stripping has been given by Neeb.[7]

Several different kinds of electrode have been used in this field; solid electrodes[1] have been found to give erratic results because of surface contamination and a mercury pool electrode[1] has poor sensitivity because of diffusion of the deposited metal within the mercury. A levelled-off mercury thread[1] has been used, but a more widely used electrode is the hanging mercury drop,[2,3,6] the applications of which have been discussed by Kemula and Kublik.[6] Recently, several workers have used wax-impregnated carbon electrodes[4] and carbon-paste electrodes,[5] which have low residual currents and a wide usable anodic range. It is obviously impossible to use a mercury electrode for the determination of mercury and because wax-impregnated electrodes are reputedly difficult to make, it was decided to use a carbon-paste electrode for the work described below.

EXPERIMENTAL

Reagents

Deionised water was used in all experiments.

1·8 M *Lithium sulphate solution.* Analytical reagent grade $Li_2SO_4.H_2O$ was used without further purification.

Standard mercury solution (100 μg/ml). Prepared from pure mercury.

Standard iron solution (100 μg/ml). Made from analytical reagent grade ammonium iron(III) sulphate.

"*Standard mixture*". Made by mixing standard solutions of analytical reagent grade salts cf Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, Sn, V and Zn with the lithium sulphate solution and evaporating to dryness. This gave a mixture containing 60 ppm of each of the metals with respect to lithium sulphate.

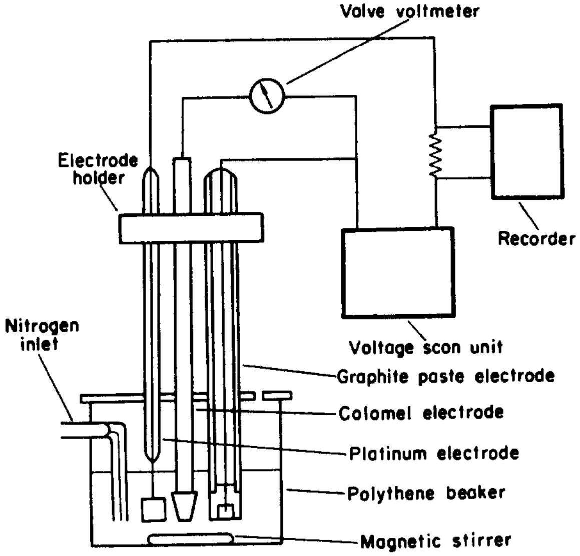

FIG. 1.—Cell assembly

Apparatus

Graphite-paste electrode (Fig. 1). The electrode[5] was fabricated from a 1-inch section of ⅜ Teflon rod, hollowed at one end and the resulting hole (¼" deep and ¼" diameter) packed with a paste made from spectrographically pure graphite (3 g) and bromonaphthalene (2 ml); electrical contact was made by means of a platinum lead.

Cell (Fig. 1). The cell was fabricated from a 50-ml polythene beaker fitted with a side arm (for flushing with nitrogen) and a magnetic stirrer. The cell was covered with a polythene lid having holes for the saturated calomel electrode, the platinum electrode and the graphite paste electrode.

Stirrer. A Baird and Tatlock stirrer (C33/0020) and paddle (C33/0034) were used. Experiments showed that the sensitivity of the technique improved with increased stirring rate and the stirring was made as fast as possible without causing splashing of solution. This setting was then retained for all subsequent work.

Voltage scan unit (Fig. 2). The unit was a transistorised Miller integrator circuit which could be set at any desired voltage between −2·0 and +2·0 V or used to scan this range at a desired rate.

Valve voltmeter. Mullard type E7555/3.

Recorder. Bristol Dynamaster (0–10 mV) connected across a resistor in series with the working electrode.

Determination of current-voltage curves

The graphite-paste electrode was immersed in pure lithium sulphate solution and electrolysed at +0·8 V for 10 min to remove electro-active impurities before each run (all voltages were measured relative to the saturated calomel electrode).

The cell was assembled as shown (Fig. 1) and 20 ml of lithium sulphate solution added. Nitrogen was bubbled through the stirred solution at 200 ml/min for 10 min to remove dissolved oxygen and was also passed over the surface of the liquid during the subsequent operations. A potential of −1·0 V was applied to the graphite-paste electrode for 15 min, during which time the solution was stirred, then the voltage supply and stirrer switched off. After 30 sec, the potential was set at 0 V and scanned to +0·6 V at a rate of 0·2 min. The resulting current-voltage curve (Fig. 3) was horizontal over the desired range and indicated a low residual current.

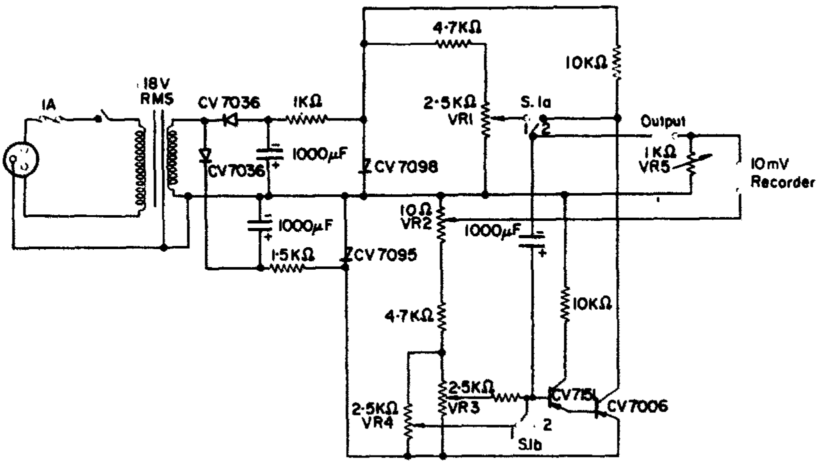

FIG. 2.—Voltage scan unit:
VR1—Set starting voltage,
VR2—Set recorder zero,
VR3—Set scan rate,
VR4—Set Miller circuit,
VR5—Set recorder range,
S.1a,b
Position 1—Circuit starting voltage,
Position 2—Auto-scan.

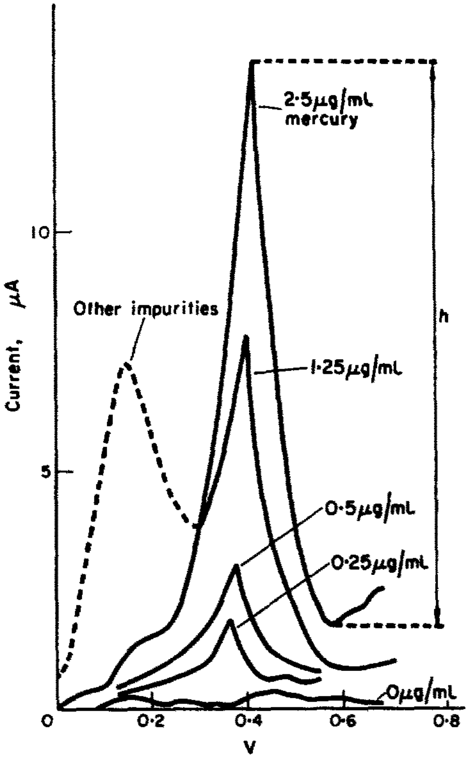

FIG. 3—Oxidation currents of mercury

The above procedure was repeated with varying amounts of mercury (0 to 50 μg) added to 20 ml of lithium sulphate solution. Fig. 3 illustrates typical peaked polarograms obtained for different concentrations. The height (h) from the peak to the minimum on the positive side was measured as shown (Fig. 3). This method was used to avoid the tail of the impurities peak. The same electrode (A) was used for all measurements and peak height plotted against mercury concentration gave a linear relationship (over the tested range of 5–50 μg of mercury) suitable for use as a calibration curve. Replicate determinations were carried out at the 2·5 μg/ml level and the 0·25 μg/ml level and no significant difference in the results was observed with different electrodes; this is consistent with earlier reports.[2] The results are recorded in Table I.

TABLE I.—REPRODUCIBILITY OF MERCURY PEAK CURRENTS

Concentration of mercury, *μg/ml*	2·50	0·25
Peak current, μA (Electrode B)	12·5, 13·5, 12·4	0·94, 1·25, 1·44
(Electrode C)	13·1, 13·1, 12·8	1·12, 0·80, 0·94
Mean, μA	12·9	1·12
Mean recovery (Fig. 4), *μg/ml*	2·55	0·25
Standard deviation, μA	0·44	0·19
μg/ml	0·09	0·04

The standard deviation of 0·04 μg/ml at the lower level indicated a 2σ detection limit of 0·08 μg/ml. The coefficient of variation was 16% at the lower level and 3·5% at the higher level.

Effect of other cations

The impurity most likely to be present in lithium sulphate is iron; the addition of iron in concentrations of up to 5 μg/ml did not have any effect on the mercury peak current. The effect of other impurities was established by adding the "standard mixture", containing Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, Sn, V and Zn to the lithium sulphate solution so that the final solution contained 2·5 μg/ml of each of these metals. The effect on the peak current, obtained from 1·25 μg/ml of added mercury, was such as to give successive recoveries increasing from 1·35 μg/ml to 1·65 μg/ml of mercury. Consistent recoveries (about the 1·35 μg/ml level) were only obtained by more drastic decontamination of the electrode before each run. It was found necessary to wash the electrode thoroughly with 1:1 nitric acid and water, before pre-electrolysing at +0·8 V for 10 min.

Current-voltage curves for the solutions containing the above metals are shown in Fig. 3. The peak at +0·1 V was attributed to copper, which was shown to give a peak at this potential when it was present alone in the lithium sulphate solution. The slight interference in the recovery of mercury can be attributed to the fact that during a large part of the plating time, mercury is deposited onto a graphite-paste electrode coated with other metals.

It was thought advisable to adopt a standard addition procedure for the analysis of actual samples of lithium sulphate, because it was considered likely that this would overcome any slight interference effects caused by the presence of other cations. It should also eliminate any differences between electrodes, although different electrodes were not, in fact, observed to give significantly different results. A solution was made up of lithium sulphate, containing 1·25 μg/ml of mercury and 2·5 μg/ml of each of the metals listed above, and the resulting peak current (h_1) measured. A known amount (25 μg) of mercury was added to a second 20-ml aliquot of this solution and the resulting peak current (h_2) measured. The mercury recovered (x) was then calculated from the equation

$$x\bigg/\left(x+\frac{25}{20}\right)=h_1/h_2 \tag{1}$$

where $\left(x+\frac{25}{20}\right)$ is the final concentration of mercury. Table II lists the recoveries from six such determinations.

TABLE II.—REPLICATE STANDARD ADDITION RESULTS

Mercury originally present, *μg/ml*	1·25
Mercury recovered, *μg/ml*	1·30, 1·45, 1·20 1·15, 1·20, 1·25
Mean, *μg/ml*	1·25
Mean recovery	100%
Standard deviation, *μg/ml*	0·10

Suggested procedure

(1) Make up the sample to give 40 ml of 1·8 M solution.
(2) Prepare graphite-paste electrodes as described above, wash well with 1 : 1 nitric acid and water, then electrolyse at +0·8 V in pure lithium sulphate solution for 10 min.
(3) Add 20 ml of the sample solution to the cell, pass nitrogen for 10 min and electrolyse the stirred solution at −1·0 V for 15 min.
(4) Switch off the current and stirrer for 30 sec.
(5) Scan anodically from 0 to +0·6 V and measure the mercury peak current (h_1).
(6) Wash and pre-electrolyse the electrode.
(7) Add a known amount of mercury (*e.g.*, 25 μg) to the other 20-ml aliquot of sample solution and repeat steps 3–5. Measure the peak current (h_2).
(8) Calculate the original mercury content (x) of the sample solution from equation (1).

CONCLUSIONS

Mercury has been determined in 1·8 M lithium sulphate solution in concentrations up to 2·5 μg/ml by an anodic stripping voltammetric technique using a graphite-paste electrode. The limit of detection was 0·08 μg/ml and the standard deviations were 0·04 μg/ml at the 0·25 μg/ml level and 0·09 μg/ml at the 2·5 μg/ml level. In the presence of other impurities, a standard addition method was found to have a standard deviation of 0·10 μg/ml at the 1·25 μg/ml level. The time required for one such determination was approximately 1 hr.

Acknowledgement—The author wishes to thank Mr. D. G. Lamb for designing and constructing the voltage scan unit.

Zusammenfassung—Die Methode der "anodic-stripping-" Voltammetrie mit einer Elektrode aus einer Kohlenstoffpaste wurde auf die Bestimmung von Quecksilber in 1,8 M Lithiumsulfatlösungen angewandt. Zwischen 0,08 und 2,5 μg/ml besteht eine lineare Beziehung zwischen Spitzenstrom und Quecksilbergehalt. Im Bereich höherer Konzentrationen ist die Standardabweichung der Ergebnisse 0,1 μg/ml, bei niedrigeren Konzentrationen fällt sie auf 0,04 μg/ml. Die Störung durch andere Kationen wurde untersucht und durch Zugabe eines Standards beseitigt.

Résumé—On a appliqué la technique de voltamétrie par dissolution anodique, avec électrode de carbone en pâte, au dosage du mercure dans des solutions 1,8M de sulfate de lithium. Dans le domaine 0,08–2,5 μg/ml, il y a une relation linéaire entre le courant de pointe et la teneur en mercure. L'écart type des résultats est de 0,1 μg/ml pour la valeur supérieure, et tombe à 0,04 μg/ml pour la valeur inférieure. On a étudié l'interférence d'autres cations, et leurs effets ont été éliminés par l'emploi d'une technique normalisée d'addition.

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A STUDY OF THE COBALT CHLORO-COMPLEXES IN DIMETHYLFORMAMIDE AND THE USE OF ONE OF THEM FOR THE SPECTROPHOTOMETRIC DETERMINATION OF COBALT

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Summary—Cobalt(II) forms deep-blue stable chloro-complexes in dimethylformamide. One of them, $(CoCl_4)^{2-}$, is used for the spectrophotometric determination of cobalt. Optimum analytical conditions have been established. Beer's law is obeyed between a cobalt concentration of 5 and 100 ppm; a wider concentration range was not investigated. Sensitivity of the colour reaction is 0·10 μg of cobalt per cm² for $\log I_0/I = 0{\cdot}001$; a large excess of many foreign ions can be tolerated; an ion-exchange separation is used when necessary. The method has been applied successfully to the determination of cobalt in steel, ferromanganese and a nickel-copper alloy.

IN an attempt to use 2,3-quinoxalinedithiol[1-3] in dimethylformamide as a spot test for cobalt it was observed that a deep-blue colour is formed when dimethylformamide alone is added to dilute cobalt chloride solutions. Further study revealed that the colour is caused by cobalt chloro-complexes. An investigation of the colour reaction and its use for the spectrophotometric determination of cobalt in several types of material is described in this paper.

EXPERIMENTAL

Apparatus

Spectrophotometers. Beckman Models DK-2 and DU with matched 1-cm Corex cells.

pH Meter. Beckman Model G.

Ion-exchange columns. The ion-exchange columns were constructed from 7-mm (o.d.) Pyrex tubing, sealed to a capillary stopcock at one end and to 10 cm of 15-mm (o.d.) Pyrex tubing at the other end. The columns were packed with a slurry of Dowex-1, 8X resin, 50 to 100 mesh. The resin bed was 25 cm in length. A glass-wool plug was used at each end of the resin bed.

Reagents

Standard cobalt solutions (1000 ppm). Dissolve 0·500 g of Johnson, Matthey's "Specpure" cobalt sponge in reagent grade 12*M* hydrochloric acid and dilute to 500 ml with 12*M* hydrochloric acid. Prepare a chloride-free cobalt standard by dissolving 0·500 g of cobalt sponge in a minimum of concentrated nitric acid and dilute to 500 ml with dimethylformamide.

Dimethylformamide (*DMF*). This compound was used as received from Matheson, Coleman, & Bell. Redistillation was not required. Eastman's DMF was also satisfactory.

Other chemicals. All other chemicals were reagent grade. Solutions were prepared using either distilled water or DMF.

PROPERTIES OF THE COBALT CHLORO-COMPLEXES IN DIMETHYLFORMAMIDE

Absorbance spectrum

The cobalt chloro-complexes have a deep-blue colour in dimethylformamide. The absorbance spectrum is shown in Fig. 1. The peaks are fairly sharp and two

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maxima occur: one near 610 mμ and another near 675 mμ. The positions of the maxima are independent of the amount of chloride in excess but their heights increase with the chloride concentration up to about a 500-fold excess, after which they become constant. Chloride solutions and DMF have very little absorbance at 610 and 675 mμ.

Rate of formation of the complexes and their stability

The cobalt chloro-complexes form instantaneously either upon mixing the reactants with DMF or upon adding sufficient DMF to their aqueous solutions. No significant difference in absorbance occurred over a period of 5 days; measurements were not made over longer periods.

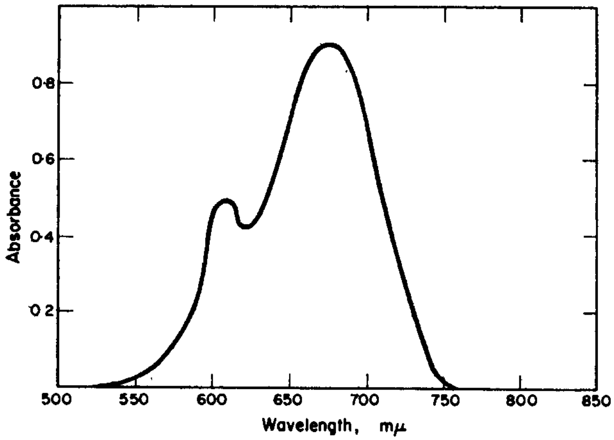

Fig. 1.—Absorbance spectrum of cobalt chloro-complexes in dimethylformamide.

Effect of pH

The absorbance of the cobalt chloro-complexes in DMF does not appear to be dependent upon the apparent pH (*i.e.*, pH meter reading) of the solution if chloride is in large excess. Moderate amounts of strong acids, such as nitric, sulphuric, perchloric and phosphoric, have no effect. Basic solutions were difficult to test because of the low solubility of alkali in DMF. Ammonia begins to interfere at an apparent pH of 4·5 to 5, perhaps because of cobalt ammine formation, and hence cannot be used.

Effect of order of addition of reactants

The order of addition of the cobalt, chloride and DMF has no effect on the absorbance if the ratios are correct. Hence, the reactants may be mixed in any order.

Valence state of cobalt in the complexes

It is fairly certain that the cobalt in the complexes is in the bivalent state. Indeed, the complexes can be formed in the presence of reducing substances, such as hydroxylamine; in fact, hydroxylamine hydrochloride can be used as the source of chloride.

Mole ratio studies

The empirical formulae of the cobalt chloro-complexes *in solution* were established by the mole ratio method of Yoe and Jones[4] and by the continuous variations method of Job,[5] as modified by Vosburgh and Cooper.[6] The data are plotted in Figs. 2 and 3. A rigorous interpretation of Fig. 2 indicates very small changes in slope at mole ratios of 1 to 1 and 1 to 2, though the differences are only slightly greater than the experimental error. A stronger indication of a 1 to 3 species, $(CoCl_3)^-$, exists, though rounding of the absorbance curve in this area is pronounced because of dissociation of the complex. The curve finally becomes horizontal above mole ratios of about 1 to 500 at an absorbance of 0·401. Extrapolation of either the "best" straight line through the first several points or any of the first three segments intersect the line representing an absorbance of 0·401 near a mole ratio of 1 to 4. This leaves little doubt that the final species formed is $(CoCl_4)^{2-}$.

Sufficient concentrations to observe the 1 to 4 complex in the continuous variations method could not be used, but it did confirm the formation of the lower complexes (see Fig. 3). Hence, the formation of 1 to 1, 1 to 2, 1 to 3, and 1 to 4, cobalt chloro-complexes, *i.e.*, $(CoCl)^+$, $CoCl_2$, $(CoCl_3)^-$ and $(CoCl_4)^{2-}$ are indicated. These findings

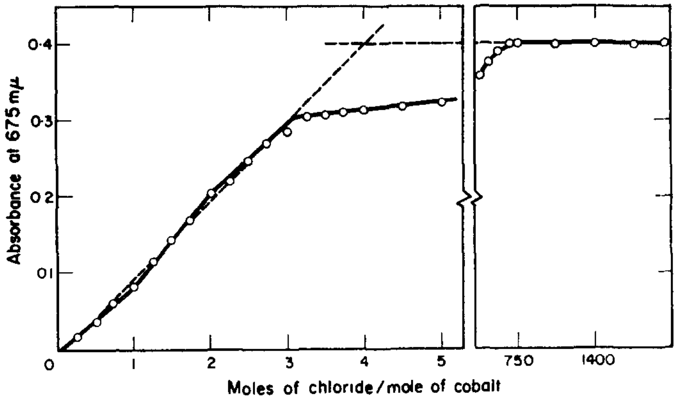

FIG. 2.—Mole ratio of cobalt chloro-complexes by Yoe and Jones method.

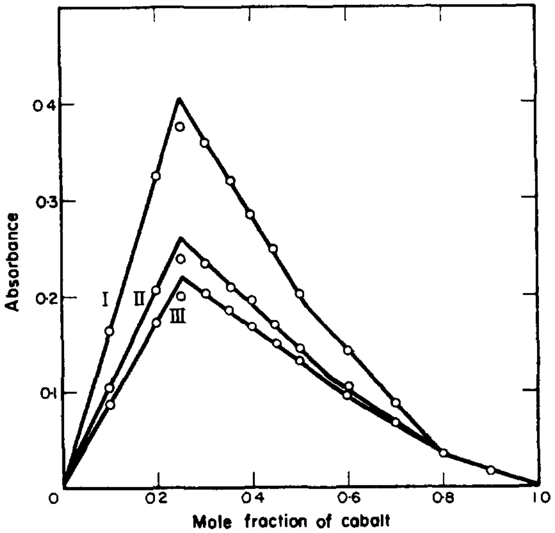

FIG. 3.—Mole ratios of cobalt chloro-complexes by continuous variations method.

are in broad agreement with those of Baaz *et al.*[7] who used other organic solvents but disagree with those of Bobtelsky and Spiegler[8] who found no evidence for a 1 to 3 complex. It is not surprising that a large excess of chloride is required to force a fourth chloride into the negative $(CoCl_3)^-$ co-ordination sphere. Ligands other than chloride which may be in the co-ordination sphere have been omitted and were not studied.

Structure of the complexes

It seems plausible to postulate a tetrahedral $(CoCl_4)^{2-}$ anion as the species used for the cobalt determination.[9]

Absorbance spectra between 400 and 750 mμ of 1 to 1, 1 to 2, 1 to 3 and 1 to 4 cobalt-chloride ratios have the same general shape, much like that shown in Fig. 1. Only one isosbestic point occurs at 585 mμ, which is believed to be caused by unreacted cobalt which has a maximum absorbance at 525 mμ. This indicates the formation of a single blue chloro-species from the pink cobalt nitrate solutions, unless the various chloro-species have about the same characteristics over the wavelength range 400 to 750 mμ. These spectra can be explained, however, if the cobalt in the absence of chloride is assumed to be octahedrally co-ordinated, as indicated by its pink colour,[9] and to shift to a tetrahedral co-ordination upon the addition of a single chloride, followed by stepwise substitution of three more chlorides. The complexes are much more stable in DMF than in water but are still highly dissociated, requiring a large excess of chloride to produce $(CoCl_4)^{2-}$ with a maximum and reproducible absorbance.

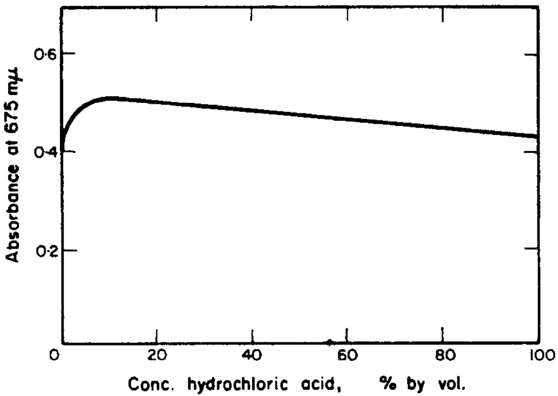

Fig. 4.—Effect of hydrochloric acid concentration on the absorbance of the cobalt chloro-complex in dimethylformamide.

DETERMINATION OF COBALT

Selection of a suitable chloride

Because the solubility of metallic chlorides that do not form chloro-complexes is very low in DMF and because a large excess of chloride is required to produce maximum absorbance by the cobalt chloro-complex, $(CoCl_4)^{2-}$, hydrochloric acid was chosen as the chloride source. The effect of the hydrochloric acid concentration was studied by maintaining the cobalt concentration at 50 ppm and varying the hydrochloric acid concentration from 0 to 100 volume %, *i.e.*, 0 to 12*M* HCl. The results are plotted in Fig. 4 and show that a nearly constant maximum absorbance occurs between 4% and 20% (by volume) concentrated acid, *i.e.*, between 0·5*M* and 2·5*M* hydrochloric acid in DMF.

Recommended calibration procedure

Transfer 0·05, 0·10, 0·20, 0·40, 0·60, 0·80 and 1·00 ml, respectively, of a standard cobalt solution (1000 ppm) in 12*M* hydrochloric acid, to 10-ml volumetric flasks and add sufficient 12*M* hydrochloric acid to make 1 ml. The series will contain 5, 10, 20, 40, 60, 80 and 100 ppm of cobalt, respectively, when diluted to volume (10 ml). Add to each solution 6–8 ml of DMF, mix and allow to cool. Make to volume (10 ml) with DMF, mix thoroughly, and measure the absorbance at 675 mμ against a reagent blank. Construct a graph of absorbance as a function of concentration.

Reproducibility

The average, standard deviation and percentage error for one standard deviation for six determinations at each of the seven concentrations used in preparing the calibration curve are listed in Table I.

TABLE I.—DATA FOR CALIBRATION CURVE

Co, *ppm.*	Absorbance average	Std. Dev. σ	Error, %
5	0·052	0·003	5·77
10	0·102	0·002	1·96
20	0·202	0·003	1·49
40	0·401	0·004	1·00
60	0·599	0·003	0·50
80	0·790	0·006	0·76
100	0·994	0·009	0·91

Effect of temperature

Normal variations in laboratory temperature cause no significant change in absorbance.

Effect of water

The effect of water upon the results obtained using the calibration procedure was studied by keeping the cobalt concentration constant at 40 ppm and varying the volume percentage of water from 0 to 25%. The results are plotted in Fig. 5 and show that the absorbance begins to decrease between 3 and 4% of water. The decrease does not become appreciable, however, until water concentrations greater than 6% are reached.

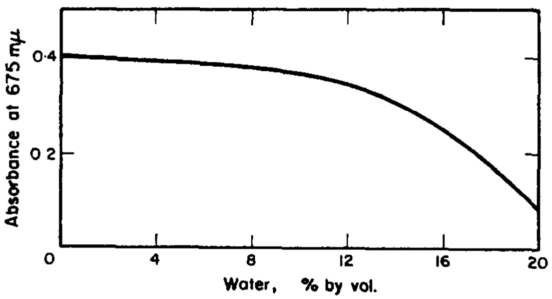

FIG. 5.—Effect of water on the cobalt determination.

Effect of foreign ions

A cobalt concentration of 30 ppm was used for this study. Because of the limited tolerance to water, many of the less common ions were tested at a 2-fold excess; the more common ions were tested at a 20-fold excess. A change in absorbance of ±2% (about 2σ) or less was considered as "no interference." None of the common inorganic anions interfered, nor did acetate, citrate, oxalate, tartrate or EDTA. The common mineral acids can be tolerated up to at least 0·5 ml per 10 ml of solution. Ge(IV), Rh(III), Nb(V) and Ta(V) ions formed precipitates in the DMF but they usually settled quickly and the supernatant liquid gave the same absorbance as the cobalt solution alone. Removal of the precipitates by filtration also produced satisfactory results. Of the common cations tested only Cr(III), Ni(II) and Cu(II) caused a deviation in absorbance greater than 2% at a 20-fold excess. Vanadium(V), however, was not tested above a 2-fold excess and might interfere at higher concentrations. The chlorides of lead, silver and mercury(I) did not precipitate from the DMF-HCl mixture.

Tolerance to Cr(III), Fe(III), Ni(II) and Cu(II) was arbitrarily set at that concentration which caused a change in absorbance of ±2% and ±5%, respectively. The results are given in Table II.

Table II.—Tolerance of the cobalt determination (30 ppm of cobalt) to interfering ions

Ion	Limiting concentration, *ppm* ±2%	±5%
Cr(III)	110	190
Fe(III)	1000	2500
Ni(II)	60	150
Cu(II)	250	600

This procedure is able to tolerate interferences better than that based on the same complex in ethanol.[10]

Discussion of the determination of cobalt

Beer's law is obeyed over a cobalt concentration range of 5 to 100 ppm. A wider concentration range was not tested. Absorbance values between 0·2 and 0·7 were chosen as the optimum range[11] and correspond to a cobalt concentration range of 20 to 70 ppm. The sensitivity is 0·10 μg of cobalt per cm^2 for log $I_0/I = 0{\cdot}001$, *i.e.*, one part of cobalt in ten million parts of solution.

The use of 1 ml of 12*M* hydrochloric acid per 10 ml allows the samples, after appropriate dissolution, to be diluted to volume with 12*M* hydrochloric acid. The sample size and dilution should be adjusted so that a 1-ml aliquot will contain sufficient cobalt (0·2–0·7 mg when using a 10-ml volumetric flask) for one analysis.

Prevention of interference by foreign ions

Interference by foreign ions is not a serious problem because a considerable excess of most of them can be tolerated. The interference caused by large amounts of chromium, iron, nickel or copper, could not be prevented by common masking agents, but ion-exchange separation[12,13] was satisfactory.

Recommended separation procedure

After appropriate dissolution, dilute the sample to volume with 9*M* hydrochloric acid. Place an aliquot containing between 0·2 and 0·7 mg of cobalt on a resin column which has been conditioned with 9*M* hydrochloric acid. Because the distribution coefficient of cobalt on Dowex-1, 8X resin in 9*M* hydrochloric acid is about 80, elution with this solution can be continued until all unabsorbed ions are removed. Nickel and chromium are easily removed. Then elute the cobalt with 4*M* hydrochloric acid, evaporate almost to dryness, and determine as described under the recommended calibration procedure.

Copper, iron and zinc remain on the column and may be removed by elution with 0·005*M* hydrochloric acid. The column may then be re-used.

ANALYSIS OF NBS SAMPLES

To evaluate the method, three National Bureau of Standards samples (Nos. 153, 162 and 68) were analysed for cobalt. Twelve samples of No. 153 were analysed without separation. The cobalt values obtained ranged between 8·34% and 8·56%, the average being 8·46% and the standard deviation ± 0·95%. This compares favourably with the Bureau's range of 8·40% to 8·54% and average value of 8·45%. NBS Nos. 162 and 68 required removal of interferences by ion-exchange before analysis. Five samples of each were analysed. The results are summarised in Table III.

TABLE III.—DETERMINATION OF COBALT IN NBS SAMPLES

NBS sample	NBS % Co		New Method % Co	
	Range	Average	Range	Average
No. 153 Steel	8·40–8·54	8·45	8·34–8·56	8·46
No. 162 Ni-Cu alloy	0·53–0·54	0·54	0·529–0·544	0·534
No. 68 Ferromanganese	0·07[a]	—	0·068–0·075	0·072

[a] Represents the result of only one NBS analyst.

Zusammenfassung—Kobalt(II) bildet in Dimethylformamid tiefblaue stabile Chlorokomplexe. Einer davon, $(CoCl_4)^{2-}$, wird zur spektralphotometrischen Bestimmung von Kobalt benützt. Die besten analytischen Arbeitsbedingungen wurden ermittelt. Das Beersche Gesetz gilt bei Kobaltkonzentrationen von 5 bis 100 ppm; ein größerer Konzentrationsbereich wurde nicht untersucht. Die Empfindlichkeit der Farbreaktion ist 0,10 μg Kobalt pro cm² bei log $I_0/I = 0{,}001$. Ein großer Überschuß vieler Fremdionen ist zulässig; nötigenfalls wird durch Ionenaustausch abgetrennt. Die Methode wurde mit Erfolg auf die Bestimmung von Kobalt in Stahl, Ferromangan und einer Nickel-Kupfer-Legierung angewandt.

Résumé—Le cobalt(II) forme, en diméthylformamide, des chlorocomplexes bleu-foncé stables. L'un d'eux $(CoCl_4)^{2-}$ est utilisé pour le dosage spectrophotométrique du cobalt. On a établi les conditions analytiques optimales. La loi de Beer est respectée pour des concentrations en cobalt comprises entre 5 et 100 ppm. On n'a pas étudié un plus grand domaine de concentrations. La sensibilité de la réaction colorée est de 0,10 μg de cobalt par cm² pour log $I_0/I = 0{,}001$. Un gros excès de nombreux ions étrangers peut être toléré; si nécessaire, on a recours à une séparation par échange d'ions. On a appliqué la méthode avec succès au dosage du cobalt dans l'acier, le ferromanganèse, et dans un alliage nickel-cuivre.

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VANADIUM COMPOUNDS IN REDUCTIMETRIC TITRATIONS—I

STANDARDISATION OF VANADIUM(II) SULPHATE WITH IRON(III) SOLUTION

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Summary—Methods of standardisation of vanadium(II) sulphate against iron(III) solutions are described. The standardisation can be carried out visually at a temperature of about 80° using acetylacetone, or meconic, salicylic or sulphosalicylic acids as internal indicators. The titration can be carried out at room temperature if copper(II) is used as a catalyst; the end-point can be detected with methylene blue, gallocyanine or potentiometrically as well as by the indicators listed above. The copper(II) catalyses the oxidation of vanadium(III) to vanadium(IV), which is slow at room temperature.

BI-, ter- and quadrivalent vanadium compounds have been used for a number of reductimetric titrations. Vanadium(II) compounds are powerful reducing agents[1] and have been employed for visual,[2–7] potentiometric[8–12] and amperometric[13,14] titrations of various oxidising agents. A number of organic compounds[2,5,15] belonging to different groups have also been determined, including nitro compounds[5] that are difficult to reduce.

Maass[8] carried out the standardisation of vanadium(II) sulphate with iron(III) solution potentiometrically. Banerjee[2] has claimed that the above titrations are possible at room temperature using thiocyanate as internal indicator. Recently, Ellis and Vogel,[5] in agreement with Gapchenko and Sheintsis[16] and contrary to the experience of Banerjee,[2] found that the use of thiocyanate as indicator at the laboratory temperature is unsatisfactory. With the help of potentiometric titrations they showed that the following two stages of oxidation of vanadium(II) with iron(III) are involved:

$$V^{2+} \rightarrow V^{3+} + e \text{ (a rapid reaction)}$$
$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e \text{ (a comparatively slow reaction).}$$

They found that the oxidation of vanadium(III) to vanadium(IV) is a comparatively slow reaction, which does not reach completion when the vanadium(II) solution is added to the iron(III) solution at the normal titration rate. This results in high as well as erratic titres when the titration is carried out by the method recommended by Banerjee. Ellis and Vogel,[5] therefore, preferred the reverse addition of the solution and used the one electron change *i.e.*, vanadium(II) to vanadium(III), with phenosafranine as visual indicator.

In a previous communication by Mittal, Tandon and Mehrotra,[6] it was shown that the change of vanadium(II) to vanadium(IV) can be indicated satisfactorily by carrying out the titration at about 80°, and using methylene blue or gallocyanine as visual indicators.

In the present investigations, it has been found that a small amount of copper(II) catalyses the oxidation of vanadium(III) to vanadium(IV) and even at the normal speed of titration, the titre, when both a visual and a potentiometric end-point were used, corresponded to the two-electron change of vanadium(II) to vanadium(IV). With this modified technique, titrations with vanadium(II) are at least as convenient as the conventional titrations with titanous salts. In some analytical application the possibility of oxidation stages(III) and (IV) might be turned to some advantage. For visual titrations, methylene blue, gallocyanine, acetylacetone, and meconic, salicylic and sulphosalicylic acids have been successfully used as indicators.

The use of acetylacetone as an internal indicator in the titration of iron(III) with EDTA was described by Singh, Sahota and Gupta.[16] Salicylic and sulphosalicylic acids were used in the determination of iron(III) against ascorbic acid by Erdey and Bodor.[17] Meconic acid was used in the titration of iron(III) solution against titanium(III) chloride by Kolthoff.[18]

The use of copper(II) in catalysing a number of reactions is well known. Both organic[19,20] as well as inorganic[21,22] compounds have been determined in the presence of cupric ions.

A number of methods have been described for the preparation of vanadium(II) solutions. Reduction of vanadium(V) and vanadium(IV) compounds with metals or amalgams[5,9,11,15,23] or electrolytic reduction at a platinum or lead cathode[2,8] are some of the well known techniques. Electrolysis with a mercury cathode has been used for preparative purposes[23,24] and in electrochemical studies.[1,26] In the present investigations vanadium(II) solution was prepared by reducing vanadyl sulphate with amalgamated zinc in the presence of dilute sulphuric acid as described by Lingane and Pecsok,[27] and then stored in an inert atmosphere of purified hydrogen in an apparatus described in an earlier communication.[6]

EXPERIMENTAL

Reagent:

Vanadium(II) solution. Prepare approximately 0.05*M* vanadium(II) sulphate solution by dissolving 20 g of reagent grade vanadyl sulphate in 1 l. of distilled water containing 30 ml of concentrated sulphuric acid. Alternatively, dissolve 6 g of reagent grade ammonium metavanadate in boiling water and reduce the solution by sulphur dioxide until a clear blue solution is obtained. Remove the excess of sulphur dioxide by passing carbon dioxide through the solution. Add 30 ml of concentrated sulphuric acid and make up the solution to 1 l. Stand the solution overnight in contact with amalgamated zinc. Complete reduction is marked by a change in colour from blue to violet. Standardise the vanadium(II) solution against standard potassium dichromate.[5]

Iron(III) solution. Prepare 0.1 *M* iron(III) sulphate solution by dissolving about 5.6 g of reagent grade iron wire. Standardise the solution with potassium dichromate after reduction with stannous chloride.

0.1M Copper(II) sulphate solution

Indicators. Prepare a 0.2% aqueous solution of methylene blue or gallocyanine, 2% aqueous solution of sulphosalicylic acid and 2% alcoholic solution of acetylacetone, meconic and salicylic acids.

Apparatus

Visual titrations are carried out in a 100-ml conical flask fitted with a rubber bung with three holes, which accommodate inlet and outlet tubes for carbon dioxide and the tip of a burette.

Potentiometric titrations are performed with a bench-type Cambridge pH meter with a platinum indicator electrode and a saturated calomel reference electrode. A 100-ml Pyrex beaker, fitted with a rubber bung with five holes to accommodate inlet and outlet tubes for carbon dioxide, the electrodes and the tip of a burette, is used.

Standardisation of vanadium(II) solution against iron(III) sulphate using methylene blue and gallocyanine as visual indicators

Place 10 ml of iron (III) solution and 2 ml of copper solution in the titration vessel and bubble carbon dioxide through the solution for about 10 min. Add 2–3 drops of the indicator, and titrate the solution slowly with vanadium(II) solution, to a light blue colour. The indicators are reversible, as reported earlier; an indicator correction of 0.1 ml had to be applied. A few results are given in Table I.

TABLE I.—VISUAL INDICATORS FOR TITRATION OF IRON(III) WITH VANADIUM(II)

Indicator used	Vanadium(II) present, *mmoles*	Vanadium(II) found		
		In presence of copper(II), *mmoles*	At 80°C, *mmoles*	Potentiometrically, *mmoles*
Methylene blue	0·4714	0·4714	0·4714	0·4714
Gallocyanine	0·4714	0·4714	0·4714	0·4714
Methylene blue	0·4998	0·4998	0·4998	0·4998
Gallocyanine	0·4998	0·4998	0·4998	0·4998
Methylene blue	0·4807	0·4807	0·4807	0·4807
Gallocyanine	0·4807	0·4807	0·4807	0·4807
Acetylacetone	0·4999	0·4999	0·4999	0·4999
Acetylacetone	0·4704	0·4712	0·4712	0·4712
Meconic acid	0·4999	0·4999	0·4999	0·4989
Meconic acid	0·4704	0·4712	0·4712	0·4688
Salicylic acid	0·4999	0·4999	0·4999	0·4999
Salicylic acid	0·4704	0·4712	0·4712	0·4688
Sulphosalicylic acid	0·4999	0·4999	0·4999	0·4999
Sulphosalicylic acid	0·4704	0·4712	0·4712	0·4688

DISCUSSION AND RESULTS

Effect of varying concentrations of copper(II) sulphate

The effect of different concentrations of copper(II) on the visual end-points was studied in detail and it was observed that for every 5 ml of 0·1 *M* iron(III) solution, 1 ml of 0·1 *M* copper(II) sulphate was the minimum required (see Table II). The effect of acidity was also noted and it was found that satisfactory results were obtained in an over-all acidity of about 2*N*. At higher acid concentrations there was an increase in the titres.

TABLE II.—EFFECT OF COPPER(II) SULPHATE ON THE TITRATION OF IRON(III) WITH VANADIUM(II) USING VISUAL INDICATORS

Copper(II) sulphate added, *mmoles*	Vanadium(II) present, *mmoles*	Vanadium(II) found, *mmoles*
0·01	0·2499	0·2500
0·05	0·2499	0·2497
0·10	0·2499	0·2499
0·20	0·2499	0·2499
0·40	0·2499	0·2499
0·50	0·2499	0·2499

Standardisation of vanadium(II) solution against iron(III) sulphate in presence of other visual indicators.

Besides methylene blue and gallocyanine, other suitable visual indicators are acetylacetone, and meconic, salicylic and sulphosalicylic acids. The procedure followed is the same as in the case of methylene blue and gallocyanine, although the indicator correction is negligible in these cases. Some typical results are shown in Table I.

Effect of diverse ions

Zinc(II), cobalt(II), nickel(II) and manganese(II) do not interfere, whereas cerium(IV), manganese(VII), chromium(VI), vanadium(V), tungsten(VI) and molybdenum(VI) do interfere and should not be present.

Standardisation of vanadium(II) solution against iron(III) sulphate potentiometrically

Potentiometric titrations were performed under three different experimental conditions: (i) at normal titration speed, (ii) slowly, allowing 2–3 min between each drop at least 1 ml before the end-point, and (iii) at normal speed and in the presence of copper(II) sulphate. The results in the first two cases were found to be in agreement with those of Ellis and Vogel.[5] However, in the presence of copper(II) satisfactory results could be obtained at normal titration speed and without much waiting near the end-point. It was possible to complete the titration within a period of about 15 min. Some typical results obtained are shown in Table III.

TABLE III.—POTENTIOMETRIC TITRATION OF IRON(III) WITH VANADIUM(II) UNDER DIFFERENT CONDITIONS

	Vanadium(II) found, *mmoles*		
Vanadium(II) present, *mmoles*	Normal speed of titration time taken about 15 min	Slow titration time taken about 40 min	In presence of copper(II) time taken about 15 min
0·5095	0·5248	—	—
0·5095	—	0·5095	—
0·5095	—	—	0·5074
0·4712	0·4804	—	—
0·4712	—	0·4682	—
0·4712	—	—	0·4712
0·4713	0·4822	—	—
0·4713	—	0·4713	—
0·4713	—	—	0·4713

CONCLUSION

In the present investigation it has been shown that the standardisation of vanadium(II) solution with iron(III) sulphate can be successfully carried out at the laboratory temperature in the presence of copper(II) as catalyst. The end-point corresponds to the two-electron change of vanadium(II) to vanadium(IV) and can be indicated either visually or potentiometrically with almost the same accuracy. In the absence of copper(II), however, the second stage of oxidation, vanadium(III) to vanadium(IV), is comparatively slow and does not reach completion at normal titration speed and is marked by high and erratic titres. For satisfactory results the titration must be carried out slowly or at a temperature of about 80°. A few other common catalysts [nickel(II), manganese(II), mercury(II), silver(I), iodine monochloride and oxalic, citric and tartaric acids] were also tried but these were found to be unsuccessful.

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Zusammenfassung—Methoden zur Einstellung von Vanadium(II)-sulfat gegen Eisen(III)-sulfat werden beschrieben. Die Einstellung kann bei etwa 80° visuell ausgeführt werden, wobei Acetylaceton, Mecon-, Salicyl- oder Sulfosalicylsäure als Indikatoren in der Lösung verwendet werden können. Mit Kupfer(II) als Katalysator kann bei Zimmertemperatur titriert werden; der Endpunkt kann mit Methylenblau, Gallocyanin oder potentiometrisch, ferner mit den oben aufgezählten Indikatoren festgestellt werden. Kupfer(II) katalysiert die Oxydation von Vanadium(III) zu Vanadium(IV), die bei Zimmertemperatur langsam verläuft.

Résumé—On décrit des méthodes de titrage du sulfate de vanadium(II) au moyen de sulfate de fer(III). Le dosage peut être mené visuellement à une température d'environ 80°, en utilisant, comme indicateurs internes, l'acétylacétone, ou les acides méconique, salicylique ou sulfosalicylique. On peut mener le dosage à température ambiante si l'on emploie du cuivre(II) comme catalyseur; le point final peut être détecté au bleu de méthylène, à la gallocyanine ou potentiométriquement, ainsi qu'avec les indicateurs énumérés cidessus. Le cuivre(II) catalyse l'oxydation du vanadium(III) en vanadium(IV), qui est lente à température ambiante.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—VI*

CHELOMETRIC DETERMINATION OF COPPER

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Summary—A study of the determination of copper by titration with EDTA, using biamperometric detection of the end-point with two stationary platinum electrodes, is reported. The influence of pH, applied potential, temperature and rate of stirring on the course and accuracy of the titration are examined. The selectivity of the titration is investigated and possible analytical applications discussed.

THE possibility of the chelometric determination of copper with amperometric indication, using two polarisable electrodes at constant applied potential, has already been mentioned.[1] As in the determination of iron(III),[2,3] the exact evaluation of the titration curves for copper is not possible on the basis of the corresponding current-potential curves, which is usually recommended in the case of biamperometric methods (dead-stop).[4] The reason for this statement has been published earlier.[3] The electrode reactions occurring during the titration with EDTA are now being studied and the results will be published later.

The present paper is a continuation of the previously reported studies of the amperometric method using two identical polarisable electrodes. It deals with the titration of copper with EDTA using an indication system of two stationary platinum electrodes.

EXPERIMENTAL

Reagents

All chemicals used were of the highest grade of purity (reagent grade). The exact concentrations of solutions of metallic salts were determined by recommended procedures.

Buffer solutions. Prepared from 1*M* solutions of trichloracetic, monochloracetic, formic, acetic and aminoacetic acids, by neutralisation with aqueous ammonia under potentiometric pH control.

Standard solutions of copper. Prepared by dissolving copper metal (99·99%) in a minimum amount of nitric acid (1:1) and, after evaporation to remove oxides of nitrogen, the solution was diluted with water so that 1 ml contained 1·00 mg of copper (standardised by electrolysis). Standard solutions of copper in perchloric, sulphuric and hydrochloric acids were prepared similarly.

0·05*M* EDTA *solution.* Prepared by dissolving 37·22 g of Chelaton 3 (Lachema, Prague, Czechoslovakia) and diluting to 2000 ml. The titre of this solution was determined against standard lead nitrate solution using Xylenol Orange as indicator.[5]

Apparatus

Amperometric titrations were carried out using apparatus identical to that described previously.[2,3] The electrodes were two platinum plates (5 × 6 × 0·2 mm). When not in use these electrodes were

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[*] Part V: reference 5.

maintained immersed in distilled water. A micro ammeter DLL (Metra Blansko) with a maximum deflection of 750 μA was used as the indication instrument. pH was measured with an electronic pH meter (Multoscop V, Lab. potřeby, Prague, Czechoslovakia) and a glass electrode.

Procedure

A known amount of standard copper solution was diluted to 100–120 ml and the pH adjusted either with nitric acid (1:1) or with aqueous ammonia (1:1) or with 20 ml of buffer solution. When on other conditions are given, this solution was titrated with 0·5*M* EDTA at pH 2·5 and a temperature of 20°. The applied potential was maintained at 1·4 V; the rate of stirring was 1600 rpm. All titrations were started 3 min after immersing the electrodes into the titration solution. Change of current was plotted against volume (ml) of titrant added. The stabilisation of current (especially near the equivalence point) was very rapid. Results of all titrations represent the arithmetic mean of three measurements.

RESULTS AND DISCUSSION

Influence of pH

With respect to the specificity of the method, the course of the titration was examined especially in an acidic (buffered and unbuffered) medium. The titration curves obtained in unbuffered solutions of nitric and hydrochloric acids are presented on Fig. 1, and in buffered solutions in Fig. 2. The results show the possibility of determining copper above pH 1·9 in a nitric acid medium and above pH 2·5 in buffer solutions of trichloracetic acid/ammonia and of formic acid/ammonia. In hydrochloric acid solutions and in monochloracetic acid/ammonia buffer solutions (pH 2), detection of the end-point is more difficult. Similar results have also been observed in buffered solutions of perchloric and sulphuric acids. Experiments carried out in the pH range 5·1–11·3 (buffered solutions) gave satisfactory results up to pH 10·7 (see Fig. 3). Above this pH, detection of the end-point was not accurate.

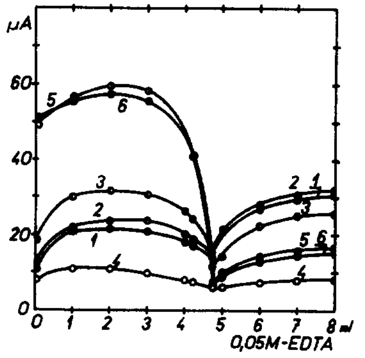

FIG. 1.—Influence of pH on titration of copper in unbuffered medium:

HNO_3	HCl
1. 1·9	4. 2·0
2. 2·8	5. 4·8
3. 4·0	6. 5·4

[15·00 mg of copper; total volume: 120 ml; 20°; applied potential: 1·4 V]

Influence of applied potential

The influence of applied potential on the biamperometric determination of copper was studied over the range 1·4–2·0 V in unbuffered solutions and in the interval 1·0–2·0 V in buffered solutions. No influence was observed except in the case of an

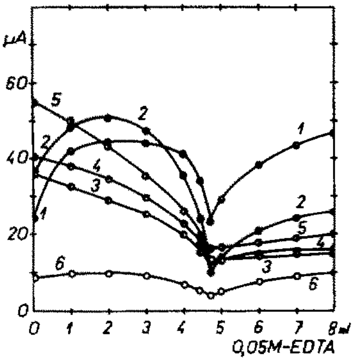

FIG. 2.—Influence of pH on titration of copper in a buffered (non-complex forming) medium:

Trichloracetic acid/ammonia	Formic acid/ammonia	Monochloracetic acid/ammonia
1. 2·5	3. 4·5	6. 2·5
2. 2·8	4. 5·2	
	5. 6·7	

[15·00 mg of copper; total volume: 120 ml; 20°; applied potential: 1·4 V]

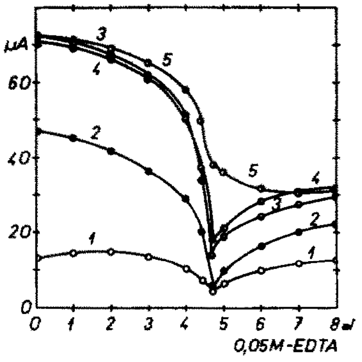

FIG. 3.—Influence of pH on the titration of copper in a buffered (acetic acid/ammonia) medium:

1. 5·1
2. 7·0
3. 8·5
4. 10·7
5. 11·3

[15·00 mg of copper; total volume: 120 ml; 20°; applied potential: 1·4 V]

applied potential of 1·0 V (titration curve not well developed); detection of the equivalence point is sharp enough. The mean error in the determination of 150 mg of copper is ±0·1 % rel.

At pH 6 (unbuffered solution) and an applied potential of 1·0–1·6 V, layers of copper are formed on the surface of the negative indicator electrode which either dissolve during the titration or remain stable. Under these conditions the determination is impossible.

Influence of temperature

At room temperature (20°) there are no irregular changes in the current. At a higher temperature (70°) the course of the titration remains unchanged and also at lower applied potentials. Stabilisation of the current during the titration is better at a higher temperature.

Influence of stirring

No influence of the rate of stirring was observed between 600–3400 rpm.

"Passivation" of indicator electrode

The influence of the products of the electrode processes on a series of subsequent titrations was studied. These titrations were all carried out under identical conditions without any chemical or mechanical treatment of the surface of the electrodes. A series of 25 EDTA titrations was carried out over an interval of 5 hr. The results confirmed the unfavourable influence of the products of the reactions on the perennial decrease of current (Fig. 4). However, the accuracy of the detection of the end-point is not affected by this phenomenon. Deposits on the electrode surface dissolve very well if the electrodes are immersed in warm (70°) nitric acid (1:1) (Fig. 4, curve 7). The error in a series of determinations of 15·00 mg of copper did not exceed 0·1 % rel.

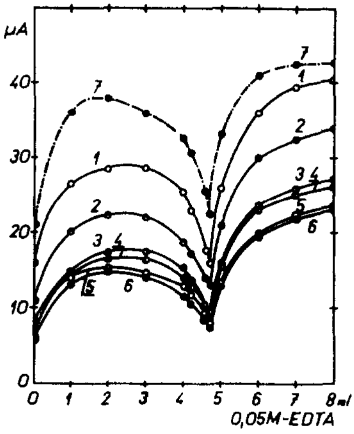

Fig. 4.—Course of titration of copper in a series of 25 determinations:

1. titration 1
2. titration 5
3. titration 10
4. titration 15
5. titration 20
6. titration 25
7. after immersion in warm HNO_3 (1:1)

[15·00 mg of copper; total volume: 120–150 ml; 20°; pH: 2·5 (unbuffered); applied potential: 1.4V]

The decrease of current from the moment of insertion of the electrodes was also examined. Fig. 5 shows the dependence of current on time in an acidic medium, nearly neutral medium and alkaline medium. Stabilisation of the current sets in after 3 min.

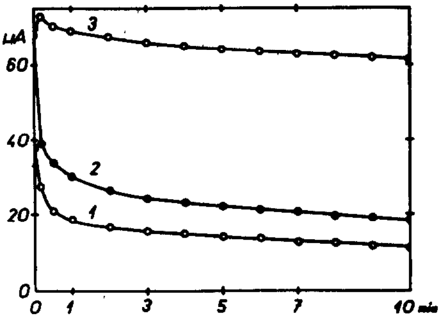

Fig. 5.—Current-time curves during stabilisation of the current in the titration of copper:

1. pH 2·5 (unbuffered)
2. pH 6·0 (buffered)
3. pH 9·5 (buffered)

[15·00 mg of copper; total volume: 120 ml; 20°; applied potential: 1·4 V]

Concentration range and accuracy

The described procedure enables the determination of 1–150 mg of copper in a volume of 120 ml with greater accuracy than is possible in a visual indicator titration. Some results of such determinations are summarised in Table I. The mean relative error does not exceed ±1%, with the exception of the determination of 1 mg of copper when the error is magnified by the small consumption of the titrant.

Table I

Cu, *mg*		0·05*M*-EDTA, *ml*		Difference	
Taken	Found	Calculated	Found	*mg*	*%rel.*
1·00	1·02	0·315	0·32	+0·02	+2·00
5·00	4·99	1·571	1·57	−0·01	−0·99
15·00	14·93	4·721	4·70	−0·07	−0·47
50·00	49·94	15·738	15·72	−0·06	−0·12
100·00	100·23	31·504	31·55	+0·23	+0·23
150·00	149·32	47·214	47·00	−0·68	−0·46

Selectivity

The selectivity was examined by the titration of 15·0 mg of copper in a total volume of 120 ml at pH 2·5 and an applied potential of 1·2–1·4 V, in the presence of various metal ions. Even high concentrations of acetate, nitrate, sulphate, chloride, phosphate, perchlorate, borate, tartrate, oxalate and fluoride do not interfere with the determination; neither do the following metal ions interfere: aluminium, calcium, cadmium, manganese, silver, titanium, uranium(VI) and zinc. On the other hand, cobalt, indium, iron(III), lead, mercury, nickel, thallium, thorium, zirconium and thiocyanate interfere.

In a buffered alkaline medium (pH 9·5) triethanolamine, ascorbic acid, aminoacetic acid, calcium and cobalt interfere with the determination. Magnesium, barium, hexamethylenetetramine, tartrate, chloride, oxalate, formate, nitrate, sulphate and perchlorate do not interfere.

The influence of some interfering ions can be masked by suitable masking agents. Thus, iron(III) ions can be screened by ascorbic acid, which enables the determination of 15·0 mg of copper in the presence of 500 mg of iron.[6]

Analytical Application

The developed procedure can be used successfully in metallurgical analysis.[6] It makes possible a reduction in the time of analysis of some metallurgical materials, ores, minerals and flotation products. It can also be applied to the determination of copper in pure chemicals and concentrated acids. The use of extremely dilute EDTA solutions enables the determination of very small quantities of copper to be made.[7]

Zusammenfassung—Es wird über eine Untersuchung berichtet, bei der der Endpunkt der Kupfertitration mit EDTA biamperometrisch mit zwei ruhenden Platinelektroden bestimmt wurde. Der Einfluß von pH, angelegter Spannung, Temperatur und Rührgeschwindigkeit auf Verlauf und Genauigkeit der Titration wurden geprüft. Die Selektivität der Titration wird untersucht und mögliche analytische Anwendungen diskutiert.

Résumé—On d'écrit une étude sur le dosage du cuivre par titrage à l'EDTA, en utilisant une détection bi-ampérométrique du point final au moyen de deux électrodes stationnaires en platine. On examine les influences du pH, du potentiel appliqué, de la température et de la vitesse d'agitation sur la marche et la précision du dosage. On étudie la sélectivité du dosage et discute des applications analytiques possibles.

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DETERMINATION OF DEACTIVATED OLEFINES ON THE SUBMICRO SCALE

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Summary—Olefines which do not undergo the normal addition reactions with electrophilic reagents can be reacted with the nucleophilic reagent morpholine to form a tertiary amine. A submicro method using this reagent has been developed. When the addition product is basic it is titrated after acetylation of the excess morpholine; when it is neutral the excess of morpholine is titrated.

The submicro method[1] for the determination of olefinic unsaturation, based on the addition of bromine monochloride to the double bond, was successfully applied to the analysis of $\alpha\beta$ unsaturated acids. However, when a group more strongly electron attracting than —COOH, *i.e.*, —COOEt, —C≡N or —F, was conjugated to the double bond, the electron availability was found to be lowered to such an extent that bromine monochloride (and other electrophilic reagents) was no longer effective. This type of compound is, however, susceptible to attack by nucleophilic reagents at the incipient positively-charged carbon atom. A method has been described by Critchfield, Funk and Johnson[2] in which the nucleophilic reagent morpholine, is reacted with deactivated olefines to form a tertiary amine. With the majority of olefines the addition product is basic, so that it can be titrated with standard perchloric acid in a non-aqueous medium after acetylation of the excess of morpholine. If, however, an electron-attracting group is attached to the carbon atom and to the nitrogen, the addition product is weakly basic or even neutral, and a modification of the general method is then necessary to deal with this class of compound.

In the development of the submicro method it was first of all necessary to find the optimal concentration of morpholine reagent. Because the excess of morpholine is removed by conversion to *N*-acetylmorpholine, it would appear that the actual concentration of morpholine, provided that it was present in excess, would have little effect on the reaction. It was found, however, that too large an excess of morpholine caused the indicator colour change in the titration of the tertiary amine to be less distinct than when lower concentrations of morpholine were used. The indicator used in the preliminary investigation, screened Thymol Blue, was the one recommended by Critchfield *et al.*[2] The colour change of this indicator in the submicro procedure was not very sharp (yellow-pink) and a more distinctive change was found with pyridine-2′-azo-*p*-dimethylaniline,[3] which changes from red to purple at the end-point.[4]

The indicator end-point was further improved by changing the solvent to 2-methoxyethanol alone instead of the 2-methoxyethanol/methanol solvent system used in the original method. A potentiometric study of the indicator end-point was carried out, partly to examine the suitability of various indicators for the titration and also to investigate the influence of the nature of the olefine on the basicity of the addition compound. A Weston standard cell was connected in series with the electrodes in order to obtain a reading on the pH-meter. The backing-off potential could be adjusted through a 1-Megohm variable resistance.

Table I.—Results obtained by Procedure A

Compound	C=C found, %
Acrylonitrile* (94·88 μg; C=C theory: 45·25%; 15 min)	44·26, 45·90, 42·86, 43·59 45·38, 44·68
Ethyl acrylate* (88·80 μg; C=C theory: 24·08%; 15 min)	23·16, 22·85, 23·84, 24·15
Acrylic acid* (64·28 μg; C=C theory: 33·42%; 60 min; 100°; HAc catalyst)	31·68, 30·69, 32·39, 31·70
Acrylamide (37·08–116·24 μg; C=C theory: 33·87%; 30 min; HAc catalyst)	32·84, 32·91, 33·69, 34·96, 34·26

* Standard solution in 2-methoxyethanol

The results obtained with olefines which react with morpholine to give a basic tertiary amine addition product are shown in Table I. A potentiometric titration curve was plotted for each compound (Fig. 1) because this gives an indication of the basicity of the tertiary amine. The results obtained with those compounds which formed a neutral or weakly basic addition compound are shown in Table II.

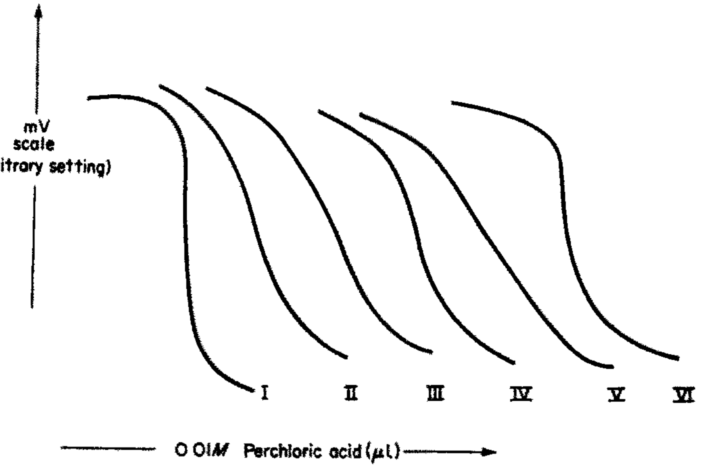

Fig. 1.—Potentiometric titration curves:
I. 2-Amino-2-hydroxymethyl-1,3-propane diol
II. Acrylonitrile,
III. Acrylamide,
IV. Ethyl acrylate,
V. Acrylic acid,
VI. Morpholine.

The results obtained from the addition of morpholine to fluoro-olefines indicate that further investigation of the mechanism of the addition is necessary. With hexafluoro-1,2-difluoro-pent-1-ene, addition of morpholine in 2-methoxyethanol solution gave results which only corresponded to 60–70% of the theoretical double-bond content. A possible reason for the low results could be attributed to reaction between the sample and the solvent.

TABLE II.—RESULTS OBTAINED BY PROCEDURE B

Compound	C=C found, %
Tetracyanoethylene (58·80—122·43 μg; C=C theory: 18·75%)	18·66, 17·33, 17·01, 16·87
1-Aminophenyl-2,2′-dicyanoethylene (68·29–80·74 μg; C=C theory: 14·20%)	13·89, 13·39, 13·36
Hexafluoro-1,2-difluoro-pent-1-ene* (87·90 μg; C=C theory: 11·33%)	10·59, 11·50, 10·31, 10·64 10·93, 11·26

* Standard solution in diethyleneglycol dimethyl ether

A similar type of reaction has been studied by Pruett.[5] Although the occurrence of this reaction was not definitely proved, when the solvent was changed to diethyleneglycol dimethyl ether (diglyme) in the present study the results obtained were much improved. This solvent was used in all subsequent investigations. The results obtained for hexafluoro-1,2-dichloro-pent-1-ene were all less than 50% of the theoretical value, and for the unsubstituted compound hexafluoro-pent-1-ene, no reaction at all was observed. This would seem to indicate that the necessary deactivation is only achieved when the fluorine is attached to the double-bond carbon atom.

EXPERIMENTAL

Apparatus

pH Meter. (E.I.L. Vibron Model)

Electrodes. These were glass and silver/silver chloride[6] incoporating a salt bridge of 0.1 *M* sodium perchlorate in glacial acetic acid.

Weston standard cell

Titration vessels. Borosilicate glass test-tubes (3 × 1 cm) were used in the potentiometric titrations, but for all other routine determinations the conventional submicro titration vessels were used.[1]

Reagents

Morpholine. Reagent grade

2-*Methoxyethanol.* Reagent grade

Acetic anhydride. Analytical reagent grade

Acetic acid solution. A 1:1 solution of glacial acetic acid (analytical reagent grade) in 2-methoxyethanol.

0·05% *Pyridine-*2*-azo-*p*-dimethylaniline solution.* 0·05 g of the solid indicator was dissolved in 100 ml of 2-methoxyethanol.

Diethyleneglycol dimethyl ether (diglyme). Reagent grade

Procedure A (where the addition product is basic; Table I)

Add 0·05 ml of morpholine from an Agla micrometer syringe to approximately 0·5 μequiv of the olefine, followed by 0·2 ml of 2-methoxyethanol and 0·05 ml of acetic acid solution. The time allowed for the addition reaction to reach completion depends on the reactivity of the olefine, but 30–90 min is generally sufficient. Then add 0·1 ml of acetic anhydride to acetylate the excess of reagent and allow 5 min for the reaction solution to cool to room temperature. Add 0·4 ml of 2-methoxyethanol together with 0·02 ml of the indicator solution and titrate with standard 0·01*M* perchloric acid to the first appearance of a purple colour. A simultaneous blank determination should be carried out.

Procedure B (where the addition product is neutral; Table II)

Add a measured excess of a standard morpholine solution in diethyleneglycol dimethyl ether to a measured amount of the olefine (approximately 0·5-1·0 μequiv) and then add a further 0·2 ml of diethyleneglycol dimethyl ether to the solution. Allow 0·5 hr for the reaction to reach completion, then add 0·4 ml of diethyleneglycol dimethyl ether together with 0·02 ml of indicator solution; titrate the excess of morpholine with the standard perchloric acid solution. A simultaneous blank determination should be carried out.

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Zusammenfassung—Olefine, die mit elektrophilen Reagentien nicht die normalen Additionsreaktionen eingehen, können mit dem nukleophilen Morpholin zu tertiären Aminen umgesetzt werden. Eine Submikromethode mit diesem Reagens wurde entwickelt. Ist das Additionsprodukt basisch, so wird es nach Acetylierung des überschüssigen Morpholins titriert; ist es neutral, so wird das überschüssige Morpholin titriert.

Résumé—Les oléfines qui ne subissent pas les réactions normales d'addition avec les réactifs électrophiles peuvent réagir avec le réactif nucléophile morpholine, pour former une amine tertiaire. On a élaboré une sub-micro-méthode utilisant ce réactif. Lorsque le produit d'addition est basique, on le dose après acétylation de l'excès de morpholine; lorsqu'il est neutre, on dose l'excès de morpholine.

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SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM(V) WITH BROMOPYROGALLOL RED

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Summary—Bromopyrogallol Red reacts with niobium(V) in a tartrate medium at pH 6·0 to form an intense blue coloured 3:1 reagent: metal complex ($\epsilon_{610\,m\mu} = 60{,}000$); the reaction is gelatin sensitised. In a medium made $10^{-2}M$ with respect to EDTA a 2:1 complex is formed and though the sensitivity decreases slightly ($\epsilon_{610\,m\mu} = 53{,}000$), the reaction becomes highly selective towards niobium. After the addition of masking agents to complex the few interfering ions, no interference is found from 1000-fold excesses of the 34 cations examined, including tantalum, tungsten, molybdenum, titanium, zirconium, beryllium and thorium, or from any of the common complexing anions, including phosphate and fluoride. The conditional stability constant for the 3:1 complex is $2{\cdot}7 \times 10^{18}$ and for the 2:1 complex, 1×10^{12}. The colour system is stable and reproducible and the proposed method seems to be the most sensitive visible-range spectrophotometric method so far proposed for niobium(V).

Bromopyrogallol Red has been shown recently to possess unique sensitivity and conditional selectivity as a spectrophotometric reagent for the determination of trace amounts of silver because of the formation of a ternary complex between 1,10-phenanthroline, Bromopyrogallol Red and silver ion in an acetate buffered medium at pH 5·8.[1] This blue ternary complex (λ_{max} 635, $\epsilon = 51{,}000$) has entirely different characteristics from the yellow coloured binary system between silver and Bromopyrogallol Red reported earlier by the same workers.[2] We have made a preliminary report[3] on the colour reaction between Bromopyrogallol Red (BPR) and niobium; the present paper gives a detailed account of our examination of the reaction.

Preliminary studies showed that the blue complex formed between niobium(V) and BPR in an acetate/tartrate medium (*ca.* pH 5·8) could be formed equally well in the presence or absence of a considerable excess of EDTA. This indicated that a method based on the use of BPR should be very selective. However, it was found that the colour systems were stable for maximal periods of only 10–20 min and various attempts were, therefore, made to achieve stabilisation. The addition of water-miscible solvents and of indifferent electrolytes showed no marked improvement, nor did variation of pH over the working range of the system. However, during these experiments it was observed that when the colour system was developed in a small volume before dilution to the mark, a much more intense colour was obtained, but that this colour was more unstable than that developed following immediate dilution. This suggested that the coloured complex was colloidal and the latter was further substantiated because the complex could be collected at the interface when the

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aqueous system was shaken up with water-immiscible solvents, such as benzene, carbon tetrachloride or chloroform. Because of the presence of sulphonic acid groups in the metallochrome it was not expected that either the BPR or its blue niobium complex would be extracted; this was confirmed. It is also relevant to note that in these early experiments the blue complex produced in aqueous media settled out on standing overnight and adhered to the walls of the glassware.

The above findings suggested that stabilisation could be achieved through the action of protective colloids. These can act in several ways, *e.g.*, by prevention of coagulation, if the system involves a suspensoid; by prevention of precipitation, if an insoluble compound is being formed from an initially 'soluble' species or by prevention of fading of such a system as it ages. In addition, Feigl[4] has noted a sensitisation effect whereby the colour of a system is enhanced or even the absorption band shifted to other wavelengths because of adsorption of a coloured complex on a protective colloid or *vice versa*.

In our initial experiments we used 1,10-phenanthroline because of its previous use[1] and because it is capable of producing the same effect as a protective colloid and is readily available in a pure state. Its addition resulted in complete stabilisation of the colour system, and fading no longer occurred on dilution. Furthermore, there was found to be considerable sensitisation. In the absence of EDTA, maximum colour development was achieved in 90 min and in its presence in 2 hr. A very slight further increase occurred overnight. In the process of establishing the optimum pH, time of development, *etc.*, it was found that the response of the system, at constant pH, was critically dependent on the nature of the buffer and on its concentration. The greatest sensitivity was achieved with an ammonium acetate buffer, and, for a given concentration of the latter, maximum absorbance for the niobium complex was found to occur in the range pH 5·8–6·6.

In an attempt to eliminate the variation of sensitivity with buffer concentration it was found that the use of gelatin instead of 1,10-phenanthroline overcame the problem completely. With gelatin, the optimum pH range was found to be 5·7–6·4. An ammonium acetate buffer at pH 6·0 was subsequently used in all other experiments. Variation of buffer concentration in the range 5–20 ml had no effect on the colour system. The optimum time for colour development was 90 min in the presence of EDTA and 75 min in its absence. Both solutions showed a small increase in absorbance overnight and after standing for several days the colour separated out as a blue precipitate. The order of addition of the gelatin appeared to be uncritical, but as a matter of routine it was added to the niobium test solution immediately after the other reagents. The recommended order of addition of reagents is EDTA, BPR, buffer, gelatin. In all subsequent work, the colour was allowed to develop for 90 min after addition of all the reagents, then the solution was diluted to 100 ml with water *after* this time had elapsed.

Fig. 1 shows the absorption spectra of BPR (A); of the same amount of reagent with $\frac{1}{3}$ mole proportion of niobium solution (B); with $\frac{1}{2}$ or 1 mole proportion of niobium (C) and spectrum (B) repeated in the presence of a 1000-fold excess of EDTA (D).

The formation of the 2:1, BPR:niobium complex proceeds with a bathochromic shift of the wavelength of maximum absorption in the visible region of the spectrum, (curves A → C in Fig. 1) and with a pronounced hyperchromic effect. On the basis of later evidence, *q.v.*, and the isosbestic point on Fig. 1 common to curves A, B and D, it may be assumed that a 3:1 complex (curve B) has been formed, but incompletely (shoulder at 610 mμ still present and indicative of the presence of some 2:1 complex and isosbestic point indicative of free reagent); curve D shows the breakdown of the 3:1 complex to give free reagent (maximum now back at 560 mμ) and the 2:1 complex (shoulder at 610 mμ now more pronounced).

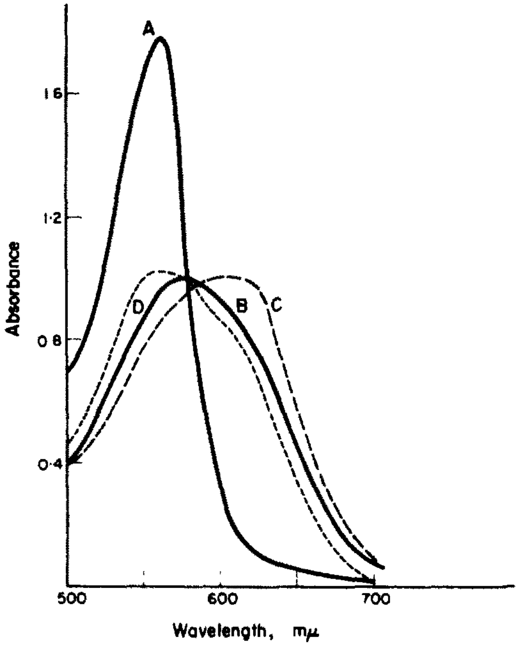


FIG. 1.—Absorption spectra of Bromopyragallol Red and its niobium(V) complexes at pH 6·0:

(A) 10 ml of $10^{-4}M$ BPR + 10 ml of buffer solution in 100 ml; 4-cm cuvettes against water.

(B) As (A) with addition of 3·33 ml of $10^{-4}M$ niobium(V) solution + 1 ml of 1% gelatin.

(C) As (A) with addition of 5·0 ml of $10^{-4}M$ niobium(V) solution + 1 ml of 1% gelatin.

(D) As (B) with addition of 10 ml of $10^{-1}M$ EDTA.

Obviously, the formation of the niobium complex of BPR may be followed by measurements at 560 mμ, the band maximum for the reagent, or at 610 mμ, the point of maximum divergence between the spectra of the complex and the BPR. All future measurements were made at the latter wavelength. The analytical potentiality of the procedure was checked against the Lambert-Beer law performance of the colour system (Fig. 2A). Straight-line calibration curves were obtained over the range 9–45 μg of niobium (0·09–0·45 ppm in final solution), but no attempt was made to establish the upper limit of the linear relationship [Fig. 2A, curve (i)]. A similar calibration curve was obtained in a $10^{-2}M$ EDTA medium [Fig. 2A, curve (ii)], from which it will be seen that there is only a slight reduction in sensitivity. From these curves, the molar absorptivity is $\epsilon_{610\,m\mu} = 60{,}000$ and in the presence of EDTA $\epsilon_{610\,m\mu}^{10^{-2}M\ EDTA} = 53{,}000$. The corresponding sensitivity indices are 0·0015 μg/cm^2 and 0·0017 μg/cm^2, respectively.

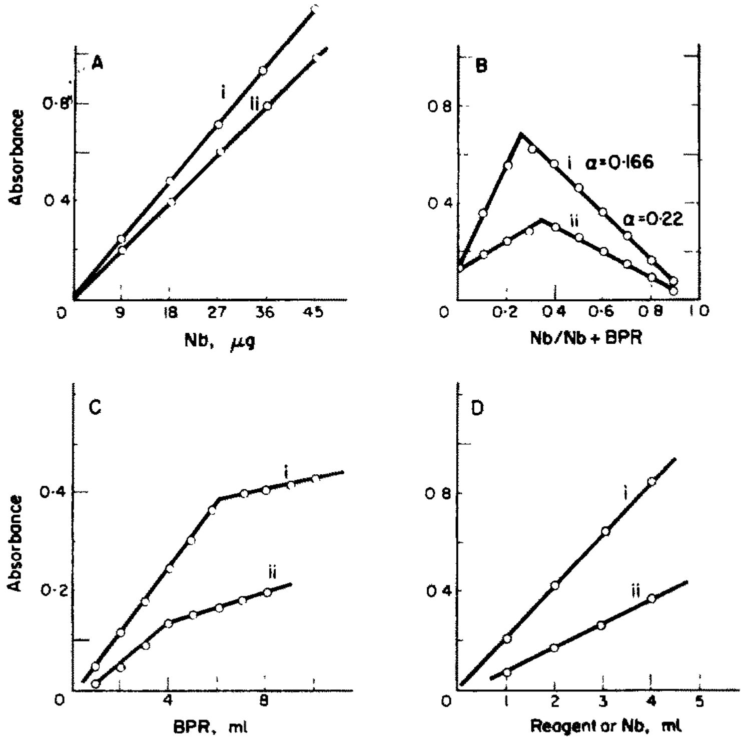


FIG. 2.

(A) *Calibration Curves:*

(i) 1–5 ml of $10^{-4}M$ niobium(V) solution + 10 ml of $2{\cdot}5 \times 10^{-4}$ M BPR + 10 ml of buffer solution + 1 ml of 1% gelatin in 100 ml; 4-cm cuvettes, 610 mμ against reagent blank.

(ii) As (i), but with addition of 10 ml of $10^{-1}M$ EDTA added before other reagents.

(B) *Continuous Variation Plots:*

(i) Total molar concentration of BPR + niobium(V) = 10 ml of $10^{-4}M$ solutions + 10 ml of buffer solution + 1 ml of 1% gelatin in 100 ml; 4-cm cuvettes, 610 mμ against water.

(ii) As (i), but with the addition of 10 ml of $10^{-1}M$ EDTA.

Both curves are uncorrected for reagent blank.

(C) *Mole-Ratio Plots:*

(i) 2 ml of $10^{-4}M$ niobium(V) solution + 10 ml of buffer solution + x ml of $10^{-4}M$ BPR + 1 ml of 1% gelatin in 100 ml; 4-cm cuvettes against x ml of BPR reagent blank at 610 mμ.

(ii) As (i), but in presence of 10 ml of $10^{-1}M$ EDTA + 5 ml of 10% potassium chloride solution.

(D) *Slope-Ratio Plot:*

Concentration of invariable component: 10 ml of $10^{-3}M$ solution; variable component: 1–4 ml of $10^{-4}M$ solution; buffer, EDTA and gelatin as before in 100 ml; 4-cm cuvettes at 610 mμ against water (niobium invariable) or same amount of BPR (BPR invariable).

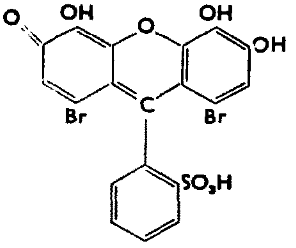
An examination of the data presented in Table I shows that BPR is considerably more sensitive than conventional reagents. Calibration curves are reproducible and, as will be shown subsequently, the proposed procedure is also more selective than most of the others.

TABLE I.—SENSITIVITY OF NIOBIUM REAGENTS

Reagent/masking medium	Molar absorptivity	Sensitivity index
BPR	$\epsilon_{610\,m\mu} = 60{,}000$	0·0015
BPR in $10^{-2}M$ EDTA	$\epsilon_{610\,m\mu} = 53{,}000$	0·0017
BPR in $10^{-2}M$ EDTA + 2% tartrate	$\epsilon_{610\,m\mu} = 47{,}500$	0·0018
PAR[5]	$\epsilon_{550\,m\mu} = 38{,}700$	0·0024
PAR in $2 \times 10^{-3}M$ EDTA[5]	$\epsilon_{550\,m\mu} = 35{,}600$	0·0026
PAR in $2 \times 10^{-3}M$ EDTA + 5%[5] tartrate[5]	$\epsilon_{550\,m\mu} = 23{,}500$	0·0039
Thiocyanate (acetone addition)[6]	$\epsilon_{385\,m\mu} = 35{,}000$	0·0027
Thiocyanate (ether extraction)[7]	$\epsilon_{385\,m\mu} = 32{,}400$	0·0029
Xylenol Orange[8]	$\epsilon_{535\,m\mu} = 16{,}000$	0·0058
8-Hydroxyquinoline[6]	$\epsilon_{385\,m\mu} = 10{,}000$	0·009
Tribromopyrogallol[9]	$\epsilon_{410\,m\mu} = 6{,}170$	—
Hydrogen peroxide[6]	$\epsilon_{340\,m\mu} = 892$	0·110

Composition of niobium-BPR complex

The niobium solutions used in this particular part of the work were prepared from a stock solution which had been standardised by a gravimetric *N*-benzoylphenylhydroxylamine procedure in which the precipitate is ignited to niobium pentoxide. The BPR reagent was assayed by potentiometric titration with sodium hydroxide solution. On the basis of its structure it should be possible to titrate the sulphonic acid proton and one of the phenolic protons; the other two phenolic protons are less readily removed because of strong hydrogen bonding to quinone oxygen atoms. This proved to be the case. An inflection occurred at 1·95 moles of base to 1 mole of reagent (*ca.* pH 7·5), giving a purity of *ca.* 98% for the reagent used in this work.



Bromopyrogallol Red (BPR)

Continuous variation plots showed a 3:1 BPR:Nb complex in the absence of EDTA [Fig. 2B (i)] and a 2:1 complex in a $10^{-2}M$ EDTA medium (*ca.*1000-fold excess) [Fig. 2B (ii)]. From Yoe and Jones mole-ratio plots similar evidence was obtained for 3:1 and 2:1 complexes in the absence [Fig. 2C (i)] and presence [Fig. 2C (ii)] of EDTA. In the latter instance no clear break was obtained on the curve except when the electrolyte concentration of the medium was increased (0·8*M* potassium chloride). Harvey-Manning slope-ratio plots (curve 2D) gave unequivocal evidence of the 2:1 BPR:niobium complex both in the absence and presence of EDTA, but showed no evidence of the 3:1 complex revealed clearly by the other two procedures. This evidence supports the thesis that the 2:1 complex is the strongest of the three possible complex species, but this aspect was not pursued further because both the previous methods and the absorption spectra (Fig. 1) show clear evidence in favour of the existence of the 3:1 species. Moreover, because BPR reacts with very many cations and still reacts with niobium in the presence of an excess of EDTA (Fig. 1, curve C), it is obvious that the analytically important species is the 2:1 complex, because the reagent would normally only be used in conjunction with EDTA as a mass-masking agent. Calculations of the degree of dissociation (α) of the two complexes from the continuous variations studies in Fig. 2B give conditional stability constants of $2{\cdot}7 \times 10^{18}$ for the 3:1 complex and 1×10^{12} for the 2:1 complex in the presence of $10^{-2}M$ EDTA.

These studies clearly reveal the stoichiometry of the colour body, but do not present any evidence of its physical nature. The only pertinent evidence available from this study is that the complex precipitates out readily from solution and is easily coagulated at the interface of water-immiscible solvent systems. This, despite the presence of sulphonic acid groups in the periphery of the organic reagent remote from the chelating centre of the molecule, is indicative of a colloidal body and suggests that an adsorption system, *i.e.*, lake formation, may be involved. This is further substantiated by: (a) the gelatin stabilisation and sensitisation of the colour system; (b) the observation of Feigl[10] that, *inter alia*, niobium is precipitated quantitatively by gelatin from an acid solution, and (c) the ease of destruction of the colour system by heat. Against this, it may be noted that the presence of indifferent electrolyte appears to favour colour formation, whereas it usually destroys adsorption compounds and additionally, the blue complex, though unstable, may be formed in the absence of gelatin. The definite 2:1 and 3:1 stoichiometry of the colour bodies also favours the view that a complex of definite composition is formed, which is of colloidal nature and stabilised by adsorption of gelatin, or by adsorption on gelatin. It is also to be concluded that EDTA possibly takes part in the stoichiometry of the 2:1 complex and the very beneficial effect of ammonium ions on the colour system may also be significant. The sensitivity of the colour reaction of BPR towards niobium(V) and insensitivity towards tantalum(V) suggests the probability that in these polyhydric phenol reagent complexes the visible region spectra produced by niobium may be caused by electron transfer reactions between niobium(V) and the phenol. The ease of reduction of niobium(V) relative to tantalum(V) may explain the lack of colour production with the latter.

It is concluded that the two adjacent phenol groups in BPR are involved in the complex formation because of the well known affinity of niobium for reagents containing vicinal phenolic groups, *e.g.*, pyrogallol, catechol, gallic acid. The possibility of complex formation through the $> \mathrm{C(OH)}{-}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}{-}$ group in the molecule also exists, but molecules containing this group, *e.g.*, 2,3,7-trihydroxy-9-phenyl-6-fluorone and 9-(*p*-dimethylaminophenyl)-2,3,7-trihydroxyfluorone, usually show a greater affinity for tantalum than for niobium: the BPR reagent shows little reactivity towards tantalum. From the evidence available the empirical compositions of the complexes are most probably $\mathrm{NbOY_3}^{3-}$ and $\mathrm{NbOY_2}^{-}$, where Y^{2-} represents the BPR molecule with its two readily dissociated protons removed. The entry of EDTA into the colour complex or association of the coloured anionic species with ammonium ions, is not precluded. An anionic complex is also suggested by its extractability into amine-containing solvents. This behaviour would not be expected from an adsorption compound of BPR on hydrated niobium pentoxide.

Interference studies

Because of the sensitivity of BPR towards many cations, the interference of various ions in the niobium method was examined in a medium which was $10^{-2}M$ with respect to EDTA. The anions examined at a 1000-fold g-ion excess relative to niobium level were citrate, cyanide, fluoride, oxalate, phosphate, sulphide and sulphite, *viz.*, those ions likely to be added as masking agents. Of these, only citrate produced a definite diminution in colour intensity (*ca.* 7%) and sulphide yielded a turbidity. Sulphide would not normally survive the processes by which niobium is brought into solution, and citrate only causes a slight diminution even when present in a 1000-fold excess, so that were its presence essential, it could be tolerated by incorporation of approximately similar amounts in the calibration solutions. Tartrate and acetate are, of course, present in the recommended procedure in considerable concentrations. The tolerance of the procedure towards fluoride and phosphate is noteworthy, particularly because it seems that they interfere in all the conventional spectrophotometric methods.

The cations examined at *ca.* a 1000-fold g-ionic excess relative to niobium included: aluminium, arsenic(III), barium, beryllium, bismuth, calcium, cadmium, cerium(III), cerium(IV), chromium(III), cobalt(II), copper(II), iron(II), iron(III), lanthanum, lead, magnesium, manganese(II), mercury(II), nickel, silver, strontium, thorium, tin(IV), uranium(VI), vanadium(V), zinc and zirconium. Of these cations, only aluminium, cerium(IV), silver, thorium, uranium(VI) and vanadium(V) caused interference. With bismuth and mercury(II) it was observed that colour development was slowed down considerably, but full recovery was, in fact, obtained after 4 hr. The addition of a small amount of ascorbic acid reduced the higher oxidation states of cerium and vanadium and they no longer interfered, whilst the addition of fluoride overcame the interference of aluminium and thorium. Phosphate addition similarly overcame the interference of 0·5–1 mg amounts of uranium(VI) and zirconium, and the addition of cyanide overcame the interference of silver.[1] Thus, the addition of reducing or masking agents removed the few interferences amongst the 29 cations first examined.

A second series of potential interfering cations was next examined in the realisation that these would be more difficult to overcome.[1] Those were antimony(V), molybdenum(VI), tantalum(V), titanium(IV) and tungsten(VI). All interfered seriously with the determination of *ca.* 18 μg of niobium when present in milligram amounts, although none of them showed much colour formation with BPR in the absence of gelatin. Several separation methods are available for the preliminary separation of niobium from these ions and, as will be described in a subsequent paper, the niobium -BPR complex itself can be extracted into di-n-octyl methylamine in amyl acetate, but a simpler expedient was simply to increase the tartrate concentration. We have already noted that the interference of large amounts of tantalum in the procedure using 4-(2-pyridylazo)-resorcinol (PAR) can be eliminated by the addition of a convenient concentration of tartrate.[5]

In the present instance with BPR, it was found that the presence of 2% w/v of ammonium tartrate in the final solution reduces the molar absorptivity $\varepsilon_{610\,\mathrm{m}\mu} = 60{,}000$ to $\epsilon_{610\,\mathrm{m}\mu}^{2\%\ \mathrm{tartrate}} = 49{,}000$ and in the EDTA medium from $\epsilon_{610\,\mathrm{m}\mu}^{10^{-3}M\ \mathrm{EDTA}} = 53{,}000$ to $\epsilon_{610\,\mathrm{m}\mu}^{10^{-3}M\ \mathrm{EDTA}/2\%\ \mathrm{tartrate}} = 47{,}500$. In the latter medium it was found that there was no interference from milligram amounts of any of these ions (*cf.* Table II).

TABLE II.—DETERMINATION OF NIOBIUM IN PRESENCE OF ANTIMONY AND SOME REFRACTORY METALS (*cf. Experimental* for conditions)

Interfering ion present	Absorbance
18 μg of Nb	0·380
18 μg of Nb + 1·5 mg of Mo^{VI}	0·375
18 μg of Nb + 2·5 mg of W^{VI}	0·380
18 μg of Nb + 1 mg of Ta^{V}	0·375
18 μg of Nb + 0·5 mg of Ti^{IV}	0·375
18 μg of Nb + 0·25 mg of Sb^{V}	0·380

Discussion of results

The proposed procedure (and sub-procedures) for niobium is completely free from the interference of 34 cations and 7 anions, almost all of which would be expected to interfere in some way with the colour system. In a few cases, which are noted in the recommended procedure, it is necessary to make addition of a soluble masking agent. The sensitivity and freedom from interference from elements usually associated with niobium provide an attractive procedure for the determination of trace amounts of niobium. The addition of tartrate to the extent of 2% eliminates the interference from milligram amounts of antimony and the refractory metals molybdenum, tantalum, titanium and tungsten, and although this reduces the sensitivity of the routine method by *ca.* 10%, it is still more sensitive than the other methods (*cf.* Table I). In addition to high sensitivity and selectivity, the method also maintains the excellent reproducibility and stability of colour system which are associated with the PAR procedure.[5] In contrast to the latter, however, it should be noted that the reagent formulation is subject to oxidation and for good reproducibility it should be prepared afresh every 7 days.

EXPERIMENTAL

Reagents

$10^{-4}M$ *Standard niobium*(V) *solution.* Fuse 0·266 g of niobium pentoxide (BDH Ltd., England) with 7·5 g of potassium hydrogen sulphate in a silica or porcelain crucible and extract the cooled melt with a boiling solution of 20 g of tartaric acid in water. Filter, cool and dilute to 1 litre with distilled water. Standardise the solution gravimetrically by precipitation of niobium *N*-benzoylphenylhydroxylaminate and ignition to Nb_2O_5.[11] From this stock solution transfer the calculated amount required for 1 litre of $10^{-4}M$ niobium (V) solution (*ca.* 50 ml) to a beaker. Add 20 g of tartaric acid and neutralise to pH 5·8–6·4 (pH paper). Allow to cool, transfer to a 1-litre flask and dilute to volume with distilled water:

1 ml of $10^{-4}M$ niobium(V) solution = 9·29 μg of niobium.

$2{\cdot}5 \times 10^{-4}M$ *Bromopyrogallol Red solution.* Dissolve 0·1396 g of Bromopyrogallol Red (BDH Ltd., England) in 500 ml of absolute ethanol and dilute to 1 litre with water. *This solution is best prepared afresh every 7 days.*

Buffer solution (*pH* 6·0). Dissolve 80 g of analytical reagent grade ammonium acetate in water, treat with 6 ml of glacial acetic acid and dilute to 1 litre.

$10^{-1}M$ *EDTA solution.* Dissolve 37·225 g of EDTA (disodium salt dihydrate) in 1 litre of water.

1% *Gelatin solution.* Dissolve 1 g of gelatin in warm water and, after cooling, dilute to 100 ml.

Apparatus

Unicam SP 600 spectrophotometer operated from a 12-V transformer; 4-cm cuvettes.

Calibration curve

Transfer 1–5 ml aliquots of $10^{-4}M$ niobium(V) solution to 100-ml standard flasks, add 10 ml of $10^{-1}M$ EDTA, 10 ml of $2{\cdot}5 \times 10^{-4}M$ BPR reagent, 10 ml of buffer solution and 1 ml of 1% gelatin. Do *not* dilute the mixture at this stage, but allow to stand for 90 min before doing so. Measure the absorbance of the niobium-containing solutions against a reagent blank, similarly prepared but containing no niobium, in 4-cm cuvettes at 610 mμ.

Procedure

Take an aliquot of niobium solution, containing 45 μg of niobium, in 2% tartaric acid and nearly neutralised with sodium hydroxide to pH 5·7–6·6, and determine the niobium content by the procedure described above under *Calibration curve*.

Special precautions

In the presence of cerium(IV) or vanadium(V), add sufficient solid ascorbic acid to reduce them to cerium(III) or vanadium(IV).

In the presence of aluminium or thorium, add 5 ml of $0{\cdot}2M$ sodium fluoride. This will cater for up to milligram amounts of these ions. In the presence of uranium(VI) or zirconium (up to 1 mg), add 5 ml of a $0{\cdot}1M$ solution of sodium phosphate; in the presence of silver add sufficient of a 1% solution of cyanide. There is no need to modify the calibration curve procedure for any of these additions. Care must, however, be taken not to exceed the capacity of the buffer when dealing with solutions of hydrolysable metals.

In the presence of milligram amounts of tantalum, titanium, tungsten(VI), molybdenum(VI) or antimony(V), use the above procedure, but add 10 ml of 20% ammonium tartrate before the addition of the BPR reagent. In this instance it is necessary to add a similar amount of ammonium tartrate to the solutions from which the calibration curve is made.

Résumé—Le rouge de bromopyrogallol réagit avec le niobium (V) en milieu tartrique à pH 6,0 pour former un complexe réactif: métal 3:1 intensément coloré en blue ($\epsilon_{610\ m\mu} = 60000$); là réaction est sensibilisée à la gélatine. Dans un milieu 10^{-2}M en EDTA, il se forme un complexe 2:1 et, quoique la sensibilité décroisse légèrement ($\epsilon_{610\ m\mu} = 53000$), la réaction devient hautement sélective du niobium. Après addition d'agents dissimulants pour complexer les quelques ions interférants, on n'a pas trouvé d'interférence avec des quantités 1000 fois plus élevées des 34 cations examinés, comprenant les tantale, tungstène, molybdène, titane, zirconium, beryllium et thorium. Les anions complexants communs, y compris phosphate et fluorure, n'interfèrent également pas. La constante de stabilité du complexe 3:1 est $2{,}7 \times 10^{18}$ et celle du complexe 2:1, 1×10^{12}, dans les conditions données. Le système coloré est stable et reproductible, et la méthode proposée semble être, dans le visible, la méthode spectrophotométrique la plus sensible proposée jusqu'à présent pour le niobium (V).

Zusammenfassung—Brompyrogallolrot reagiert mit Niob(V) in Tartratmedium bei pH 6,0 zu einem intensiv blauen 3:1-Reagens: Metall-Komplex ($\epsilon_{610\ m\mu} = 60000$). Die Reaktion wird durch Gelatine sensibilisiert. In einem Medium mit 10^{-2}M EDTA wird ein 2:1-Komplex gebildet. Obwohl die Empfindlichkeit schwach abnimmt ($\epsilon_{610\ m\mu} = 53000$), wird die Reaktion hochselektiv für Niob. Nach Zugabe von Maskierungsmitteln, um die wenigen störenden Ionen komplex zu binden, stören weder 1000-fache Überschüsse der 34 untersuchten Kationen, darunter Tantal, Wolfram, Molybdän, Titan, Zirkon, Beryllium und Thorium, noch die häufigsten komplexbildenden Anionen, darunter Phosphat und Fluorid. Unter den angegebenen Bedingungen ist die Stabilitätskonstante des 3:1-Komplexes $2{,}7 . 10^{18}$, die des 2:1-Komplexes $1 . 10^{12}$. Die Färbung ist stabil und reproduzierbar; die vorgeschlagene Methode ist offenbar die empfindlichste, die bisher im sichtbaren Bereich für Niob(V) vorgeschlagen wurde.

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SHORT COMMUNICATIONS

Analysis of metal chelates—IV:* Simultaneous polarographic determination of metals and 8-hydroxyquinoline in metal 8-hydroxyquinolates

(*Received* 11 *November* 1964. *Accepted* 14 *March* 1965)

INORGANIC ions and organic substances are usually determined independently by d.c. or a.c. polarographic methods. The authors are attempting to determine inorganic and organic substances simultaneously by polarography,[1-6] and in the present investigation have studied the determination of the metal and 8-hydroxyquinoline contents of various metal 8-hydroxyquinolates.

8-Hydroxyquinoline has been widely used for the gravimetric determination of metals, but it reacts with many metallic ions and the precipitates to be examined are apt to be contaminated with foreign ions. We have determined the contents of cadmium, copper, zinc, lead, bismuth, nickel and 8-hydroxyquinoline in the 8-hydroxyquinolates of these metals, in order to investigate the extent of coprecipitation. Various methods have been published for the polarographic determination of these metals, and a few reports on the polarography of 8-hydroxyquinoline have appeared, but these have mainly referred to the determination of metal ions.

EXPERIMENTAL

Reagents

All chemicals used were analytical reagent grade. Solutions of cadmium, copper zinc, lead and bismuth at about $0{\cdot}1M$ concentration were prepared from suitable salts and standardised by EDTA titration. A 2% solution of 8-hydroxyquinoline in ethyl alcohol was used.

Apparatus

An a.c. polarograph (model PA-102, Yanagimoto Co., Kyoto, Japan) was used. This type of a.c. polarograph was developed using the principle of the bridge polarograph.[4]

Procedure

The precipitation of the metal 8-hydroxyquinolates was carried out according to a conventional gravimetric procedure[7] as follows. Aliquots of each metal solution were transferred to 200-ml beakers and diluted with water to about 100 ml. Four g of sodium acetate trihydrate were added to the cadmium solution, 1 ml of $6M$ acetic acid and 5 g of sodium acetate trihydrate to the copper solution, 1 ml of $6M$ acetic acid and 4 g of sodium acetate trihydrate to the zinc solution, 3 ml of $1M$ sodium citrate solution and 2 g of sodium acetate trihydrate to the lead solution followed by the addition of $2M$ sodium hydroxide solution to adjust the pH to about 10, and 2 ml of $6M$ acetic acid, 1 g of sodium citrate and 6 g of sodium acetate trihydrate added to the bismuth solution. After heating these solutions to 60°, 8-hydroxyquinoline solution equivalent to twice the quantity of each metal was added with continuous stirring. The precipitates were filtered on sintered glass filters and washed with boiling water.

All the precipitates except the lead complex were dissolved in 20 ml of $2M$ hydrochloric acid; lead 8-hydroxyquinolate was dissolved in a mixture of 20 ml of $2M$ hydrochloric acid and 10 ml of $1M$ sodium citrate. To the solutions of cadmium, copper and zinc 8-hydroxyquinolates 10 ml of $1M$ sodium citrate and 5 ml of concentrated phosphoric acid (sp. gr. $1{\cdot}71$) were added and the solutions diluted with water to 250 ml in volumetric flasks. To the solution of lead 8-hydroxyquinolate 5 ml of concentrated phosphoric acid were added followed by dilution with water as described above. To the solution of bismuth 8-hydroxyquinolate 10 ml of $1M$ sodium citrate solution were added followed by dilution. A portion of each solution was transferred to a polarographic cell and dissolved

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* Part III: *Talanta*, 1965, **12**, 179.

oxygen removed by passing purified hydrogen through the solution for 10 min. Metals and 8-hydroxyquinoline were determined by a.c. polarography in the voltage range 0 to −2·0 V *vs.* the mercury pool at 25°.

RESULTS AND DISCUSSION

Polarography of cadmium, copper, zinc, lead, bismuth and 8-hydroxyquinoline

About 30 mg of each metal were precipitated and the metals and 8-hydroxyquinoline determined by a.c. polarography as mentioned above. The polarograms obtained are shown in Fig. 1. Cadmium, copper, lead and bismuth, which are reduced reversibly, give well-defined a.c. polarographic waves which are separated from each other except in the case of copper and bismuth. 8-Hydroxyquinoline gives an a.c. polarographic wave at a higher potential, and which can be measured separately from the waves of the metal ions. The a.c. polarographic wave of 8-hydroxyquinoline corresponds to the A wave of 8-hydroxyquinoline studied by Stock and may represent reduction to the dihydro compound.[5] The wave also corresponds to the first wave reported by Carruthers[1] and by Stone and Furman;[2] the corresponding d.c. polarographic wave has been used to determine 8-hydroxyquinoline.[1-3] In general, the a.c. polarographic waves obtained from irreversible systems are comparatively small and broad.[6] The wave of 8-hydroxyquinoline is very small and broad in comparison with the waves of the metal ions, as shown in Fig. 1, so that it would appear that the reduction of 8-hydroxyquinoline is irreversible at the dropping mercury electrode. The wave can, however, still be used for the determination of 8-hydroxyquinoline as described below.

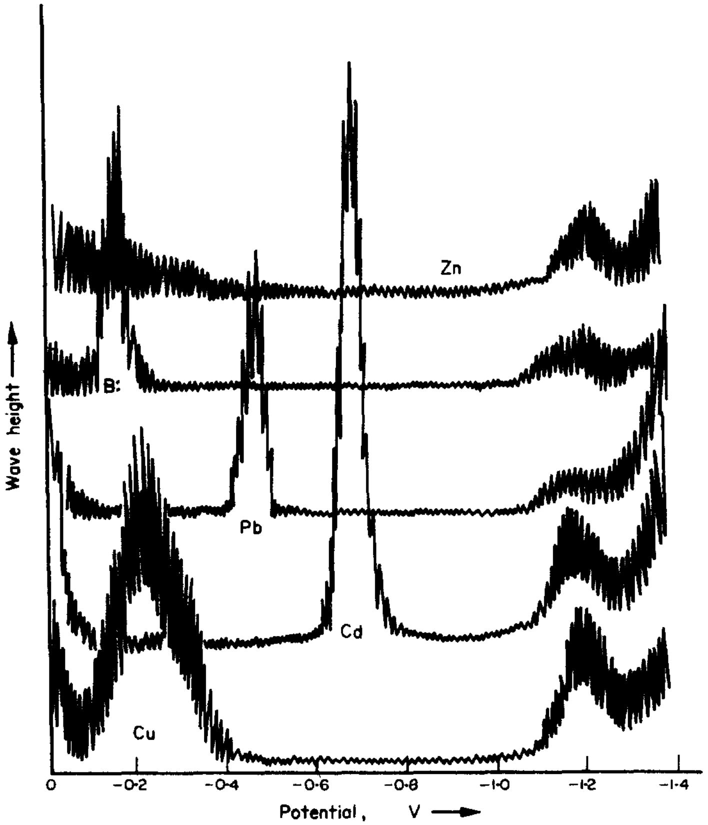

FIG. 1.—A.C. polarograms of bismuth, cadmium, copper, lead, zinc and 8-hydroxyquinoline.

The summit potentials of the a.c. polarograms obtained are shown in Table I.

The cadmium, copper, lead and bismuth solutions were buffered to pH values of 0·30, 0·30, 0·50 and 1·00, respectively. The summit potential of 8-hydroxyquinoline varied with pH, and moved to higher potentials with increasing pH.

The solution obtained from zinc 8-hydroxyquinolate gave only one wave (Fig. 1). When zinc solution was added to this solution the height of the wave did not change, but when 8-hydroxyquinoline was added the wave height increased. It appears that the polarographic wave is due only to 8-hydroxyquinoline. In pure solution the zinc wave appeared at −1·13 V in the supporting electrolyte used; it is suggested that a complex is formed between zinc and 8-hydroxyquinoline in the supporting electrolyte used. Nickel behaved in the same way as zinc. These effects will be studied later.

TABLE I.—SUMMIT POTENTIALS OF A.C. POLAROGRAMS.

Reducible species	Summit potential *V*
Cadmium	−0·67
Copper	−0·22
Lead	−0·47
Bismuth	−0·18
8-Hydroxyquinoline	−1·13 to −1·20

In the present work calibration curves for cadmium, copper and 8-hydroxyquinoline have been plotted. The heights of the waves for cadmium, copper and 8-hydroxyquinoline were linearly proportional to concentration in the range 1–16 mg of cadmium, 5–25 mg of copper and 2–100 mg of 8-hydroxyquinoline in 250 ml of the final solution, respectively.

By means of the method described, metal ions and 8-hydroxyquinoline in metal 8-hydroxyquinolate can be determined simultaneously by a.c. polarography.

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Summary—Studies of the simultaneous determination of metal and 8-hydroxyquinoline in metal 8-hydroxyquinolates have been made by a.c. polarography, after precipitation of the chelates by a conventional procedure and re-solution in a suitable medium. Cadmium, copper, lead and bismuth may be determined, together with 8-hydroxyquinoline but the zinc peak cannot be distinguished from that of the 8-hydroxyquinoline under the conditions employed. Some aspects of the results are discussed.

Zusammenfassung—Die gleichzeitige Bestimmung von Metall und 8-Hydroxychinolin in Metall-8-hydroxychinolaten wurde wechselstrompolarographisch untersucht. Die Chelate wurden dabei auf herkömmliche Weise gefällt und in einem geeigneten Medium wieder gelöst. Cadmium, Kupfer, Blei und Wismut können zusammen mit 8-Hydroxychinolin bestimmt werden; der Zink-Peak kann unter den verwendeten Bedingungen nicht von dem des 8-Hydroxychinolins unterschieden werden. Die Ergebnisse werden unter einigen Gesichtspunkten diskutiert.

Résumé—On a étudié, par polarographie en courant alternatif, le dosage simultané du métal et de la 8-hydroxyquinoléine dans les 8-hydroxyquinoléinates métalliques, après précipitation des chélates par une technique usuelle, et remise en solution dans un milieu convenable. Le cadmium, le cuivre, le plomb et le bismuth peuvent être dosés avec la 8-hydroxyquinoléine, mais le sommet du zinc ne peut être distingué de celui de la 8-hydroxyquinoléine dans les conditions utilisées. On discute de quelques aspects des résultats.

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Applications de la chelatométrie—XVII:* Dosage volumétrique des ions argent par réduction a l'état élémentaire

(*Reçu le* 1 *fevrier* 1965. *Accepté le* 14 *mars* 1965)

On sait que la constante de stabilité du composé formé entre l'E.D.T.A et les ions Argent-I n'atteint que 7,3 et, de ce fait, est trop faible pour permettre un dosage chélatométrique direct de ces ions. Les procédés indirects sont fort peu nombreux; le principal d'entre eux consiste dans la libération d'ions nickel-II à partir du complexe tétracyano-nickelique de façon à permettre le titrage de ces ions libérés en présence de murexide comme indicateur; ce procédé, dû à Flaschka et Huditz,[4,5] a été appliqué notamment au dosage de l'argent dans les alliages cuivreux[1] et dans les films photographiques,[13] et au dosage indirect des halogénures,[4,5] des iodures en présence de chlorures,[24] du brome organique[16,19] et de l'arsenic organique.[25] Nous l'avons utilisé nous-mêmes pour l'évaluation des halogènes organiques,[8,9] de la mercaptopurine,[11] des sulfamides,[10] et des vic-polyols; il est à remarquer, toutefois, que le virage n'est pas toujours facile à saisir avec netteté et cette observation a conduit Gedansky et Gordon[6] à utiliser une lecture photométrique tout en conservant la murexide, et Klein et Skřivánek[23] à remplacer cet indicateur par la thymolphtalexone en présence d'un peu de jaune de diméthyle.

Une méthode chélatométrique récente emploie une suspension de diéthyl-dithiocarbamate de cuivre;[12] les ions-cuivre-II mis en solution sont mesurés aprés filtration. Cabrera et West[29] ont dosé les sels d'argent en direct au moyen des acides thioglycolique, β-mercaptopropionique, ou mercaptosuccinique; la *p*-diméthylamino–benzalrhodanine peut être utilisée comme indicateur en présence de xylène-cyanol qui facilite la perception du virage; les mesures potentiométriques avec une électrode indicatrice d'argent donnent de très bons résultats.

Les modes de réduction des ions Argent–I en argent élémentaire sont nombreux; si on utilise un agent réducteur minéral, on peut envisager le dosage d'un excès de ce réactif ou celui du composé oxydé obtenu après réaction. En 1953, Přibil, Doležal et Simon[17] avaient utilisé le caractère réducteur du complexe ferreux de l'E.D.T.A.; le point final était observé par ampérométrie ou par potentiométrie. Les sels manganeux, en milieu alcalin, constituent un réactif convenable pour les ions Argent-I,[26] et nous avons essayé d'utiliser le complexe manganeux de l'E.D.T.A. dans le but de mesurer la quantité d'E.D.T.A. libérée après précipitation du bioxyde de manganèse; mais ce réactif, en milieu alcalin, s'est révélé beaucoup trop sensible vis-à-vis de l'oxygéne atmosphérique pour être utilisable d'une manière pratique.

La réduction par les métaux alcalins[2] est bien connue, de même que celle obtenue par le cadmium; le zinc, l'aluminium,[27] le plomb,[13] le bore[15] et l'oxyde cuivreux;[18] l'isolement de l'argent par le zinc est quantitatif et peut être utilisé pour une séparation analytique;[14] Senderens,[20–22] dit que le poids de réducteur employé ne correspond pas à celui de l'argent précipité de son nitrate et ce, par suite d'une légère réduction de l'anion nitrique; Doležal et Žýka[3] ont néanmoins décrit tout récemment une technique utilisant les amalgames de zinc ou de bismuth avec titrage des ions zinc-II ou bismuth-III formés après réaction. Nous avons essayé l'action des métaux seuls dans les mêmes conditions et avons finalement obtenu des résultats satisfaisants avec le cuivre.

PARTIE EXPERIMENTALE†

Réactifs utilisés

Cuivre. Nous avons choisi ce métal sous la forme de fil d'une épaisseur de 0,1 mm; pour l'emploi, le fil était coupé en longueurs d'environ 5 mm.

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† Avec la collaboration de Michel Berteleau (Ecole Superieure de Chimie de Paris)

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ON sait que la constante de stabilité du composé formé entre l'E.D.T.A et les ions Argent-I n'atteint que 7,3 et, de ce fait, est trop faible pour permettre un dosage chélatométrique direct de ces ions. Les procédés indirects sont fort peu nombreux; le principal d'entre eux consiste dans la libération d'ions nickel-II à partir du complexe tétracyano-nickelique de façon à permettre le titrage de ces ions libérés en présence de murexide comme indicateur; ce procédé, dû à Flaschka et Huditz,[4,5] a été appliqué notamment au dosage de l'argent dans les alliages cuivreux[1] et dans les films photographiques,[13] et au dosage indirect des halogénures,[4,5] des iodures en présence de chlorures,[24] du brome organique[16,19] et de l'arsenic organique.[25] Nous l'avons utilisé nous-mêmes pour l'évaluation des halogènes organiques,[8,9] de la mercaptopurine,[11] des sulfamides,[10] et des vic-polyols; il est à remarquer, toutefois, que le virage n'est pas toujours facile à saisir avec netteté et cette observation a conduit Gedansky et Gordon[6] à utiliser une lecture photométrique tout en conservant la murexide, et Klein et Skřivánek[28] à remplacer cet indicateur par la thymolphtalexone en présence d'un peu de jaune de diméthyle.

Une méthode chélatométrique récente emploie une suspension de diéthyl-dithiocarbamate de cuivre;[12] les ions-cuivre-II mis en solution sont mesurés aprés filtration. Cabrera et West[29] ont dosé les sels d'argent en direct au moyen des acides thioglycolique, β-mercaptopropionique, ou mercapto-succinique; la *p*-diméthylamino–benzalrhodanine peut être utilisée comme indicateur en présence de xylène-cyanol qui facilite la perception du virage; les mesures potentiométriques avec une électrode indicatrice d'argent donnent de très bons résultats.

Les modes de réduction des ions Argent–I en argent élémentaire sont nombreux; si on utilise un agent réducteur minéral, on peut envisager le dosage d'un excès de ce réactif ou celui du composé oxydé obtenu après réaction. En 1953, Přibil, Doležal et Simon[17] avaient utilisé le caractère réducteur du complexe ferreux de l'E.D.T.A.; le point final était observé par ampérométrie ou par potentiométrie. Les sels manganeux, en milieu alcalin, constituent un réactif convenable pour les ions Argent-I,[26] et nous avons essayé d'utiliser le complexe manganeux de l'E.D.T.A. dans le but de mesurer la quantité d'E.D.T.A. liberée après précipitation du bioxyde de manganèse; mais ce réactif, en milieu alcalin, s'est révélé beaucoup trop sensible vis-à-vis de l'oxygéne atmosphérique pour être utilisable d'une manière pratique.

La réduction par les métaux alcalins[2] est bien connue, de même que celle obtenue par le cadmium; le zinc, l'aluminium,[27] le plomb,[13] le bore[15] et l'oxyde cuivreux;[18] l'isolement de l'argent par le zinc est quantitatif et peut être utilisé pour une séparation analytique;[14] Senderens,[20–22] dit que le poids de réducteur employé ne correspond pas à celui de l'argent précipité de son nitrate et ce, par suite d'une légère réduction de l'anion nitrique; Doležal et Zýka[3] ont néanmoins décrit tout récemment une technique utilisant les amalgames de zinc ou de bismuth avec titrage des ions zinc-II ou bismuth-III formés après réaction. Nous avons essayé l'action des métaux seuls dans les mêmes conditions et avons finalement obtenu des résultats satisfaisants avec le cuivre.

PARTIE EXPERIMENTALE†

Réactifs utilisés

Cuivre. Nous avons choisi ce métal sous la forme de fil d'une épaisseur de 0,1 mm; pour l'emploi, le fil était coupé en longueurs d'environ 5 mm.

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* Article précédent: *Talanta*, 1965, **12**, 420.

† Avec la collaboration de Michel Berteleau (Ecole Superieure de Chimie de Paris)

Tampon (pH-8). 54 g de chlorure d'ammonium sont dissous dans 800 ml d'eau distillée; de l'ammoniaque est ajouté jusqu'à ce que la solution accuse un pH égal à 8; le tout est complété à un litre.

Murexide. 75 mg sont dissous dans 50 ml d'éthylène-glycol; cette solution reste stable pendant plusieurs semaines.

0,01*M* E.D.T.A. 3,7 g d'éthylène diamino-tétracétate disodique sont dissous dans l'eau distillée en complétant à un litre. On détermine la molarité exacte à partir d'un poids connu de magnésium en utilisant le noir ériochrome T comme indicateur.

Mode opératoire

La solution contenant le sel d'argent doit être neutre (pH 5,5 à 6,0). Si besoin est, la neutralisation pourra être faite au moyen d'une solution de carbonate de potassium. 20 ml de solution, contenant 0,2 à 1 mmole d'argent, sont introduits dans une fiole jaugée de 100 ml; on ajoute 250 mg environ de cuivre, bouche la fiole et agite énergiquement pendant quinze minutes. Le contenu de la fiole est complété à 100 ml au moyen deau distillée fraîchement bouillie et la fiole est abandonnée pendant quelques minutes pour permettre à la plus grande partie de l'argent réduit de se déposer;† 50 ml du liquide surnageant sont prélevés au moyen d'une pipette et introduits dans une fiole d'Erlenmeyer; on ajoute 100 ml environ d'eau distillée; 20 ml de Tampon pH-8 et une quantité de murexide juste suffisante pour obtenir une légère coloration jaune plus ou moins verdâtre.

Ajouter la solution d'E.D.T.A. 0,01*M* au moyen d'une burette jusqu'au virage de l'indicateur; on peut utiliser une burette de 25 ml graduée en 0,05 ml pour une teneur en argent supérieure à 40 mg et une burette de 10 ml graduée en 0,02 ml pour une teneur inférieure; le virage a lieu du jaune au violacé en passant par une teinte grisâtre que nous avons choisie comme point final du dosage.

Le nombre de milligrammes d'argent contenu dans l'échantillon dosé est donné par la formule:

$$p = 431{,}5 \times V \times N'$$

V = nombre de millilitres de solution d'E.D.T.A.,
N′ = molarité exacte de cette solution.

TABLEAU I

nombre de mg d'argent présent	nombre de mg d'argent trouvé	Rapport, %	Déviation, %
21,575	21,61	100,16	+0,16
53,94	53,71	99,57	−0,43
—	53,55	99,28	−0,72
75,52	75,95	100,57	+0,57
—	75,66	100,18	+0,18
107,88	107,56	99,70	−0,30
—	108,20	100,30	+0,30
—*	107,62	99,76	−0,24
—*	108,26	100,36	+0,36

* Réduction effectuée en présence de 4 mmoles de nitrate de potassium.

Résultats obtenus

La présente technique a été experimentée sur des volumes de solutions 0,1*M* et 0.02*M* de nitrate d'argent contenant 0,2 à 1 millimole; les résultats obtenus sont réunis dans le tableau I.

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CLAUDE HENNART

Résumé—Les ions argent—I sont réduits quantitativement par le cuivre élémentaire; les ions Cuivre—II formés sont dosés, sans filtration, au moyen dé l'E.D.T.A. avec la murexide comme indicateur.

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† La présence de petites quantités d'argent réduit en suspension ne perturbe pas le dosage mais une trop forte quantité peut gêner la perception du virage. On pourra vérifier sur quelques millilitres du liquide, l'absence d'argent par l'addition d'une goutte d'acide chlorhydrique.

Summary—Silver(I) ions are determined *via* their quantitative reduction with elemental copper; the copper(II) ions formed are titrated, without filtration, by EDTA using Murexide as indicator.

Zusammenfassung—Silber(I) wird über die quantitative Reduktion mit elementarem Kupfer bestimmt; das gebildete Kupfer(II) wird ohne Filtration mit EDTA und Murexid als Indikator titriert.

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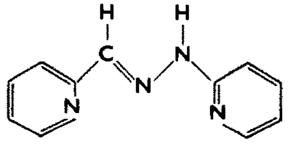
Spectrophotometric determination of palladium with pyridine-2-aldehyde-2-pyridylhydrazone

(*Received* 12 *February* 1965. *Accepted* 18 *March* 1965)

MANY analytical procedures using an organic reagent have been devised for the determination of palladium and the wide range of reagents available has been the subject of several recent reviews.[1-3]

There are increasing applications for thiophene and pyridine derivatives in the analysis of metals. For example, in the case of palladium, 2-thiophene aldoxime has been used for its gravimetric analysis[4] and the oximes, phenyl-2-pyridyl ketoxime[5] and 2-pyridine aldoxime[6] for its spectrophotometric determination.

Metal complexes of the tridentate ligand pyridine-2-aldehyde-2-pyridylhydrazone, (PAPHY),



I

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Zusammenfassung—Silber(I) wird über die quantitative Reduktion mit elementarem Kupfer bestimmt; das gebildete Kupfer(II) wird ohne Filtration mit EDTA und Murexid als Indikator titriert.

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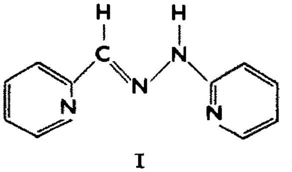
Metal complexes of the tridentate ligand pyridine-2-aldehyde-2-pyridylhydrazone, (PAPHY),



I

I, have been prepared by Lions and his coworkers in the course of extensive studies on the chelating properties of multidentate ligands.[7,8] It was pointed out[8] that the co-ordination of PAPHY to a metal ion increases the acidic character of the hydrogen attached to the nitrogen of the hydrazine residue with the result that this is readily detached as a proton. The interaction between PAPHY and a transition metal ion generally produces a coloured cationic complex which, on treatment with alkali, is converted by loss of a proton to a neutral, water-insoluble species. The possible analytical applications have been discussed.[10] Therefore, there is the possibility of using this type of chelate for the gravimetric and spectrophotometric determination of palladium over different ranges of pH.

In the present investigation, the complexes of palladium and PAPHY have been studied and the experimental conditions determined for their use in the analysis of palladium.

EXPERIMENTAL

Apparatus

Spectrophotometers. Spectra were measured on the Optika Recording Spectrophotometer. Absorbance measurements at a particular wavelength were made on the Unicam SP 500 Spectrophotometer.

Pye Universal pH Meter

Reagents

Palladium solutions. A standard palladium solution, $9{\cdot}4 \times 10^{-3}M$, was prepared by dissolving 417 mg of palladium chloride in 25 ml of 6*M* hydrochloric acid and diluting to 250 ml. A $3{\cdot}76 \times 10^{-4}M$ solution, containing 40 ppm of palladium, was prepared by 25-fold dilution of the standard solution.

Pyridine-2-aldehyde-2-pyridylhydrazone. Pyridine-2-aldehyde-2-pyridylhydrazone was prepared by the reaction in ethanolic solution between equimolar quantities of redistilled pyridine 2-aldehyde and 2-pyridylhydrazine. The latter was made by reaction between 2-chloropyridine and hydrazine.[11] PAPHY was recrystallised from ethanol to constant melting-point (179°). The reagent is commercially available from the Aldrich Chemical Co. Inc., Milwaukee, 10, Wisconsin, U.S.A. A solution of PAPHY was prepared by dissolving the required weight in ethanol. The ethanolic solution showed no decomposition after 1 week and the solid appeared to be stable indefinitely.

Other solutions. These were all prepared from reagent grade chemicals.

Ethanol. Reagent grade

RESULTS

Palladium complex of pyridine-2-aldehyde-2-pyridylhydrazone

A deep-red sparingly soluble complex is formed over the pH range 1–4 when 15 ml of an ethanolic solution of PAPHY containing 0·15 g of reagent is added to 100 ml of palladium(II) chloride solution containing 0·0417 g of palladium chloride (a molar ratio of 3:1) and the pH adjusted by the addition of hydrochloric acid or sodium hydroxide.

Analysis of the complex showed: C, 38·00; H, 3·00; N, 14·95; Cl, 11·22; Pd, 30·73%;
$Pd(C_{11}N_4H_9Cl)$ requires: C, 38·95; H, 2·65; N, 16·5; Cl, 10·5; Pd, 31·4%.

Spectrophotometric Studies

The absorption spectra of a series of solutions, obtained by mixing equal volumes of 35·8 ppm of PAPHY and 5·3 ppm of palladium(II) chloride to give a molar ratio of 6:1 and buffered to various pH values, were measured. These are characterised by a broad absorption band in the visible region with λ_{max} varying between 510 and 540 mμ (Fig. 1). The reagent itself in ethanolic solution shows no absorption at this wavelength and so the absorbance at 520 mμ can be used as a measure of the palladium present.

The absorbance varied with pH, reaching a maximum at pH values between 11·5 and 11·8. Beer's Law is obeyed over the range 0·8–9·6 ppm of palladium at pH 11·6. The range of most accurate measurement is 2·0–9·6 ppm palladium. The colour is fully developed 2 min from the time of mixing and remains constant for at least a further 30 min. Some slight decrease in absorbance may occur if the solution is allowed to stand for longer periods.

The composition of the coloured complexes in solution at pH 11·6 and 4 was determined both by Job's method of continuous variation and the mole ratio method. Fig. 2 shows the Job plots obtained from measurements at 510 mμ. Absorbance measurements at 470 and 550 mμ confirmed that at both pH values the ratio of ligand molecules to metal ions is 1:1. From this, the molar absorptivity of the complex at 520 mμ and at pH 11·6 was found to be 13,960.

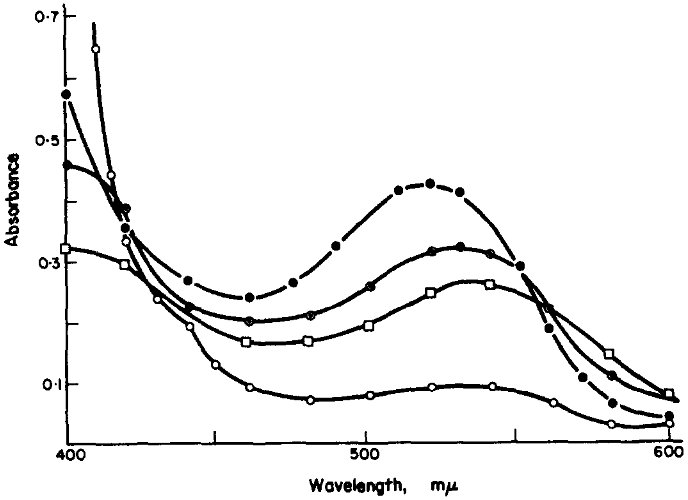


Fig. 1.—Absorption spectra of the palladium complex of pyridine-2-aldehyde-2-pyridylhydrazone in aqueous solutions of varying pH (concentration of complex, 8·01 × $10^{-5}M$):

○ pH = 1·7 ○ pH = 4·7 □ pH = 8·3 ● pH = 11·6.

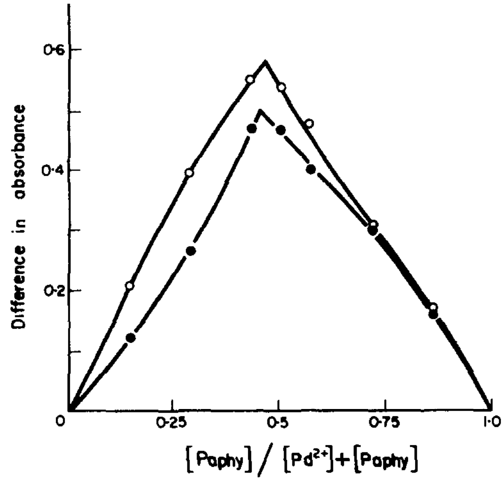


Fig. 2.—Determination of the composition of the complex between palladium and PAPHY by the method of continuous variation [measurements at 510 mμ; concentration of reagents (equimolecular), 5·27 × $10^{-4}M$]:

○ pH = 11·6 ● pH = 4·0.

Effect of other ions

The criterion for significant interference was taken to be a measured value of absorbance which differed by more than 2% from that found with palladium alone.

In a solution containing 40 μg/25 ml of palladium (1·6 ppm) and excess reagent, up to 40 μg of iron(III), silver(I), zinc(II), iridium(IV), platinum(IV), rhodium(III), ruthenium(III) and (IV), and gold(III), when present separately, did not interfere. Smaller amounts of nickel(II) and copper(II) (> 10 μg) and cobalt(II) (> 1 μg) caused interference, but up to 40 μg of these cations separately had no effect on the absorbance in the presence of a 3-fold molar excess of EDTA.

The anions sulphate, nitrate and halides did not interfere.

Recommended procedure for palladium

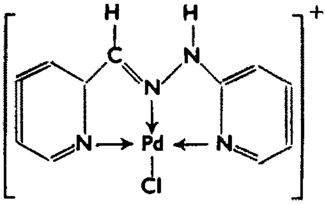
Dissolve the sample by appropriate means. *Aqua regia* may be used, provided the nitric acid is removed subsequently by fuming down several times with hydrochloric acid.

Pipette 1 ml of the sample solution ((20–250 μg Pd and 0·025*M* with respect to HCl) into a 25 ml volumetric flask and add 8 ml of the ethanolic solution of pyridine 2-aldehyde 2-pyridyl hydrazone (0·5 g/l). Allow the solution to stand for five minutes, then add 1 ml of 1*M* sodium hydroxide solution and dilute to 25 ml.

Read the absorbance at 520 mμ, and calculate the weight of palladium present from a previously prepared calibration curve.

DISCUSSION

Precipitation from solution is incomplete below pH 2 although the development of a red colour is consistent with the formation of the complex ion II. Loss of a proton (from the >NH group) produces an uncharged complex which precipitates from solution over the pH range 1–4. The analysis of the solid confirms that this uncharged complex has the composition $Pd(C_{11}N_4H_9)Cl$.



II

At pH values above 4, aqueous solutions again contain a complex cation, as indicated by ion-exchange experiments. This cation could result from the uncharged complex by replacement of the chloride ion with a water molecule.

Palladium behaves differently from most other transition metal ions in forming a 1:1 complex with PAPHY. This is presumably due to the tridentate ligand occupying three of the four co-ordination positions at the corners of a square plane. When the fourth position is occupied by a chloride ion, the complex has a single positive charge. Dipositive transition metal ions which are usually hexa-co-ordinate, form complexes with PAPHY in which the ratio of metal atoms to ligand molecules is 1:2. Then the complex cations formed in acid solution have two positive charges and so do not precipitate until the pH is high enough to remove both acidic hydrogens.

CONCLUSIONS

Pyridine-2-aldehyde-2-pyridylhydrazone is a selective reagent for the spectrophotometric determination of palladium. Maximum sensitivity is reached in aqueous alkaline solutions of pH greater than 11; the few metals which interfere can be successfully masked with EDTA.

Acknowledgement—The authors wish to express their grateful thanks to International Nickel Ltd., London, for the provision of the platinum metals used in this investigation.

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Summary—Palladium(II) and pyridine-2-aldehyde-2-pyridylhydrazone form a red complex in aqueous solution with maximum development of colour at pH values between 11·5 and 11·8 (λ_{max} = 520 mμ). A procedure is described for the accurate spectrophotometric determination of 1–10 μg of palladium. Only a few metal ions interfere and their interference can be prevented by the addition of EDTA.

Zusammenfassung—Palladium(II) und Pyridin-2-aldehyd-2-pyridylhydrazon geben in wäßriger Lösung einen roten Komplex mit maximaler Farbtiefe bei pH 11,5–11,8 (λ_{max} = 520 mμ). Eine Arbeitsvorschrift zur genauen spektralphotometrischen Bestimmung von 1–10 μg Palladium wird angegeben. Nur wenige Metallionen stören; die Störung kann durch Zugabe von EDTA verhindert werden.

---

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Résumé—Le palladium(II) et la pyridine 2-aldéhyde 2-pyridylhydrazone forment en solution aqueuse un complexe rouge avec développement maximal de la coloration aux pH compris entre 11,5 et 11,8 ($\lambda_{max} = 520\,m\mu$). On décrit la technique pour le dosage spectrophotométrique précis de 1 à 10 μg de palladium. Quelques ions métalliques seulement interfèrent, et leur interférence peut être évitée par l'addition d'EDTA.

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LETTERS TO THE EDITOR

Chemical species to be determined

SIR,

Whenever one wishes to discuss the general principles underlying analysis, particularly when considering the evaluation and errors of analytical results, it is necessary frequently to use the term *chemical species to be determined* or its equivalent. This term is cumbersome and yet, to the best of my knowledge, there is no single word that may be substituted. I believe that a word is needed to fill this gap in analytical terminology.

I would suggest that the term *determinand* be used to denote *that which is to be determined.* The word is analogous to other terms, such as titrand, multiplicand and legend, and is formed from well known Latin roots. General acceptance of this suggestion would simplify the phraseology of analysis and I should be interested to hear of the views of your readers on this suggestion.

A. L. WILSON

Analytical Chemistry Section
Central Electricity Research Laboratories
Cleeve Road, Leatherhead, Surrey, England
16 *April* 1965

Selectivity index

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I have read with interest the letters from Professor Belcher and Dr. Betteridge that have recently appeared in this journal.[1] The points made by Dr. Betteridge in support of the Selectivity Index are telling, but I believe that the compression and elimination of so much analytical detail might well lead to confusion and ambiguity. However, the main purpose of my letter is to argue against the definition of an interference proposed by Dr. Betteridge. The following points seem to me of importance:

1. Chemical species other than ions may cause interference but, of course, this point could be covered by a simple change of the definition.
2. It seems desirable to avoid the use of the same word, *i.e.*, interference, for both the effect and its cause. I would suggest that interference be reserved for the effect and interfering species for the cause. Again, this point, if accepted, could be covered by a simple change of the definition.
3. The proposed definition implies a model of interference in which the relative effect of the interfering species, present in a 100-fold (molar) excess, is independent of the concentration of the determinand.* When the interference does not conform with this model, the definition may lead to ambiguity. Thus, for a constant (molar) ratio of the interfering species and the determinand, the concentration of the latter may affect the magnitude of the interference. An example of this type of interference is afforded by the effect of phosphate in the spectrophotometric determination of silicon.[2] A further possibility is that the interference caused by a certain species may pass through a maximum or minimum as its concentration is increased. The effect of phosphate in the spectrophotometric determination of silicon[2] also provides an example of this type of effect.

Such deviations from the model implied by the proposed definition of interference will, in general, lead to ambiguity because the concentration of the determinand and the arbitrary choice of the 100-fold excess of another species *X* may determine whether or not *X* is classed as an interfering species.

4. In practical analysis, one is often concerned with the situation where the interfering species is present in a reasonably constant concentration, and the concentration of the determinand varies. It is then of interest to know whether or not the magnitude of the interference is independent of the concentration of the determinand. The proposed definition does not cover this point, and might even tend to restrict the amount of detailed investigation made on interference.
5. The magnitude of the interference caused by a species may depend markedly on the concentrations

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* The term *determinand* has been suggested in a previous letter in this issue of *Talanta.*

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LETTERS TO THE EDITOR

Chemical species to be determined

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Whenever one wishes to discuss the general principles underlying analysis, particularly when considering the evaluation and errors of analytical results, it is necessary frequently to use the term *chemical species to be determined* or its equivalent. This term is cumbersome and yet, to the best of my knowledge, there is no single word that may be substituted. I believe that a word is needed to fill this gap in analytical terminology.

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1. Chemical species other than ions may cause interference but, of course, this point could be covered by a simple change of the definition.
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Such deviations from the model implied by the proposed definition of interference will, in general, lead to ambiguity because the concentration of the determinand and the arbitrary choice of the 100-fold excess of another species *X* may determine whether or not *X* is classed as an interfering species.

4. In practical analysis, one is often concerned with the situation where the interfering species is present in a reasonably constant concentration, and the concentration of the determinand varies. It is then of interest to know whether or not the magnitude of the interference is independent of the concentration of the determinand. The proposed definition does not cover this point, and might even tend to restrict the amount of detailed investigation made on interference.
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of the reagents. Two examples are provided by the effect of the concentration of bathophenanthroline on the interference caused by copper in the spectrophotometric determination of iron,[3] and the effect of the concentration of ammonium molybdate on the interference caused by phosphate in the spectrophotometric determination of silicon.[4] Thus, depending on the particular values chosen for the concentrations of the reagents, the same species might or might not be classed as an interfering species. Such situations would tend to cause confusion.

6. If the proposed definition were adopted, a species *X* causing a systematic relative error of 4% would not be termed an interfering species. On the other hand, such an error may often be regarded as an important effect, and the natural tendency, following the custom of many years usage, would be to call *X* an interfering species. It seems likely that the literature might evolve with the same species being classed both as an interfering and a non-interfering species. Such a situation is clearly undesirable, particularly in view of the proliferation of the literature and the increasing use made of abstracting journals.

This difficulty could be overcome by deciding to use a new word to denote those species that cause systematic errors less than 5%, but this seems too artificial. It is clear that this problem of terminology arises because of the choice of an arbitrary magnitude of error (*i.e.*, 5%) in the definition; merely changing the value assigned to this error does not eliminate the problem.

7. From the points above, the question obviously arises: what is the best way to define an interfering species? It seems desirable that the definition should depart as little as possible from currently-held views, and yet should contain no arbitrary elements. On this basis, I would suggest the following definition which is, of course, far from original.

For a given analytical method, any species present in the sample that causes systematic error in the analytical result shall be called an interfering species for that method.

Professor Belcher and Dr. Betteridge both emphasised that it is a reaction rather than a reagent that is selective. My suggested definition extends this concept so that it is the complete analytical method that is regarded as selective. This seems to be more correct than to emphasise one particular reaction, because usually a number of equilibria and experimental parameters jointly determine the magnitude of the interference caused by different species.

It follows from this definition that no species can be proved not to be an interfering species. This statement is a consequence of the fact that random errors affect all measurements, and lead to uncertainties in quantitative statements based on experimental results. Therefore, after experimental tests, all that can be said is that the effect of a species *X* is less than a certain value that is determined by the magnitude of the random errors. Thus, my proposed definition implies that all species must be regarded as potentially-interfering species, but this leads to no difficulty in practice because of the following considerations.

To those concerned with investigating, developing or applying analytical methods, it is essential that those species present in the sample should not cause more than a tolerable systematic error that will vary from one application to another. If the literature or new experimental tests show that the systematic error caused by a particular species is greater than can be tolerated, then a different analytical method must be used. This is a simple approach, and no recourse need be made to some arbitrary choice of the magnitude of systematic error that constitutes interference. It seems possible that my definition may lead to greater attention being paid to the subject of interference than if Dr. Betteridge's proposal were adopted.

I suppose the substance of my letter can be summarised by saying that I think no compromise on the definition of interference should be attempted.

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16 *April* 1965

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PRECISION OF THE DETERMINATION OF COPPER AND GOLD BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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(*Received* 19 *May* 1964. *Revised* 29 *January* 1965. *Accepted* 29 *March* 1965)

Summary—Copper and gold can be determined by atomic absorption spectrophotometry using hollow cathode lamps which produce the resonance lines of 3247 Å and 2428 Å, respectively. Optimal experimental conditions have been ascertained. In the case of copper calibration curves are presented for 10–100 as well as for 100–700 ppm, and in that of gold for 5–50 as well as for 50–500 ppm. The influence of several cations and anions has been examined. Precision calculations have been made by a method suggested previously by the authors.

ATOMIC absorption spectrophotometric methods are becoming more and more widely used in science and industry. However, a thorough study of the optimal experimental conditions and of the best attainable precision is lacking in almost all cases. We have previously recommended an improved method for calculation of the precision of quantitative spectrophotometric measurements.[1] This method can also be used as the basis for evaluation of the results of atomic absorption measurements. We have already investigated the optimum conditions for determination of zinc[2] and silver.[3] Atomic absorption methods for copper[4–6,10] and gold[7,8] have already been described by various authors. Our present aim was to ascertain those conditions under which the precision of measurements for these two elements are best, even if the sensitivity of the method decreases somewhat.

EXPERIMENTAL

Reagents

Copper nitrate standard solution. Prepared from analytically pure copper nitrate and standardised by titration with disodium ethylenediaminetetra-acetate standard solution, using Murexide as indicator. From a stock solution appropriate dilutions were made to obtain the standard working solutions needed.

Gold chloride standard solution. Prepared from commercially available $AuCl_3{\cdot}HCl{\cdot}3H_2O$ by dissolution in water. Standardisation was made by titrating the solution with standard iron(II) sulphate using potentiometric end-point detection.[9]

Solutions for investigation of cationic interferences. Prepared from analytically pure reagents. Their concentrations were adjusted by weighing only. Metal nitrates were used whenever possible, or metals, metal oxides or metal carbonates were dissolved in nitric acid by heating. Nitric acid was present in all cases in a slight excess. Stock solutions were prepared in all cases, containing at least 20 mg/ml of the relevant cation.

Solutions for investigation of anionic interferences. Prepared from analytically pure ammonium salts. Their concentrations were adjusted by weighing. The stock solutions contained at least 20 mg/ml of the relevant anion.

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* Assistant Professor, Cairo University, Faculty of Science, Chemistry Department, Giza, Egypt, U.A.R.

Apparatus

The Hilger Uvispec spectrophotometer was used with its atomic absorption attachment. Air pressure was controlled by a fine manometer, while illuminating gas was introduced into the burner directly from a laboratory gas tap. The gas pressure seemed to be constant, and, when measured by a flow manometer, had a value of 40 mm of water. The determinations of copper were made on the 3247 Å copper resonance line, using the brass hollow cathode lamp supplied with the instrument. Gold determinations were made with another hollow cathode lamp, which emitted the resonance line 2428 Å of gold.

INVESTIGATION OF EXPERIMENTAL CONDITIONS

Air pressure

Because the amount of liquid sprayed into the burner depends mainly on the air pressure, absorbancies at various pressures are different. By using higher pressures the number of atoms capable of absorption will increase in unit time, *i.e.*, the sensitivity of the measurement increases in this case. The air pressure cannot, however, be increased to extremely high values, because an unstable flame occurs, which causes a high scattering in the absorbancy readings. At the same time, the calm, laminary flow of the solutions changes stepwise to a turbulent one, which also results in a decreased reproducibility of the measurements. To investigate the optimal air pressure, we made absorbancy measurements of solutions of 100, 500 and 1000 ppm of copper and 50, 150 and 300 ppm of gold, respectively, at pressures of 0·2, 0·3 and 0·4 kg/cm^2 overpressure. A slit width of 0·1 mm was chosen on the basis of preliminary measurements. A lamp current of 40 mA was used in all cases. Results are shown in Tables I and II for copper and gold, respectively. In the case of copper a 0·3 kg/cm^2 air overpressure seemed to give the most steady flame, while in the case of gold 0·4 kg/cm^2 was chosen because of a better sensitivity.

Variation of lamp current

We also made measurements using various lamp currents. The air pressure was adjusted in all cases to 0·4 kg/cm^2, while slit widths were adjusted arbitrarily to 0·15 mm. The results in Tables III and IV for copper and gold, respectively, indicate that in both cases a lamp current of 40 mA provides the best working condition. Currents were applied in increasing order, and 30 min were allowed to elapse before each series to ensure complete heat equilibrium between the hollow cathode and its environment. In all further investigations a 40-mA lamp current was used.

Variation of slit width

For the sake of accuracy of the measurements the use of adequate slit width is essential. Therefore, we carried out a series of measurements using various slit widths and measuring the optical densities from copper solutions of 100, 500 and 1000 ppm, and from gold solutions of 100, 250 and 400 ppm. In all cases six parallel readings were made, and the standard deviations of these were calculated. The results are presented in Tables V (copper) and VI (gold). In both cases a slit width of 0·15 mm gives the most precise and also the most sensitive result. Thus, this slit width can be recommended for practical measurements.

Optimal concentration limits

As previously pointed out,[1] reliable results can be expected in quantitative spectrophotometric measurements only if the optical density of the solution to be analysed

TABLE I.—VARIATION OF ABSORBANCY OF COPPER SOLUTIONS WITH AIR PRESSURE

Air overpressure, *kg/cm*^{2}	Absorbancy		
	Copper, *ppm*		
	100	500	1000
0·20	0·180	0·655	0·982
0·30	0·382	1·027	1·350
0·40	0·450	1·050	1·500

TABLE II.—VARIATION OF ABSORBANCY OF GOLD SOLUTIONS WITH AIR PRESSURE

Air overpressure, *kg/cm*^{2}	Absorbancy		
	Gold, *ppm*		
	50	150	300
0·20	0·043	0·118	0·235
0·25	0·069	0·160	0·321
0·30	0·085	0·200	0·374
0·35	0·113	0·262	0·465
0·40	0·134	0·303	0·535

TABLE III.—VARIATION OF LAMP CURRENT IN COPPER DETERMINATIONS

Lamp current, *mA*	Absorbancy		
	Copper, *ppm*		
	100	500	1000
20	0·290	0·740	0·823
33	0·270	0·773	0·870
40	0·295	0·797	1·050
60	0·270	0·780	0·940

TABLE IV.—VARIATION OF LAMP CURRENT IN GOLD DETERMINATIONS

Lamp current, *mA*	Absorbancy		
	Gold, *ppm*		
	50	150	300
10	0·091	0·202	0·353
18	0·085	0·203	0·353
28	0·080	0·202	0·348
38	0·085	0·202	0·375
44	0·095	0·210	0·375
60	0·085	0·202	0·321

lies within 0·2 and 0·8. Our experiments have shown that these limits correspond to concentrations of 60 and 400 ppm of copper and of 100 and 500 ppm of gold. These should be the lowest and highest concentrations on which atomic absorption measurements should be made. For practical purposes, however, we prepared two calibration curves for each metal, covering the concentration ranges 10–100 and 100–700 for copper, and 5–50 and 50–500 ppm for gold. The optimal experimental conditions are shown in Tables VII and VIII for copper and gold, respectively.

TABLE V.—VARIATION OF SLIT WIDTH IN COPPER DETERMINATIONS

Slit width, *mm*	Absorbancy and standard deviations		
	Copper, *ppm*		
	100	500	1000
0·10	0·335	0·900	1·223
	±0·0133	±0·0448	±0·0485
0·15	0·400	1·09	1·253
	±0·0065	±0·0155	±0·0158
0·20	0·35	0·88	1·12
	0·01	0·04	0·05

TABLE VI.—VARIATION OF SLIT WIDTH IN GOLD DETERMINATIONS

Slit width, *mm*	Absorbancy and standard deviations		
	Gold, *ppm*		
	100	250	400
0·1	0·164	0·350	0·511
	±1·30	±0·60	±0·72
0·15	0·153	0·337	0·502
	±1·31	±0·62	±0·71
0·2	0·163	0·339	0·495
	±1·93	±0·98	±0·77
0·25	0·149	0·298	0·433
	±1·95	±1·04	±0·90

TABLE VII.—OPTIMAL EXPERIMENTAL CONDITIONS FOR DETERMINATION OF COPPER

Line: 3247 Å copper resonance line
Lamp current: 40 mA
Air pressure: 0·3 kg/cm^2 (overpressure)
Slit width: 0·15 mm
Calibration curves:
for 10–100 ppm of copper
$E = 0·0009 \pm 0·009 + (0·00367 \pm 0·00015)$ C
for 100–700 ppm of copper
$E = 0·269 \pm 0·0028 + (0·001281 \pm 0·0000062)$ C

TABLE VIII.—OPTIMAL EXPERIMENTAL CONDITIONS FOR DETERMINATION OF GOLD

Line: 2428 Å gold resonance line
Lamp current: 40 mA
Air over pressure: 0·4 kg/cm^2 (overpressure)
Slit width: 0·1 mm
Concentration limits 5–50 and 50–500 ppm of gold(III)
Calibration curves:
  for 5–50 ppm of gold(III)
  $E = -0{\cdot}0002 \pm 0{\cdot}000113 + (0{\cdot}0026 \pm 0{\cdot}0000037)\, C$
  for 50–1500 ppm of gold(III)
  $E = 0{\cdot}0671 \pm 0{\cdot}0026 + (0{\cdot}001506 \pm 0{\cdot}0000084)\, C$

Precision

The precision of the measurement of a concentration can be calculated in the following way:[1]

$$\frac{s_c}{c}100 = \frac{s_E}{E-a}100 + \frac{s_a}{E-a}100 + \frac{s_b}{b}100$$

where $(s_c/c)100$ is the standard deviation of the concentration measurement, s_E is the standard deviation of the absorbancy measurements, E is the absorbancy itself, a is the intercept and b is the slope of the absorbancy *vs.* concentration curve, and s_a and s_b are the standard deviations of these quantities, respectively. We made the precision calculations for both ions in all concentration regions; the results are shown in Tables IX–XII. Especially the determination of gold seems to be precise from this point of view; it can be carried out with an average 2% total relative precision at higher concentrations. The photometric precision $[(s_E/E - a)100]$ is favourably small in all cases.

TABLE IX.—PRECISION OF COPPER DETERMINATIONS WITHIN A CONCENTRATION OF 10–100 PPM

Concentration, *ppm*	$\frac{s_E}{E-a}100$	$\frac{s_a}{E-a}100$	$\frac{s_b}{b}\cdot 100$	$\frac{s_c}{c}\cdot 100$
10	4·7	23·7	4·2	32·6
20	4·1	11·7		20·0
30	4·9	8·4		17·5
40	3·9	6·5		14·6
50	0·8	4·8		9·8
60	1·1	4·1		9·4
70	0·8	3·5		8·5
80	1·8	3·1		9·1
90	1·9	2·7		8·8
100	1·0	2·4		7·6

Effect of foreign ions

We examined the effect of added foreign cations on the absorbancy measurements by adding 10- and 100-fold amounts of the ions to solutions of 100, 500 and 1000 ppm of copper as well as 40- and 100-fold amounts to 50, 100 and 150 ppm solutions of gold. Because we did not find any influence from the 10- and 40-fold concentrations, we mixed together more of the cations and measured the effect of these mixtures. It must be emphasised that, in a given group of metals, each ion was present in a 10-, 40- or 100-fold excess; therefore, the results were obtained in the presence of a very

TABLE X.—PRECISION OF COPPER DETERMINATIONS WITHIN A CONCENTRATION OF 100–700 PPM

Concentration, *ppm*	$\frac{S_E}{E-a}100$	$\frac{S_a}{E-a}100$	$\frac{S_b}{b}.100$	$\frac{S_c}{c}.100$
100	4·9	2·1	0·5	7·5
200	6·7	1·1		8·2
300	4·2	0·7		5·4
400	3·1	0·6		4·2
500	1·3	0·4		2·2
600	1·6	0·4		2·4
700	0·4	0·3		1·2

TABLE XI.—PRECISION OF GOLD DETERMINATIONS WITHIN A CONCENTRATION OF 5–50 PPM

	Photometric precision			Total precision
Concentration, *ppm*	$\frac{S_E}{E-a}.100$	$\frac{S_a}{E-a}.100$	$\frac{S_b}{b}.100$	$\frac{S_c}{c}.100$
5	7·57	0·85	0·14	8·56
10	4·96	0·43		5·53
15	3·82	0·28		4·14
20	3·32	0·22		3·68
25	1·99	0·17		2·30
30	2·85	1·15		3·14
35	1·52	0·12		1·78
40	1·82	0·11		2·07
45	1·45	0·10		1·69
50	1·61	0·08		1·83

TABLE XII.—PRECISION OF GOLD DETERMINATIONS WITHIN A CONCENTRATION OF 50–500 PPM

	Photometric precision			Total precision
Concentration, *ppm*	$\frac{S_E}{E-a}.100$	$\frac{S_a}{E-a}.100$	$\frac{S_b}{b}.100$	$\frac{S_c}{c}.100$
50	4·60	4·00	0·56	9·16
100	1·20	1·75		3·51
150	1·20	1·20		2·96
200	0·74	0·87		2·17
250	0·66	0·67		1·89
300	0·87	0·55		1·98
350	0·43	0·48		1·47
400	0·41	0·43		1·40
450	0·40	0·39		1·35
500	0·40	0·35		1·31

TABLE XIII.—EFFECT OF FOREIGN IONS ON DETERMINATION OF COPPER

Foreign ions	Copper solution, *ppm*	Absorbancy in presence of 0	10	100
		fold amounts of foreign ions		
$Hg_2^{2+} + Hg^{2+}$	100	0·263	0·262	0·254
	500	0·686	0·707	
	1000	0·900	0·900	
$Cd^{2+} + Pb^{2+} + Bi^{3+}$	100	0·263	0·263	0·271
	500	0·686	0·707	
	1000	0·900	0·880	
$Mn^{2+} + Co^{2+} + Zn^{2+} + Ni^{2+}$	100	0·263	0·266	0·265
	500	0·686	0·675	
	1000	0·900	0·883	
$Fe^{3+} + Al^{3+}$	100	0·263	0·262	0·285
	500	0·686	0·695	
	1000	0·900	0·870	
$Ca^{2+} + Sr^{2+} + Ba^{2+} + Mg^{2+}$	100	0·263	0·270	0·285
	500	0·686	0·718	
	1000	0·900	0·900	
Cl^-, SCN^-	200		0·310	0·305
	400		0·402	0·402
	600		0·477	0·477
SO_4^{2-}, CH_3COO^-	200		0·310	0·310
	400		0·402	0·400
	600		0·477	0·472
$S_2O_8^{2-}$, NO_3^-	200		0·310	0·322
	400		0·402	0·438
	600		0·477	0·490
Br^-, $(COO)_2^{2-}$	200		0·310	0·350
	400		0·402	0·440
	600		0·477	0·500

high concentration of foreign ions. Deviations are not high even in the presence of a 100-fold excess. The metals were added in the form of their nitrates.

To examine the effect of anions we added ammonium salts to 200, 400 and 600 ppm of copper and to 50, 100 and 150 ppm solutions of gold, using a 10-fold excess in the case of copper and a 40- and 100-fold excess in the case of gold. No remarkable effect was found if a 10-fold excess of anions was present in the case of copper, but in the case of a 100-fold excess the deviations were remarkable. Here only peroxydisulphate, bromide and oxalate ions have marked effects. The results for gold are even better; only oxalate ions have any effect, forming a precipitate with the gold ions in the solution. The results of these measurements are shown in Table XIII for copper and in Table XIV for gold.

TABLE XIV.—EFFECT OF FOREIGN IONS ON DETERMINATION OF GOLD

Foreign ions	Gold solution, *ppm*	Absorbancy in presence of 0	40	100
		fold amounts of foreign ions		
$Cu^{2+} + Cd^{2+} + Bi^{3+} + Pb^{2+}$	50	0·130	0·110	0·087
	100	0·218	0·187	
Cd^{2+}	50	0·130	0·125	0·128
	150	0·290	0·287	
Cu^{2+}	50	0·129	0·127	0·110
	100	0·216	0·215	
Bi^{3+}	50	0·130	0·130	
	150	0·289	0·292	
Pb^{2+}	50	0·130	0·130	0·126
	100	0·217	0·217	
$Fe^{3+} + Al^{3+} + Cr^{6+}$	50	0·130	0·123	
	100	0·218	0·199	
	150	0·290	0·263	
$Fe^{3+} + Al^{3+}$	50	0·130	—	0·127
$Zn^{2+} + Mn^{2+} + Co^{2+} + Ni^{2+}$	50	0·130	0·131	0·130
	100	0·215	0·215	
	150	0·288	0·286	
$Mg^{2+} + Ca^{2+} + Sr^{2+} + Ba^{2+}$	50	0·130	0·130	0·130
	100	0·219	0·216	
	150	0·290	0·286	
Cl^-	50	0·128	0·125	0·125
	100	0·217	0·206	
	150	0·289	0·269	
Br^-	50	0·127	0·117	0·127
	100	0·216	0·200	
	150	0·288	0·260	
SCN^-	50	0·130	0·127	0·132
	100	0·218	0·214	
	150	0·288	0·286	
CO_3^{2-}	50	0·130	0·133	0·134
PO_4^{3-}	50	0·130	0·127	0·120
$SO_4^{2-} + S_2O_8^{4-}$	50	0·130	0·130	0·127
	100	0·218	0·214	
	150	0·288	0·283	
$NO_3^- + CH_3COO^-$	50	0·130	0·128	0·131
	100	0·217	0·216	
	150	0·287	0·288	

Zusammenfassung—Kupfer und Gold können bestimmt werden durch atomare Absorptionsspektralphotometrie mit Hohlkathodenlampen, die die Resonanzlinien 3247 Å bzw. 2428 Å emittieren. Die besten Arbeitsbedingungen wurden festgelegt. Bei Kupfer werden Eichkurven für 10–100 und 100–700 ppm vorgelegt, bei Gold für 5–50 und 50–500 ppm. Der Einfluß verschiedener Kat- und Anionen wurde geprüft. Nach einer früher von den Autoren vorgeschlagenen Methode wurde die Genauigkeit berechnet.

Résumé—On peut doser le cuivre et l'or par spectrophotométrie d'absorption atomique en utilisant des lampes à cathode creuse qui produisent les raies de résonance de 3247 Å et 2428 Å, respectivement. On a déterminé les conditions expérimentales optimales. Avec le cuivre, les courbes d'étalonnage sont présentées pour 10–100 et pour 100–700 p.p.m., et avec l'or pour 5–50 et 50–500 p.p.m. On a examiné l'influence de quelques cations et anions. Les calculs concernant la précision ont été faits selon une méthode antérieurement suggérée par les auteurs.

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APPLICATION OF CIRCULAR THIN-LAYER CHROMATOGRAPHY TO INORGANIC QUALITATIVE ANALYSIS

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Summary—After separation of metal ions into Groups 1–5 of the classical hydrogen sulphide scheme of qualitative analysis, the metal ions in each Group are separated by circular thin-layer chromatography. Several solvents and spray reagents for the Group analyses are reported. The method is simple and convenient; development of a chromatoplate is complete within 2 min.

THIN-LAYER chromatography (TLC) for the separation of mixtures of substances otherwise difficult to separate possesses the advantages of shortness of running time of the solvents and uniformity of the chromatographic support obtained by using a standardised gel preparation.

Circular chromatography is considered to be a very convenient and versatile analytical tool for the separation of a mixture which is not quite resolved by linear development. Many workers have tried to carry out circular thin-layer chromatography but because the horizontal development requires the solvent to be fed to the layer by a wick, no convenient and satisfactory modification has so far been devised. For example, Bryant's apparatus[1] for horizontal development consists of a chromatoplate inverted over a petri dish and solvent is fed to the film by a cotton wick held at the centre of the dish. In Stahl's modification[2] of this technique, a cotton feeder is plugged into a small hole drilled through the chromatoplate; this requires great skill. Mottier[3] tried to achieve the advantages of horizontal development in radial technique. The principle of the method is first to draw the pattern on the film with a fine needle, then to scrape the unwanted adsorbent off the glass with a spatula.

Meinhard and Hall[4,5] employed developing pipettes for circular chromatography and illustrated their usefulness in the analysis of mixtures of iron and zinc[4] and of copper and nickel[5] salts. Though the method is convenient, it required further refinement because it is difficult to keep the atmosphere saturated with the solvent by the use of a simple pipette. The preliminary results of Meinhard and Hall[4,5] were not very satisfactory, but these authors were still of the opinion that thin-layer chromatography would prove useful in inorganic chemical analysis. However, the inorganic field was virtually ignored[6] until 1960. Since then some studies have been reported on the separation and subsequent identification of inorganic ions[7–9] on thin films but, generally speaking, these researches have involved only a small number of ions.

In the present paper a simple and convenient modification of Meinhard and Hall's technique,[5] which involves the use of a developing chamber and an irrigating pipette for circular thin-layer chromatography, is described. This enables the metal ions of Groups I–V of the classical hydrogen sulphide scheme of qualitative analysis, previously separated into these Groups by conventional means, to be separated using alumina and silica adsorbents. Development of the chromatogram is complete within 2 min. A number of spray reagents on alumina and silica glass plates have also been studied and several solvents for the separation of different groups of cations are reported.

EXPERIMENTAL

Reagents

All reagents were of analytical grade or comparable purity.

Aluminium oxide (D-5, containing 5% calcium sulphate as binder, Camag) and silica gel (D-0, without binder, Camag) were used for preparation of the thin films. Both were used without further treatment.

Apparatus

The apparatus consists of a developing chamber and irrigating pipette, both being all glass (Fig. 1). The developing chamber is like an inverted funnel with a circular solvent cup fused to its inner wall. The open top of the chamber is of such a diameter as to provide a tight fit with the irrigating pipette inserted through it. The surface of the developing chamber, which touches the film surface, is ground to produce a leak-proof joint.

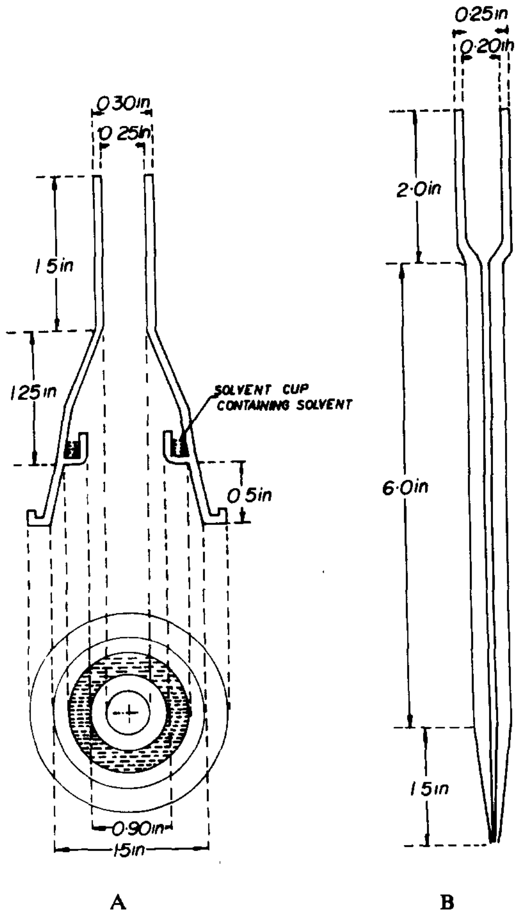

FIG. 1.—Circular thin layer chromatography apparatus: A—developing chamber; B—irrigating pipette.

The irrigating pipette consists of a capillary drawn to a fine jet at one end, the other end being fused to a piece of wide-bore glass tubing. Several irrigating pipettes with varying jet cross-sectional areas are needed for the proper handling of liquids of different viscosity.

The applicator (Camag, Muttenz, Homburgerstrasse 24, Switzerland) consists of a spreading trough of stainless steel fixed to an aluminium bed on which glass plates can be aligned. It can accommodate 10-cm or 20-cm width glass plates of any thickness or length.

Preparation of thin films

Five g of alumina or silica gel are mixed thoroughly with 16 ml of water using a pestle and mortar; the slurry is placed in the applicator and glass plates are coated to a uniform thickness (*ca.* 200 μ). The plates are dried overnight at room temperature (30–32°).

Silica gel film which has been allowed to dry overnight in the atmosphere at room temperature is about as active as that which has been heated to 110° for 30 min.[10] In the present procedure the thin films are exposed to the atmosphere for a considerable time during use and would re-absorb moisture if they had been heat-activated. In order to avoid the non-linear behaviour of thin films because of re-absorption of moisture, it was found best to dry the films at room temperature overnight.

Development of chromatoplates

A very fine hole is made in the prepared surface with a small pin. About 1–2 μl of the test solution to be chromatographed is applied to the plate with a micro pipette (2512: Shandon Scientific Co. Ltd., London, England) taking care that the solution does not spread in the film, thus forming a larger spot. This pipette has a flat mouth and cannot be used alone, so that a very fine capillary, having a suitable diameter to fit tightly, was placed in its mouth. The volume of test solution applied depends on the concentrations of the individual cations and on the sensitivity of the spraying reagents to be used. The spot is allowed to dry and the developing chamber is placed over the spot with its solvent cup filled with the solvent with which the film is to be irrigated. A small piece of filter paper is placed in the solvent cup in such a way that its lower end dips into the solvent while the upper end spreads towards the top of the chamber; this helps to saturate the atmosphere in the developing chamber more quickly. After 10–15 min, when the atmosphere in the chamber has been saturated with the solvent, the cork closing the top of the solvent chamber is removed and the irrigating pipette containing the solvent inserted into the developing chamber in such a way that its capillary tip touches the plate where the test solution was originally spotted. Development of the chromatoplate is complete in 1–2 min. The plate is then dried and sprayed with the appropriate reagent to locate the position of the different rings.

Details of the spray reagents together with the treatment after spraying are given in Table I. Treatment with ammonia can be carried out simply by exposing the plates to ammoniacal vapours.

TABLE I.—SPRAY REAGENTS FOR LOCATION OF METAL IONS

Reagent	Solution	Treatment after spraying
Sodium sulphide (SS)	0·5% aqueous	NH_3 atmosphere
Alizarin (AZ)	Saturated in 96% ethanol	NH_3 atmosphere
Dimethylglyoxime (DG)	Saturated in ethanol containing 25% ammonia	
Sodium rhodizonate (SR)	1% aqueous, freshly prepared	
Dithizone (DZa)	0·05% in 80% acetone	NH_3 atmosphere
Dithizone (DZc)	0·05% in chloroform	NH_3 atmosphere
Rubeanic acid (RA)	Saturated in 96% ethanol	NH_3 atmosphere

Analysis of mixtures

In order to analyse an unknown mixture, it is essential to separate the cations by conventional means into the various Groups of the classical hydrogen sulphide scheme of analysis.[11] Solutions are then prepared from the various Group precipitates and processed by the procedure detailed above.

A solution, containing the nitrates of Ag^+, Pb^{2+}, Hg_2^{2+}, Hg^{2+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Co^{2+} Ni^{2+}, Zn^{2+}, Ba^{2+}, Ca^{2+} and Sr^{2+}, the chlorides of Sb^{3+}, Sn^{4+}, Al^{3+}, Mn^{2+}, together with sodium arsenite and chromium oxide, was prepared in dilute hydrochloric acid, followed by filtration in order to separate the chlorides of Group I. The chlorides of silver, mercury(I) and lead thus separated, were dissolved in concentrated nitric acid, the solution heated to dryness and the residue extracted with a small amount of concentrated nitric acid, followed by suitable dilution for analysis by TLC.

The sulphides of Group II were separated into Groups IIA and IIB by the use of yellow ammonium sulphide. The cations of Group IIA were dissolved in a mixture of potassium chlorate and hydrochloric acid and the resulting solution, after removing excess acid by successive concentration and dilution, was analysed by TLC. The sulphides of Group IIB were reprecipitated with dilute hydrochloric acid, then dissolved in *aqua regia*. After removing excess acid by successive concentration and dilution, the solution was used for TLC. The hydroxides of Group III were dissolved in hot dilute hydrochloric acid and this solution used directly for TLC analysis. Group IV sulphides were dissolved in *aqua regia*, excess acid removed by successive concentration and dilution, before the solution was analysed by TLC. Finally, the carbonates of Group V were dissolved in concentrated hydrochloric acid and the solution used directly for TLC analysis.

RESULTS AND DISCUSSION

Nine different solvents have been investigated for the separation of cations into different groups (Table II). Though some of the solvents contain the same reagents as used previously,[8] their composition is different to suit the separation of different cations under the present experimental conditions. Nitric acid has been used instead of hydrochloric acid for the separation of the Group I cations, otherwise precipitation of the cations would occur.

TABLE II.—SOLVENTS FOR SEPARATION OF METAL IONS

Solvent	Composition, *v/v*	Group
A	n-Butyl alcohol, acetone, nitric acid (conc.) 23:23:4	I
B	n-Butyl alcohol, acetone, acetylacetone, nitric acid (conc.) 20:20:6:4	I
C	n-Butyl alcohol, methanol, hydrochloric acid (8*M*), acetylacetone 28:15:4:3	IIA
D	n-Butyl alcohol, hydrochloric acid (8*M*), acetylacetone 43:4:3	IIA
E	n-Butyl alcohol, acetone, hydrochloric acid (8*M*), acetylacetone 33:10:4:3	IIA
F	Acetone, hydrochloric acid (8*M*), acetylacetone 48:1:1	IIB
G	Acetone, hydrochloric acid (4*M*), acetylacetone 97:2:1	III, IVB
H	Acetone, hydrochloric acid (4*M*), acetylacetone 46:2:2	IVA
J	Acetone, hydrochloric acid (4*M*) 97:3	V

The maximum diameter to which the solvent is allowed to spread is about 1 inch and R_f-values are measured with a fine geometrical divider of the type generally used by a draughtsman. To minimise the error, R_f-values are evaluated by measuring the diameters of the rings obtained on spraying. Special care must be taken in applying spots on chromatoplates because the spot size is of great importance. Spots of smaller size give better results. The function of the irrigating pipette is that of a wick in circular chromatography.

The irrigating pipette may be marked to deliver equal amounts of solvent to run a chromatoplate. Such chromatoplates are found to have an almost reproducible solvent flow diameter.

The R_f-values of various cations are given in Table III. In Group IIA, the

R_f-values of cadmium(II) and mercury(II) are almost the same but their bands can be distinguished by their specific colour. It is difficult to obtain reproducible R_f-values, though the order of separation always remains the same. Hence, cations are identified according to their sequence and their specific colour reactions.

TABLE III.—R_f VALUES OF METAL IONS‡

Group	Absorbent	Cation	Spray reagent* and colour	Solvent† R_f		
				A	*B*	
I	Alumina (D-5)	Ag^+	dark brown (SS)	0·63	0·63	
		Hg_2^{2+}	tan (SS)	0·80	0·78	
		Pb^{2+}	dark brown (SS)	0·44	0·43	
				C	*D*	*E*
IIA	Alumina (D-5)	Cu^{2+}	dark brown (SS)	0·96	0·95	0·96
		Cd^{2+}	yellow (SS)	0·75	0·64	0·60
		Hg^{2+}	tan (SS)	0·73	0·59	0·62
		Bi^{3+}	brown (SS)	0·61	0·36	0·46
		Pb^{2+}	dark brown (SS)	0·47	0·27	0·36
				F		
IIB	Silica Gel (D-0)	Sb^{3+}	red-orange (DZc)	1·00		
		As^{3+}	yellow (DZc)	0·93		
		Sn^{4+}	violet (DZc)	0·86		
				G		
III	Silica Gel (D-0)	Fe^{3+}	blue-violet (AZ)	1·00		
		Al^{3+}	yellowish-orange (AZ)	0·34		
		Cr^{3+}	violet (AZ)	0·13		
				H		
IVA	Alumina (D-5)	Ni^{2+}	blue (RA) red (DG)	0·17		
		Co^{2+}	dark-brown (RA) brown (DG)	0·49		
		Mn^{2+}	red-brown (RA) red (DG)	0·30		
		Fe^{3+}	brown (RA) yellowish-green (DG)	1·00		
				G		
IVB	Alumina (D-5)	Ni^{2+}	blue (DZa)	0·40		
		Zn^{2+}	red-violet (DZa)	0·56		
		Cu^{2+}	green (DZa)	1·00		
				J		
V	Silica Gel (D-0)	Ba^{2+}	brick-red (SR)	0·00		
		Sr^{2+}	red (SR)	0·28		
		Ca^{2+}	violet (AZ)	0·81		

* *Cf.* Table I.

† *Cf.* Table II.

‡ R_f-values represent averages of 3 separate runs for each Group.

The sensitivity of detection of various metal ions on thin films is given in Table IV, which indicates the smallest amount of each metal ion which can be identified.

Seiler and Seiler[7] separated the acid-hydrogen sulphide group cations [mercury(II), bismuth, lead, copper and cadmium] with a development time of 2 hr and the ammonium sulphide group cations [iron(III), chromium(III), aluminium, cobalt, nickel, manganese(II)] in 15–20 min. With the present procedure the separation of each Group takes place within 2 min.

It is advisable to use a chloroform solution of dithizone for location of Group IIB cations because an acetone solution of dithizone does not work satisfactorily.

The analysis of a mixture containing all the cations from Groups I–V was carried out by separating the cations into the various Groups, then analysing each Group by TLC (see *Experimental*). This avoids interference from the cations of one Group in another Group. The identification of each cation in the different Groups was quite satisfactory. When analysing an unknown mixture, it is not necessary to run standard chromatograms because the sequence of separation of different cations remains the same, although the R_f-values may differ slightly from those given in Table III. The procedure described in this paper is not a comprehensive scheme for the identification of cations from unknown mixtures until these are separated into different Groups by the classical hydrogen sulphide analytical scheme before proceeding for TLC.

Table IV.—Sensitivity of metal ions on thin films

Ion	Sensitivity, µg	Ion	Sensitivity, µg
Ag^+	2 (SS)*	Al^{3+}	3 (AZ)
Hg_2^{2+}	3 (SS)	Cr^{3+}	7 (AZ)
Pb^{2+}	2 (SS)	Ni^{2+}	0·6 (DG)
Cu^{2+}	3 (SS)		0·5 (RA)
	1 (DZa)		0·8 (DZa)
Cd^{2+}	5 (SS)	Co^{2+}	1 (DG)
Hg^{2+}	3 (SS)		1 (RA)
Bi^{3+}	2 (SS)	Mn^{2+}	5 (DG)
Sb^{3+}	15 (DZc)		10 (RA)
As^{3+}	6 (DZc)	Zn^{2+}	3 (DZa)
Sn^{4+}	2 (DZc)	Ba^{2+}	2 (SR)
Fe^{3+}	5 (AZ)	Sr^{2+}	2 (SR)
	20 (RA)	Ca^{2+}	2 (AZ)
	10 (DG)		

* *Cf.* Table I.

From an unknown mixture, the Group IV cations were separated with solvent H (*cf.* Table II). The chromatograms were sprayed with a saturated solution of rubeanic acid for location of nickel, cobalt and manganese, while the outermost ring due to zinc (having an R_f of 0·55) was visible only when the same chromatogram was sprayed with dithizone solution in chloroform.

Attempts were made to include the analysis of mixtures of sodium, potassium and magnesium, but no spray reagent was found satisfactory for location of the cations of this Group.

Zusammenfassung—Nach Trennung der Metallionen in die 5 Gruppen des klassischen Schwefelwasserstofftrennungsganges der qualitativen Analyse werden die Ionen jeder Gruppe durch ringförmige Dünnschichtchromatographie getrennt. Verschiedene Lösungsmittel und Sprühreagentien für die Gruppenanalysen werden angegeben. Die Methode ist einfach und bequem; die Entwicklung eines Chromatogramms dauert 2 Minuten.

Résumé—Après séparation des ions métalliques en groupes I–V au moyen d'hydrogène sulfuré, selon le schéma classique de l'analyse qualitative, on sépare les ions métalliques dans chaque groupe par chromatographie en couche mince circulaire. On décrit plusieurs solvants et réactifs de pulvérisation pour l'analyse des groupes. La méthode est simple et commode; le développement d'une chromatoplaque est achevé en 2 minutes.

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SUBSTOICHIOMETRIC DETERMINATION OF COPPER IN HIGH-PURITY METALS BY ACTIVATION ANALYSIS

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Summary—A selective and very simple substoichiometric determination of copper in high-purity aluminium, silicon, iron, gallium, zinc and tin by activation analysis has been developed. The radiochemical procedure is based on the extraction of copper diethyldithiocarbamate into chloroform from an aqueous alkaline medium. The only interfering elements are mercury, palladium, silver, osmium and gold.

THE determination of traces of impurities of the order of $10^{-4}\%$ and lower can be carried out by destructive activation analysis.

In order to prepare a radiochemically pure sample for counting, a laborious and time-consuming isolation may be necessary and the chemical yield may need to be determined. Determinations can be done very much quicker if the technique of gamma-spectrometry is used for the measurements. In this case the requirements for radiochemical purity of the counted sample are not as high as for the counting of beta-activity. Even in this case it may be desirable partially to separate radiochemically the activity to ensure that peaks in the gamma-spectrum do not overlap; here again it would be necessary to determine the chemical yield.

A substantial reduction in the complexity of the chemical isolation can be achieved by using the principle of substoichiometry suggested by Růžička and Starý.[1] The main advantage of this principle lies in the greatly enhanced selectivity of the radiochemical separation. Using exactly the same quantity of carrier and reagent for both the test sample and the standard solution, the two chemical yields are the same and need not be estimated. The above-mentioned authors have successfully applied the substoichiometric method in activation analysis, *e.g.*, for the determination of zinc and copper in germanium dioxide by extraction with dithizone,[2] of silver also by dithizone extraction,[3] of molybdenum by extraction with 8-hydroxyquinoline,[4] *etc.*

For the determination by activation analysis of traces of copper in high-purity aluminium, silicon, iron, zinc, gallium and tin, we have now used the substoichiometric method by extracting copper diethyldithiocarbamate into chloroform. The extractability of metal carbamates decreases in the order: mercury, palladium, silver, copper, thallium(III), *etc.*[5] Therefore, using a substoichiometric amount of reagent, the organic phase will contain, besides copper, only mercury, palladium and silver, and with gamma-spectrometry it should be possible to perform a selective analysis for copper.

EXPERIMENTAL

Apparatus

200-Channel gamma-spectrometer, Intertechnique SAI 332 (Intertechnique, 94 Avenue de Paris, Versailles; France). NaI(Tl) crystal 1 × 1·5 inch.

Reagents

Copper carrier solution. An aqueous solution containing 10 mg of copper/ml in the form of $Cu(NO_3)_2$.

Copper standard solution. Prepared by diluting the carrier solution in the ratio 1:50.

Screening solutions. 25% Aqueous citric acid, 5% aqueous disodium ethylenediaminetetra-acetate (EDTA).

Sodium diethyldithiocarbamate (NaDDTC) *solution.* Prepared by dissolving 680 mg of the reagent in 100 ml of water (1 ml of reagent solution $\simeq$ 1·27 mg of copper).

The purity of all reagents used was *Pro Analysi.*

Test substances. Samples of high-purity aluminium, silicon, gallium and tin, spectrally pure iron, pure zinc, sodium carbonate (*Pro Analysi*) were used.

Irradiation

The test samples of high-purity metals, weighing 0·08–0·5 g, were irradiated in aluminium containers for 1–20 hr in a VVR-S reactor in the Institute of Nuclear Research, Řež, in a flux of about 10^{13} neutron.cm^{-2}.sec^{-1}; zinc was irradiated in a thermal column in a flux of 10^{11} neutron.cm^{-2}.sec^{-1}. The standards, prepared by evaporating to dryness 0·1 ml of carrier solution in quartz ampoules, were also enclosed in the aluminium containers.

Some of the samples (zinc, gallium, tin) give resonance peaks in the epithermal region of neutron flux. It was, therefore, necessary to estimate the extent of the possible modification of copper analysis from the absorption of neutrons in the matrix. By irradiation of copper both inside and without a cadmium capsule it was revealed that the contribution of epithermal neutrons to the total activity amounted only to 5·6% for irradiation in the core and 0·4% for irradiation in the thermal column. Epithermal resonance absorptions exert, therefore, no substantial influence on the copper activity. Moreover, the resonance peaks of gallium and tin do not overlap the resonance peaks of copper and are located at relatively high energies.[6] Auto-absorption of thermal neutrons in the present experiments is negligible.[7]

Procedure

The irradiated test sample was dissolved in hydrochloric acid to which 1 ml of carrier solution and a small quantity of nitric acid were added. For dissolution of silicon a mixture of nitric and hydrofluoric acids was used. After dissolution, 15 ml of 25% citric acid solution and 15 ml of 5% EDTA solution were added and the solution made alkaline using Alizarin Yellow R as indicator (pH 12). The solution was then transferred to a 50-ml separatory funnel, exactly 5 ml of NaDDTC solution were added and copper was extracted with 20 ml of chloroform for 3 min. After washing the mixture with 25% citric acid solution and 5% EDTA solution at pH 12, the chloroform layer was discharged into a 25-ml graduated flask, diluted to the mark with chloroform and the gamma-spectrum measured by means of a 200-channel analyser. The standard solution was treated similarly; the residue from evaporation was washed out quantitatively from the quartz ampoule with 5 ml of conc. nitric acid and diluted with water to the mark in the graduated flask. For the actual determination a suitable portion was taken, 1 ml of copper carrier solution added and treated in exactly the same way as the test sample. By comparing the areas of the annihilation gamma-peaks of ^{64}Cu in the test sample and in the standard solution, the copper content of the test sample was measured.[8]

RESULTS AND DISCUSSION

Extraction of copper with sodium diethyldithiocarbamate can be used for the selective separation of copper either from slightly acidic or alkaline solutions. The extraction of copper from an alkaline medium of pH above 10 in the presence of citric acid and EDTA[9] has been found most suitable for its substoichiometric separation from solutions containing up to gram-quantities of various test materials. Under these conditions the determination is highly selective[5,9] and only mercury, palladium and silver—and perhaps also osmium—will be co-extracted with copper. Gold is slowly reduced to the metal by the diethyldithiocarbamate, any non-reduced gold also being extracted.[9] Of the possible interfering radionuclides, only ^{193}Os gives photopeaks, corresponding to gamma-rays of energies 0·46 and 0·56 MeV, in the vicinity of the annihilation peak (0·511 MeV) of ^{64}Cu (Table I). However, these peaks could be differentiated.

TABLE I[10,11]

Isotope	Half-life	Photon energies, *MeV*	Activation cross-section, *barn*
^{64}Cu	12·8 hr	0·51 ann; (1·34)	4·3
^{108m}Ag	5 year	0·72; 0·62; 0·43	—
^{108}Ag	2·3 min		44
^{110m}Ag	253 day	0·66; 0·88	3·2
^{110}Ag	24 sec	0·66	110
^{185}Os	94 day	0·65; 0·88; 0·87	200
^{191m}Os	14 hr	0·74	—
^{191}Os	15 day	0·129; 0·042	8
^{193}Os	31·5 hr	0·073; 0·281; 0·46 0·39; 0·56;	1·6
^{198}Au	2·7 day	0·412	96
^{197m}Hg	25 hr	0·164; 0·133	—
^{197}Hg	65 hr	0·077	—
^{199m}Hg	43 min	0·16	—
^{203}Hg	47 day	0·279	4
^{205}Hg	5·1 min	0·20	0·4

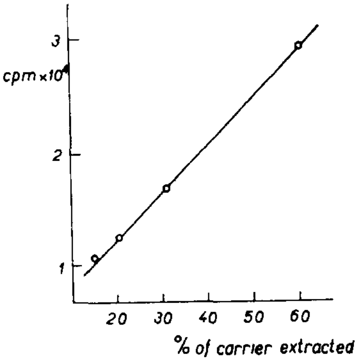

FIG. 1.—Extraction of carrier solution (labelled with ^{64}Cu) using an increasing (substoichiometric) amount of sodium diethyldithiocarbamate solution and a fixed volume of chloroform (stoichiometry equals 100% of carrier extracted; activity of organic phase expressed in cpm; extraction at pH 10).

In order to ensure the highest possible purity of the extracted copper, a substoichiometric quantity of the reagent solution, corresponding to about 63% of the carrier added, was used for its extraction. Also, this substantially reduced the duration of the determination, because it was unnecessary to determine the chemical yield. In order to estimate the reproducibility, extractions of carrier solution (labelled with ^{64}Cu) with increasing substoichiometric amounts of sodium diethyldithiocarbamate solution and a fixed amount of chloroform were studied (Fig. 1). A number of such experiments was also carried out in the presence of target materials. Reproducible results were obtained in all cases and so it has been proved that substoichiometric amounts of sodium diethyldithiocarbamate can be used for the extraction of copper. In almost all analyses of target materials, pure ^{64}Cu was obtained in a single extraction (see, for instance, Fig. 2). Even if some other isotopes were extracted (Table I), they would not affect the chemical yield because their quantity by

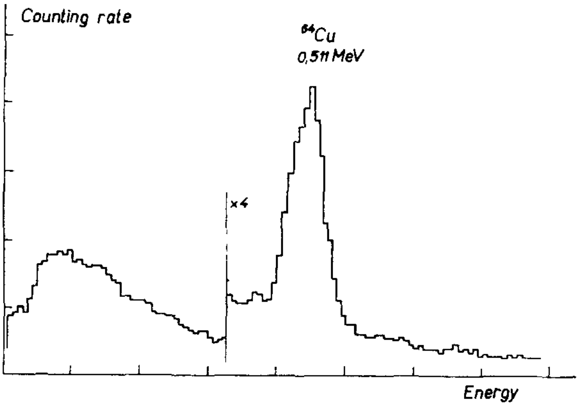

FIG. 2.—Gamma-spectrum of ^{64}Cu isolated in determination of copper in silicon.

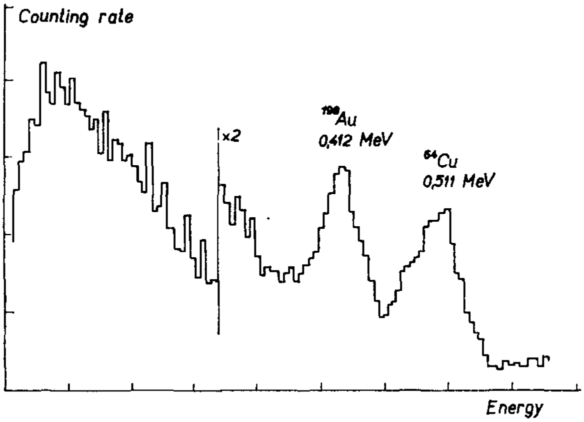

FIG. 3.—Gamma-spectrum of ^{64}Cu isolated in determination of copper in aluminium.

weight is negligible. They can be easily distinguished in the gamma-spectrum. In fact, in two instances the gamma-spectra showed the presence of traces of ^{198}Au and ^{197,203}Hg (Figs. 3 and 4). In several cases, the purity of the sample was also checked by measurement of the decay beta-activity and of the annihilation peak (0·511 MeV), *e.g.*, in the sample in which the presence of gold was proved. This measurement confirmed either the radiochemical purity of the sample or the absence of foreign activities in the energy range around 0·511 MeV.

Using the developed method it was found possible to determine even submicrogram amounts of copper in aluminium, silicon, tin and gallium of high purity. The copper content of spectrally pure iron is considerably higher. For the determination of copper in zinc, only zinc with a high copper content was available. The results of the latter determination, therefore, confirm only the possibility of carrying out a simple and rapid determination of copper in this metal. The results from our analyses are given in Table II. The method is also applicable for the determination of copper in specially pure reagents and acids, *e.g.*, in sodium carbonate (*Pro Analysi*). It permits the determination of less than 10^{-8} g of copper. The chemical treatment

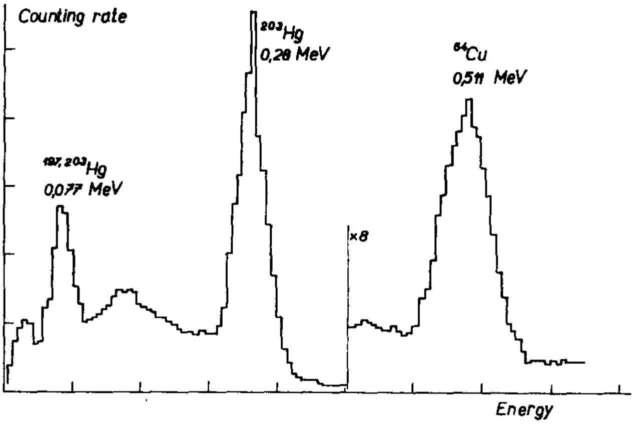

FIG. 4.—Gamma-spectrum of ^{64}Cu isolated in determination of copper in gallium.

TABLE II

Sample	Cu found*, *ppm*
Aluminium	1·60
Silicon	0·25
Iron	49·50
Zinc	41·20
Gallium	24·10
Tin	1·44
Na_2CO_3	3·14

* Average of 3 experiments.

required is very simple. Most time in the analysis is needed for dissolving the high-purity materials; the chemical separation proper lasts only 5–10 min. The use of the gamma-analyser facilitates the copper determinations without the need to measure the half-life even in the case when the extraction is not quite specific.

Zusammenfassung—Eine selektive und sehr einfache unterstöchiometrische Methode zur Bestimmung von Kupfer in hochreinem Aluminium, Silicium, Eisen, Gallium, Zink und Zinn durch Aktivierungsanalyse wurde entwickelt. Die radiochemische Arbeitsweise beruht auf der Extraktion von Kupferdiäthyldithiocarbamat aus wäßrig alkalischem Medium mit Chloroform. Es stören nur Quecksilber, Palladium, Silber, Osmium und Gold.

Résumé—On a élaboré une méthode de dosage substoechiométrique, sélective et très simple, du cuivre dans les aluminium, silicium, fer, gallium, zinc et étain de haute pureté, par analyse par activation. La technique radiochimique est basée sur l'extraction du diéthyldithiocarbamate de cuivre en chloroforme à partir d'un milieu aqueux alcalin. Les seuls éléments qui interfèrent sont le mercure, le palladium, l'argent, l'osmium et l'or.

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REDUCTION OF ALKYL DISULPHIDES WITH TRIPHENYLPHOSPHINE

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Summary—Alkyl disulphides are reduced to thiols by triphenylphosphine in aqueous methanol, with the phosphine being converted to the oxide. Water is believed to be the source of the hydrogen and oxygen required. The reductions are rather slow; heating for periods of several hours is necessary. Maximum yields of 70–80% are generally obtained, although some substituted alkyl disulphides, such as cystine and dithiodiglycolic acid, are quantitatively reduced. The principal analytical application of this reduction appears to be the determination of aromatic disulphides in the presence of alkyl disulphides, because the aromatic compounds are reduced at a much greater rate.

INTRODUCTION

TRIPHENYLPHOSPHINE has been found to be an effective agent for reducing aromatic disulphides, in aqueous methanol, to thiols.[1] This reduction was first reported for phenyl disulphide by Schonberg[2] and was mentioned later in a report by Schonberg and Barakat[3] on the reaction of triphenylphosphine with a series of disulphides:

$$RSSR + (C_6H_5)_3P + H_2O \rightarrow 2RSH + (C_6H_5)_3PO.$$

Several acyl and thioacyl disulphides and 4,4′-dithio-bis-*N*,*N*′-dimethylaniline were found to react with triphenylphosphine to yield the corresponding monosulphide and triphenylphosphine sulphide. This reaction was later reported for allyl disulphide[4] and for a number of alkenyl disulphides:[5,6]

$$RSSR + (C_6H_5)_3P \rightarrow RSR + (C_6H_5)_3PS.$$

Schonberg and Barakat[3] reported that ethyl, benzyl, benzhydryl, and 9-fluorenyl disulphides did not react with triphenylphosphine in refluxing benzene. Moore and Trego[5] found that benzyl disulphide did not interact with triphenylphosphine after several hours at 80° in benzene. These authors also reported that isopropyl, tert-butyl and n-butyl tetrasulphides were converted to the disulphides on refluxing with excess triphenylphosphine in benzene and that there was no reaction beyond this point.

We have found that a number of alkyl disulphides are reduced to thiols on reaction with triphenylphosphine in aqueous methanol containing perchloric acid. The reductions, generally, are not quantitative but yields of 90% were found for some compounds. Only a small amount of reduction occurs after several hours at room temperature. Because of the great difference in ease of reduction of aromatic disulphides with triphenylphosphine as compared to alkyl disulphides it is possible to obtain selective reduction of aromatic disulphides in the presence of alkyl disulphides. This paper reports a study of the reaction of a variety of alkyl disulphides with triphenylphosphine and the selective reduction of aromatic disulphides.

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DISCUSSION

The reduction of alkyl disulphides to thiols with triphenylphosphine is considerably more difficult than for aryl disulphides, requiring several hours of heating for even partial reduction. Aryl disulphides are quantitatively reduced at room temperature in a few minutes. This difference in the ease of reduction is also reflected in the polarographic behaviour of these disulphides. Aromatic disulphides are reduced at the dropping mercury electrode in the region of −0·5 V *vs.* S.C.E. in acetate buffer while alkyl disulphides require a potential of approximately −1·75 V. Only a few substituted alkyl disulphides are quantitatively reduced by triphenylphosphine and these only after heating for 1–2 hr. Although alkyl disulphides can be much more easily reduced by other procedures, the great difference in rate of reduction of aromatic disulphides and alkyl disulphides with triphenylphosphine allows the quantitative determination of the aryl compounds in the presence of the aliphatic substances.

Polarographic studies

The presence of the alkyl thiols was detected by polarographic observation of the reaction solutions. All of the alkyl thiols showed an oxidation wave at the dropping mercury electrode with a half-wave potential at +0·05 V *vs.* S.C.E. in 0·1*M* perchloric acid (Fig. 1). It has been suggested that this is caused by the formation of the mercurous salt of the thiol.[7] These waves are somewhat erratic; sometimes a pronounced "dip" in the plateau of the wave, from +0·2 to +0·3 V *vs.* S.C.E., appears. This oxidation wave is greatly dependent on acidity, with the half-wave potential occurring at approximately −0·35 V *vs.* S.C.E. in sodium acetate–acetic acid solutions in aqueous methanol.

The reactions of the alkyl disulphides were followed by observing the polarographic reduction waves in the region of −1·75 V *vs.* S.C.E. The loss of the disulphide was shown by the decrease in the wave height. In most cases the decrease in disulphide concentration correlated fairly well with the amount of thiol formed. In some experiments there was some discrepancy in that the reduction wave had almost gone whilst the titre showed 60–70% reduction. This is possibly because of loss of thiol through the reflux condenser. In most cases the coolant for the condensers was maintained at about −10° by use of a refrigerant bath.

Amperometric titrations

Results for the titrations of the alkyl disulphides are shown in Table I. As stated previously, yields become almost quantitative after several hours of refluxing. The

TABLE I.—REDUCTION OF VARIOUS DISULPHIDES

Compound	RSSR[a], *mg*	Time, *hr*	Temperature	RSH, *mg*	Reduction, %[b]
Benzyl disulphide	12·7	20	Room	5·3	40
	14·4	4	Reflux	13·7	95
Butyl disulphide	12·5	5	Room	1·0	8
	12·5	6	Reflux	11·6	93
Ethyl disulphide	10·1	5	Reflux	8·1	80
Propyl disulphide	11·1	4	Reflux	8·1	73
Dithiodiglycolic acid	11·1	4	Room	9·1	82
	12·1	2	Reflux	12·7	105
Cystine	11·6	3	Reflux	12·6	109

[a] The ratio of $(C_6H_5)_3P$ to RSSR was 1·5 to 2·0.

[b] Elemental sulphur added before titration, to react with excess phosphine.

two substituted alkyl disulphides seem to be easier to reduce with triphenylphosphine than the unsubstituted compounds. Essentially quantitative reduction was obtained for cystine and dithiodiglycolic acid in 1-2 hr. This agrees with the difference in ease of polarographic reduction. Cystine is reduced at −0·6 V *vs.* S.C.E. in 0·1*M* perchloric acid and dithiodiglycolic acid at −1·4 V *vs.* S.C.E. in acetate buffer, whilst the unsubstituted disulphides are not reduced until −1·7 to −1·8 V *vs.* S.C.E. in acetate solutions.

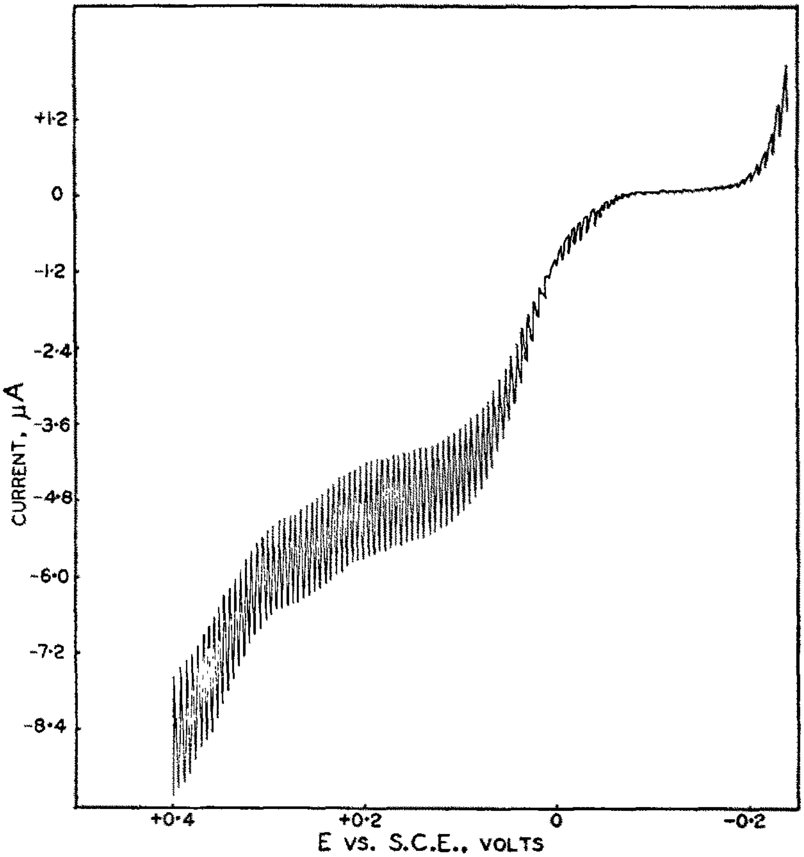

FIG. 1.—Polarogram of n-propanethiol produced by reaction of n-propyl disulphide with triphenylphosphine

It was found that the presence of unreacted triphenylphosphine leads to high results in the amperometric titration of the thiols with silver nitrate, because of the interaction of the phosphine with silver ion. Several organic phosphines are known to form complexes with silver ion.[8] The only simple means to overcome this difficulty appeared to be the addition of elemental sulphur to form the phosphine sulphide:

$$(C_6H_5)_3P + S \rightarrow (C_6H_5)_3PS.$$

Because the mole ratio of triphenylphosphine to disulphide was usually 2 : 1 (in order to increase the yield of thiol) the addition of sulphur was normally necessary. Neither triphenylphosphine oxide nor sulphide exhibited any interaction with silver ion. However, the presence of excess sulphur did lead to complications in the titrations of the thiols. Sulphur is reported to react with mercaptides forming a monoalkyl disulphide ion, which will then react with silver ion producing silver sulphide and an organic trisulphide:[9]

$$RSH + S \rightarrow RSSH$$
$$2RSSH + 2Ag^+ \rightarrow R_2S_3 + Ag_2S.$$

It is still possible to determine thiols in the presence of sulphur by titration with silver and even to estimate the amount of sulphur from the inflections in the potentiometric curve.[9] However, some difficulties are encountered if the solutions containing sulphur and thiol are allowed to age for very long.

In acidic aqueous methanol solutions containing thiol and sulphur addition of silver nitrate caused the appearance of a yellow, then orange colour with an early cloudiness, which resulted in a dark precipitate on aging for a few minutes. The colour is redder when aryl thiols are involved. In the titration of a solution containing *p*-aminothiophenol and sulphur with silver ion a deep red colour with no cloudiness resulted. There was no precipitation until the titration had been concluded. A dark precipitate formed after a few minutes and the colour disappeared. The titration of the thiol was quantitative. The nature of the interaction between thiols and sulphur and the subsequent reaction with silver ion has not been experimentally defined. In spite of the complex behaviour of these systems, the thiols can be titrated quantitatively so that sulphur can be used to react with excess triphenylphosphine.

Applications

Perhaps the most useful analytical application of the triphenylphosphine reduction would be the determination of aromatic disulphides in the presence of alkyl disulphides. Results from the reduction of aromatic disulphides in the presence of benzyl disulphide and butyl disulphide are shown in Table II. These reductions were carried out at room temperature. It is probable that the reduction of almost any alkyl disulphide would be sufficiently slow so that there would not be enough alkyl thiol produced to cause error in the determination of the aromatic disulphides. The reductions were terminated in 20 min by adding sulphur to react with the phosphine. This time

TABLE II.—SELECTIVE REDUCTION OF AROMATIC DISULPHIDES

Compound	ArSSAr[a], *mg*	Benzyl disulphide, *mg*	Butyl disulphide, *mg*	ArSH, *mg*	Reduction, %[b]
Phenyl disulphide	10·8	13·1		10·8	100
	10·1		8·1	10·2	101
p-Tolyl disulphide	13·2	12·6		12·3	93
	14·3		8·1	14·1	98
Bis(*o*-nitrophenyl)disulphide	18·8	16·6		18·3	99
	13·8		8·1	13·5	98
4,4′-Dithiodianiline	13·8	12·8		13·6	98
	13·4		8·1	13·2	98

[a] 32–36 mg of $(C_6H_5)_3P$ present.

[b] Reaction time was 20 min; elemental sulphur added before titration.

could be shortened in the event of interference because small amounts of aromatic disulphides are reduced in 5–10 min by triphenylphosphine.

Detection of triphenylphosphine oxide

The presence of triphenylphosphine oxide in reaction residues was detected by infrared studies. The oxide shows a strong absorption band at 1190 cm^{-1}, which has been attributed to the P-O vibration.[10] Infrared spectra of the reaction residues for the reactions involving cystine, dithiodiglycolic acid and butyl disulphide showed a prominent absorption peak at the P-O frequency. It is possible that some oxidation could occur by dissolved or atmospheric oxygen although it has been shown that triphenylphosphine is not readily oxidised in a stream of oxygen.[11] Triphenylphosphine alone when put through the same procedure as that used to obtain the reaction residues showed little evidence of oxide formation on infrared examination.

EXPERIMENTAL

Apparatus

Polarography. Polarograms were recorded with a Sargent Model XV recording polarograph. A conventional "H" cell mounted on a Sargent constant head dropping mercury electrode assembly was employed. The amperometric titrations were performed using a Sargent synchronous rotator with a platinum electrode. Current was measured with a Hewlitt-Packard vacuum-tube voltmeter.

Infrared spectrophotometer. Beckman IR-5 spectrophotometer

Reagents

Dithiodiglycolic acid and triphenylphosphine oxide were obtained from Chemicals Procurement Laboratories. Triphenylphosphine, cystine, benzyl disulphide and the alkyl disulphides were Eastman white label grade chemicals. All solvents and reagents used were the best available materials.

Procedure

The reactions were usually conducted in 10% aqueous methanol which was $0{\cdot}1M$ in perchloric acid or sodium acetate and acetic acid. For the polarographic studies of the disulphides, a mixed solvent of 40% methanol, 40% isopropanol, and 20% water containing tetramethylammonium nitrate ($0{\cdot}1M$) was used.

Stock solutions of the liquid disulphides were prepared in methanol and aliquots were taken for the reactions. The solid disulphides and triphenylphosphine were weighed directly and dissolved in a small volume (1 ml) of acetone or benzene, then diluted to 100 ml with the aqueous methanol solvent. Solutions were refluxed for periods of from 1 to 6 hr. The reflux condenser was cooled to $-10°$ in most instances to prevent loss of the volatile thiols. Polarograms were then recorded for some of the reaction solutions to detect the presence of the thiols and observe the decrease in concentration of the disulphides. The yields of thiols were determined by amperometric titration with $0{\cdot}01M$ silver nitrate employing a rotating platinum electrode with a saturated calomel electrode as reference. The titration procedure was essentially the same as that of Kolthoff and Harris.[12]

Acknowledgment—The support of the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

Zusammenfassung—Alkyldisulfide lassen sich in wäßrigem Methanol mit Triphenylphosphin zu Mercaptanen reduzieren, wobei das Phosphin in Phosphinoxyd übergeht; Vermutlich stammen der benötigte Wasserstoff und Saurerstoff aus dem Wasser. Die Reduktionen gehen langsam; mehrstundiges Erhitzen ist notwendig. Im allgemeinen lassen sich Ausbeuten bis zu 70–80% erzielen; indessen werden einige substituierte Alkyldisulfide, wie Cydin und Dithioglycolsäure, quantitativ reduziert. Die Wichtigste analytische Anwendung dieser Reduktion ist offenbar die Bestimmung aromatischer Disulfide in Gegenwart aliphatischer, da die aromatischen Verbindungen mit viel größerer Geschwindigkeit reduziert werden.

Résumé—Les disulfures d'alcoyle sont réduits en thiols au moyen de triphényl-phosphine en méthanol aqueux, avec conversion de la phosphine en son oxyde. On pense que l'eau est la source de l'hydrogène et de l'oxygène nécessaires. Les réductions sont lentes; il est nécessaire de chauffer pendant plusieurs heures. On obtient en général des rendements maximaux de 70–80%, bien que la réduction soit quantitative avec quelques disulfures d'alcoyle substitués, comme la cydine et l'acide dithioglycolique. L'application analytique principale de cette réduction semble être le dosage des disulfures aromatiques en présence des disulfures aliphatiques, les composés aromatiques étant réduits beaucoup plus rapidement.

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SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM AFTER EXTRACTION OF THE STANNOUS-CHLORO COMPLEX BY HIGH MOLECULAR WEIGHT AMINES

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Summary—An investigation of the complex formed between platinum(IV) and tin(II) in hydrochloric acid solutions has been carried out, and its extractibility by various long-chain high molecular weight amines (HMWA) in organic solvents examined. The orange coloured platinum(IV)–tin(II) complex is quantitatively extractable from an aqueous phase into an organic phase of a wide range of high molecular weight amines in chloroform or benzene. On the basis of this extractability a method has been developed for the spectrophotometric determination of platinum in the presence of many other elements. Comparison of the absorption spectra of the coloured species in the aqueous and amine phases indicates the presence of the same absorption species in each medium. The extractability of the complex by HMWA suggests that the coloured species is anionic and not cationic as reported by earlier authors.

INTRODUCTION

HIGH molecular weight amines (HMWA), particularly the highly branched alkyl amines, have been used for the separation of several pairs of metals as anions[1–4] and for the extraction of metals such as uranium, thorium and plutonium.[5–8] In several cases the elucidation of the structure of anionic species on the basis of extraction information has been possible.[9–12] The most popular method of extraction of metals is as the halo-complexes from hydrochloric acid into an organic phase containing the amine.

In the present work a survey of the literature revealed that extraction of metals of the platinum group into HMWA as the stannous-chloro complexes had not previously been employed.

The reaction of tin(II) with platinum(IV) was first observed by Wohler,[13] who attributed the colour formation to colloidal platinum, analogous to the "purple of Cassius" when gold is similarly treated. Sandell[14] studied the method and found that the system obeyed Beer's law but was subject to marked interference from palladium and other platinum group metals. Ayres and Meyer[15] carried out a detailed spectrophotometric study of the platinum(IV)–tin(II) chloride system in aqueous solution and in amyl and ethyl acetate extracts. He found that the colour on extraction faded rapidly, probably because of atmospheric oxidation, and that almost all the platinum group metals form similarly coloured products, which are extractable into the organic phase. Further, co-extraction of tin (mostly stannic) into the organic phase was an undesirable feature.

In a study on the nature of the platinum(IV)–tin(II) chloride complex Meyer and Ayres[16] identified it as a tetrapositive cation, $(PtSn_4Cl_4)^{4+}$, in which platinum exists in zero valency, analogous to the zero valent metal in tetracyanonickelate and -palladate.[17] Shukla,[18] however, demonstrated, by electrophoretic studies, the presence of an anionic species, support for which was recently given in correspondence on the subject.[19,20]

In the belief that the species was more likely to be anionic than a tetrapositive cation, investigations were begun in this laboratory with the aim of using HMWA to extract the species and, if possible, use it for the spectrophotometric determination of platinum. The investigations carried out to this end, and the results obtained are reported below.

EXPERIMENTAL

Apparatus

Hilger Uvispek Spectrophotometer (S.P.700)

Reagents

Platinum chloride solution. Exactly 1 g of grade I platinum thermocouple wire (purity 99·99%) was dissolved in *aqua regia*, evaporated almost to dryness and the mass taken up with 20 ml of 1:1 hydrochloric acid. The evaporation and hydrochloric acid treatment was repeated three times to remove all the nitric acid and to destroy any nitrosoplatinic acid. Finally, the residue was taken up in 90 ml of concentrated hydrochloric acid and the solution diluted to 1 litre, giving a concentration of 1 mg of platinum/ml. The concentration of this solution was checked by precipitating platinum with formic acid, igniting and weighing as the metal.[21]

Tin(II) chloride solution. 23 g of tin(II) chloride dihydrate were dissolved in 100 ml of 3·5*M* hydrochloric acid.

Organic solvents. Chloroform was redistilled before use, but benzene (thiophene free) was used without any additional purification.

High molecular weight amines. The amines used are listed below; all were used without further purification:
primene 81-R ($t\text{-}C_{12-14}H_{25-29}NH_2$), mol. wt. 185–213, from Lennig Chem. Co., Ltd; tribenzylamine, mol. wt. 287, from B.D.H. (reagent grade); tri-n-hexylamine, mol. wt. 269, from Aldrich Chemical Co; tri-n-octylamine, mol. wt. 354, from L. Light & Co., Ltd.

Each amine was used as a 0·2*M* solution in benzene or chloroform, which was shaken with 3*M* hydrochloric acid before use.

Procedure for determination of platinum in presence (or absence) of palladium

When palladium is present, the amount should not exceed that of platinum and the aliquot taken for the determination should not contain more than 100 μg of each element.

To the solution in a 50-ml beaker, add dropwise 5% (v/v) aqueous ammonia from a burette until the solution just turns alkaline. Add a drop or two in excess and stir the solution thoroughly for 0·5–1 min, then add 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride solution without delay. Transfer the solution to a separatory funnel and add 5 ml of amine solution, which has been treated with hydrochloric acid. Shake for 2 min and allow the phases to separate. Filter the amine layer through a small filter paper into a 10-ml flask and make up to the mark with pure solvent. Measure the absorbance at 400 mμ and compare with a calibration curve prepared by taking standard amounts of platinum through the same procedure.

Notes. 1. 0·5–1 min is sufficient time to form the ammine of palladium. Longer periods allow the platinum to form the ammine salt and interference with the determination of platinum arises.

2. If only platinum is present, the addition of aqueous ammonia is unnecessary.

Procedure for determination of platinum in presence of rhodium

The amount of rhodium should not exceed the amount of platinum. An aliquot containing not more than 100 μg of platinum is suitable for the determination.

Take an aliquot of 5 ml, containing platinum and rhodium in 0·10–0·11*M* hydrochloric acid. Add 5 ml of 0·2*M* pretreated amine in organic solvent and shake for 2 min. Allow the phases to separate and draw off the aqueous phase, which contains almost all the rhodium. Wash the amine phase with 10 ml of 0·1*M* hydrochloric acid by shaking for 0·5–1 min (the wash liquid may appear turbid but no platinum will be stripped). Discard the aqueous phase and determine the amount of platinum in the amine phase. To do this shake the amine phase in a separatory funnel containing 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride solution in 50 ml of water. Continue the shaking for 2 min. Allow the phases to separate, collect the organic phase in a 10-ml flask and finish according to the procedure above.

As a final check on the method, the following "unknowns" were analysed by one of us (M.A.K.). The results are shown in Table II.

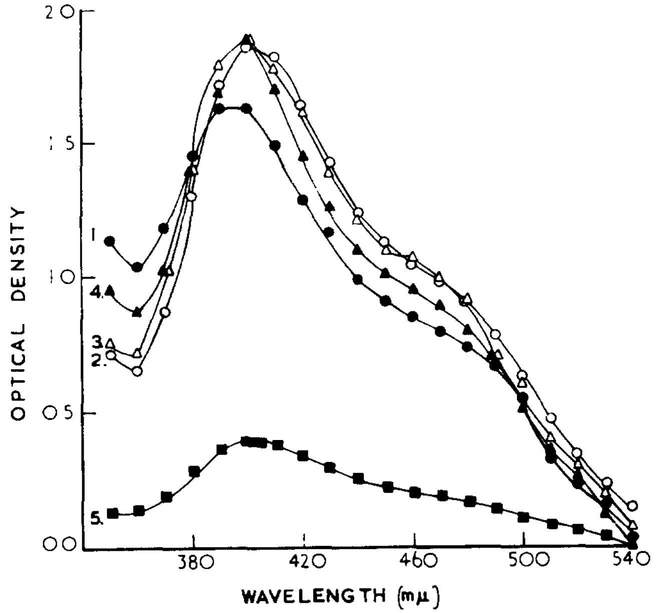

FIG. 1.—Absorption spectrum of platinum(IV)–tin(II)–chloro complex extracted by various amines in chloroform (0·2*M*) and the absorption spectrum of the same amount of platinum(IV) in the aqueous phase:
●—primene, ○—tri-n-benzylamine,
△—tri-n-hexylamine, ▲—tri-n-octylamine,
■—platinum colour developed in aqueous phase.

RESULTS

Formation of platinum(IV)*–tin*(II)*–chloro complex and extraction by* HMWA

The complex, orange in colour, was readily formed by treating 500 μg of platinum(IV) with 7 ml of concentrated hydrochloric acid and 1 ml of tin(II) chloride solution and making the volume up to 50 ml. It could be extracted by following the procedure given under *Experimental.*

To investigate the influence of HMWA, the procedure was followed using each amine in turn. All the complex was found to be removed from the aqueous phase in one extraction by all the amines used. This would appear to indicate that the complex is anionic, thus confirming the observations of Shukla and others.

Absorption spectrum

The platinum(IV)–tin(II) complex, after formation and extraction as outlined above, was examined spectrophotometrically and the absorption curve prepared in the range 350–600 mμ. In Figs. 1 and 2 the absorption spectrum for different amines in chloroform and benzene, respectively, is shown. From the figures it will be seen that all the curves are identical, showing maximum absorption at 400 mμ. A second absorption maximum occurs around 310 mμ. However, below 325 mμ the absorption of the blank is so great that this maximum is unsuitable for use. The absorption spectra of the complex in different amines closely resembles that of the platinum(IV)–tin(II) complex in aqueous solution, where the maximum occurs at 403 mμ.[15]

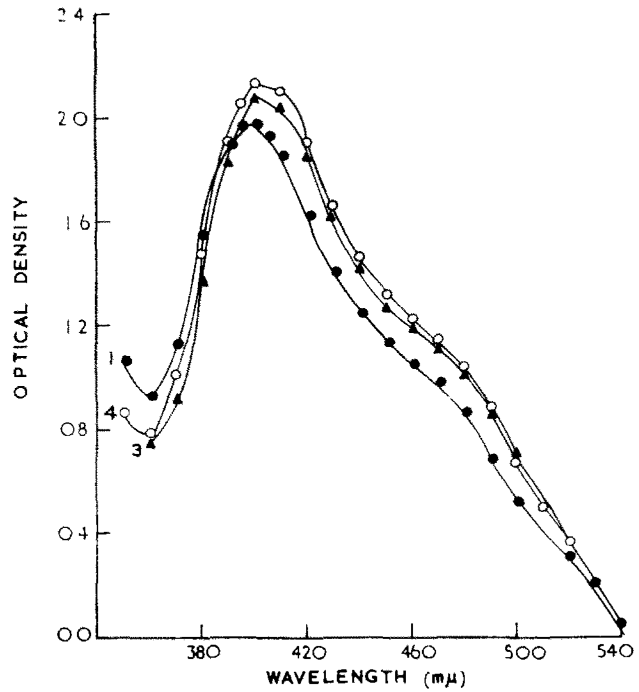

FIG. 2.—Absorption spectrum of platinum(IV)–tin(II)–chloro complex extracted by various amines in benzene (0·2*M*): ●—primene, ▲—tri-n-hexylamine, ○—tri-n-octylamine.

It would appear, therefore, that the coloured platinum(IV)–tin(II) complex is extracted from aqueous solution into the amine/organic phase, probably with little change in structure. Further, the fact that pure chloroform or benzene does not extract the complex from aqueous solution, whereas amine solutions of the solvents extract the complex with great efficiency, would indicate that it is anionic in nature, agreeing with the suggestions of Skukla[18] and the findings of Young *et al.*,[23] but disagreeing with the structure of Meyer and Ayres.[16]

Calibration and sensitivity

Known concentrations of platinum were extracted by the foregoing procedure and optical densities measured at 400 mμ. For solutions containing between 10 and 500 μg/10 ml, Beer's law was closely obeyed. An optical density of 0·1 corresponded to 25 μg when chloroform was the solvent and to 27 μg when benzene was used. The sensitivity of the amine-extracted complex showed an increase in sensitivity five-fold over the amount of platinum(IV)–tin(II) complex in the aqueous phase.

Effect of hydrochloric acid concentration

To prevent precipitation of tin(II) chloride the presence of hydrochloric acid is essential. Various concentrations of acid were examined and a concentration in the range 1·3–1·5*M* was found to be most suitable for efficient extraction. Further, in this range the extract was stable and clear. Within limits the amount of tin(II) chloride had little effect on the intensity of the colour. However, for all subsequent determinations the amount of tin(II) chloride was kept to a minimum (1 ml) which was sufficient to produce maximum colour intensity.

Extraction efficiency

In earlier work involving the extraction of the platinum(IV)–tin(II) complex the solvents used were iso-amyl acetate and ethyl acetate.[15] The extracts were, however, found to be unstable, particularly in the former solvent. Further, the extinction coefficient, and hence the sensitivity in both solvents was about the same as in the aqueous phase. The instability of the complex in these solvents probably arises from the fact that the negatively-charged species is not strongly bound by the solvent and decomposes into entities of indefinite composition on standing. On the other hand, there is a great affinity of HMWA for anions, which increases in the series primary > secondary > tertiary.[24] The high extraction efficiency of these high molecular weight amines for the complex can be judged by the fact that 5 ml of 0·2*M* amine in chloroform or benzene will extract the complex quantitatively from 50 ml of aqueous phase in a single extraction.

Stability

The stability of the amine/organic solvent extract was found to be dependent on three factors (1) hydrochloric acid concentration, as discussed above, (2) the type of solvent, and (3) the type of amine.

Solvent effect. When chloroform is used as the solvent, the extract is stable for 2 hr, but cloudiness then appears, probably because of the co-extraction of tin in the stannic form. However, despite the cloudiness the intensity of the colour remains unchanged even after standing overnight, if the tin(IV) is filtered off before measurement.

A benzene solution of the amine, when used as extractant, gives a very clear solution, which remains clear for a considerable period of time. No trace of turbidity is produced on standing overnight. An interesting point for which no explanation can be offered at present, is that, all conditions being the same, the amine/benzene system gives a greater intensity at the absorption maximum than the amine/chloroform system, although there is no shift in the absorption maximum.

Type of amine. All the amine extracts were stable and without cloudiness, except in the case of primary amines using chloroform. Tri-n-hexylamine and tri-n-octylamine in benzene solution gave excellent phase behaviour and the best extraction efficiency. Tribenzylamine in benzene gave a precipitate with the aqueous phase. No curve is shown for it in Fig. 2.

Interferences

The effect of tin(II) chloride in hydrochloric acid on a number of elements was examined by adding, to the solutions of a number of associated elements, hydrochloric acid and tin(II) chloride.

The following results were obtained with the different elements examined:

Osmium. The test solution itself has a faint amber colour. No colour change took place on the addition of the reagents and there was no evidence of extraction or interference in the determination of platinum.

Iridium. The test solution was bright orange in colour. Addition of the reagents decolourised the solution leaving only a faint yellow colour in solution. There was no evidence of extraction or interference in the determination of platinum. A third layer forms at the interface of the two phases, gel-like in appearance. This is, however, retained by the filter paper and presents no problem.

Ruthenium. The test solution was dark-blue in colour. Addition of the reagents changes this to a very pale blue. There was no evidence of extraction or interference in the determination of platinum.

Palladium. The test solution was light-orange. An intense red-orange colour develops instantaneously on addition of the reagents. The colour is completely and efficiently extracted into the amine phase and, under such conditions, interferes with the determination of platinum. Interference is, however, removed by the addition of dilute aqueous ammonia before the reagents. By this treatment palladium is converted into the cationic complex $[Pd(NH_3)_4]^{2+}$ which, under controlled conditions, does not interfere with the platinum determination. Platinum treated with aqueous ammonia before adding tin(II) solution does not show a tendency to form an ammine complex, unless left for some time.

Rhodium. This element forms two species when reduced with tin(II) chloride.[22] A hydrochloric acid solution of rhodium slowly develops a red colour when heated with tin(II) chloride. Such a solution on dilution with $2M$ or stronger hydrochloric acid retains its colour, but changes to a yellow solution on dilution with water. Neither coloured species has been identified. Both species are completely extractable into the amine phase, indicating anionic complexes; both interfere with the determination of platinum. Investigations showed, however, that the distribution ratio for the rhodium species in HMWA was very low in $0{\cdot}1M$ hydrochloric acid, whereas that for platinum is a maximum in acid of this strength. For equal amounts of platinum and rhodium contained in $0{\cdot}1M$ hydrochloric acid this difference in the distribution ratios enabled platinum to be determined.

Molybdenum. This element when treated with the reagent gives a blue colour, which on dilution turns reddish-orange. However, under the conditions used for platinum, molybdenum is not extracted. Even a one hundred-fold excess of molybdenum, which gives an intensely coloured aqueous phase, does not show the slightest sign of extraction. Molybdenum does not, therefore, interfere in the determination of platinum.

The following cations and anions caused no interference with the method: osmium(IV), ruthenium(IV), iridium(IV), cobalt(II), nickel(II), iron(III), sulphate, nitrate and perchlorate (Table I).

DISCUSSION

As indicated above, the complex formed between platinum(IV) and tin(II) is readily extracted into HMWA, from which it is supposed that the complex is anionic in nature and that "liquid anion exchange" occurs between the charged complex and the high molecular weight amine. The over-all reaction for this type of ion exchange might be represented by:

TABLE I.—DETERMINATION OF PLATINUM IN THE PRESENCE OF DIVERSE IONS

Diverse ion	Amount, μg	Platinum, μg		Error, μg
		Taken	Found	
Osmium(IV)	1000	400	402	+2
Ruthenium(III)	1000	400	400	0
Iridium(IV)	1000	400	397	−3
Palladium(II) (a)*	100	100	101	+1
(b)	100	100	102	+2
(c)	100	100	100	0
(d)	100	100	103	+3
Palladium(II)†	100	100	62·5	−37·5
Rhodium(IV) (a)	100	100	102	+2
(b)	100	100	100	0
(c)	100	100	100·5	+0·5
(d)	100	100	101	+1
Nickel(II)	1000	200	202	+2
Cobalt(II)	1000	200	200	0
Iron(III)	1000	200	198	−2
Chromium(III)	1000	200	200	0
Copper(II)	1000	200	200	0
Nitrate	1 g	400	398	−2
Chlorate		400	402	+2
Sulphate		400	400	0

* Allowed to stand for up to 1 min before addition of reagents.
† Allowed to stand for 5 min before addition of reagents.

TABLE II.—ANALYSIS OF "UNKNOWN" SAMPLES

Sample No.	Platinum, μg/ml		Error, μg	Other elements, μg/ml
	Present	Found		
I	5·0	5·1	+0·1	Pd, 5; Rh, 0
		4·95	−0·15	
		5·05	+0·05	
II	25	24·6	−0·4	Pd, 0; Rh, 10
		25·1	+0·1	
		25·05	+0·05	
III	4·0	4·4*	+0·4	Pd, 10; Rh, 0
		4·5	+0·5	
		4·5	+0·5	

* In this "unknown" the amount of palladium present was greater than that of platinum and, as expected, gave higher results.

$$RNH_{2(org)} + H^+A^-_{(aq)} \rightleftharpoons [RNH_3^+A^-]_{(org)}$$

$$n[RNH_3^+A^-]_{(org)} + [MX]^{n-}_{aq} \rightleftharpoons ([RNH_3^+]_n\,[MX]^{n-})_{(org)} + nA^-_{(aq)}$$

where $H^+A^-_{(aq)}$ in the present case represents hydrochloric acid, and $[MX]^{n-}_{(aq)}$

represents the platinum(IV)–tin(II) complex in aqueous solution. The conclusion that the complex is anionic in nature confirms the contention of Shukla.[18]

Further, from the fact that the absorption spectra of the complex species is the same with all the amines and organic solvents used would indicate that the absorbing species is the same in each case.

Rhodium forms two different kinds of complex with tin,[25] but both are extractable in a similar manner to the platinum(IV)–tin(II) complex. Palladium behaves in the same way, suggesting that the coloured species of both elements are also anionic in nature. It is assumed that, in the case of rhodium, the yellow complex differs from the red in the number of chlorine atoms in the molecule.

It may be that in the metal-tin complexes investigated, the metal is reduced by tin(II) chloride, then the tin(II) chloride enters the co-ordination sphere, giving rise to a metal-tin bond.

A study of the structure of the complexes of ruthenium, rhodium, iridium and platinum with tin(II) chloride has recently been reported by Young *et al.*[23] In this laboratory a study of the palladium–tin chloride complexes is at present in progress. Results will be reported later.

Résumé—On a effectué des recherches sur le complexe formé entre le platine(IV) et l'étain(II) en solutions chlorhydriques, et étudié son extractibilité par diverses amines à longue chaîne et haut poids moléculaire (HMWA) en solvants organiques. On peut extraire quantitativement le complexe platine(IV)–étain(II), coloré en orangé, à partir d'une phase aqueuse, dans une solution en chloroforme ou benzène d'une grande variété d'amines à haut poids moléculaire. Sur la base de cette extractibilité, on a élaboré une méthode de dosage spectrophotométrique du platine en présence de nombreux autres éléments. La comparaison des spectres d'absorption des espèces colorées en phases aqueuse et aminée indique la présence de la même espèce absorbante dans chaque milieu. L'extractibilité du complexe par HMWA suggère que l'espèce colorée est anionique et non cationique, ainsi qu'il a été dit antérieurement par d'autres auteurs.

Zusammenfassung—Der Komplex zwischen Platin(IV) und Zinn(II) in salzsauren Lösungen wurde untersucht sowie seine Extrahierbarkeit mit verschiedenen langkettigen Aminen großen Molekulargewichts (HMWA) in organischen Lösungsmitteln. Der orange gefärbte Platin(IV)–Zinn(II)-Komplex läßt sich quantitativ aus einer wäßrigen Phase mit sehr vielen Aminen hohen Molekulargewichts in Chloroform oder Benzol extrahieren. Auf Grund dieser Extrahierbarkeit wurde eine Arbeitsvorschrift zur spektralphotometrischen Bestimmung von Platin in Gegenwart vieler anderer Elemente entwickelt. Vergleich der Absorptionsspektren der farbigen Spezies in wäßriger und Aminphase zeigt, daß in beiden Medien die selbe absorbierende Spezies vorliegt. Die Extrahierbarkeit des Komplexes durch HMWA weist auf anionische Natur der farbigen Spezies hin, im Gegensatz zur Ansicht früherer Autoren.

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TALANTA REVIEW*

A CRITICAL EVALUATION OF COLORIMETRIC METHODS FOR DETERMINATION OF THE NOBLE METALS—III†‡

PALLADIUM AND PLATINUM

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Summary—Spectrophotometric methods for palladium and platinum recorded subsequent to 1958 are critically reviewed. Associated with the descriptions of each metal there is included a table which identifies reagents recorded before 1958 together with pertinent references.

INTRODUCTION

The number of spectrophotometric methods for the noble metals published during the past two decades probably exceeds the total number of all other reported quantitative methods for these metals. Simultaneously, new systems of analysis for alloys, solutions, ores, *etc.*, which contain traces of noble metals have been reported. Many of these analytical systems involve separational techniques, such as chromatography, ion exchange and extraction with immiscible solvents, which processes lend themselves especially to final spectrophotometric determinations. Arising out of these areas of research there has been developed a variety of methods for the determination of even fractions of micrograms of noble metals in kilogram amounts of sample. Systems for which no analytical methods were previously available may now be treated with simplicity and accuracy. A case in point is the separation and determination of microgram amounts of rhodium and iridium.

Ironically, this surplus of methods has created the usual problems associated with superabundance. Thus, the choice of method has now become a difficulty and this, in turn, has created a more critical attitude towards the content of pertinent publications. In general, the spectrophotometric methods are concisely and effectively recorded. However, there remain difficulties of interpretation and application and it is with a hope for the extended usefulness of spectrophotometric methods that the author, who has struggled under, and contributed to these difficulties, offers the following comments.

Practically all of the spectrophotometric methods for the determination of the noble metals deal with the problem of interfering constituents. Indeed, many authors justify their contributions with the claim for an improved degree of selectivity. In general, the technique used to ascertain the toleration for impurities is based on a prescribed small percentage departure from a specific absorbance resulting from a measured addition of the interfering constituents being tested. Thus, it is assumed that the identity of the dissolved constituent is fixed and permanent and irresponsive

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

† Part II: see reference 11.

‡ Part III: to be continued.

to the influences of dissolution processes, variations in acidities, age of solutions and air oxidation, *etc.*

It is clearly evident that too little attention has been given to the effect on the colour-forming capacity of noble metal solutions resulting from aging. It may be noted that a determination of the effects of aging require simultaneous variations in acidity, temperature, salt content, *etc.* In general, aging effects are not made evident by determining separately the effect of changes of temperature, of acidity, *etc.*

Among the noble metals there is no more striking example of the effect of long standing on solution composition than that visibly evident when an iridium metal or salts are fused with sodium peroxide and subsequently acidified with hydrochloric acid. Recently, Ryan[1] noted the effect of long standing on the chloroform-extraction properties of an iridium solution treated with 4,5-dimethyl-2-mercaptothiazole. As early as 1924 Ardagh *et al.*[2] recorded that aged solutions of chloroplatinate developed a colour with potassium iodide more rapidly than freshly prepared solutions. Recently, it has been shown that the cation isolation of ruthenium from base metals by Dowex 50 × 8 is adversely affected if the solution is allowed to age.[3]

Perhaps one of the most enlightening examples of the influence of long standing or aging on the colour-forming capacity is found with the osmium-thiourea reaction. Solutions of osmium made by distilling octavalent oxide into sulphur dioxide-hydrochloric acid yield an immediate pink on the addition of thiourea. With continued standing a solution, similarly prepared, may fail to produce a colour. This failure which has been erroneously ascribed to losses of osmium is, in fact, the result of changes in dissolved osmium constituents.

Recently, Nemac, Berka and Zýka[3a] recorded a titrimetric method for ruthenium which involves a titration of Ru^{4+} or $[RuCl_6]^{2-}$ with lead tetra-acetate. The authors state,

"In order to achieve a satisfactory course of the titration it is, however, necessary that the solutions of tetravalent ruthenium in dilute HCl which are titrated should be older than 14 days (from the day of their preparation).

The colour of tetravalent ruthenium stock solutions in dilute HCl (0·7N) changes after some time from the red-brown colour of freshly prepared solutions to a dark-brown to violet-brown color. Only sufficiently old solutions of the latter color can be used for the oxidation with $PbAc_4$ to be described."

Examples of the deleterious influence on solution composition of a previous fuming with sulphuric acid as opposed to the direct addition of a sulphate are numerous. It has been stated that large amounts of added sulphate can be tolerated in the spectrophotometric determination of platinum by 5-(*p*-dimethylaminobenzylidene)-rhodanine while a previous fuming cannot be tolerated.[4] The classical precipitation of rhodium by hydrogen sulphide requires a treatment with hydrochloric acid in those instances where rhodium solutions have been subjected to a period of fuming with sulphuric acid. Furthermore, the latter process applied to solutions of platinum chloride prevents the quantitative oxidation of platinum to the quadrivalent state which is required for hydrolytic separation from the remaining noble metals.[5] In these instances and others the direct addition of comparable amounts of sulphate ion provides relatively little interference with subsequent spectrophotometric and other determinations.

From these data, together with the voluminous literature dealing with the complexities of solution compositions of the noble metals, it would appear reasonable that consideration should be given to the interrelated effects of dissolution techniques, acidities, ion concentrations, period of aging, *etc.*, in the determination of the optimum conditions for the colour formation of reagent-noble metal constituents. This necessity may be further emphasised by a consideration of the unpredictable behaviour of hydrochloric acid solutions of iridium, which metal can be separated from other noble metal constituents by reductants from whose potentials one would predict a complete precipitation of iridium. The explanation for this anomaly may lie, not in incorrect potentials, but in a lack of information concerning the solution composition of the simple iridium solution.

Despite these instances of environmental difficulties, the tolerances for potentially interfering cations and anions determined by mixing the required solutions will in some cases prove to be acceptable data. This is particularly true when the investigator has made some effort to duplicate the character of the dissolved constituents, perhaps only by using salts whose oxidation states would correspond to those obtained by dissolution processes involving the commonly used oxidants such as nitric acid.[6] Furthermore, one cannot expect investigators to provide interference data derived from the many and various methods of dissolution. However, in those instances where dissolution may be accomplished by a simple treatment with *aqua regia* or with fuming sulphuric acid, some effort should be made to subject the mixed solution to a comparable procedure, and in any case careful consideration should always be given to the character of the noble metal salts used and the data should be accompanied by clearly defined descriptions of the environment used for colour development. Perhaps it should be stressed that the analytical chemist who is concerned about interference from specific constituents should, when it is practicable, determine for himself the tolerances applicable to his own techniques.

Here, perhaps one may suggest also that researchers in the field of spectrophotometric methods for noble metals have been traditionally and sometimes unduly preoccupied with immiscible solvent extractions as a means of accomplishing selectivity and eliminating interferences; relatively little attention has been given to the use of ion-exchange techniques as part of a colorimetric procedure. Contrary to the opinion that these techniques involve the treatment of large volumes of solutions, one may, by applying the full capacity of an exchanger, accomplish excellent separations with volumes at least comparable to those involving solvent extractions. In the areas of noble-metal determination, one may collectively separate large proportions of many associated base metals with an efficiency exceeding that often accomplished by the use of immiscible solvents. There is here a potentially useful adjunct to trace methods of analysis.

A clear recognition of the effect on colour formation of environmental influences may dictate favourable procedural techniques.

Colour reagents which require media of low acidity usually offer some difficulty. The fact that, with the exception of quadrivalent platinum, these metals are quantitatively precipitated as hydrated oxides at a pH approaching neutrality will sometimes dictate a specific order of reagent addition and heating techniques. In general, when a pH of about 2–7 is required, the reagent, *etc.*, should be added before an adjustment to the required acidity and before any required heating period. These procedures may avoid low values resulting from the appearance of colloidal hydrated oxides which are usually insensitive to the colour reagent. Examples of this difficulty are found in the determination of ruthenium by acetylacetone,[7] in which case the pink complex is formed most rapidly at pH 5–6, and in the determination of osmium with anthranilic acid which requires a pH of 5·5–6·5 for colour development.[8]

Spectrophotometric procedures which belong to this category may prove discouraging to the practising analyst who wishes to achieve a good degree of precision and accuracy.

Almost invariably, published reports of new spectrophotometric procedures contain some expression of reaction sensitivity. The confusion concerning a precise meaning of sensitivity, evident in the early literature which deals with qualitative detection, has been removed largely by the work of Feigl who distinguished between quantity sensitivity and concentration sensitivity.[9] To express the former Feigl used the term identification limit, which is the mass limit of the constituent, usually expressed in micrograms, which can be detected. The limiting value to which this identification limit may be diluted is expressed as the "limiting concentration", "dilution limit" or "concentration limit".

Obviously, spectrophotometric techniques as they are presently described do not allow the use of the term identification limit. However, it is encouraging to note in a few recent reports the inclusion of data describing dilution limits for those reactions which produce visible colour changes. These data may well provide useful procedures for the detection of noble metals, particularly for the much needed field tests.

An approach to the use of dilution limits for spectrophotometric determinations was recommended by Sandell,[10] who defined sensitivity as "the number of micrograms of element, converted to the coloured product, which in a column of solution having a cross section of 1 cm^2 shows an absorbance of 0·001". "Sensitivity", thus defined, assumes that the Beer-Lambert Law holds to infinite dilution and thus cannot be applied to those methods which require working curves. Recently, various authors have expressed sensitivies in terms of absorbances greater than 0·001, *e.g.*, 0·01, and in addition have provided data concerning concentration sensitivity as expressed by Feigl.

The greater number of recently recorded spectrophotometric methods include data denoting the optimum range of concentrations. Presumably, the most favoured methods are those with a wide range of applicable concentrations and exceptionally high sensitivities. Perhaps too little attention has been given to those methods which apply only to concentrations which fall within the range of classical methods. Not infrequently, such methods are of considerable value in industrial laboratories when large numbers of samples must be analysed and rapidity of determination is of primary importance and high accuracy only of secondary importance.

Reports of procedures involving new reagents generally include data dealing with accuracy and precision. In common with all analytical methods, any expression of these terms for spectrophotometric methods must involve the efficient functioning of some mechanical equipment as well as the efficiency with which the unit is operated and with which the associated techniques are manipulated. An adequate recognition of the variability in human frailties requires acceptance with reservations of data concerning accuracy and precision. Thus, in some instances an experienced operator may increase the accuracy of a spectrophotometric method beyond that designated by the author or there may be failure to achieve this limit. Generally, one may hope to reach an accuracy of about ±1 to 3% from most direct spectrophotometric methods. Very few if any of these methods applied to the determination of noble metals achieve an accuracy in excess of 1%, which is also the approximate limit for such competitive methods as optical and X-ray spectrographic analysis. In general, the authors determine the accuracy of their method over a quoted optimum range of concentrations. Because of the relatively low accuracy as compared with many classical analytical methods, the problem of achieving high precision is of less importance. However, one must hope that newly proposed methods will contain some expression of precision and preferably these expressions should be confined to those commonly recognised and perhaps confined to those generally useful in the ranges of concentration to which spectrophotometric procedures apply. In the present author's opinion, few, if any, of the recorded spectrophotometric methods for noble metals, except perhaps in certain restricted areas of routine practice, provide an accuracy which could justify the inclusion of complete statistical expressions. Perhaps an adequate description of precision would be achieved by recording the number of determinations, the arithmetical mean and the average deviation. The more statistically useful "standard deviation" is seldom required and such terms as relative analytical error, *etc.*, often add to confusion and uncertainty of meaning. In any case, uniformity in expressions of accuracy and precision would add to the clarity achieved by the recent improvements in the symbology of expression for the Beer-Lambert Law.

With respect to the numbers of spectrophotometric methods now available, one may note the deficiency of methods for iridium and ruthenium and the relative abundance of methods for palladium. This situation exists also in all classical methods. One could hope that the efforts expended in the development of methods for palladium might be applied to the discovery of methods for the remaining platinum metals for most of which there is some deficiency of reagents. In defence of the rapidly accumulating methods for palladium it has been stated that a newly proposed method, despite any lack of obvious advantages, may supply a special need in some unforseen application. In the case of palladium the present author entertains reservations concerning this opinion and, in any case, perhaps here and in related situations one may conserve printed space through limiting the content of such reports to the degree that a record of the new reagent will not be lost.

The present review deals with the spectrophotometric methods recorded subsequent to the author's second review.[11] The seven tables, one for each noble metal, contain a complete list of reagents, including those discussed in the first and second reviews, together with the recommended range of concentration for each method and the reference to the pertinent publication. In general, these ranges are expressed as optimum ranges and in those instances in which the range is an expression only as that over which the Lambert-Beer Law applies, it is so indicated by the symbol B.L. In a very approximate way the reagents are listed in the order of an increasing lower limit of the concentration range. In some instances this arrangement is ignored; in general, this discontinuity is infrequent and appears especially in instances when there is a very close similarity of reagent structure.

Even a casual examination of the tables will reveal the superfluity of palladium reagents and a more detailed examination of the recorded descriptions of each palladium method may well serve to discourage a researcher who wishes to publish a new method for palladium and who seeks to find some justification for its publication.

On the other hand, the tables indicate a deficiency of methods for the remaining noble metals and strangely, this is the case with even the more common of the noble metals, *e.g.*, gold and platinum. Because spectrophotometric methods are generally applied subsequent to some method of concentration and because the concentration frequently involves the use of fusion mixtures, chlorination and mixtures of mineral acids, such as *aqua regia*, perchloric acid, fuming sulphuric acid, *etc.*, the spectrophotometric methods which may be integrated with these dissolution processes are especially useful. These preliminary processes invariably involve the necessity of transfering and washing and there are, therefore, difficulties in maintaining small volumes. Methods which allow colour development in volumes of noble metal solutions of the order of 10 ml or more are advantageous.

Much of the present author's research over the past three decades has included the application of spectrophotometric determinations subsequent to the use of the above dissolution and concentrating techniques. Initially, each researcher is required to make a choice of methods appropriate to his problem. It may be of interest to note that, despite the wide variety of preliminary treatments to secure the noble metal solution, and the variety of sensitivities and ranges involved, the following selection of methods is almost invariably made:

for platinum and palladium—tin(II) chloride and *p*-nitrosodimethylamine,
for rhodium —tin(II) bromide or tin(II) chloride,
for iridium —tin(II) bromide,
for osmium and ruthenium —thiourea.

PALLADIUM

Palladium has been determined by an extraction with ethylene chloride of a complex formed by mixing with palladium chloride solution, first a potassium iodide solution, then tetra-ethyleneglycoldimethyl ether to form the tetra-iodopalladate(II) salt.[12] The palladium solution was evaporated to remove nitric acid and adjusted to 3% in hydrochloric acid. Subsequent to the addition of the iodide and reagent solution, three to four extractions were made with ethylene chloride. The organic phase was filtered into a volumetric flask, made to volume with the organic extractant and the absorbance measured at 340 mμ. Large proportions of rhodium, nickel and cobalt are tolerated, but there is interference from copper(II), gold(III), iron(III), and platinum(IV) chloride.

Beer's Law applied over the range of 0–6 ppm of palladium with a sensitivity of about 0·2 μg/cm^2.* Better methods are available from the point of view of tolerance and of freedom from cumbersome techniques. Exposure of the organic extract to sunlight or extended exposure to daylight must be avoided. The required time of extraction is stated as 10 min.

N,N′-Bis-(2-sulphethyldithio-oxamide) was used by Goeminne *et al.*[13] to produce two complexes with palladium. With at least a four-fold excess the complex has a mole ratio of platinum to reagent of 1:2. With a deficiency of reagent the mole ratio is 1:1. The former is the more stable and is formed in 5–6*M* hydrochloric acid solutions. Maximum absorbance, measured at 425 mμ, was reached in 30 min and remained constant for 30 min. The applicable range of concentration is 0·02–0·2

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* The expression for sensitivity used throughout this review is that proposed by Sandell and described above.

ppm of solution. The sensitivity is 0·0083 μg/cm^2; the molar extinction coefficient is 12,860. There is interference from relatively small proportions of copper, iron, gold, platinum and ruthenium, less interference from rhodium and iridium, and relatively little interference from nickel and cobalt. Buffered solutions (pH 3–8) may also be used for the determination. The absorbance is then measured at 392 mμ. Tolerance for associated base and platinum metals is less than that for the determination in acid solutions.

A spectrophotometric method less susceptible to interferences from associated metals was described by Gustin and Sweet.[14] The method was used over the range of 2–150 μg/50 ml of the sample, which volume is recommended in the procedure. Thus the sensitivity on this basis is 0·04 ppm of solution. The reagent, 8-aminoquinoline, reacts with palladium at an acidity of pH 2·5 or less to form an insoluble yellow chloride complex with bivalent palladium with a mole ratio of palladium to reagent of 1:2. The precipitate is converted to a violet, insoluble complex at pH 10·2 or higher. This complex is extracted by chloroform to form a violet solution with an optimum absorbance at 590 mμ, which absorbance must be measured within 1 hr. Applied to synthetic samples containing the associated platinum metals with copper, iron, chromium(III), nickel, *etc.*, the results obtained indicated appreciable freedom from interferences. Iridium interferes in relatively small proportions. However, the proposed method requires the use of EDTA. The effect of gold was not determined.

One of the most effective methods of determining traces of palladium in the presence of the base metals frequently associated in such natural occurrences as ores, concentrates and alloys involves the selective isolation of palladium by coprecipitation with tellurium by tin(II) chloride. This method, applied to sulphide minerals, meteorites, *etc.*, was described by Sandell.[10] The method was modified by Marhenke and Sandell[15] to the extent that the precipitate of tellurium-palladium is treated to allow for an extraction by diethyl oxalate, which is preferred to the usual extractants, such as isopropyl ether and n-butanol, because of its lesser volatility, its density of 1·05 and its greater insolubility in water. Separation from water is clean and the palladium–*p*-nitrosodiphenylamine complex is stable in the extractant. The absorbance is measured at 525 mμ. Over the range 0·2–0·5 μg of palladium the recovery is 90% or greater. Presumably, the slightly low results arise from adsorption of palladium by coprecipitated metastannic acid.

The procedure requires a treatment of the sample with nitric and hydrochloric acids, removal of nitric oxides, addition of tellurium solution to the 3*M* hydrochloric acid solution, and finally addition of tin(II) chloride solution to precipitate the tellurium along with the palladium. The mixed precipitate is converted to a chloride solution, 0·01*M* in hydrochloric acid, treated with the reagent and then extracted with diethyl oxalate. As one would expect, the reduction procedure would ensure simultaneous precipitation of gold and silver. Treatment of the mixed precipitate would result in the formation of silver chloride which has a marked tendency to adsorb palladium. Thus, the amount of silver in the sample should not exceed 0·1 mg. In the case of gold, dissolution of the mixed precipitate would result in an association of gold with the palladium, the former causing high results by giving a colour with the reagent. The ratio of gold to palladium should not, therefore, exceed ten if the error in palladium is to be kept below 10%. Undoubtedly, an extraction of gold chloride following dissolution of the mixed tellurium precipitate would serve to remove this interference. There is practical value in the fact that the method tolerates as much as 100 μg of the associated platinum metals as well as large proportions of the base metals, iron, copper, nickel, cobalt, lead and chromium. The amount of selenium should not exceed 100 μg.

The authors predict a successful application of the method to meteorites, dunites, *etc.* It may be noted that a comparable separation of gold from a specific ore by McBryde and Yoe[16] yielded promising results. However, predictions of this nature should be accepted with some reservations. The complexities of the compositions of rocks, ores and natural alloys, along with the variations in solution composition resulting from even presumably consistent techniques of dissolution, will, not infrequently, render inapplicable a procedure which has proved eminently satisfactory when applied to synthetic materials.

8-Mercaptoquinoline (thio-oxine) was used by Bankovskii and Ievin'sh[17] to form a red chelate, $Pd(C_9H_6NS)_2{\cdot}H_2O$, insoluble in water and extractable with chloroform, chlorobenzene and bromobenzene. In these solvents the colour is an intense orange or rose. Extractions are made from 4–6*M* hydrochloric acid and with chloroform the three absorption maxima are 272, 286 and 485 mμ. The corresponding sensitivities are 0·024, 0·003 and 0·14 μg/cm^2 of palladium. Beer's Law applies up to 27 μg/ml in 6*M* hydrochloric acid; 2 μg/25 ml can be determined quantitatively. As much as 20 mg of platinum and 1–2 mg of osmium and ruthenium can be masked by thiourea. Iridium and rhodium do not react with thio-oxine in the strongly acid solution. Tervalent iron does not interfere in amounts up to 80 mg; larger amounts can be complexed by sodium hypophosphite. Copper, silver, gold and mercury react with thio-oxine and while the salts are not soluble in chloroform, they interfere, and to avoid this, thiourea is added to the mixtures of immiscible solvents subsequent to an initial shaking to remove the palladium complex. Molybdenum interferes and a modification of the method is required in its presence. Oxidising reagents must be absent.

In a later paper[18] these authors discussed the analytical applications of 8-mercaptoquinoline with the platinum metals. A significant feature of these reactions is that the complexes with platinum and palladium are salts of the type MeR_2 and with iridium, rhodium, osmium and ruthenium, of the type MeR_3. In the case of the platinum and palladium complexes, prepared in a pyridine medium, there is some coprecipitation of the oxidation product, thio-oxine-8,8′-diquinolylsulphide. The thio-oxinates of the remaining platinum metals do not coprecipitate with the oxidation product.

Xavier[19] used 2-mercaptoquinoline, whose sensitivity limit for palladium is 0·05 ppm. Colour development occurred at pH 1·4–2·8 and the absorbance was measured at 450 mμ. There was interference from associated base and noble metals.

Potassium thiocyanate in 100-fold excess can be used to form $Pd(SCN)_4{}^{2-}$, whose maximum absorbance in solution occurs at 310 mμ.[20] From 0·1 to 2 μg of palladium can be determined in the presence of a 300-fold amount of iron(III). Moderate amounts of platinum, iridium and rhodium may be tolerated if the absorbance is measured immediately. Thiocyanate was previously used by Przheva'shiĭ *et al.*[21] to produce a red complex, $[Pd(SCN)_4]_2{}^{2-}$, extractable with isoamyl alcohol or with butyl alcohol at a pH below 5. There was no interference from platinum(IV). Excess of thiocyanate ion prevented interference from iridium. Iron was complexed with disodium hydrogen phosphate.

Two of the most promising spectrophotometric reagents for palladium were proposed by Busev and Naku.[22] 1-Mercaptopropionic-*p*-anisidide and the corresponding *p*-toluidide produced yellow precipitates in an acidic medium with relatively high concentrations of palladium and a yellow colour with low concentrations. The yellow constituents were extractable by chloroform and benzene to give yellow solutions. The mole composition of the yellow constituent is 1:2 for palladium to the reagent. The absorption maximum in chloroform or benzene was 410 mμ for both reagents. Beer's Law applied over the range 0·2–12 μg of palladium/ml. The procedure for colour development required the use of 2–140 μg of palladium in 10–15 ml of solution. In chloroform the molar extinction coefficient for the aniside reagent was 15,700 with a sensitivity of 0·14 μg/cm^2. These data were comparable for the toluidide reagent and for benzene solvents. Optimum absorbance was attained over the range 0·1–3*M* hydrochloric acid. There was a slight decrease in absorbance at higher acidities. At least a 6-fold excess of reagent was necessary for the chloroform extracts of the palladium complexes of both reagents; with a sufficient excess in 1*M* hydrochloric acid the colour of the complex reached a maximum value after 30 min and remained constant for 24 hr. Before extracting, the reaction mixture required shaking for a few seconds and standing for 5–10 min. A single extraction with chloroform, made over a period of 2 min, was sufficient for quantitative recovery. Absorbance was measured 30 min after extraction.

With the described procedure there was no interference from the associated platinum metals, platinum(IV), rhodium(III), iridium(IV) and osmium(IV), in proportions of 1000:1. In weakly acidic solutions these metals produce precipitates, which are, however, insoluble in chloroform or benzene. Cobalt and nickel form grey-black precipitates at pH 6–8 only; they do not interfere in the prescribed procedure. Molybdenum (MoO_4^{2-}) interferes but can be masked by tartaric acid, the latter also masking interference from iron(III), bismuth(III), zinc(II), lead(II) and tin(II).

The single difficulty with the proposed method seems to be the interference from copper, which metal is often associated with the platinum metals. The experimental data recorded by the authors, all of it in the microgram range, indicates very satisfactory recoveries and it may be hoped that the method will receive further attention.

Chrome Azurol S (Colour Index No. 43825; trisodium salt of 3″-sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid) was used by Sangal and Dey[23] to produce at pH 4 a violet chelate whose composition indicated a mole ratio of palladium to reagent of 1:1. The maximum colour was developed in 5 min and remained insensitive to temperatures of 5° to 95°. The colour conformed to Beer's Law over the range 0·33–7·3 ppm. The sensitivity was 0·04 μg/cm^2; for an absorbance of 0·01 the sensitivity was 0·4 μg/cm^2. Absorbance was measured at 580 mμ. Interferences were determined by the direct addition of cation and anion constituents. In general, associated base and noble metals interfered.

Sangal and Dey[24] have added 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulphonate (Thoron) to their list of new reagents for the colorimetric determination of palladium. The reddish-violet 1:1 complex has a maximum absorbance at 525 mμ, a sensitivity of 0·0106 μg/cm^2 and an applicable range of 0·35–25·4 ppm of palladium. Colour formation is instantaneous over the optimum pH range of 2·0–10·0 and it is insensitive to a wide range of temperatures. A large number of cations and ions interfere.

2-Mercaptobenzimidazole and 2-mercaptobenzothiazole were used for the spectrophotometric determination of palladium by Majumdar and Chakrabartty.[25] These reagents and their red coloured complexes with palladium show high absorbance in the ultraviolet region and less high in the visible, where there are no sharp absorbance peaks. Absorbance measurements must be made from a rather limited wavelength region where there is minimum absorbance by reagent and maximum absorbance by the coloured palladium complex. These reagents offer such advantages as the stability of reagent and of the coloured complex, the wide optimum pH range and the useful range of palladium concentrations. However, they are not especially selective.

2-Mercaptobenzimidazole was also used by Xavier[26] who preferred a pH range of 1·0–2·6. Absorbance measurements were made at 380 mμ, 10 min after adding the reagent. There is interference from gold, platinum, silver and iron. Iron(III) is complexed with phosphate. Small amounts of cobalt, nickel, copper and iron(II) are tolerated. The sensitivity is recorded as 0·04 ppm of palladium.

Quinoxaline-2,3-dithiol was used by Ayres and Janota[27] for the range 0·4 to 3 ppm of palladium. The reagent is insoluble in water, chloroform, benzene, *etc.* It was used as a 0·1 % solution in dimethylformamide, but to ensure stability protection from light was necessary. Measurements with the red complex were made at 548 mμ; a yellow complex was also detected with a maximum absorbance at 466 mμ. The colour develops rapidly and is reasonably stable. There is interference from platinum, iron, cobalt and nickel. The reagent has also been applied for the simultaneous determination of palladium and platinum.[28] Palladium concentrations from 0·40 to 2.80 ppm, and platinum concentrations from 1·03 to 7·18 ppm, and concentration ratios of palladium:platinum varying from 0·056:2·8 were applicable. The most suitable wavelengths were 624 and 548 mμ, slightly less precision being obtained at 624 and 517 mμ.

The reagent in dimethylformamide produces a red complex with palladium and a blue complex with platinum. The required bivalency for platinum is achieved by tin(II) chloride and the formation of insoluble complexes is avoided by the addition of *N*,*N*-dimethylformamide. In a previous report Ayres and Janota[27] indicated that platinum, osmium, nickel, cobalt and iron(III) interfered seriously. In a recent report on the successful use of the reagent for the spectrophotometric determination of platinum, Ayres and McCrory[29] found interference from copper, cobalt, nickel and rhodium. With both determinations the data obtained indicated relatively little interference from sulphate and a variety of other anions, frequently used for the purpose of dissolution and separation of the noble metals. It should be noted that these conclusions were based on the direct addition of the anion or cation to a solution of the platinum or palladium. Therefore, one must not conclude that similar results will obtain when the foreign ions are associated with the noble metal throughout the processes of dissolution or of any prior separations.

5-(*p*-Dimethylaminobenzylidene)-rhodanine in ethyl alcohol reacts with palladium in neutral or slightly acid solutions to form a violet precipitate.[30,31] Relatively stable solutions of the palladium complex are formed in formic or propionic acid solutions. With the former solvent the absorbance maximum is 515 mμ and with the latter, 530 mμ. In hydrochloric acid the maximum absorbance occurs at 515 mμ. Different lots of the reagent give slight differences of absorbance maxima and recalibration is necessary for each new lot of reagent. Absorbance increases slightly with excesses of reagent. The optimum range is about 0·4–2·5 ppm of palladium. In propionic acid, maximum colour is attained at room temperature in 10–15 min, and is stable for more than 2 hr. There is interference from platinum, ruthenium, iridium, iron, chromium, copper and gold.

Other reagents for the lower range limit of about 0·4 ppm of palladium contain 5-membered rings with nitrogen and sulphur and the reactive mercapto group. Among these are derivatives of thiodiazoles, benzimidazole and benzothiazole. The first of these derivatives applied to the colorimetric determination of palladium was 2-mercapto-4,5-dimethylthiazole. Ryan[32] used this reagent for the range 0·5–8 ppm. As would be expected with this type of reagent, precipitates are formed with palladium and amounts of the latter beyond the recommended range may produce a turbidity. Beer's Law is not obeyed over the optimum range.

However, the method is not sensitive to variations in acidity or salt content and only platinum interferes. To separate the latter the usual hydrolytic separation may be used. If necessary, palladium can be isolated by an ethyl acetate extraction of the palladium-diphenylamine complex. Subsequently, the organic matter is destroyed before treatment with the dimethylthiazole reagent. This separation is unnecessarily cumbersone. Although the method has the advantage that comparable concentrations of gold do not interfere, the obvious disadvantage is the interference of platinum which is the almost constant associate of palladium. The effective concentration range allows for some application to the analysis of assay beads. It should be noted, however, that when sulphuric acid is used as a parting acid the hydrolytic separation from platinum is only applicable after a fuming and ashing process.

An examination of 2-mercapto-4,5-dimethylthiazole as a reagent for palladium was also made by Radford.[33] It was found that, when the absorbance was measured in the ultraviolet region using a mercury-vapour lamp and Wood's glass filters, there was an increase of 160% in sensitivity and that the coloured constituents obeyed Beer's Law. Increases in the concentration of hydrochloric acid caused slightly higher absorbance values, and the acidity must, therefore, be controlled. It was also found that the addition of ethanol to prevent turbidity was unnecessary.

The data described above for rhodanine apply also to the thiosalicylic-acid method recorded by Dema and Voicu.[34] The range for this reagent is 0·5–2·6 ppm of palladium and the acidity for colour development is pH 2–4 in an acetone medium. There is here, an advantage in the non-interference of gold, copper, iron and nickel. This advantage is to a degree vitiated by the interference from both platinum(II) and platinum(IV). Rhodium also interferes.

Ayres and Alsop[35] recorded two procedures for the determination of palladium by tin(II) salts. For the range 0·5–2·5 ppm tin(II) phosphate was used in a medium of phosphoric and perchloric acids; for the range 8–32 ppm in 1-cm cells tin(II) chloride was used in a hydrochloric and perchloric acid medium. For the latter reagent the absorbance peak occurs at 635 mμ. The green colour reaches maximum intensity in about 20 min at room temperatures and remains stable for about 30 min. The applicable range of acidity for colour development is 1·5–2·1M and the optimum perchloric acid concentration is 0·5M, and the maximum concentration for phosphoric acid is 2M. Beyond these proportions an unstable colour is developed. Tin(II) chloride concentrations in the final solution should be 0·02–0·04M. The presence of chloride ion is essential and should not fall below 0·92M. Lower concentrations result in low absorbance values. The order of addition of reagents should be palladium solution, dilute mixed acids and finally the reagent tin(II) chloride. The total volume of solution is somewhat critical. For a final volume of 25 ml the addition of tin(II) chloride reagent to 17 ml or less of palladium and acid mixture, gives reproducible absorbancies. The rate of addition of reagent and temperature variations are not critical. There are objectionable interferences from all of the noble metals, but relatively large amounts of iron and cobalt can be tolerated. Nitrate and sulphate ions do not interfere. No method of colour extraction has yet been recorded.

The palladium-tin(II) phosphate system produces a red-violet colour in the absence of chloride ion and the presence of perchlorate ion. The narrow absorbance band has its maximum at 487 mμ and the colour system obeys Beer's Law. Maximum colour develops within 10 min at room temperature and is stable for 1·5 hr. The absorbance for a fixed amount of palladium is dependent upon the concentrations of perchloric and phosphoric acid. The identity of the coloured tin(II) complex is not known.

Useful reagents applicable to about the same range of palladium concentration as the tin(II) method are found with the naphthol derivatives. Some of these are discussed in previous reviews.[11,36]

A variety of thio-organic compounds was examined by Burke and Yoe[37] with a view to their use as spectrophotometric reagents for palladium. Each of five reagents provided absorption curves of approximately the same general shape with absorption maxima at 270 mμ, and with about the same sensitivity of 0·01 μg of palladium/cm^2. The spot plate sensitivity was 0·5 μg/0·05 ml and the limit of dilution was 1 in 5.

1-Thioglycerol was selected from the five reagents for detailed study. The identity of the yellow constituent was not determined and it was concluded that the complex was ionic and unstable. Beer's Law was obeyed over the range 0·5–9 ppm. The colour was insensitive to pH, the absorbance remaining constant over the pH range 2–7, and while buffers could be used if desired, in their presence the order of addition of reagents became an important factor; a 5% decrease in absorbance was observed if the buffer was added after colour development. Variations in room temperature did not effect the absorbance values. The degree of interference from associated base and noble metals was determined by direct addition of the constituents before colour development. Within this limitation only nickel of the associated metals could be tolerated in reasonable proportions. The reported non-interference of sulphate and nitrate ions is acceptable only with the reservations discussed previously in this paper. This spectrophotometric method will have only very restricted applications. The absorbance is measured in the ultraviolet range, the sensitivity and the applicable concentration range offer little or no advantages compared to other recorded reagents and the high degree of interferences will in general require a previous isolation of palladium.

Diethyldithiophosphate has been used for spectrophotometric, titrimetric and gravimetric determinations of palladium. Busev and Ivanyutin[38] provided a detailed description of the various applications of the reagent, which was used as the nickel salt dissolved in carbon tetrachloride. The yellow complex of 1 atomic weight of palladium to 2 moles of reagent has a maximum absorbance at 295 mμ, and a sensitivity of 0·0034 μg/cm^2. Beer's Law holds over the range of 0·6 to about 4 ppm for a 1-cm cell. For the range of about 6 to 40 ppm measured at 340 mμ, visual colorimetry can be employed. The method involves the formation of the insoluble palladium complex, acidification and extraction with carbon tetrachloride and subsequent washings with water and sodium hydroxide solution to remove excess reagent. Associated base and platinum metals interfere; to a limited degree interference from copper, iron platinum, gold, *etc.*, can be eliminated by previous precipitations and selective solvent extractions. The method was used to determine palladium in the presence of lead and this application is worthy of further examination, because with some modification, it may thus be used to determine palladium in assay alloys.

2-Nitroso-1-naphthol-4-sulphonic acid[39] reacts with palladium to form a red complex whose composition is 1 atomic weight of palladium to 2 moles of the reagent. The complex can be extracted by isoamyl alcohol from solutions of nitric or sulphuric acids. Beer's Law is followed for 0·6–18·7 μg of palladium/ml. The optimum wavelength is 525 mμ, measured in 7M acetic acid solution. There is interference from associated base and platinum metals.

Chromotrope 2 R (disodium 2-phenylazo-1,8-dihydroxynaphthalene-3,6-disulphonate) reacts with palladium to form a complex whose mole ratio is 1 to 1.[40] Maximum absorbance was obtained at pH 2·1–5·1 and measured at 574 mμ. Beer's Law holds over the range 0·6–12·3 ppm of palladium.

Xylenol Orange has been used for the spectrophotometric determination of palladium to form an orange complex with an absorption maximum at 518 mμ. The reported molar absorptivity of 26,000 indicates a sensitivity of 0.004 μg/cm^2. The composition of the complex is 2 moles of reagent to 1 of palladium. Beer's Law applies over the range 0·2–4·0 ppm of palladium with an optimum range of 0·8–3·2 ppm of palladium. Because of the interference of chloride ion and in order to increase selectivity, Otomo[41] used a concentrated perchloric acid medium for the reaction with maximum and constant absorbance at a concentration range of 1·1–1·7M. An excess of reagent was required and a short period of boiling was necessary. No conclusive statement was made concerning the influence of associated base and noble metals. Distinct advantages of the method are the solubility in water of the orange palladium complex and the high sensitivity. One may hope that efforts will be made to apply the method to natural and artificial products containing palladium.

Other reagents for palladium containing the mercapto group are 2,5-dimercapto-1,3,4-thiodiazole (Bismuthiol-I) and 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazole-2-one (Bismuthiol-II). Majumdar and Chakrabartty[42] used Bismuthiol-I over the range of 0·8–8·0 ppm at wavelengths between 400 and 410 mμ. There are no sharp absorbance peaks. The colour develops instantaneously, is independent of pH and is acceptably stable under the conditions recommended. The palladium complex is fairly soluble in water. Bimuthiol-II was used by Majumdar and Chakrabartty[42] for the range 0·4–8 ppm of palladium. At a wavelength between 410 and 430 mμ the colour intensity is relatively insensitive to pH change, remaining stable between pH 3 and 10. The red coloured constituent forms immediately and because of its insolubility in water the addition of acetone or methyl cellosolve is required. The claim for a sensitivity greater than the *p*-nitrosodiphenylamine reagent is incorrect. Furthermore, the latter reagent has a lower limit of both detectability and sensitivity expressed as an absorbance-weight response. The extent of interference and the range of applicability of Bismuthiol-II is comparable to the mercaptans included above and none of these has advantages superior to the more established reagents.

Kodama[43] used *o*-nitrosoresorcinolmonomethyl ether for the range 0·8–2 ppm of palladium. The procedure involves a fuming period with perchloric or sulphuric acid which allows adaptions to various stages of fire assay techniques, *e.g.*, parting of the silver bead. The fumed solution is mixed with coniferin and chloroform in a separatory funnel and the chloroform extract treated with sodium carbonate solution. The absorbance is measured at 420 mμ.

An interesting spectrophotometric method, used by Komatsu and Taki[44] for the range 1–30 ppm of palladium, involves the use of a large excess of the reagent 1-phenylthiosemicarbazide, which redissolves the initial orange-brown precipitate to form an orange-yellow solution. The wavelength used is 372 mμ and the optimum acidity is $3M$ in acetic acid. As would be expected, there is interference from associated base metals and some of the noble elements. Platinum forms an insoluble green precipitate. EDTA is used to remove interference from copper and silver and sodium fluoride is used for iron. Gold is removed by solvent extraction with ether.

2-Nitroso-1-naphthol has been used to determine palladium in uranium fission alloys.[45] There is no interference from uranium, ruthenium, zirconium and rhodium. The method is a combination of that proposed by Alvarez[46] and Cheng.[47] Palladium is quantitatively extracted by toluene along with excess reagent in the pH range 1.0–2.0; EDTA serves as a buffer and masking reagent. The excess reagent is scrubbed from the organic phase with dilute sodium hydroxide solution. Initial pH adjustments are made with aqueous ammonia rather than with sodium hydroxide solution because the latter produces low and erratic results. However, sodium hydroxide as the scrub solution, produces improved precision.

A second paper was recorded by Larsen and Ross.[48] Palladium was determined as its complex with 2-nitroso-1-naphthol after separation by the extraction of the complex in toluene; ruthenium was separated by distillation of its octavalent oxide, collection in a caustic solution of sodium hypochlorite and a subsequent spectrophotometric determination.

1,2-Nitrosonaphthol and the 2,1-derivative were used by Kodama[49] in perchloric or sulphuric acid solution and the resulting palladium complex was then extracted with chloroform. For the 1,2-complex the absorbance was measured at 298 mμ or at 441 mμ; for the 2,1-derivative, 308, 376 or 385 mμ could be used. The most sensitive wavelength is 308 mμ.

A method which is useful for the simultaneous determination of platinum and palladium was recorded by Pyle and Jacobs.[50] The reagent, dibenzyldithio-oxamide, produces a yellow palladium complex and with platinum a rose-coloured complex, both insoluble in aqueous media but extractable with chloroform. The absorption maxima are, respectively, 450 and 520 mμ. The applicable range of concentration is approximately 1–4 ppm or to 5 ppm in the case of platinum. The complexes contain a ratio of 1 mole of bivalent metal to 2 moles of reagent. The sensitivities are 0·0055 μg/cm^2 for palladium and 0·0075 μg/cm^2 for platinum. Colour development is optimum in hydrochloric acid solutions of a molarity of 8 or greater, with an immediate development in the case of palladium and with platinum, for which a sodium sulphite reduction is recommended, the optimum colour development requires 30 min. Two chloroform extractions remove the complexes and the colour remains stable for a least 48 hr. The recommended ratio of added reagent:metal is 31:1 for palladium and 76:1 for platinum. For the simultaneous determination the reagent: metal ratio is that used for platinum. The method is surprisingly free from interferences from associated noble and base metals. In the case of palladium, with iron, nickel,cobalt, copper, chromium, the permitted proportions are about 1 μg of palladium to 5000 μg of the base metals. Gold interferes, except in the presence of sodium sulphite, which probably produces metallic gold. With the obvious exception of platinum the interference from the remaining noble metals is not excessive; in the case of osmium it may be noted that the use of osmium(VI) for determining the degree of interference does not necessarily duplicate the dissolved osmium constituent which would result from the author's preparation of the platinum-palladium solution. However, in any case, interference from osmium is readily removed by previous oxidation. In the case of platinum the interferences from similar associated metals was invariably greater than for palladium. Indeed, for most practical purposes any claim for freedom from interference is invalid, *e.g.*, the deleterious effects of copper, nickel and, of course, palladium reduces the value of the method. Any interference from gold is eliminated by reduction with the added sulphite.

Jacobs *et al.*[51] applied the didodecyl derivative of dithio-oxamide for the determination of palladium to produce a yellow water-insoluble complex in hydrochloric acid solutions of about 7·5*M*. The optimum concentration range is about 1–4 μg of palladium/ml of solution. The sensitivity is 0·005 μg/cm^2; the colour is stable for at least 48 hr and its development requires about 15 min. The required ratio of reagent to palladium is at least 4 moles to 1 formula weight of palladium; larger ratios are recommended. This method will prove useful for the determination of palladium in the presence of platinum(IV). The permitted ratio is about 1 to 160, respectively. Gold interferes, except in the presence of sodium sulphite, which reagent disallows the presence of platinum and increases the tolerance for iron. The tolerance indicated for sulphate should not be interpreted to indicate the tolerance for sulphate solutions prepared, as they usually are in practice, to include a fuming process. The high tolerance for rhodium and iridium will have value only in relatively few analytical processes.

With palladium, tartrazine forms a stable orange complex which may be used for determinations in the range 1·23–9·83 ppm of palladium in the presence of 150-fold amounts of platinum(IV). The colour is developed in a sodium acetate solution at pH 5·5–5·75 and the absorbance is measured at 496 mμ.[52]

The spectrophotometric determination of palladium by sodium 1-nitroso-2-naphthol-3,6-disulphonate (Nitroso-R salt)[53] provides some advantages as compared to other nitrosonaphthols. The red complex is soluble in water and no extraction is required; the colour reaction is rapid, Beer's Law is obeyed, and the colour intensity is constant when measured 15 min after preparation and remains stable up to 24 hr. Furthermore, the reagent solution is stable for several months. While the maximum absorbance occurs at 430 mμ, there is some significant absorbance of the reagent at this wavelength and the plateau at 500–510 mμ is more suitable for measurements. The most sensitive range of concentration is 1·28–4·27 ppm of palladium. There is no interference from platinum, rhodium, osmium and gold, although in the presence of $HAuCl_4$ the colour changes slowly and the absorbance measurements should be made within 1 hr after colour development. The best results are obtained at an acetic acid concentration of 0·2*M* and at a pH of about 2·6. Hydrochloric acid solutions at a pH of about 2 can also be used. It is desirable to use an excess of reagent because the absorbance is thereby somewhat increased.

The application of nitroso-R salt was also discussed by Garcia and Garride,[54] who found that Beer's Law was obeyed over the range 5–13 ppm. The absorbance was measured at 520–560 mμ. The suitable pH range for colour formation was reported as 3·25–6·85. An excess of reagent was required and the colour reaction was insensitive to temperature changes.

Quinoline-2-aldoxime was used by Oi[55] to produce a yellow palladium complex at pH 5, which could be extracted by chloroform. Beer's Law applies over the range 1·5–70 μg/ml. Interference from copper or platinum is avoided by the use of EDTA.

Phenyl-1-pyridyl ketoxime is a useful reagent for the spectrophotometric determination of palladium. Sen[56] included a recipe for preparation of the reagent but it has recently been made available commercially.* This ketoxime forms a yellow, water-insoluble compound containing 1 mole of palladium to 2 moles of ketoxime. The chloroform extract exhibits absorbance peaks at 410 and 340 mμ. Beer's Law applies over the range 0·5–14 ppm of palladium with a 1-cm light path. The optimum range at 340 mμ is 1·5–8 ppm and at 410 mμ it is 2–10 ppm of palladium. The corresponding sensitivities are 0·0021 μg/cm^2 and 0·0036 μg/cm^2.

Because there is some absorbance by the reagent at 340 mμ, the maximum at 410 mμ is recommended when excesses of reagent are unavoidable. The most favourable acidity for formation and extraction of the palladium chelate is between pH 8·5 and 10. Maximum colour development is instantaneous and the colour remains stable for at least 2 weeks. Temperature variations between 0° and 45° are without significance. The reagent forms coloured complexes with iron(II), cobalt, nickel and copper, which are simultaneously extractable. These interferences are avoided by the addition of EDTA which does not interfere when the absorbance is measured at 410 mμ. At 340 mμ EDTA must be included in the blank. Of the noble metals, only gold interferes. The complexes of the platinum metals, lead and iron(III) are not extracted by chloroform.

Jacobs[57] used *N*,*N'*-bis-(3-dimethylaminopropyl)-dithio-oxamide to produce a yellow, water-soluble chelate containing 1 mole of palladium and 2 moles of reagent. Beer's Law was followed over the range 0·20–8·0 ppm of palladium with the optimum range 1·6–5·7 ppm. The sensitivity of the reaction is 0·008 μg/cm^2; the absorbance maximum is at 427 mμ. Colour develops immediately at room temperatures and is independent of temperatures over the range 15–45° and stable for at least 4 hr. With a 7·5-fold or greater excess of reagent the absorbance remains constant. For maximum sensitivity the molarity of hydrochloric acid should be above approximately 3·4. Compared to most colorimetric methods for palladium there is relatively little interference from the platinum group, gold and nickel. Interference from osmium and ruthenium is of little consequence because these metals are readily removed and, particularly in this case, because nitrate and sulphate may be tolerated. In the presence of platinum the absorbance of the palladium complex is measured within 10–15 min because platinum slowly produces a rose colour. Copper and iron interfere.

The above reagent is also used for platinum[58] and for the simultaneous determination of palladium through a calculation involving the known molar absorbitivies of the two complexes. With platinum the rose coloured complex contains a ratio of reagent to platinum of 2:1. The sensitivity is 0·009 μg/cm^2, which is considerably higher than the tin(II) chloride method but less than the *p*-nitrosodimethylaniline method. Absorbance is measured at 515 mμ. The optimum range is 1·8–6·5 ppm.

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* From G. Frederick Smith Co., Columbus, Ohio, U.S.A.

As in the case of palladium, the acid strength is adjusted to 4·8*M*. The colour is developed, subsequent to reduction of platinum by sodium sulphite, and a 10-min development period is required. An 18-fold or greater excess of reagent is required.

Because the absorbances of the complexes of both platinum and palladium are additive, and Beer's Law is obeyed at both 427 and 515 mμ, a simultaneous determination of platinum and palladium may be achieved. A technique such as this encourages applications for routine determinations. However, in those instances where there is a great difference in the proportions of the two constituents, the errors associated with the determinations of the constituent present in large proportions may become additive to the errors incident to the determination of the second constituent.

The method applied to platinum alone does not tolerate large proportions of associated noble or base metals. Gold, iridium, ruthenium, nickel and iron are tolerated in proportions of about 15 parts to one of platinum. Toleration of palladium, ruthenium, osmium, rhodium and copper is low.

5-Amino-2-benzimidazolethiol in excess produces an orange coloured complex with a ratio of 1 atomic weight of metal to 2 formula weight of reagent.[59] Maximum absorbance occurs at 390 mμ and the solution obeys Beer's Law between 1 and 8 ppm with an optimum range of 2–7 ppm. The sensitivity is 0·008 μg/cm^2. Colour is developed at room temperature, remaining constant at a pH between 2 and 4 for 24 hr. Platinum and osmium interfere and must be separated. The claim for no interferences from other associated platinum and base metals is based on a permitted ratio of 4 ppm of palladium to about 8 ppm of foreign metal. In general, there is some increase in tolerance in the presence of EDTA.

Thiomalic acid, used by Wagner and Yoe[60] as a spectrophotometric reagent, provides the advantages that it is water soluble and commercially available, and reacts instantaneously with palladium over a wide acidity range, although maximum absorbance is obtained over a pH range of 1·1 to 2·6. Maximum absorbance of the yellow complex occurs at 350 mμ. The reagent does not absorb above 290 mμ and a water blank is satisfactory. The complex obeys Beer's Law over the range 0·4–10 ppm and it is stable for several days. Temperature variations over the range 15–35° are without significant effect.

The practical sensitivity of the reaction is about 0·05 ppm and the optimum range of concentration is 2–7 ppm of palladium. Although the reagent is unstable, solutions may be used over a period of 24 hr. While the order of addition of reagents is not critical, if the absorbance is to be measured immediately, the buffer must be added last, otherwise 1 hr is required for the colour reaction to reach a maximum intensity. The absorbance remains constant for at least 3 days. An excess of reagent is desirable because the absorbance of the complex is thus somewhat increased and the tolerance to several interferences is also increased. The reagent presumably forms two compounds, one of which is a stable complex consisting of 2 molecules of thiomalic acid to 1 formula weight of palladium and a lesser stable complex with a 1:1 ratio which absorbs to a lesser extent. Because the usual organic solvents fail to extract the yellow complex it is assumed to be ionic in aqueous solution. This extraction failure is unfortunate because, in spite of a claim for unusual specificity, there is interference from most of the noble metals, copper and iron(III). There is a large tolerance for nickel, cobalt, sulphate and nitrate.

1-(2-Pyridylazo)-2-naphthol, previously used for rhodium and iridium by Stokely and Jacobs,[61] has been applied by Hayashi[62] for the determination of palladium. The green 1:1 mole-ratio complex, soluble in chloroform and isoamyl alcohol, forms in weakly acid solution. In chloroform the absorbance is measured at 678 mμ. Beer's Law applies over the range 1–20 ppm of palladium. Colour is developed by heating for a few minutes on a water bath. There is no interference from moderate amounts of rhodium, platinum, gold, silver and mercury. This reagent was also applied to determine traces of palladium and platinum in high-purity gold. Subsequent to the dissolution of the sample, gold was extracted with isopropyl ether and then palladium dimethylglyoxime with chloroform. The palladium was next converted to the above naphthol derivative (at a pH of 1·5–3·5). Platinum in the aqueous phase was reduced by tin(II) chloride, extracted with dithizone in carbon tetrachloride and the absorbance measured at 730 mμ; 0·2 ppm of palladium or platinum could be determined.

Busev and Kiseleva[63] used a 1% solution of 1-(2-pyridylazo)-2-naphthol in methyl alcohol for a chloroform extraction at pH 2·5 and for a range of 6–14 ppm of palladium. The extract has absorbance maxima at 620 and 675 mμ; the latter wavelength is preferable when the proportion of platinum is high. The method is reasonably free from noble metal interferences. Cobalt behaves similarly to palladium. The associated base metals can be extracted with isoamyl alcohol.

This naphthol derivative was also used by Sawada and Kato[64] for the determination of palladium in titanium alloys. Colour was developed at pH 3·0–3·5 and heating at 100°. The sensitivity was recorded as 0·006 μg/cm^2.

Two new reagents containing the *o*-hydroxyazo group have been used for the determination of palladium(II). Sodium 1-azophenyl-2-hydroxy-6,8-naphthalene disulphonate at pH 6·5–6·8 was used to determine 1·04–14 ppm of palladium; sodium 1-phenyl-3-methyl-5-hydroxy-4-(*p*-sulphophenyl)-pyrazole reacts at pH 1 to determine palladium over the range of 12·61–189·22 ppm. It is stated that these reagents may be used for determinations in ores and that platinum, gold, nickel and mercury do not interfere.[65]

Among the numerous thiol reagents for the determination of platinum metals, 2-mercaptobenzoxazole was selected by Arita and Yoe[66] to produce an orange-yellow complex, with a mole ratio of reagent to metal of 1:1. The complex is soluble in a mixture of cyclohexanone and dioxan. Absorbance measurements are made at 375 mμ, the optimum concentration range is 15–30 ppm and Beer's Law applies over the range 2–40 ppm. The sensitivity for an absorbance of 0·001 is 0·08 μg/cm^2; for an absorbance of 0·005 the sensitivity is 0·4 ppm; the spot plate sensitivity is 0·05 μg/0·05 ml.

The colour reaction is instantaneous but the complex is somewhat unstable, the intensity decreasing 1% in 10 min. There is also a decrease in stability with increasing basicity although this is accompanied by an increase in colour intensity. The addition of buffers encourages precipitation and measurements are, therefore, made in dilute hydrochloric acid solutions. Absorbance is measured at 375 mμ and is independent of the normal laboratory temperature changes and of the order of addition of reagents. The degree of interference from associated noble and base metals was determined by direct addition of the constituents before colour development. Except for cobalt, and to a lesser degree for nickel, there was interference from small proportions of associated metals, *e.g.*, 3 ppm of platinum salt added to 20 ppm of palladium produced an error of ±2%.

Nitrilotri-acetic acid has been used for the spectrophotometric determination of palladium.[67] Except perhaps for very specific purposes the method will have little application. The optimum range of concentration is 20–220 ppm. Measurements are made at 330 mμ, and there is interference from the remaining platinum metals. No data were provided to indicate the effects of gold or associated base metals. In the presence of platinum metals, palladium is first removed by precipitation with dimethylglyoxime. The method offers no advantage over the many useful alternative methods.

Bis-(allylthiocarbamyl)-hydrazine (Dalzin) was used by Dutt and Sarma[68a] to produce an orange, insoluble complex with a 1:1 mole ratio of metal to reagent. The optimum acidity is pH 1·2–1·3. The chloroform extract shows a maximum absorbance at 365 mμ. In a later paper[68b] the authors recommended a pH of 3–6 and extracted the complex in the presence of EDTA. Beer's Law applied over the range of 1–20 ppm. The complex was found stable for several hours at 25–40°. Associated base metals, silver and mercury(I) did not interfere.

Nioxime was used by Pshenitsyn and Ivonina,[69] who added an aqueous solution of the reagent to the palladium solution adjusted to pH 1. After 10–15 min the complex palladium salt was extracted by chloroform.

Derivatives of nioxime are finding increasing use as analytical reagents for palladium. Banks and Smith[70] used 4-methyl-1,2-cyclohexanedione dioxime for palladium contents of 2·5–250 μg. The solution is adjusted to pH 2 by a hydrochloric acid-potassium chloride buffer and allowed to stand for 1 hr. The insoluble complex is extracted by chloroform and the absorbance measured at 280 mμ using 1-cm cells. Interference from copper, cobalt and iron can be avoided by masking reagents but ruthenium must be removed. One should note that the working range of palladium concentration in a method such as this one is determined partly by the efficiency of the initial precipitation, together with the completeness of the complex formation, and not by the sensitivity in the organic extract which, in the case of this 4-methylnioxime reagent is 0·07 μg of palladium/cm^2.

Benzildioxime was also used[69] with palladium solutions at pH 2 and the absorbance of the chloroform extract is measured at 280 mμ.

Dimethylglyoxime, perhaps the most generally useful reagent for the gravimetric determination of palladium, was used by Kodama[49] for the spectrophotometric determination of palladium in preference to 1,2-nitrosonaphthalene when one must avoid interference from chloride.

The determination of palladium as its iodide compounds in nickel plating solution was studied by Frantsevich-Zabludovskaya, Kalimanova and Sharafan.[71] This is an interesting and useful examination of the palladium iodide reactions. It was found that the optimum absorbance of the brown solution reaches a maximum at a molar ratio of potassium iodide to palladium of 2:1, and subsequently remains constant up to a 50:1 ratio. The absorbance then decreases in the presence of a larger excess of potassium iodide, finally increasing again and at a 200-fold excess of the potassium iodide it remains constant, the solution now being coloured red. This dissolved constituent is $K_2(PdI)_4$; the maximum absorbance at a ratio of 2:1 presumably resulting from a colloidal suspension. The red constituent had previously been used by Fraser *et al.*[72] for the spectrophotometric determination of palladium. Frantsevich-Zabludovskaya applied this method successfully to the determination of palladium in activating solutions contaminated with detergent. It was found that the absorbance was constant over the potassium iodide:palladium molar range from 200:1 to complete saturation of the solution of potassium iodide; it remained constant for 6 hr, decreasing after 24 hr and it was unaffected by acidity over the pH range 2·5–10. Maximum absorbance of the red complex reported by Fraser *et al.*[72] occurs at 410 mμ. Frantsevich-Zabludovskaya *et al.* used a blue filter of the FEK-M photoelectric colorimeter.

In the case of the brown solutions resulting from low ratios of potassium iodide: palladium, the authors[71] were unable to identify the coloured constituent. However, it was noted that the absorbance was constant with time; the solution conformed to Beer's Law and the molar extinction coefficient, albeit regarded as arbitrary, was calculated as $4{\cdot}3 \times 10^3$. While the brown solution examined by an ultramicroscope failed to reveal colloidal particles, the dialysis data clearly indicated a colloidal suspension. It should be noted here that the present author[73] used potassium iodide for the gravimetric determination of palladium. An excess of at least 10 times the calculated weight of the iodide could be used and PdI_2 was applied successfully as the weighing form.

In a previous publication the present author expressed the opinion that the palladium iodide spectrophotometric method, because of its sensitivity to oxidising and cation interferences would find little practical application. Clearly this was an erroneous prediction.

1-Benzoyl-2-methylglyoxal dioxime was used by Schekochikhina, Peshkova and Shlenskaya[74] to react with palladium at pH 1·25–3·60, forming a yellow crystalline salt, soluble in alkaline solution. A chloroform extract eliminated interferences and the complex showed a maximum absorbance at 280 mμ.

2-Chloropyridine was used by Egli[75] to separate and to determine palladium and platinum. The separation was made in a special flask constructed from an Erlenmeyer flask in which the sample was weighed, reduced in hydrogen, dissolved in mixed acids and the solutions evaporated to form chloride solutions. The latter solution was then treated with 40% sodium nitrate solution followed by the 2-chloropyridine which must be pyridine free. Immediately after the addition of the chloropyridine, the solution was mixed, the layers were allowed to separate and the strongly acid aqueous layer, which contained most of the impurities, was drained off. The organic layer was washed with a solution of 40% sodium nitrate and nitric acid and the washings discarded. There was then added consecutively a 1:1 solution of acetic acid and butanol, an aqueous solution of anhydrous sodium acetate and sodium toluene sulphonate. The chloropyridine layer containing the palladium was drawn off into a 100-ml flask containing 50 ml of dimethylformamide.

The upper layer was similarly extracted with a solution of 2-chloropyridine, butanol and acetic acid, adding the extract to a calibrated cylinder. The aqueous layer with the platinum was treated immediately with 20% hydrochloric acid, a solution of tin(II) chloride and pure hydroquinone. The technique of the above extraction must be applied with precision. Variations in time, after the addition of the chloropyridine, will alter the distribution of the platinum in the two phases because of the dissociation of the platinum-chloropyridine complex. On standing there was a decrease in the amount of platinum in the aqueous layer and, furthermore, the complex may partially precipitate.

For the colorimetric determination of palladium the extract was now diluted to volume with dimethylformamide. A measured volume of this solution was transferred to a measuring flask and diluted with dimethylformamide, then solutions of acetic acid and sodium hydroxide were added. This was followed by a solution of potassium iodide and the volume was made up to the mark with dimethylformamide and allowed to stand in the dark overnight at 20°. The absorbance of the red colour was measured at 525 mμ.

For platinum the yellow tin(II) complex was extracted with acetic ester within a 24-hr period, the extracts were made up to volume and the absorbance was measured at 401 mμ against a blank containing acetic ester and hydroquinone. Correction factors were proposed to compensate for losses of platinum resulting from a variety of compositions and extraction conditions. Small errors of palladium may occur with high ratios of palladium to platinum. However, only traces of palladium should appear in the platinum phase. The use of a glass stirring rod rather than the Teflon protective rod, induced crystallisation of the platinum-palladium complexes. The claim by the author of an accuracy of palladium determination greater than that obtained from the iodide method is unsubstantiated. Maximum intensity of colour was achieved after 15 hr. The platinum-tin(II) method was modified by the use of hydroquinone rather than by resorcinol. Presumably, iridium interfered with the platinum determination and gold with the palladium determination. Quantities of the associated base metals, copper, iron, nickel, cobalt, chromium, lead, *etc*., comparable to the amounts of platinum and palladium, introduce interference of less than 0·5%.

No data were provided to indicate the accuracy which can be achieved and it would seem that in the development of the equipment and of the technique of dissolution, some effort was made to add to the complexity and the difficulty of what is normally a relatively simple operation. Compared to the ease of application of a standard rose crucible the use of a specially constructed flask of 100-ml capacity, with the associated difficulty of weighing milligram amounts of metal by difference, is an unnecessary complication.

Although thionalide is a general precipitant for heavy metal cations it may be used for the spectrophotometric determination of palladium.[76] The complex has a mole ratio of metal to reagent of 1:2 and is extracted from 2–3*M* hydrochloric acid by a 2:1 chloroform-isoamyl alcohol mixture. Absorbance at 375 mμ is measured 10–15 min after a single extraction. Beer's Law is obeyed over the range of 0·4–12 μg/ml and the sensitivity is 0·2 μg/ml. The claim is made that palladium can be determined in the presence of 1000 times its amount of platinum, rhodium, iridium, osmium, cobalt and nickel. Tartaric acid is used to mask the presence of molybdate, iron(III), bismuth(III), zinc, lead(II) and tin(IV). Presumably, the degree of interferences was determined by the addition of constituents. An accuracy of ±5% is claimed.

The related reagent thioglycollic acid has been used for the determination of palladium in titanium ores.[77] In the presence of tartaric acid the reaction produces a stable yellow colour. Maximum absorbance occurs at 371 mμ and the colour developed at pH 4 can be extracted by butyl alcohol. Copper, iron and molybdenum interfere; platinum does not.

4-(2-Thiazolylazo)-1-naphthol[78] produces a blue-green chelate with a mole ratio of reagent to metal of 1:1 and a purple chelate with a 1:2 ratio. The former is obtained with a large amount of palladium and the latter with an excess of reagent.

TABLE I.—SPECTROPHOTOMETRIC METHODS FOR PALLADIUM

No.	Reagent	Range of concentration, *ppm*
1.	Tetra-ethyleneglycoldimethyl ether + potassium iodide[12]	0–6 B.L.
2.	*N*,*N*′-Bis-(2-Sulphethyldithio-oxamide)[13]	0·02–0·2
3.	8-Aminoquinoline[14]	0.04–30
4.	*p*-Nitrosodiphenylamine[10,15,79–82]	0·05–0·3
5.	*p*-Nitrosodimethylaniline[79,10]	0·25–1
6.	3-Hydroxy-1-(*p*-sulphonatophenyl)-3-phenyltriazine[297]	0·2–6
7.	8-Mercaptoquinoline (thio-oxine)[17–19]	0·2–10 0–27 B.L.
8.	Thiocyanate[20,21]	0·2–9
9.	1-Mercaptopropionic-*p*-aniside[22]	0·2–12 B.L.
10.	Chrome Azurol S{Trisodium salt of 3″-sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid}[23]	0·33–7·3 B.L.
11.	1-(*o*-Arsonophenylazo)-2-naphthol-3,6-disulphonate (Thoron)[24]	0·35–25·4
12.	5-Mercapto-3-phenyl-2-thiol-1,3,4,-thiodiazole-2-one [Bismuthiol-II][42]	0·4–8
13.	2-Mercaptobenzothiazole and 2-mercaptobenzimidazole[25,26]	0·4–6 1·0–2·6
14.	Quinoxaline-2,3-dithiol[27–29]	0·4–3 0·4–2·8
15.	5-(*p*-Dimethylaminobenzylidene)-rhodanine[30,31]	0·4–2·5
16.	Thionalide[76]	0·4–12
17.	2-Mercapto-4,5-dimethylthiazole[32,33]	0·5–8
18.	Thiosalicylic acid[34]	0·5–2·6
19.	Tin(II) phosphate[35]	0·5–2·5
20.	1-Nitroso-2-naphthol[11,36]	0·5–5
21.	1-Thioglycerol[37]	0·5–9 B.L.
22.	Diethyldithiophosphate[38]	0·6–4 B.L. 6–40 visual
23.	2-Nitroso-1-naphthol-4-sulphonic acid[39]	0·6–18·7 B.L.
24.	Chromotrope 2R (disodium 2-phenylazo-1,8-dihydroxynaphthalene-3,6-disulphonate[40]	0·6-12·3 B.L.
25.	Xylenol Orange [3,3′-bis-*N*,*N*-di(carboxymethyl)-aminomethyl-*o*-cresolsulphonaphthalein][41]	0·8–3·2
26.	Thiourea[83]	0·8–24
27.	2,5-Dimercapto-1,3,4-thiodiazole (Bismuthiol-I)[42]	0·8–8·0
28.	*o*-Nitrosoresorcinolmonomethyl ether[43]	0·8–2
29.	Tin(II) bromide[84]	1–10 B.L.
30.	1-Phenylthiosemicarbazide[44]	1–30
31.	α-Furildioxime[85]	1–5
32.	2-Nitroso-1-naphthol[45–49,86]	1–5
33.	Dibenzyldithio-oxamide[50]	1–4
34.	Didodecyldithio-oxamide[51]	1–4
35.	Tartrazine[52]	1·23–9·83
36.	Sodium 1-nitroso-2-naphthol-3,6-disulphonate (Nitroso-R salt)[53,54]	1·28–4·27 5–13 B.L.
37.	Quinoline-2-aldoxime[55]	1·5–70 B.L.
38.	Phenyl-1-pyridyl ketoxime[56]	1·5–8(340 mμ) 2–10 410 mμ)
39.	*N*,*N*′-Bis-(3-dimethylaminopropyl)-dithio-oxamide[57,58]	1·6–5·7
40.	5-Amino-2-benzimidazolethiol[59]	2–7
41.	Thiomalic acid[60]	2–7

TABLE I.—SPECTROPHOTOMETRIC METHODS FOR PALLADIUM (*continued*)

No.	Reagent	Range of concentration, *ppm*
42.	β-Furaldioxime[87,88]	2·4–6
43.	*N,N′*-Ethylene-bis-(4-methoxy-1,2-benzo-quinone-1-oxime-2-imine)[89]	4–100
44.	Catalytic with molybdenum blue[91]	4–11
45.	EDTA[90]	5–200 B.L.
46.	1-(2-Pyridylazo)-2-naphthol[61–64]	6–14
47.	Sodium 1-azophenyl-2-hydroxy-6,8-naphthalene disulphonate;[65]	1·04–14
	Sodium 1-phenyl-3-methyl-5-hydroxy-4-(*p*-sulphophenyl) pyrazole[65]	12·61–189·22
48.	Tin(II) chloride[92,93]	8–32
49.	2-Mercaptobenzoxazole[66]	15–30
50.	Nitrilotri-acetic Acid[67]	20–220
51.	Bromide ion[94]	37–360
52.	Dimethylglyoxime and salicylaldoxime[95]	
53.	2-Mercaptoquinoline[19]	
54.	Bis-(allylthiocarbamyl)-hydrazine (Dalzin)[68]	
55.	Dithio-oxamide (Rubeanic acid)[96]	
56.	Nioxime[69]	
57.	4-Methyl-1,2-cyclohexanedione dioxime[70]	
58.	Benzildioxime[69]	
59.	Dimethylglyoxime[49]	
60.	Potassium iodide[71–73]	
61.	1-Benzoyl-2-methylglyoxal dioxime[74]	
62.	2-Chloropyridine[75]	
63.	Thionalide[76]	
64.	Thioglycollic acid[77]	
65.	4-(Thiazolylazo)-1-naphthol[78]	

The purple complex has a sensitivity of 0·006 μg/cm^2 and can be extracted with isoamyl alcohol.

PLATINUM

Tin(II) chloride remains one of the most useful and generally applicable spectrophotometric reagents for platinum. Recently, it has been used for the determination of trace amounts of platinum dissolved from platinum anodes during the electrolysis of sodium chlorate.[97]

Platinum was separated from interfering constituents by coprecipitation with copper sulphide. One milligram of copper was sufficient for the collection of microgram quantities of platinum from a 3*M* hydrochloric acid solution. The mixed sulphide precipitate was collected, treated with *aqua regia* and converted to chloride. The chloride solution was treated with tin(II) chloride reagent and the platinum complex extracted with ethyl acetate. Absorbance was measured at 420 mμ. The deleterious effect of chromium was eliminated by the ethyl acetate extraction. Gold did not interfere. No data were included to indicate interferences from copper, nickel or the associated base metal. However, the method was designed for, and applied successfully to solutions of sodium chloride, sodium chlorate and sodium bichromate. Following reduction of the oxidants by careful addition of concentrated hydrochloric acid, the platinum-copper sulphide precipitation was completed. For the range of 0·0–0·02 ppm of platinum an accuracy of 5–10% was obtained.

Berman and Goodhue[98] introduced a variation in the tin(II) method to achieve a sensitivity five times greater than that realised by the method proposed by Ayres and Meyer.[92] This was accomplished primarily by a larger reduction in the amount of tin(II) chloride and the addition of sulphuric and perchloric acids to stabilise the coloured constituent and to effect a hypsochromic shift in the absorption band from the tin(II) reagent.

In the absence of perchloric acid there is a marked fading caused, at least partially, by light. In the presence of 5 ml of concentrated perchloric acid the yellow colour develops within a few minutes and remains stable for at least 4 hr. The amounts of sulphuric acid are not critical but fuming should be avoided. If this inadvertently takes place, addition of several millilitres of hydrochloric acid and boiling to remove the volatile acid restores the colour systems. Too little sulphuric acid produces low results. The absorbance is measured at 310 mμ and the recommended range is 0·4–6 ppm with 1-cm cells, and 0·08–1·2 ppm with 5-cm cells. Quartz cells are used because 310 mμ is beyond the limit of 320 mμ, recommended for Corex glass cells. However, to avoid the necessity of ultraviolet accessories the authors determined that a tungsten lamp source and Corex glass cells could be used with a 3-fold increase in slit width. The method is particularly suitable for solutions containing nitric acid because the procedure accomplishes its removal. Interferences from associated metals have been properly examined by carrying the constituents through the complete treatment before measurements. In general, the platinum metals interfere, with iridium providing the least effect. Of the associated base metals, chromium, iron and copper provide the least interference. It is recommended that here, as with most other spectrophotometric methods for platinum, a previous separation of the latter be effected.

The stability of the tin(II)-platinum complex is not critically affected by the proportions of the reagent although minimum amounts are recommended. For the applicable range of platinum, 2 ml of the freshly prepared reagent is the optimum amount.

Tin(II) chloride in solutions of sulphuric and perchloric acids was used by Pilipenko and Sereda[99] for the simultaneous determination of platinum and palladium. Samples containing 0·4–10 μg of the metals/ml were heated with concentrated sulphuric acid. Perchloric acid was added and the absorbance of the tin(II) chloride colour for palladium was measured at 630 mμ. The absorbance at 310 mμ, less that calculated from the palladium concentration, was used to determine platinum. There was little or no interference with the palladium determination from osmium, rhodium and iridium. Iridium, rhodium and ruthenium interfered with the platinum determination.

Tin(II) chloride was also used by Mizuike and Ujihira[100] to determine traces of platinum in chlorate cell liquor. Mercury and the tin(II) chloride solution were mixed. The mercury alloy of platinum was isolated followed by volatilisation of the mercury at 350° in a nitrogen stream. The platinum residue was then prepared for the tin(II) spectrophotometric method with the absorbance being measured at 420 mμ.

Faye and Inman introduced a useful variation in the tin(II) method.[101] The procedure followed a separation of platinum from palladium by an anion-exchange column, then stripping by perchloric acid and subsequent fuming with sulphuric acid. Following treatment in the presence of hydrochloric acid, the platinum was extracted by a solution of tin(II) chloride and tributyl phosphate-hexane. The organic phase was centrifuged and the absorbance was measured in a 1-cm Corex cell.

It should be noted that the efficiency of the tin(II) method for platinum subsequent to stripping from an exchanger may be vitiated by the presence of organic matter. Coburn *et al.*[102] have recorded that nitric-sulphuric mixtures failed to destroy the organic matter but mixtures of perchloric and nitric acids were effective.

The tin(II) method was applied to binary alloys containing uranium and less than 5% of platinum. Larger proportions were determined gravimetrically. Wagner[103] and Shmulyakovskii[104] used the tin(II) method for platinum in catalysts and a procedure for determining platinum in cathode slimes with and without extraction was recorded by Struszynski and Chwastowska.[105]

5-(*p*-Dimethylaminobenzylidene)-rhodanine, previously used for the spectrophotometric determination of palladium over the range of 0·4–2·5 ppm,[30,31] has been applied by Piercy and Ryan to the determination of platinum over the range of 0·5–6 ppm.[4] While maximum absorbance occurs at 545 mμ, the appreciable absorbance of reagent required the use of 590 mμ, at which wavelength the reagent showed 100% transmittance. The procedure required reduction to platinum(II) by ascorbic acid although the mole ratio of metal to reagent proved to be 1:3. The dark red complex is developed at a pH between 2 and 4 and heating at 65–75° for 5 min. An extraction is made with propionic acid in which the red colour remains stable for 1 hr. There is interference from silver, copper, gold, rhodium and palladium. Interference from palladium can be reduced somewhat by the addition of dimethylglyoxime; 25 ppm of palladium to 2 ppm of platinum can be tolerated.

2,3-Quinoxalinedithiol (QDT), used by Ayres and Janota[27] for palladium was also applied for the spectrophotometric determination of platinum.[29] The method is applicable over the range 1·4–5 ppm. The procedure requires the use of *N*,*N*-dimethylformamide as a solvent and previous treatment with tin(II) chloride solution. With freshly prepared reagents full colour was developed within 50 min with constant absorbance up to 50 hr. Aged reagents decreased the period of stability. The tin reagent could be used for about 2 weeks and the QDT reagent in the dimethylformamide for about 4 days. The method was not sensitive to excess reagent or to acid content, but large proportions of tin(II) chloride resulted in a lack of precision. Associated base and platinum metals interfered and a previous separation of platinum is required. Although the authors failed to suggest a method of separation, a series of hydrolytic separations, both in the presence and in the absence of nitrite, ought to be effective. Convincing evidence was provided by the authors to indicate a platinum to reagent mole ratio of 1:2, providing a blue dissolved constituent with maximum absorbance occurring at 624 and 585 mμ and an intermediate minimum at 599 mμ. Each of these wavelengths was equally suitable for platinum determinations.

Potassium iodide was used by Karpova and Gut'ko[106] to determine rhodium, iridium and platinum in mixed solutions. Beer's Law was obeyed over the respective ranges of 30–3500, 1·6–160 and 0·4–64 μg/ml, the respective maximum absorbances being 502, 488 and 494 mμ.

A potentially useful method for a range of platinum of 10–100 ppm in the presence of copper, selenium, and tellurium was described by Ginzburg and Sal'skaya.[107] Absorbance measurements could be made at 370–450 mμ. Beer's Law was obeyed over the range 5–120 μg/ml. The procedure required a conversion of the platinum salts by perchloric acid to hexabromoplatinic acid. During the fuming process the solution may become turbid if the larger amounts of platinum are present but dissolution is accomplished upon the required addition of hydrobromic acid. The method has been applied successfully to industrial products containing high proportions of copper, selenium and tellurium. The unsubstantiated claim is made that the method tolerates approximately equal amounts of platinum, selenium and iron, 4-fold proportions of tellurium and copper and 17-fold amounts of nickel. Before this work, hexachloroplatinate(IV) had been applied by Kirkland and Yoe[108] for the range of 3–11 ppm and with measurements made at 262 mμ. As in the proposed method, the platinum metals interfered.

TABLE II.—SPECTROPHOTOMETRIC METHODS FOR PLATINUM

No.	Reagents	Range of concentration, *ppm*
1.	Tin(II) salt[92,97–105,115 121]	0·4–6 0·5–2 3–25
2.	5-(*p*-Dimethylaminobenzylidene)-rhodanine[4,30,31]	0·5–6
3.	*p*-Nitrosodimethylaniline[122,123]	0·7–2·4
4.	Dibenzyldithio-oxamide[60]	1–5 (see Palladium Table No. 33
5.	2,3-Quinoxalinedithiol[29]	1·4–5
6.	Potassium iodide[106,123,210]	1·8–5
7.	*N,N′*-Bis-(3-dimethylaminopropyl)-dithio-oxamide[57,58]	(see Palladium Table No. 39)
8.	Hexachloroplatinate(IV)[108] and hexabromoplatinate(IV)[107]	3–11 5–120 B.L. 10–100
9.	*o*-Phenylenediamine[109]	4–12
10.	Thiosemicarbazide[110,124,125]	10–90
11.	Anthranilic acid[111,112]	16–48
12.	*o*-Aminophenol-*p*-sulphonic acid[111]	8–24
13.	Diacetoimidoplatinum[124]	250–900
14.	Dithizone[113,114]	
15.	Phenylthiosemicarbazide[126]	
16.	Alkali fluoroplatinate[127]	
17.	2-Chloropyridine[75]	(See Table I, No. 62)

o-Phenylenediamine forms an orange solution with platinum(IV).[109] The optimum range is 4–12 ppm and the optimum wavelength is 450 mμ; the sensitivity is 0·003 μg/cm². The complex is formed in 25 min at pH 3–4 and remains stable for 1 hr. Absorbance increases up to pH 3 and decreases beyond pH 4·0. The complex contains a mole ratio of platinum to reagent of 1:2. There is interference from associated base and platinum metals.

Thiosemicarbazide was used by Barkovskiĭ[110] to determine platinum in silver alloys without the removal of silver. The alloy was dissolved in nitric and hydrochloric acids and the silver chloride was dissolved by ammonium thiocyanate; then ammonia and sodium acetate were added. To an aliquot of the resulting liquid were added, in order, ammonium thiocyanate, gelatin, an aqueous solution of the thiosemicarbazide, sodium acetate and the absorbance was measured in a 3-ml cell with a green filter.

Anthranilic acid[111] produces a reddish-violet complex with a mole ratio of platinum(IV) to reagent of 1:1 and a maximum absorption at 500 mμ. The optimum concentration range is 16–48 ppm of platinum. The sensitivity is 0·068 μg/cm^2. Beer's Law is obeyed over the range of 4–64 ppm of platinum. Unfortunately, there are insufficient data included in the published report to make clear the effects of acidity, salt content, *etc.* However, the data in the original thesis[112] indicate that the optimum pH is 5 with a tolerance of ±0·5 unit. An increase of 4 ml of reagent solution above the recommended 3 ml is also without effect. Larger amounts result in a decrease of absorbance. The rate of colour formation is slow but the maximum colour intensity can be achieved by heating on a steam bath for 15–20 min; longer periods reduce the absorbance. As might be expected, the reagent is far from specific; copper, nickel, iron, rhodium and ruthenium interfere. Palladium and iridium can be tolerated up to ratios of 1:1. Nitric acid is removed by conventional methods.

It was found[111] that *o*-aminophenol-*p*-sulphonic acid also forms a coloured complex with platinum(IV) which showed a maximum absorption at 420 mμ and a sensitivity of 0·025 μg/cm^2. The conditions for colour reactions were 1 ml of 1% reagent, a pH range of 5–6 and a reaction period of about 2 hr for maximum colour development. The optimum concentration was 8–24 ppm and Beer's Law was obeyed over the range 1–26 ppm. This reagent is a useful alternative to the more established reagents.

Dithizone in benzene has been used for the extraction of platinum(II) from sulphuric acid solutions of iron, nickel and chromium. Interfering elements can be removed by washing the extract with hydrochloric acid or by treating the sample solution with concentrated dithizone in benzene before the reduction of platinum with tin(II) chloride. Absorbance could be measured at either 490 or 720 mμ.[113]

The acidities required for the benzene-dithizonate extractions were also recorded by Kawahata, Mochizuki and Misaki.[114] These were for palladium, $<15N$ and <pH 5, for platinum(II), 1·0–10·5*N*, for gold $> 7N$. The molar absorptivities were respectively, 3·8 × 10^4 at 450 mμ and 3·2 × 10^4 at 640 mμ; 4·1 × 10^4 at 490 mμ, and 3·8 × 10^4 at 720 mμ, 2·6 × 10^4 at 450 mμ.

Zusammenfassung—Es wird eine kritische Übersicht über die nach 1958 veröffentlichten spektralphotometrischen Bestimmungsmethoden für Palladium und Platin gegeben. Zusammen mit den Beschreibungen des Verhaltens der Metalle wird eine Tabelle vorgelegt, die vor 1958 beschriebene Reagentien mit den einschlägigen Literaturzitaten registriert.

Résumé—On passe en revue, de façon critique, les méthodes spectrophotométriques de dosage du palladium et du platine publiées postérieurement à 1958. A la description de chaque métal est joint un tableau identifiant les réactifs mentionnés avant 1958 avec les références correspondantes.

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SHORT COMMUNICATIONS

Spectrophotometric determination of selenium in technical sulphuric acid by *o*-phenylenediamine

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INTRODUCTION

TECHNICAL-grade sulphuric acid frequently contains a small amount of selenium. 3,3′-Diaminobenzidine is widely used to determine this selenium, but, when a large amount of sulphate is present, the reagent tends to form an insoluble sulphate (*cf.* with benzidine, which is a well known precipitant for sulphate). Therefore, the selenium is best separated from the sulphate by coprecipitation on hydrated iron(III) oxide, then dissolving this precipitate in hydrochloric acid and masking the iron(III) with EDTA before the colour development.[1] Alternatively, to prevent the interference of sulphate by precipitation a large amount of ammonium chloride can be added;[2] the time needed for colour development is then more than 3 hr. However, because the calibration curve varies with the amount of sulphate ion present, a new curve must be prepared for each different sulphate concentration.

In a previous paper,[3] one of the present authors stated that *o*-phenylenediamine was even better than 3,3′-diaminobenzidine for the spectrophotometric determination of selenium because the sensitivity was about twice as large and sulphate did not interfere. Furthermore, although the pH for colour development is almost the same in the case of both reagents, with 3,3′-diaminobenzidine the pH must be adjusted to 6–7 for the extraction (the free diamine tends to be air oxidised at this pH). An improved method for the determination of selenium in technical-grade sulphuric acid based on the use of *o*-phenylenediamine is now reported.

EXPERIMENTAL

Reagents

o-Phenylenediamine hydrochloride. This should be purified as follows. Fifty g of commercial *o*-phenylenediamine hydrochloride are dissolved in 150 ml of water and the solution decolourised with active carbon. The solution is filtered and the procedure repeated until the filtrate becomes colourless. The colourless filtrate is poured into 150 ml of concentrated hydrochloric acid, when *o*-phenylenediamine hydrochloride deposits as white crystals. The latter are filtered on a sintered-glass filter and dried over sodium hydroxide in a desiccator. The reagent thus obtained is stored in a coloured bottle. A 0.2% aqueous solution is freshly prepared before use.

Standard selenium solution (1·000 *μg of selenium/ml*). Prepared by diluting a stock solution which contains 1·4053 g of selenium dioxide in 1 litre of water.

85% Formic acid, 0·1*M* EDTA and 0·4*M* urea solutions are used; other reagents are of analytical reagent grade.

Apparatus

Spectrophotometric measurements were made with a Shimazu Model QR-50 spectrophotometer using 1-cm cells and pH measurements with a Tôa Dempa Model HM-5A glass-electrode pH meter.

Procedure

Weigh an amount of technical sulphuric acid, containing about 20 μg of selenium, by means of a weight pipette and transfer to a 100-ml beaker containing water. Heat the solution with 2 ml of 0·4*M* urea solution for 1 min above 80°. After cooling, neutralise with concentrated ammonia solution. Add 2 ml of 0·1*M* EDTA solution and adjust the pH to between 1·5 and 2·5 with formic acid. Dilute to approximately 50 ml with water. Add 2 ml of 0.2% *o*-phenylenediamine and set aside for 2 hr at room temperature. Transfer to a 125-ml separatory funnel, add exactly 10 ml of toluene and shake vigorously for 30 sec. Centrifuge the toluene layer for a few minutes. Separate the toluene layer and determine its absorbance at 335 mμ against a reagent blank.

Calibration curve

The absorbance is virtually unchanged when 15 μg of selenium are present in 0–1·5 g of pure sulphuric acid. The calibration curve is prepared according to the above *Procedure* and is the same as Fig. 8 in a previous paper.[3]

Interference studies

Of many different ions contained in technical sulphuric acid, arsenic, lead, magnesium, ammonium, chloride and nitrate do not interfere, but iron(III) and nitrous acid interfere. Sulphuric acid from the chamber process always contains nitrous acid, which reacts with *o*-phenylenediamine to form a yellow product. Nitrous acid can be effectively removed by heating with a urea solution. Iron(III) can be masked by adding EDTA.

Table I.—DETERMINATION OF SELENIUM IN CHAMBER SULPHURIC ACID

Sample	Sample taken, *g*	Selenium added, μg	Absorbance	Se found in sample	
				μg/g	%
*Glover acid No. 1	0·2238	0	0·264	57·6	
	0·3027	0	0·365	58·4	
	0·2937	5	0·453	57·9	0·0058
	0·1626	5	0·295	57·4	
*Glover acid No. 2	0·0933	0	0·204	107	
	0·1326	0	0·294	108	
	0·0860	5	0·294	108	0·0108
	0·1272	5	0·384	107	
*Glover acid No. 3	0·1643	0	0·287	84·6	
	0·1630	0	0·285	84.9	
	0·1651	5	0·395	85·9	0·0085
	0·2289	5	0·507	85·8	
1st chamber acid No. 1	0·9110	0	0·308	16·4	
	0·3987	0	0·131	16·1	
	1·1549	5	0·486	16·2	0·0016
	1·0069	5	0·426	15·6	
1st chamber acid No. 2	0·7052	0	0·215	14·8	
	0·7113	0	0·217	14·9	
	0·7727	5	0·341	14·9	0·0015
	0·7568	5	0·335	14·9	
1st chamber acid No. 3	0·2929	0	0·154	25·8	
	0·2956	0	0·157	25·1	
	0·2948	10	0·369	25·2	0·0025
	0·2940	10	0·370	25·2	

* Red elemental selenium is precipitated in these acids. Selenous acid dissolved in the supernatant clear liquors was determined and thus the data does not show the total selenium.

Determination of selenium in technical sulphuric acid

The determination of selenium in sulphuric acid made by the chamber process was carried out by the above *Procedure*. The results were summarised in Table I. Selenium in the samples is calculated by deducing the added selenium from the determined selenium.

Acknowledgement—The authors are indebted to Kōnoshima Chemical Co. Ltd. for a donation of technical sulphuric acid.

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Summary—*o*-Phenylenediamine reacts quantitatively with selenium to form piaselenol even when a large amount of sulphate is present. Piaselenol is extracted by toluene and the absorbance at 335 mμ measured to determine the amount of selenium in technical sulphuric acid. Interference from iron(III) and nitrous acid can be conveniently eliminated by adding EDTA and urea before colour development.

Zusammenfassung—*o*-Phenylendiamin reagiert mit Selen quantitativ zu Piaselenol, auch in Gegenwart eines großen Sulfatüberschusses. Das Piaselenol wird mit Toluol extrahiert und die Extinktion bei 335 mμ gemessen, um die Selenmenge in technischer Schwefelaäure zu bestimmen. Die Störung von Eisen(III) und salpetriger Säure läßt sich bequem beseitigen durch Zusatz von EDTA und Harnstoff vor der Farbentwicklung.

Résumé—L'*o*-phénylène diamine réagit quantitativement avec le sélénium pour former un piasélénol, même en présence d'une forte quantité de sulfate. On extrait le piasélénol au moyen de toluène et mesure son absorption à 335 mμ pour déterminer la teneur en sélénium de l'acide sulfurique technique. On peut aisément éliminer les interférences du fer (III) et de l'acide nitreux par addition d'EDTA et d'urée avant le développement de la coloration.

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Reversible indicators for titrations with hypochlorite

(*Received* 27 *March* 1965. *Accepted* 19 *May* 1965)

HYPOCHLORITE (sodium or calcium) is one of the most versatile redox titrants available,[1] but its application has probably been restricted because of the lack of good indicators. An excess of hypochlorite is usually added to the test solution and the residual oxidant determined either by indirect iodimetry, or by addition of a slight excess of arsenic(III), which is then titrated with hypochlorite in the presence of a suitable indicator. The first indicators were irreversible, but later two reversible indicators were described: Quinoline Yellow[2] and Tartrazine.[3] Both indicators have the disadvantage that the colour change is from yellow to colourless; hence, if the titrant is added carelessly the end-point may be missed because when a few drops of excess titrant have been added the solution becomes yellow because of formation of hypobromite.

TABLE I

Indicator	End-point*	Colour change	Change in	
			Wavelength	Optical density
BTB	+	blue → green-yellow	none	slight decrease
TB	+	blue → yellow	increase	increase
MTB	+	blue → yellow	increase	increase
BCP	+++	purple → yellow	none	decrease
CR	++	red → yellow	increase	decrease
XO	++	red → yellow	increase	decrease

* BTB is taken as the norm, with one plus sign. Increase in the number of plus signs denotes better qualities, *i.e.*, sharpness, contrast, *etc.*, as apparent to the eye.

Summary—*o*-Phenylenediamine reacts quantitatively with selenium to form piaselenol even when a large amount of sulphate is present. Piaselenol is extracted by toluene and the absorbance at 335 mμ measured to determine the amount of selenium in technical sulphuric acid. Interference from iron(III) and nitrous acid can be conveniently eliminated by adding EDTA and urea before colour development.

Zusammenfassung—*o*-Phenylendiamin reagiert mit Selen quantitativ zu Piaselenol, auch in Gegenwart eines großen Sulfatüberschusses. Das Piaselenol wird mit Toluol extrahiert und die Extinktion bei 335 mμ gemessen, um die Selenmenge in technischer Schwefelaäure zu bestimmen. Die Störung von Eisen(III) und salpetriger Säure läßt sich bequem beseitigen durch Zusatz von EDTA und Harnstoff vor der Farbentwicklung.

Résumé—L'*o*-phénylène diamine réagit quantitativement avec le sélénium pour former un piasélénol, même en présence d'une forte quantité de sulfate. On extrait le piasélénol au moyen de toluène et mesure son absorption à 335 mμ pour déterminer la teneur en sélénium de l'acide sulfurique technique. On peut aisément éliminer les interférences du fer (III) et de l'acide nitreux par addition d'EDTA et d'urée avant le développement de la coloration.

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XO	++	red → yellow	increase	decrease

* BTB is taken as the norm, with one plus sign. Increase in the number of plus signs denotes better qualities, *i.e.*, sharpness, contrast, *etc.*, as apparent to the eye.

More recently, Cerana[4] made the interesting discovery that Bromothymol Blue functions as a reversible indicator in the system and it has the advantage that the colour change is from deep blue to greenish-yellow. This finding suggested that other sulphone-phthaleins might be sufficiently stable to resist destruction and the following readily available compounds were examined besides Bromothymol Blue: Phenol Red, Chlorophenol Blue, Bromophenol Red, Tetrabromophenol Blue, Catechol Violet, Cresol Purple, Bromocresol Green, Pyrogallol Red, Bromopyrogallol Red, Bromocresol Purple, Cresol Red, Xylenol Orange, Thymol Blue, Methyl Thymol Blue.

Some were destroyed, some gave only a feeble indicator response, but the claims made for Bromothymol Blue[4] (BTB) were confirmed and five other indicators were found suitable: Bromocresol Purple (BCP), Cresol Red (CR), Xylenol Orange (XO), Thymol Blue (TB) and Methyl Thymol Blue (MTB); these five indicators were then examined in greater detail. In particular, the indicators were examined spectrophotometrically before and after the end-point when the original colour had been restored by the addition of a slight excess of arsenic(III). The results are summarised in Table I.

Notes. TB and MTB turn to a deeper blue just before the end-point: when reversed the colour changes to the deeper blue. CR and XO change from red to purple before the end-point and reverse to purple.

DISCUSSION

The wavelength of maximal absorption of BTB (620 mμ) does not shift, and there is only a slight change in optical density which denotes excellent stability. TB and MTB change to 620 mμ after reversal, which suggests conversion of both to BTB. The optical density increases with successive reversals; hence, it would seem that the conversion to the more intensely coloured BTB is incomplete at the first reversal.

The wavelength of maximal absorption of BCP (590 mμ) does not change, but the change in optical density shows that slight destruction takes place with each oxidation. CR and XO change to the wavelength of BCP after one oxidation, again suggesting conversion to BCP.

The differences indicated by the plus signs in Table I are very slight and may be a matter of personal preference and personal colour response. All the indicators are suitable, but there is little point in using CR, XO, TB and MTB when they are converted to BCP and BTB. BTB is undoubtedly the more stable, as indicated from the spectrophotometric measurements, but this is not apparent to the eye even after several reversals. BCP is preferred because of sharpness of end-point and colour contrast.

An excess of bromide was always added according to conventional practice; when it was not added, the indicators were destroyed. With some of the indicators it was also found advantageous to add osmic acid catalyst; the reaction then proceeded more rapidly.

Several substances[1] were determined by titration with hypochlorite using all the indicators in turn. Satisfactory results were obtained. A particularly valuable titration is that of iodide as described by Cerana;[5] hitherto it has only been possible to apply this titration with potentiometric determination of the end-point.

Other titrants for which there is a shortage of good reversible indicators because of destruction are bromate, iodate and chloramine-T. The above indicators were also examined in these systems, but it was not possible to make any special recommendation, because they were either inferior to or offered no advantage over conventional indicators. Our findings are summarised below.

Potassium bromate. Only TB, MTB and Catechol Violet (CV) were found suitable. All changed from red to yellow. MTB was immediately reversible: TB changed to orange and only to red after boiling. CV reverted slowly in the cold, but rapidly when heated. When an excess of bromide is added (according to conventional practice) the end-points are very poor; the end-points are only satisfactory when bromide is not added, but CV is not then reversible. Solutions of MTB seem to be unstable, because the colour changes slowly from orange to red after several days. Only this aged solution had good indicator properties with bromate, and also with iodate and chloramine-T. It is not changed to TB.

Chloramine-T. Only CV, MTB and TB were suitable and of these only CV and MTB were reversible; the colour changes of all three indicators were from red to yellow. In the absence of potassium bromide only MTB is reversible; in its presence CV is slowly reversible in the cold, but it reverts rapidly when heated. TB does not reverse under either set of conditions. The titrations were done in 2*M* and 1*M* hydrochloric or sulphuric acid.

Potassium iodate. Only MTB and TB were suitable and TB was not reversible; MTB is only reversible once, then there is some obvious destruction. In our opinion it is doubtful if any indicator is likely to supplant the use of chloroform or carbon tetrachloride in this titration. Although the container has to be stoppered and shaken between addition of titrant, this is only necessary near the end-point. All other indicators undergo some destruction.

General procedure. Transfer 25 ml of 0·1*N* arsenic(III) solution to a 250-ml conical flask, add 5 ml of 10% potassium bromide solution and 25 ml of 1·6% borax solution. Add 5 drops of BCP or XO (0·1% aqueous), or 10 drops of CR (0·05% in ethanol-water, 50:50) and 3 drops of osmic acid solution (0·2% aqueous). Titrate at moderate speed with 0·1*N* sodium hypochlorite solution until the indicator changes colour. When a slight excess of arsenic(III) is added, all three indicators revert to the purple colour.

Blanks (of the order of 0·03 ml of 0·1*N* hypochlorite) are determined for each indicator and the necessary corrections are applied.

Note. When TB (10 drops of 0·05% in ethanol-water, 50:50) and MTB (5 drops of 0·1% aqueous) were used, the osmic acid was not required; the blue colour of the indicators changes to deep blue. TB, MTB and BTB changed colour fleetingly as each drop of oxidant was added.

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Summary—Several sulphone-phthalein indicators have been examined to test their possible application as redox indicators in titrations with hypochlorite, bromate, iodate and chloramine-T. It was confirmed that Cerana's indicator, Bromothymol Blue, is an excellent reversible indicator for titrations with hypochlorite. Bromocresol Purple is possibly slightly better. Cresol Red, Xylenol Orange, Thymol Blue and Methyl Thymol Blue are also suitable, but there is little point in using them, because the first two are converted to Bromocresol Purple and the last two to Bromothymol Blue. In the remaining systems the indicators were inferior to or no better than conventional indicators.

Zusammenfassung—Einige Sulfonphthalein-Indikatoren wurden auf ihre Verwendbarkeit als Redoxindikatoren bei Titrationen mit Hypochlorit, Bromat, Jodat und Chloramin-T geprüft. Es wurde bestätigt, daß der Indikator von Cerana, Bromthymolblau, ein ausgezeichnet reversibler Indikator für Hypochlorit-Titrationen ist. Bromkresolpurpur ist vielleicht noch etwas besser. Kresolrot, Xylenolorange, Thymolblau und Methylthymolblau sind ebenfalls geeignet, aber ihre Anwendung bringt keinen Vorteil, da die ersten beiden in Bromkresolpurpur und die letzten beiden in Bromthymolblau umgewandelt werden. In den entstandenen Lösungen sind sie schlechter oder nicht besser als die üblichen Indikatoren.

Résumé—On a examiné plusieurs indicateurs du type sulfone-phtaléine en vue de leur application possible en tant qu'indicateurs redox dans les dosages au moyen d'hypochlorite, bromate, iodate et chloramine T. Il a été confirmé que l'indicateur de Cerana, bleu de bromothymol, est un indicateur réversible excellent pour les dosages à l'hypochlorite. Le pourpe de bromocrésol est peut-être légèrement meilleur. Le rouge de crésol, le xylénol orangé, le bleu de thymol et le bleu de méthylthymol conviennent aussi, mais leur emploi n'offre pas d'intérêt particulier, car les deux premiers sont convertis en pourpe de bromocrésol et les deux derniers en bleu de bromothymol. Dans les autres systèmes, ces indicateurs sont inférieurs ou tout au plus égaux indicateurs ordinaires.

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Formal potential of tris(2,2′-dipyridyl)iron(II) sulphate

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DIPHENYLAMINE and its derivatives and metal complexes of 1,10-phenanthroline or 2,2′-dipyridyl and their derivatives, are the two most important groups of redox indicators used in titrations with chromium(VI) and cerium(IV). Derivatives from both groups have been studied extensively over the last quarter-century, but some apparently behave anomalously and little effort has been made to find acceptable explanations.

It is well-known that tris(1,10-phenanthroline)iron(II) sulphate, commonly called ferroïn (1·06 V), is unsuitable for titrations of iron(II) with chromium(VI) because its potential is too high;[1] the equivalence potential of the system lies between 1·0 and 0·85 V. However, in the reverse titration ferroïn functions satisfactorily because a different and more favourable equivalence potential is obtained (1·2–0·85 V).[1] The behaviour of ferroïn in this system has only been fully recognised during the last decade, but other apparent anomalies have passed virtually unnoticed.[2-6]

(1) *N*-Phenylanthranilic acid (NPA) (1·08 V) is recommended as an indicator for use with both cerium(IV) sulphate and potassium dichromate, even though its reported potential is higher than that of ferroïn. Because this indicator behaves satisfactorily in both systems, either the reported potential is incorrect or factors other than potential come into play. It is now known that the former is the reason; in recent times the transition potential has been redetermined and is now reported as 0·89 V,[7] which is a figure to be expected for an indicator which functions in both systems. In any event, because *N*-phenylanthranilic acid is diphenylamine-*o*-carboxylic acid, one would not expect the introduction of a carboxyl group to raise the potential from 0·76 to 1·08 V.[2]

(2) 5,6-Dimethylferroïn (0·97 V) has been recommended as an indicator for titrations with dichromate because of its favourable potential.[1] It is known to function well in this system.[8] It would be expected that tris(2,2′-dipyridyl)iron(II) sulphate, which has exactly the same potential (and is much cheaper) would behave likewise, yet it has been found to behave exactly like ferroïn.[6]

(3) Ferroïn is unsatisfactory as an indicator in titrations with cerium(IV) in a perchloric acid medium, because of the high potential of this titrant; suitable indicators are nitroferroïn (1·25 V) and tris(2,2′-dipyridyl)ruthenium(II) chloride (1·25 V). Rao and Rao[9] examined the triphenylmethane dyestuffs, Erioglaucine A, Eriogreen B and Xylene Cyanol FF, as indicators in this system. They were found to be satisfactory and have the advantage of cheapness. However, the reported transition potential of all three indicators is 1·01 V. Hence the question arises, why should they function satisfactorily when ferroïn with a higher potential does not?

In the present communication the apparent anomaly of (2) is explained; that of (3) will be dealt with in a later communication.

At the time this examination was undertaken it was considered that the reported potential of tris(2,2′-dipyridyl)iron(II) sulphate was correct, because unlike NPA it had been determined under apparently the same conditions as those of the 1,10-phenanthroline derivatives which are known to be correct. Infrared and other studies of the complex and of 5,6-dimethylferroïn, revealed no unusual differences in structure or in complexing properties; hence all that remained was a redetermination of the redox potential.

Walden *et al.*,[10] who first recommended ferroïn and tris(2,2′-dipyridyl)iron(II) sulphate as indicators, ascribed the same potential to both, *i.e.*, 1·14 V. Hume and Kolthoff[11] redetermined the potential of ferroïn and advanced the revised figure of 1·06 V. They showed that the earlier figure was caused by an error in the original calculation. Apparently, Hume and Kolthoff did not redetermine the potential of tris(2,2′-dipyridyl)iron(II) sulphate but, because Walden *et al.* had found the same values for the two indicators, assumed that only the same error was involved and recommended that the same potential be used as for ferroïn, *i.e.*, 1·06 V. Shortly afterwards Smith and Richter[12] repeated the determinations. They agreed exactly with Hume and Kolthoff on the value for ferroïn, but reported the figure of 0·97 V for tris(2,2′-dipyridyl)iron(II) sulphate.

We redetermined the formal potentials of 5,6-dimethylferroïn and tris(2,2′-dipyridyl)iron(II) sulphate with the results shown in Table I.

TABLE I

Indicator	$E^{\circ\prime}(1F\,H_2SO_4)$, *V*
5,6-Dimethylferroïn	0·975, 0·977, 0·980; Mean: 0·977
Tris(2,2′-dipyridyl)iron(II) sulphate	1·024, 1·022, 1·024, 1·023; Mean: 1·023

The value for 5,6-dimethylferroïn is in excellent agreement with that of Smith and Richter, but the value for tris(2,2′-dipyridyl)iron(II) sulphate is significantly higher and explains exactly why this indicator is unsuitable for titrations of iron(II) with dichromate; its formal potential is too high for the system.

As a rough check on the electrometric determination, the potentials were determined using the "potentio-poised" solutions of Smith and Banick[13] (Table II).

TABLE II

Indicator	Range for E°′ (1*F* H_2SO_4), *V*
5,6-Dimethylferroïn	0·95–0·98
Tris(2,2′-dipyridyl)iron(II) sulphate	1·02–1·06

Although this method is less accurate than electrometric measurements, it provides a simple and independent means of estimating formal potentials. The results obtained are of the same order as those obtained electrometrically.

After completion of this work it was found that in 1963, Schilt[14] had redetermined the formal potential of tris(2,2′-dipyridyl)iron(II) sulphate by a different electrometric method; he reports the figure as 1·026 V which agrees well with the present measurement. Schilt ascribes the error to allowance not being made for the dissociation of the complex at acidities of 1*F* and higher. Walden *et al.*[10] considered that tris(2,2′-dipyridyl)iron(II) sulphate was less stable than ferroïn and it is probably for this reason that there are hardly any references in the literature to its use as a redox indicator. Cagle and Smith[15] examined the indicator properties of tris(2,2′-dipyridyl)iron(II) sulphate in the titration of iron(II) with cerium(IV) and found it satisfactory, provided that it did not stand in contact with excess of oxidant for long. These observations have been confirmed independently.[8] Although the indicator is quite satisfactory for normal titrations, its comparative instability is evident and we support Schilt's explanation.

It should also be noted that the transition potentials of the ferroïn-type indicators are, in general, some 60 mV higher than the formal potentials, because of the pronounced colours of the reduced forms in the presence of a considerable excess of the oxidised forms. The potential at the observed end-point of a titration in which a ferroïn-type indicator is used is thus higher by this amount. This increased potential should be used when practical applications of these indicators are being considered.

EXPERIMENTAL

The procedure used to determine the formal potentials followed standard practice.[1] A known amount of iron(II) solution and the indicator complex were titrated with cerium(IV) solution at particular concentrations of acid. The resulting titration curve showed two inflections: the first for the iron(III)/iron(II) system, the second for the oxidation-reduction of the indicator complex. The presence of the first inflection provided a useful check on the accuracy of the potential measurements. Schilt used a modified procedure,[14] in which the weighed complex is added directly to a solution containing enough cerium(IV) to oxidise exactly half the indicator complex followed by immediate measurement of the potential. This procedure seems only to be necessary at very high concentrations of acid. Under these conditions, fairly rapid dissociation of the oxidised indicator complex occurs and correction for the effect of this dissociation on the observed potential must be made. At the lower acid concentrations (1*F*) used in the present investigation, little or no trouble was experienced with fluctuating potentials, provided that the titration was carried out without undue delay in the region of the second inflection point.

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Summary—The formal potential of tris(2,2′-dipyridyl)iron(II) sulphate has been redetermined and is now reported as 1·023 V in 1*F* sulphuric acid as against the generally accepted value of 0·97 V. This new figure accounts for the hitherto inexplicable behaviour of the indicator in the titration of iron(II) with dichromate.

Zusammenfassung—Das Formal potential von Tris-(2,2′-dipyridyl-)-eisen (II)-sulfat wurde neu bestimmt und als 1,023 V in 1 F Schwefelsäure angegeben, gegenüber dem bisher angenommenen Wert von 0,97 V. Der neue Wert erklärt das bisher unverständliche Verhalten des Indikators bei der Titration von Eisen(II) mit Dichromat.

Résumé—On a déterminé à nouveau le potentiel formal du sulfate de tris (2,2′-dipyridyl) fer (II) et l'on donne maintenant 1,023 V en acide sulfurique 1 F, par opposition à la valeur généralement admise de 0,97 V. Ce nouveau chiffre rend compte du comportement jusqu'ici inexplicable de l'indicateur dans le dosage du fer (II) au moyen de bichromate.

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PRELIMINARY COMMUNICATION

3,3-Diphenylindane-1,2-dione dioxime as a highly sensitive precipitant for palladium

(*Received* 2 *April* 1965. *Accepted* 19 *May* 1965)

FOLLOWING work with indane-1,2-dione dioxime (IDD) as a precipitant for palladium,[1] an attempt has been made to increase the sensitivity of the determination. A reagent has now been prepared having essentially the same structure—a vicinal dioxime grouping on a 5-membered carbon ring system—as that of IDD but, in addition, having 'inert groups' to give a higher molecular weight. This compound, 3,3-diphenylindane-1,2-dione dioxime, also forms a 2:1 chelate with palladium(II).

The introduction of four phenyl groups around the central atom greatly reduces the solubility of the palladium chelate, not only in polar solvents such as water and ethanol, but also in non-polar solvents such as chloroform, carbon tetrachloride and carbon disulphide. In general, the reactions of the new precipitant are similar to those reported for the parent compound. The pH range (1–4) which can be used for precipitation of palladium is somewhat greater than that used in the case of IDD (2–2·5).

Full results with this new reagent and with other substituted indane-1,2-dione dioximes will be reported in due course.

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D. BRANDON

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Summary—3,3-Diphenylindane-1,2-dione dioxime has been prepared and a preliminary investigation shows it to be more sensitive than indane-1,2-dione dioxime as a precipitant for palladium(II).

Zusammenfassung—3,3-Diphenylindan-1,2-diondioxim wurde hergestellt und erwies sich in Voruntersuchungen als ein Fällungsreagens für Palladium(II), dessen Empfindlichkeit die von Indan-1,2-diondioxim übertrifft.

Résumé—On a préparé la dioxime de la 3,3-diphénylindane 1,2-dione et une recherche préliminaire montre qu'en tant qu'agent de précipitation du palladium(II) elle est plus sensible que la dioxime de l'indane 1,2-dione.

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LETTERS TO THE EDITOR

Interlingua

SIR,

The selection in Professor Wilson's letter[1] of 22 November 1964 to his successor as Editor-in-Chief of *Talanta* would be as follows in Interlingua:

> . . . un nove utensile analytic es introducite pro le analyse de moleculas fluorescente—le analyse de extinction-fluorescentia (le analyse per le extinction de fluorescentia). Iste campo de recerca habera ramnificationes extense in le analyse de micre amontas de compositos organic. Uso analytic es facite del effecto de extinction in le spectrophotofluorometria. Compositos tal como anthracena, phenanthrena, pyrena, benz(a)anthracena, benzo(a)pyrena, perylena, *etc.*, ha essite trovate a esser non-fluorescente in solution in nitromethano, sed hydrocarbures que contine le anulo fluoranthenic es fluorescente.

I am enclosing the latest issue of a little periodical, *SPECTROSCOPIA MOLECULAR*, which has been published monthly in Interlingua since May 1952, and which now goes to 400 subscribers (individuals, libraries and laboratories) in 32 countries.

FORREST F. CLEVELAND

Department of Physics
Illinois Institute of Technology
Chicago, Ill. 60616, *U.S.A.*
23 *April* 1965

REFERENCE

[1] C. L. Wilson, *Talanta*, 1964, **12**, 193.

LAST year, Dr. Rieman[1] suggested that, as an international journal, *Talanta* might consider the acceptance and encouragement of articles written in some international language such as Esperanto or Interlingua. Subsequently, he submitted to this journal a letter in Interlingua.[2] Thereafter, in response to a translation challenge in Interlingua from my predecessor as Editor-in-Chief,[3] three people have accepted the challenge.[4,5,6] The Editorial Board has considered the matter raised originally by Dr. Rieman and some of its deliberations are given below.

Amongst other things, a brochure which accompanied the copy of *Spectroscopia Molecular*,[6] stated "Published in the international language, Interlingua (readable at sight), for easiest reading by the greatest number of the world's spectroscopists." Two aspects of this statement require immediate comment.

Firstly, there are several other international languages than Interlingua, some of which enjoy even wider recognition. Therefore, assuming that Dr. Rieman's suggestion was acceptable in principle, it would be difficult to know which international language should be used. In fact, because of the dilution of effort towards the concept of an international language by adherents to the various competitors, a paper in any one of them might actually serve to diminish its number of potential readers.

Secondly, it is doubtful if Interlingua or any of its competitors can much longer remain classified as truly international. As has already been pointed out,[4] Interlingua is based on Latin roots and people knowing no Romance language will be no better off as regards reading a paper published in it. A very large proportion of the world's population has its language roots in quite different families to Indo-European, of which Romance is but one of the sub-families.[7]

A point the importance of which it is difficult to assess because none of the Editorial Board of *Talanta* is sufficiently *au fait* in Interlingua, concerns certain differences in the three translations[4,5,6] of the passage suggested by Professor Wilson.[3] While there are obviously several equally reasonable possibilities as regards translation of any single sentence, some of what are apparently the same words

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It is strongly felt that the greatest impact to the problem of international publication will not come from the isolated efforts of one or two journals. Rather the problem should be, and possibly is being tackled by such organisations as UNESCO. It is significant that IUPAC has adopted English as its official language, although its journal, *Pure and Applied Chemistry*, does include material written also in French and German. Should IUPAC make a definite recommendation for the use of an international language for scientific publication, then *Talanta* would certainly give it sympathetic consideration.

For the present, *Talanta* will continue to accept for publication papers written in English, French and German. It is emphasised that *Talanta* has made some concession towards recognition of the problems of international publication by including a Russian summary with all its published papers; this is in addition to summaries in English, French and German.

A great many letters have been received on the publication of papers in an international language, too many, in fact, to publish in the journal. The Editorial Board thanks those who have expressed their interest; it is the Board's opinion that the point has now been well made. Correspondence on the matter should, therefore, be considered as closed.

EDITOR-IN-CHIEF

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

IUPAC—*What it is*

The International Union of Pure and Applied Chemistry (IUPAC) is a voluntary non-profit organisation whose chief purposes are:

(1) To promote permanent co-operation between the chemists of the member countries.

(2) To study topics of international importance to pure and applied chemistry which need regulation, standardisation or codification.

(3) To co-operate with other international organisations which deal with topics of a chemical nature.

(4) To contribute to the advancement of pure and applied chemistry in all its aspects.

The governing body of IUPAC is the Council. It is composed of delegates appointed by the national agencies which are concerned with fundamental and applied chemistry. These agencies, representing the chemical interests in their respective areas (*e.g.*, Comité national de la Chimie, under the aegis of the Académie des Sciences, France; British National Committee for Chemistry of the Royal Society, Great Britain; Division of Chemistry and Chemical Technology of the National Research Council, USA; The Academy of Sciences in Moscow, USSR) are the Adhering Organisations to IUPAC, of which there are at present some 38 (see page 787).

The international importance of chemistry has been recognised for many years. After many attempts at collaborative action, IUPAC, as we know it today, was founded in London in November 1918, through the joint action of Sir William Pope, then President of the Society of Chemical Industry (UK), and Paul Kestner, President of the Société de Chimie industrielle (France). The International Union of Pure and Applied Chemistry was formally constituted in June 1920 in Rome.

IUPAC—*What it does*

IUPAC is concerned with both academic and industrial aspects of chemistry, for which international agreement or uniform practice is desirable. Examples are nomenclature, atomic weights, symbols and terminology, physicochemical constants, methods of analysis and assay. *Conferences* of IUPAC are held biennially. At these meetings reports by the various Divisions and constituent Sections and Commissions are presented, discussed, and, after approval, published.

Thus, IUPAC, through its Divisions, Sections and Commissions, serves as an international forum where outstanding specialists in many fields of chemical interest meet to exchange opinions and experiences with the object of reaching agreements that will promote the progress of chemistry throughout the world. The adoption of these agreements or recommendations is not mandatory for the adhering countries—it is wholly voluntary. Nevertheless, the expertness of judgement that goes into approved recommendations and the care taken to consider all points of view strongly favour their general acceptance.

IUPAC also sponsors international congresses and symposia organised by its Divisions or Commissions in their respective fields of interest.

The *XXIst International Conference* and the *XVIIIth International Congress* were held in Montreal in 1961, at the invitation of the Canadian National Research Council. The Congress covered the areas of Physical, Applied, Analytical and Organic Chemistry.

The *XXIInd International Conference* and the *XIXth International Congress* were held in London in 1963. The Congress was mainly devoted to Organic Chemistry, but also included sections on Inorganic, Analytical and Applied Chemistry.

In 1965 the *XXIIIrd International Conference* will be held in Paris at the invitation of the French Académie des Sciences and the *XXth International Congress* will be held in Moscow at the invitation of the Academy of Sciences of the USSR. The Congress will be concerned with Physical, Inorganic, Analytical and Applied Chemistry.

In addition IUPAC organises or sponsors many symposia on specialised topics. Examples include those held recently on Macromolecular Chemistry (Paris), Pesticides (London), Fungi and Yeasts (Dublin), Clinical Chemistry (Detroit), Nitro Compounds (Warsaw), Natural Products (Kyoto), Organo-Phosphorus Compounds (Heidelberg), Organic Photochemistry (Strasbourg), Reactivity of Solids (Munich) and Co-ordination Chemistry (Vienna).

IUPAC—*How it works*

The structure of IUPAC is shown in Table I. The executive agency of the Council is the Bureau, which is composed of the President, the Past-President, the Vice-President, the Secretary General, the Treasurer, the Presidents of the six Divisions, and not less than ten members elected by the Council. Thus, the total membership of the Bureau is 21 or more. The Executive Committee of the Bureau, which acts for the Bureau between meetings, consists of 8 members: President, Past-President, Vice-President (President Elect), Secretary General, Treasurer and three members of the Bureau.

The Executive Committee as elected at the XXIInd Conference consists of:

Lord TODD, President of the Union, Chemical Laboratory of the University, Lensfield Road, Cambridge (UK);
Prof. W. ALBERT NOYES, Jr., Past-President, University of Texas, Department of Chemistry, Austin 12, Texas (USA);
Prof. W. KLEMM, Vice-President, Anorganisch-chemisches Institut der Universität, Hindenburgplatz 55, Münster, Westfalen (Germany);
Dr. R. MORF, Secretary General, c/o F. Hoffmann-La Roche & Co. Ltd., 4002 Basle (Switzerland);
Prof. J. C. BAILAR, JR., Treasurer, Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill. (USA);
Prof. V. N. KONDRATIEV, Academy of Sciences, Institute of Chemical Physics, Vorobyevskoye, Chaussée 2b, Moscow V 334 (USSR);
Dr. A. L. G. REES, Commonwealth Scientific and Industrial Research Organization, Chemical Research Laboratories, GPO-Box 4331, Melbourne (Australia);
Prof. P. E. VERKADE, Ary Schefferstraat 217, The Hague (Netherlands).

The day-to-day chemical work of IUPAC is organised through six Divisions, of which five are concerned with the five principal branches of fundamental chemistry, and the sixth with the general field of applied chemistry (see Table I). The Divisions are practically autonomous except for financial matters. They elect their own officers and, subject to the approval of the Bureau, can form or dissolve Commissions. A Division may be subdivided into Sections, each of which may sponsor several Commissions, but at present, only the Division of Applied Chemistry is so organised. The titles of these Sections disclose that the great breadth of applied chemistry is the reason for this type of organisation.

The ultimate working units of IUPAC are the Commissions and Sub-Commissions. The Commissions are composed of the world's leading experts in their respective fields. Each Commission is associated with, and responsible to, a Division of IUPAC. Much of the work of the Commissions is conducted by correspondence, but it is obviously necessary, for effective collaboration, for Commissions to convene at intervals, preferably at least once in two years. To promote such meetings IUPAC grants travel and subsistence allowances to the Titular Members of the Commissions.

A very important activity of IUPAC during the past few years has been concerned with the establishment of Rules of Nomenclature.

The Physical Chemistry Division has published a manual of Physico-Chemical Symbols and Terminology (in English and French) prepared by the appropriate Commission.

The Inorganic Chemistry Division has issued "Definite Rules for Nomenclature of Inorganic Chemistry."

The Commission on Atomic Weights in agreement with the International Union of Pure and Applied Physics has calculated new tables for relative atomic weights based on the nuclidic mass of the pure carbon isotope 12. This table was published in 1961.

The Organic and the Biological Chemistry Divisions have issued Definite Nomenclature Rules as well as Tentative Rules. The Commission on Codification, Ciphering and Punched Card Techniques of the Organic Chemistry Division has issued "Rules for IUPAC Notation for Organic Compounds."

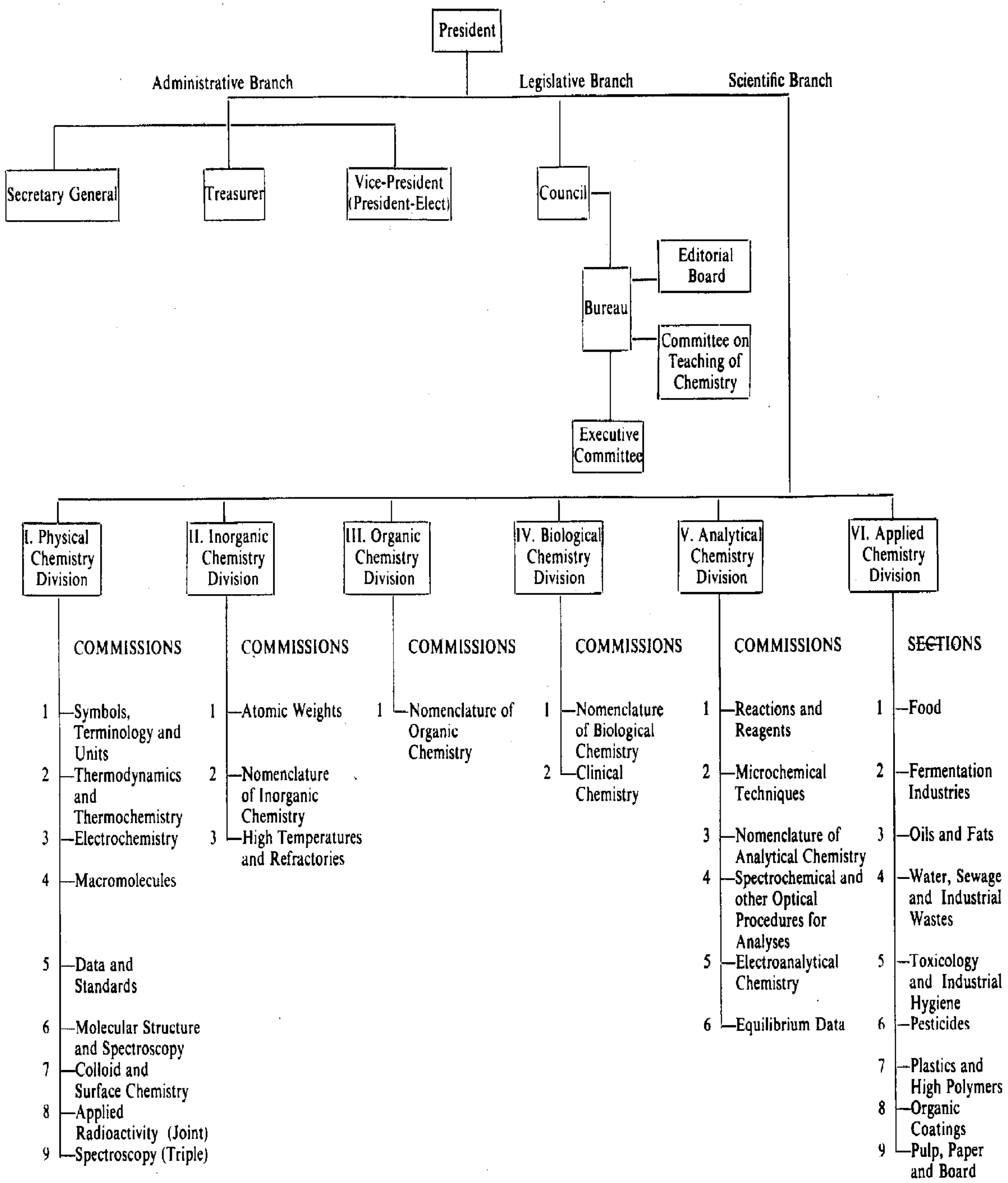
The Applied Chemistry Division, in addition to numerous reports on methods of analysis applicable to industrial use, has published a valuable treatise on the "Re-use of Water in Industry," and has assisted in the formulation of resolutions concerning the control of the industrial environment.

All these rules have been published by the official publishers of IUPAC, Messrs. Butterworths Ltd., London. The definite rules for the Nomenclature of Inorganic and Organic Chemistry and the Manual of Physico-Chemical Symbols and Terminology have been reprinted in the Journal of the American Chemical Society. Translations into several languages have been undertaken by the appropriate National Adhering Organisations.

The official journal of IUPAC, *Pure and Applied Chemistry*, initiated in 1960, has been very well received. In addition to the reports of the Commissions, the journal also publishes the main invited lectures presented at Congresses and at Symposia. This makes it an important source of scientific information that is not readily available elsewhere.

IUPAC is also very deeply interested in those problems which, although of vital importance to chemistry, are outside the mainstream of research and development. Thus a committee has recently

TABLE I.—ORGANISATION OF IUPAC



been formed to study the teaching of chemistry, for which the terms of reference have not been defined; the investigations will cover all academic levels and environments. Two other general issues which are being studied are collaboration with other international bodies, and liason with chemical industry. These latter activities should be beneficial to both IUPAC and the organisation(s) concerned.

IUPAC—*How it is financed*

All officers of IUPAC serve without remuneration. Administrative expenses are kept to a minimum. IUPAC's funds are derived from three sources—national contributions, grants-in-aid from UNESCO (with which IUPAC is affiliated through the International Council of Scientific Unions) and gifts from governmental bodies, industries and individuals. National contributions are in four categories with contributions fixed as follows: member countries in Category A, $25,000 to $2,600; member countries in Category B, $1600 to $800; member countries in Category C, $450; and in Category D, $100. As the activities of UNESCO have increased, its ability to contribute to each scientific union has decreased and, at present, the contributions from UNESCO to the Union of Pure and Applied Chemistry cover only a small fraction of the total costs. Added income has fortunately been obtained through gifts to IUPAC, but many more gifts must be received if IUPAC, through its Divisions and Commissions, is to serve the international chemical community as completely as it ought.

National Adhering Organisations

Argentina	Asociacion Química Argentina, Sanchez de Bustamante 1749, Buenos Aires
Australia	Australian Academy of Science, Gordon Street, Canberra City A.C.T.
Austria	Verein Österreichischer Chemiker, Eschenbachgasse 9, Wien I
Belgium	Comité National de Chimie, Palais des Académies, Bruxelles
Brazil	Associação Brasileira de Química, Caixa Postal 550, Rio de Janeiro
Bulgaria	Bulgarian Academy of Sciences, Street of the 7th November, Sofia
Canada	National Research Council, Division of Chemistry, Ottawa
Colombia	Ministerio de Minas y Petroleos, Laboratorio Químico Nacional Apartado 2577 Bogotá
Czechoslovakia	Czechoslovak Chemical Society, Československá společnost chemická, Hradčanske Nám 12, Prague-Hradčany
Denmark	Danske Kemiske Foreningers Foellesråd for internationalt Samarbejde, 83, Sølvgade, Copenhagen K
Finland	Suomen Kemistien Valtuuskunta, P.O.B. 58, Helsinki
France	Comité National de la Chimie, 28, rue St-Dominique. Paris-7^e
Germany	Deutscher Zentralausschuss für Chemie, Carl-Bosch-Haus, Varrentrappstrasse 40/42, Postschliessfach 9075, Frankfurt/Main
Hungary	Prof. G. Schay, Polytechnical University Budapest, Department of Physical Chemistry, Budafoki Ut. 8, Budapest XI
India	Ministry of Scientific Research and Cultural Affairs Government of India, New Delhi
Ireland	The Secretary, The Irish National Committee for Chemistry, Royal Irish Academy 19, Dawson Street, Dublin 2
Israel	The Israel Academy of Sciences and Humanities, P.O.B. 7032, Jerusalem
Italy	Consiglio nazionale delle Ricerche, Comitato per la Chimica, Piazzale delle Scienze 7, Rome
Japan	Science Council of Japan, Ueno Park, Tokyo
Luxembourg	Section des Sciences de l'Institut grand-ducal du Luxembourg, Place Auguste-Laurent, Luxembourg
Netherlands	Dr. W. F. Haak, Chemical Council of the Netherlands c/o Koninklijke Nederlandse Chemische Vereniging, Burnierstraat 1, The Hague
New Zealand	The Royal Society of New Zealand, Victoria University Buildings, P.O. Box 196, Wellington)
Norway	Norsk Kjemisk Selskap, Dr. W. Holst, Forskningsveien 1, Oslo 3
Poland	Prof. T. Urbanski, Ecole polytechnique, 75, rue Koszykowa, Varsovie
Portugal	Sociedade Portuguesa de Química e Física, Faculdade de Ciencias Rua da Escola Politecnica, Lisboa-2
Republic of China	Chinese Chemical Society, P.O.B. 609, Taipei/Taiwan
Republic of South Africa	Council for Scientific and Industrial Research, The Head, Science Cooperation Division, P.O. Box 395, Pretoria
Republic of Korea	Korean Chemical Society, 199, Dongsung-Dong, Seoul

Republic of Vietnam	Vietnamese Chemical Society, c/o Faculty of Science, Saigon
Rumania	Académie de la République populaire roumaine, Calea Victoriei 125, Bucarest
Spain	Consejo Superior de Investigaciones Científicas, Instituto Alonso Barba de Química Serrano 119, Madrid 6
Sweden	Svenska Nationalkommittén för Kemi, c/o Svenska Kemistsamfundet Wenner-Gren Center, Stockholm VA
Switerzland	Comité suisse de la Chimie, Ecole de Chimie, 22, bd des Philosophes, Genève
Turkey	Turkije Kimya Cemiyeti Merkeze Istiklâl Caddesi, Imam Sodak, 22, Kat. I-Boypglu, Istanbul 829
Union of Soviet Socialist Republics	Academy of Sciences, Leninskii prospect 14, Moscow V-71
United Arab Republic	National Research Council, Ministry of Education, Sh. al-Tahrir, Dokki, Cairo
United Kingdom	British National Committee for Chemistry, The Royal Society, Burlington House, Piccadilly, London W.1
United States of America	Division of Chemistry and Chemical Technology, National Research Council, 2101 Constitution Avenue, Washington 20418 D.C.
Yugoslavia	Union des Sociétés chimiques de la RSFY, Boîte postale 494, Belgrade

Applications have been received from:

Cuba	Comisión Nacional de la Academia de Ciencial de la República de Cuba Capitolio Nacional, La Habana
Greece	Union des Chimistes Hellènes, rue Kaningos 27, Athènes
Mexico	Sociedad Química de México, Apdo. postal 18875, Cipres 176, México 4 D.F.
Nigeria	Science Association of Nigeria, Zoology Departement, University of Ibadan, Ibadan,
Venezuela	Sociedad Venezolana de Química, Edificio Industria 2. Piso, Apartado 3895, Caracas

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TALANTA REVIEW*

A CRITICAL EVALUATION OF COLORIMETRIC METHODS FOR DETERMINATION OF THE NOBLE METALS—III†

RHODIUM, IRIDIUM, RUTHENIUM, OSMIUM AND GOLD

F. E. Beamish
Department of Chemistry, University of Toronto, Toronto 5, Canada

(*Received* 3 *December* 1964. *Accepted* 17 *May* 1965)

Summary—Spectrophotometric methods for rhodium, iridium, ruthenium, osmium and gold recorded subsequent to 1958 are critically reviewed. Associated with the descriptions of each metal is included a table which identifies reagents recorded before 1958 together with pertinent references.

RHODIUM

A 1:1 mixture of diphenylcarbazide and diphenylcarbazone reacts with rhodium(III) salts to form a purple complex of unknown structure.[1] The optimum range of concentration is 0·3–1·5 ppm and the optimum wavelength for absorption is 565 mμ. Colour is developed in a perchloric acid medium at pH 3·0. Both the acidity and the volume of water are critical. The excess of reagent, amount of buffer and period of heating beyond 30 min may be varied within reasonable limits. Preparation of the sample involves fuming with perchloric acid, which process removes the chloride and nitrate interference, volatilises both osmium and ruthenium and precipitates platinum and gold. Iridium, iron, cobalt, nickel, lead and copper interfere. Chromium(VI) and mercury(II) may be removed by volatilising chlorides.

p-Nitrosodimethylaniline was used by Wilson and Jacobs[2] to produce a cherry red complex with a sensitivity of 0·0015 μg/cm^2. The absorbance maximum was 510 mμ when measured against a reagent blank; the latter was required because of high absorbance by the reagent. Beer's Law is obeyed over the range 0·15–1·1 ppm of rhodium, with an optimum concentration of 0·3–1·1 ppm. The volume of the buffer solution, period of heating and volume of the solution heated were critical. Colour was developed at 90° with a heating period of no less than 10 min and no greater then 20 min. A large molar excess of reagent over rhodium was necessary. There was interference from associated base and platinum metals. The data provided indicated that sulphate could be tolerated in proportions of 340 ppm to 0·61 ppm of rhodium. These results were obtained by the addition of sulphate ion to the rhodium solution. One must not conclude that this degree of interference will apply to rhodium solution produced by fuming with sulphuric acid, a process frequently used for the

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

† Continued from *Talanta*, 1965, **12**, 743.

preparation of aqueous solutions of rhodium. Furthermore, because fuming with sulphuric acid is frequently used for preparation of solutions of iridium, which metal is a common associate of rhodium, one must also accept with reservations the stated degree of interference of iridium.

Ayres *et al.*[3] used tin(II) chloride for the simultaneous determination of rhodium and platinum, measurements being made at 475 and 403 mμ, or in order to reduce the absorbance of platinum in the presence of rhodium, at 560 and 403 mμ. Smith[4] used this method to determine rhodium and iridium in plutonium with no previous separation of these three metals. Under the conditions used, plutonium is reduced by tin(II) chloride to plutonium(III) which has an absorption peak at 665 mμ at which wavelength the absorbances of platinum and rhodium are negligible. For the latter two metals the absorbance was measured at 399 and 470 mμ, respectively. The absorbance of plutonium at these wavelengths is directly related to the absorbance of plutonium at 665 mμ, so that a correction may be applied by subtracting the absorbance of plutonium at 470 and 399 mμ. The method is applicable over the range 5–14 ppm of the two metals. The tin(II) chloride method was applied by Gardner and Hues[5] to the determination of rhodium in uranium. No determinations were made with less than 0·02 mg of rhodium or with more than 200 mg of uranium. A wavelength of 520 mμ was used rather than the customary 475 mμ, because with the latter, the absorbance from the uranium was significant and because the conditions of time, temperature and acid strength, which were not critical for rhodium, proved to be critical for uranium. At 520 mμ reliable blanks were obtained for even large amounts of uranium. The data obtained for approximately 1% rhodium alloys, agreed well with gravimetric results.

Tin(II) chloride was also used by Karttunen and Evans[6] for the determination of rhodium in uranium-base fission alloys. The rhodium was isolated by previous solvent extraction and treatment on a cation-exchange resin. The method of isolation of rhodium from fission products and the subsequent use of the tin(II) chloride methods for rhodium concentrations as low as 1 ppm were discussed by Cheneley, Osmond and Perry.[7]

Various efforts have been made to increase the sensitivity of the tin(II)-rhodium complexes. Markham[8] found that in the presence of iodide, tin(II) chloride gives a more intense colour than in the presence of chloride only. The sensitivity of this modification is 0·009 μg/cm^2 at 435 mμ as compared to 0·026 (475 mμ) for the red form. The method involves close control of the conditions for colour development.

Berman and Ironside[9] were able to increase materially the sensitivity of the tin(II) method through the use of tin(II) bromide. The sensitivity of the method is 0·0035 μg/cm^2 of rhodium. The yellow solutions obey Beer's Law over the range 0·8–1·6 ppm of rhodium but satisfactory results are obtained over the range 0·4–4 ppm. As in the case of tin(II) chloride, the composition of the bromide complex is unknown.* The absorption peak is 427 mμ and in the presence of chloride ion a second peak at 407 mμ may appear. To avoid the presence of the latter the tin(II) bromide was prepared by dissolving tin(II) oxide in concentrated hydrobromic acid. The instability of the coloured species and the photosensitivity of the colour development was avoided by the addition of perchloric acid before the addition of the reagent.

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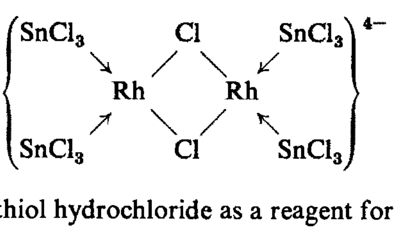
* See below, ref. [12].

The colour remains stable for at least 3 hr. While hydrobromic acid, additional to that required by the procedure, produces an increase in absorbance, the time required to achieve maximum absorbance also increases. The author's data on the effect of sulphuric acid is well worth noting. A very appreciable difference was found in the degree of interference from added sulphuric acid and a solution of rhodium fumed in the presence of sulphuric acid. The tin(II) bromide method was made applicable to fumed solutions by dilution with water, addition of concentrated hydrobromic acid and boiling vigorously for 5 min. The method usually requires the separation of rhodium from other platinum metals and associated base metals. Iridium produces the least interference and a fair estimation of rhodium can be made even when equivalent quantities of iridium are present. This procedure is perhaps the most generally satisfactory of all rhodium methods so far recorded.

A procedure for the spectrophotometric determination of rhodium by tin(II) iodide was described by Berg and Youmans.[10] Apparently these authors were unaware of the tin(II) iodide method previously described by Sandell.[11] Both methods involved a colour development in a mixed chloride–iodide medium. The method was not recommended by Sandell for very small quantities of rhodium because of the necessity of critically controlled conditions. Absorbance was measured at 435 mμ. The procedure of Berg and Youmans was applicable over the optimum range of 0·4–3 ppm. The sensitivity calculated on the basis of one atomic weight of rhodium in the coloured complex is 0·0026 μg/cm^2 measured at 460 mμ. Sandell recorded a sensitivity of 0·009 μg/cm^2 at 435 mμ. Berg and Youmans developed the brown complex by heating in a boiling water bath for a 2-min period which could be increased to 5 min without altering the results. The acid strength and the iodide concentration were not critical although the acid strength required careful control at 1*M*. Associated platinum and base metals interfered. The authors recorded a fair comparison of the three tin halide methods.

The composition of the red complex of tin(II) chloride with rhodium was investigated by Davies, Wilkinson and Young.[12] They found that a 1: 3 ratio of rhodium to tin chloride is required to form the complex and considered the composition as being



2-Diethylamino-ethanethiol hydrochloride as a reagent for rhodium was proposed by Srivastava[13] for the useful optimum range of 0·6–8·3 ppm of rhodium. Beer's Law applied over the range 0·3–15·4 ppm; the sensitivity was 0·0064 μg/cm^2 with a practical sensitivity of 0·064 μg based on an absorbance unit of 0·010. The yellow constituent of unstated composition showed maximum absorbance at 330 mμ. Maximum colour development required heating for 30 min at 90° after which period the absorbance remained constant when heating continued for 2 hr. An excess of 1: 80 of reagent was necessary for maximum colour development. The volume of the solution heated to develop the colour was of some significance; a volume in excess of that recommended required a longer heating period, and a smaller volume failed to give reproducible results. The volume of the buffer as well as the pH of the solution affected the absorbance. The colour remained stable between pH 1·5 and 3·5. A sodium acetate–hydrochloric acid buffer of pH 3·0 was recommended; other buffer systems affected the nature of the complex. The determination of interferences from associated metals and anions was made merely by adding the constituents to the rhodium system. There was interference from all of the associated base and noble metals except from nickel and gold. The latter was tolerated to a ratio of 4 ppm of rhodium to 23 ppm of gold.

5-Amino-2-benzimidazolethiol[14] produces an orange-yellow complex with a mole ratio of rhodium to reagent of 1:2. The sensitivity is 0·004 μg/cm^2. Beer's Law applies over the range 0·5–4 ppm and the optimum concentration range is 1–3·5 ppm. The maximum absorbance occurs at 370 mμ, with a working wavelength at 390 mμ where the reagent absorption is negligible. The colour development is not sensitive to acidity and the recommended pH range is 2–5. At higher pH there is a slight increase in absorbance. Colour development requires heating on the steam bath for 20 min, longer periods being without effect on the colour intensity. Excess of reagent is also without effect. There is interference from palladium, platinum, iridium and iron. Interference from copper can be masked by EDTA.

The latter reagent is also used to mask the interference from iridium in proportions greater than 1:2. With lesser proportions there is no interference from iridium. There seems to be no interference from uranium added as uranyl salts. While palladium interferes, a procedure is provided for the simultaneous determination of rhodium and palladium. The colour of the palladium constituent is developed in the cold and that for rhodium is produced after heating.

The application of *p*-nitrosodiphenylamine for the determination of rhodium was investigated by Stokeley and Jacobs.[15] Compared to the dimethyl derivative,[2] the diphenylrhodium complex required a less vigorous control of the conditions used for colour development. The sensitivity was, however, 0·0054 μg/cm^2, about one fourth of that found for the dimethyl derivative. The two procedures were approximately alike with respect to interferences. Absorbance was measured at 520 mμ against a reagent blank. The optimum range of concentration was 1·0–3·8 ppm.

Good progress has been made in providing satisfactory methods of determining rhodium and iridium in solutions of the two metals. In addition to the development of efficient methods of separating these two metal constituents and of the spectrophotometric determination of each separated metal, procedures have been recorded for the determination of both metals when present together. A simultaneous spectrophotometric determination of both metal constituents was recorded by Stokeley and Jacobs.[16] The reagent 1-(2-pyridylazo)-2-naphthol forms with rhodium chloride a green chloroform-soluble complex of unknown composition. Absorbance is measured at 598 mμ and is independent of pH over the range 4·1–5·6. Above the latter value, extraction by chloroform is complete. A heating period of 1 hr in a boiling water bath is recommended for maximum colour development and after extraction the colour remains stable for at least 24 hr. A 4-fold excess of reagent is required. The sensitivity of the reaction is 0·0052 μg/cm^2 and the optimum range of concentration is 1·1–3·8 ppm of rhodium.

In the case of iridium the reagent forms a red, chloroform-soluble complex with an absorbance maximum at 550 mμ. Because of the slight absorbance of the reagent at this wavelength, the absorbances for both metals are measured against a reagent blank. Maximum absorbance for both metals is attained over a pH range of 4·6–5·6 and complete extraction is effected over the pH range 4·6–5·9. While a heating time of 1 hr was required for rhodium, a longer period is needed for maximum colour development in the case of iridium; however, in the latter case the gain in absorbance can be neglected for practical purposes. The mole ratio of iridium to reagent is 1:2; the optimum range of application is 3·6–12·5 ppm; and the sensitivity is 0·018 μg/cm^2. The effect of associated metals was not determined for either rhodium or iridium.

The conditions necessary for the application of a simultaneous determination were satisfied and the necessary molar absorptivities for each metal at the wavelengths of 550 and 598 mμ were recorded, together with the derived equations required for the calculation of the concentration of each metal.

The reaction between bivalent rhodium and 4,5-dimethyl-2-mercaptothiazole was used by Ryan[17,18] for the separation of rhodium from iridium and for the colorimetric determination of rhodium. The amber to red complex of rhodium is formed in 3–9M hydrochloric acid by the addition of reagent followed by tin(II) chloride. The coloured complex, in a separatory funnel, is extracted by chloroform which layer is subsequently evaporated and the residue taken up with ethanol. The solution is boiled with hydrochloric acid, transferred to a standard flask and the acidity adjusted to about 1·2M. Absorbance is measured with a filter whose maximum transmittance is 430–435 mμ. The method was applied over the range 0·8 to 6 μg of rhodium/ml. The coloured complex obeys Beer's Law over the recommended range but there is a lack of stability with a 1-hr exposure to daylight or overnight standing. The method, while applicable in the presence of added sulphuric acid, produced variable and unacceptable results when applied to solutions which had been fumed with sulphuric acid. Under these conditions, substituting chromium(II) chloride for tin(II) chloride allowed the application of the method.

The author notes that, although the iridium–mercaptothiazole complex prepared from freshly prepared ammonium chloriridate is extracted by chloroform, the latter does not extract quantitatively from the same iridium solution which has stood for more than 2 weeks. The resistance developed upon aging and the effect of fuming with sulphuric, as opposed to the addition of sulphuric acid, emphasises again the reservations which must be made concerning reports of degree of interference obtained by simply mixing the constituent.

4,5-Dimethyl-2-mercaptothiazole was applied by Westland and Beamish[19] to determine rhodium before a separation from iridium by selective precipitation with antimony powder.

1-Nitroso-2-naphthol was used by Watanabe[20] to determine rhodium within the range 1–20 ppm. The complex is extracted by benzene or acetone and the absorbance is measured at 420 mμ.

Thiomalic acid may be used for the spectrophotometric determination of rhodium as well as for palladium. Wagner and Yoe[21] developed the yellow rhodium complex in solutions of pH 1–6 by heating in a boiling water bath for 40 min. The maximum absorbance occurs at 340 mμ, and the reagent does not absorb at wavelengths above 290 mμ. The complex is stable for at least 1 week and Beer's Law is obeyed over the range 1·2–10 ppm, the most sensitive range being 2–7 ppm. The composition of the complex has not been determined. The claim that the method is relatively free from interference must be interpreted with some reservations. Although acceptable results for 4 ppm of rhodium were obtained in the presence of considerably less than 4 ppm of platinum(IV), iridium(IV), gold, ruthenium(III) and osmium(VI), these proportions cannot be interpreted as non-interference, particularly when rhodium so frequently is a minor constituent. An acceptable procedure for the simultaneous determination of palladium and rhodium was also proposed by the authors.

For the range 2·4–8·3 ppm Jacobs[22] used *N,N'*-bis-(3-dimethylaminopropyl)-dithio-oxamide which produced a yellow colour showing a primary absorbance peak at 350 mμ and a secondary peak at 420 mμ. The absorbance of the reagent is very slight beyond 400 mμ. The sensitivity is 0·012 μg/cm^2 and Beer's Law is obeyed over the range 0·61–9·15 ppm. The reaction is carried out at about 7·5M hydrochloric acid which produces maximum sensitivity; it is slow and heating to 90° for 1 hr is required. There is interference from all the platinum metals and, with some toleration of cobalt and nickel, all the associated base metals interfere. Added sulphate and nitrates are tolerated. Procedures were provided for the determination of rhodium in the presence of iridium or of palladium and platinum. Attempts to determine rhodium in the presence of both platinum and iridium were unsuccessful.

The violet colour formed by the oxidation of rhodium(III) with hypobromite at pH 11 was used by Pantani[23] for a spectrophotometric determination. Absorbance was measured at 530 mμ. Maximum absorbance occurred over a pH range of 11·2–11·3 and the alkalinity must be controlled with accuracy if good precision is necessary. The optimum range of concentration is 10–60 ppm of rhodium and Beer's Law is obeyed if the absorbance is measured after stabilisation for 0·5–1 hr. The hypobromite concentration must be greater than 0·2M; the solution remains violet for several days when the reagent is 1M, but turns blue within a few hours if the reagent is 0·1M. With the latter solution an absorption maximum is found at 590 mμ which is in contrast to the 665 mμ, reported for blue solutions by Ayres and Young.[24] However, because of the different acidities employed, Pantani attributed the two colours to different ionic forms. The hypobromite reagent produces a variety of colours some of which result from variations in the hypobromite concentration. Evidence is given for rhodium(VI) in the violet solution and rhodium(V) in the blue solution. The author's data on interference can only be accepted with considerable reservations, *e.g.*, because nitrate or chloride produced no interference it is concluded that "the spectrophotometric determination can be performed on solutions obtained by treatment of the samples with *aqua regia*". Data were provided to indicate that rhodium could be determined in the presence of platinum. However, because absorption by platinum was not negligible at 530 mμ for platinum to rhodium ratios of 10 : 1, measurements were made at 540 mμ at which wavelength absorbance by rhodium was only slightly less than at 530 mμ. There was interference from iridium, palladium, osmium and ruthenium. The effect of base metals was not determined.

For the determination of rhodium in platinum alloys Aleksandrov[25] oxidised by sodium metabismuthate to form a blue-violet colour, said to be a rhodium(V) compound. It should be noted that the procedure involved a period of fuming with sulphuric acid. The absorption maximum is between 550 and 570 mμ. The method is not sensitive and is used for 20–60 ppm of rhodium. The associated base metals do not interfere and there is little interference from platinum, palladium and iridium.

EDTA has been used for the determination of 24–160 μg of rhodium/ml.[26] Maximum absorbance occurs at 350 mμ and the recommended range of concentrations is 3·27–5·70 ppm. A 2 to 3-fold excess of reagent and heating for 3 hr are required. Platinum metals interfere.

TABLE I.—SPECTROPHOTOMETRIC REAGENTS FOR RHODIUM

No.	Reagent	Range of concentration, *ppm*
1.	Sym-diphenylcarbazone and carbazide[1]	0·3–1·5
2.	*p*-Nitrosodimethylaniline[2]	0·3–1·1
3.	Tin(II) chloride;[3–8,12,27]	4–20
		5–14
	tin(II) bromide;[9]	0·4–4
	tin(II) iodide[8,10,11]	0·4–3
4.	2-Diethylamino-ethanethiol hydrochloride[13]	0·6–8·3
5.	5-Amino-2-benzimidazolethiol[14]	1–3·5
6.	*p*-Nitrosodiphenylamine[15]	1·0–3·8
7.	1-(2-Pyridylazo)-2-naphthol[16,28]	1·1–3·8
		(see palladium table No. 46)
8.	4,5-Dimethyl-2-mercaptothiazole[17–19]	1–8
		0·8–6 B.L.
9.	1-Nitroso-2-naphthol[20]	1–20
10.	Thiomalic acid[21]	2–7
11.	2-Mercaptobenzoxazole[29]	2–10
12.	*N*,*N*′-Bis-(3-dimethylaminopropyl)-dithio-oxamide[22]	2·4–8·3
13.	Sodium hypochlorite[20]	3·5–34
14.	Hypobromite[23]	10–60
15.	Metabismuthate[25]	20–60
16.	EDTA[26]	24–160

IRIDIUM

Some effort has been made to apply tin(II) iodide as a spectrophotometric reagent for iridium.[30] A stable complex is formed with maximum absorbance at 446 mμ. Beer's Law is not obeyed but reproducible results may be obtained over the range 0·8–11·7 ppm of iridium. Associated platinum and base metals interfere. It was noted that the molar absorptivity of the tin(II) bromide complex of iridium is about three times greater than that of the tin(II) iodide complex. Working ranges are similar and both methods fail to obey Beer's Law. The high toleration for sulphuric acid is cited as an advantage of the iodide method. In the light of the method used for determining tolerances this claim has little or no validity.

An unusual, nevertheless valid claim for usefulness of a spectrophotometric method was made by Robinson,[31] whose procedure for iridium possessed a distinct advantage in its lack of sensitivity which is about 0·05 μg/cm^2. The procedure is designed to allow the determination of iridium following its separation from rhodium, palladium and platinum by precipitating these metals by copper powder. Iridium, in the copper solution, is oxidised to the hexachloriridate(IV) ion by sodium chlorite and the absorbance is measured at 430 or 488 mμ. The character of the peaks varied with the concentration of sodium chlorite and in order to obtain reproducible results a minimum of 45 g/l. is required. The method is used for iridium determinations over the range 1–95 mg of iridium/l. of solution with 1- or 0·5-cm cells. There is importance in the fact that the method introduces no reagents which would interfere with a subsequent gravimetric recovery. For the latter procedure the hydrolytic precipitation followed by selective dissolution, reduction, *etc.*, is applied. In the light of recent developments more satisfactory procedures are available.

A variety of mixed acid methods for the determination of iridium has been proposed and these are discussed in previous reviews.[32,33] While the chemistry of these acid reactions has not been clarified, various postulations have been advanced. Recently, Pshenitsyn *et al.*[34] recorded that the concentrations of the sulphuric and phosphoric acids have deciding effects on the nature of the reaction. In the concentrated acid solution, irrespective of the identity of the oxidising substance, the resulting solutions have an absorption maximum at 570 mμ. The reaction products showed that quadrivalent iridium was bound in a complex anion with the acid anion and contained identical colour groups. In more dilute solutions and in solutions of perchloric acid the resulting red solutions showed an absorption maximum of 500 mμ and the authors believed that the iridium was in the form of a hydrated complex cation free from the acid anion. The valence of iridium in both the blue and red solutions was shown to be 4. In a later report Pshenitsyn *et al.*[35] stated that in dilute acid solutions intermediate compounds of quadrivalent iridium with perchloric acid or its decomposition products are formed, which are destroyed by prolonged heating or by the addition of strong acids.

TABLE II.—SPECTROPHOTOMETRIC REAGENTS FOR IRIDIUM

No.	Reagent	Range of concentration, *ppm*
1.	Leuco Crystal Violet[37]	0·5–4
2.	Tin(II) bromide[38,39]	0·5–5
3.	Tin(II) iodide[30]	0·8–11·7
4.	*p*-Nitrosodimethylaniline[40]	1·5–10
5.	Hexachloriridate(IV)[31]	1–95 1- and 0·5-cm cells
6.	*o*-Dianisidine[41]	2–20
7.	EDTA[42]	5–60
8.	Cerium(IV) oxidation[43]	2·5–25
9.	Tetraphenylphosphonium bromide[44]	2·4–60 2-cm cells
10,	Perchloric-phosphoric mixed acids[34,35,43,45]	6–100
11.	$X_2Ir(OH)_6$[36]	

The spectrophotometric application of strongly alkaline solutions of quadrivalent and tervalent iridium were discussed by Desideri and Pantani.[36] For strongly heated caustic solutions, the absorption was measured at 313 mμ and the coloured constituent was attributed to $Ir(OH_6)^{2-}$. At high concentrations of iridium the blue constituent was attributed to the polymeric form of the hydroxylated species.

RUTHENIUM

The most sensitive method for ruthenium yet recorded is a catalytic method developed by Surasiti and Sandell.[46] The recommended range is 0·001–0·1 ppm of ruthenium. The procedure involves ascertaining quantitative relationships between the proportions of ruthenium in a solution and the time required for these proportions to catalyse the oxidation of tervalent arsenic by quadrivalent cerium. The time is indicated by the period necessary to reach a predetermined transmission. Temperature is a critical factor in determining the rate of reaction and constancy to a few tenths of a degree is required. The precision for 10^{-3} μg of ruthenium is only slightly less than that obtained for standard spectrophotometric methods over the microgram ranges.

Provision is made for the removal of catalytic interferences from iodine and osmium. The proposed solvent extraction of osmium is effective within the limits prescribed, but it is well to realise that no recorded method of separating ruthenium can be relied upon to remove all constituents capable of catalysing the cerium(IV)–arsenic (III) reaction. This fact is of particular concern when one is dealing with a sample of unknown or complex composition.

1,10-Phenanthroline or its 5-methyl derivative can be used for the fluorimetric determination of ruthenium. Veening and Brandt[47] applied the method to solutions containing 1 μg/ml of ruthenium, in which case there is no interference from 25 μg of osmium. Strong oxidising reagents must be absent. Silver, manganese and palladium interfere. Palladium forms a precipitate which can be removed by centrifugation; other platinum metals do not interfere. Iron interferes seriously and must be removed before the determination. For the 5-methyl derivative the useful range of concentrations is 0·3–2·0 μg/ml of ruthenium and the fluorescence can be reproduced to within 1 % for a period of 3 days. The activation wavelength recommended is 450 mμ and the fluorescence intensity is measured at 578 mμ. The method is insensitive to variations in acidity. Changes of pH from 1·0–13·0 are without effect. Excess reagent may affect the determination.

Acetylacetone[48] reacts, at boiling temperatures, with ruthenium(III)-chloro complexes to form a stable intense pink complex of composition $Ru(C_9H_7O_2)_3$ with an absorption maximum at 505 mμ and a molar extinction coefficient of 1510. Two additional wave maxima occur, but with these there is interference from the absorbance of excess reagent. The sensitivity is 2·5 μg/cm^2 and the optimum range is 0·4–20 ppm of ruthenium; the maximum concentration is about 30 μg/ml. Thus, the sensitivity is less than with the thiourea or the *p*-nitrosodimethylaniline reactions. The method offers some advantages in that, by a chloroform extraction in the cold, at pH 1·8–2, separations from iron, titanium, *etc.*, can be effected. The effects of associated platinum metals have not been reported. The pink complex is formed most rapidly at pH 5–6, and more basic solutions will introduce difficulties because of partial precipitation, particularly if the acetylacetone complex has not been formed before neutralisation. Determinations of ruthenium in amounts of the order of 10–70 μg can be made directly from the aqueous layer, omitting the chloroform extractions. However, there is some sacrifice of accuracy and precision.

For the range 0·5–15 ppm of ruthenium, Hara and Sandell[49] used 1,4-diphenylthiosemicarbazide to form a red-violet complex extractable in chloroform with a maximum absorbance at 560 mμ. The sensitivity in chloroform is 0·010 μg/cm^2 of ruthenium. The optimum acid strength for colour development is 5·5–6·5*N*; at low acid strength the colour develops slowly; at a high acidity the rapid colour development is vitiated by fading. Heating at 100° for 10–15 min produces maximum colour. The method requires a previous distillation of the octavalent oxide which is collected in tin(II) chloride-hydrochloric acid solution. The concentration of the tin salt is critical and must be closely controlled. There is considerable advantage in the toleration of a 10-fold quantity of osmium. This method has been used successfully for the determination of ruthenium in meteorites. Although various oxidants for the iron(II) oxidation and for the simultaneous distillation of ruthenium tetroxide were found ineffective it is not unlikely that both dissolution of the meteorites and distillation of the oxide could be accomplished with perchloric acid.

Other derivatives of thiosemicarbazides have been proposed for the determination of ruthenium. A qualitative study of the reactions of thiourea derivatives was made by Steiger.[50] These were summarised by Sandell.[11] Yaffe and Voight[51] discussed the reactions of 4-phenylthiosemicarbazide and diphenylthiosemicarbazide. Six compounds structurally related to thiourea were examined by Knight *et al.*[52] with a view to their spectrophotometric applications; of these *S*-diphenylthiourea offered superior advantages. The method of application follows closely those used for thiourea and dithio-oxamide and offers no particular advantages.

2,4-Diphenylthiosemicarbazide was used by Geilmann and Neeb[53] for the range 8–30 μg of ruthenium to form a chloroform extractable complex. Twenty to thirty times as much osmium as ruthenium could be tolerated. Iridium did not interfere, but palladium, platinum and rhodium gave yellow chloroform-extractable complexes, Applying the method to a distillate of ruthenium tetroxide, Hara and Sandell[49] found that the colour intensity varied with the added reductant of sulphur dioxide or hydroxylammonium chloride. There was also an appreciable variation in the blank absorbance of the sulphur dioxide–hydrochloric acid distillate.

1-Naphthylamino-3,5,7-trisulphonic acid was used by Steele and Yoe[54] for the range 0·5–14 ppm of ruthenium. A red water-soluble complex of R_2RuO_4 is formed with a maximum absorbance at 530 mμ. The method requires a distillation from a nitric acid–potassium permanganate solution and collection of the ruthenium tetroxide in a solution of the reagent adjusted to pH 2·5–3·0. The sensitivity is 0·1 μg/cm^2 and colour development is immediate at room temperature. The acidity and amounts of reagent are not critical. The method is subject to a wide range of interferences and distillation is, therefore, a necessity. The use of nitric acid removes the osmium which also reacts with the reagent to produce a complex suitable for spectrophotometric analysis. The 4,6,8-isomer can be used with equal efficiency.

Rubeanic acid or dithio-oxamide was used by various authors for the determination of ruthenium in the range 0·60–5·9 ppm. These applications have been discussed by the author.[32] More recently, this reagent[55] has been used to determine ruthenium in the presence of large proportions of uranium, *e.g.*, in a ratio of 1: 500.

Thiocyanate was used by Belew, Wilson and Corbin[56] for the determination of ruthenium subsequent to extraction of the octavalent oxide by carbon tetrachloride. The method is applicable in the presence of nitric acid and can be used for the determination of ruthenium in steel and iron alloys. Absorbance is measured at 590 mμ, and the blue complex $[Ru(CNS)]^{+2}$ obeys Beer's Law over the range 1–15 ppm of ruthenium. The complex forms immediately and the colour develops to maximum intensity in about 30 min and is stable for at least 24 hr. The sensitivity is 0·007 μg/cm^2. Excess thiocyanate has no effect on the absorbance and maximum absorbance is obtained in approximately 0·3*M* thiocyanate. Because the ruthenium(VIII) oxide is extracted by carbon tetrachloride there is no interference from associated base and platinum metals including osmium. The usual resistance to extraction of ruthenium (VIII) oxide into the aqueous phase is overcome by salting with a solution of aluminium nitrate in nitric acid. Concentrations of nitric acid in excess of 4*M* interfere with the formation of the coloured complex. The oxidation of the ruthenium to the tetroxide is a critical step in the extraction and is accomplished with argentic oxide, only a small excess of which should be added.

Oka and Kato[57] used ammonium thiocyanate for ruthenium and measured the absorbance at 585 mμ. A molar absorptivity of 5900 was recorded as compared to 4000 found by Belew *et al.*[56]

A violet-blue complex with tervalent ruthenium is formed when ruthenium salts of varying oxidation states are treated with excess thiocyanate ion. Maximum absorbance is developed in acidities up to 1*N* on heating for 15 min at 70°. The sensitivity is about 0·02 μg/cm^2. The concentration range used was 1–15 μg of ruthenium/ml. Only osmium of the remaining platinum metals interferes.

Shlenskaya and Piskunov[58] discussed the conditions required for the application of the thiocyanate ion to ruthenium determinations applied to 24 μg of ruthenium/ml; an excess of thiocyanate to ruthenium was required. Colour was developed in a 4*M* sodium chloride medium and heating for 5 min on a water bath.

For the determination of ruthenium in the presence of uranium, Manning and Menis[59] used 2-nitroso-1-naphthol. Simple salts such as ruthenium(III) chloride could be determined in the presence of uranium without a previous separation. In the case of ruthenium-nitroso complexes a separation is necessary and Menis and Powell[60] describe the procedure, which involves a fusion with bismuthate and volatilisation of the octavalent oxide into a solution of hydrochloric acid saturated with sulphur dioxide. Absorbance of the naphthol–ruthenium complex, of unknown composition, was measured at 600 mμ. Beer's Law applied over the range 1–10 μg of ruthenium/ml. The colour was found stable for about 1 hr. The molar absorptivity was about 6500 at 600 mμ. The optimum hydrochloric acid strength was 1*M*; however, 3*M* solutions were used as the least critical concentration. Excess reagent was required. The presence of 50 mg of uranium or less had little or no effect on the determination of 400 μg of ruthenium in 50 ml of solution. For greater proportions of uranium it was essential to use standards having approximately the same proportions as the samples to be analysed.

A study of the reactions of ruthenium(III) salts with nitrosonaphthols in weakly acidic media was made by Konečny.[61] Mixtures of complexes were usually obtained; in citrate buffered media the complexes had ratios of 1: 1 and 1: 3 of metal to reagent. Both were used for the detection of ruthenium(III) salts.

Further work has been reported on the application of thiourea. Pilipenko and Sereda[62] found that the maximum colour intensity of the complex is in 6*M* hydrochloric acid and that the reaction is as follows:

$$\mathrm{Ru[SC(NH_2)_2]^{3+} + 2SC(NH_2)_2 \rightleftharpoons Ru[SC(NH_2)_2]_3}.$$

Thiourea has been used by Bergstresser[63] for the determination of ruthenium in plutonium. The method of separation is similar to that described by De Ford.[64]

For the range 2–36 ppm, Mesarić and Branica[65] distilled ruthenium tetroxide into 1*N* oxalic acid. The stable yellow colour was formed within 10 min at 80°. Of the two absorption bands, 375 and 475 mμ, the former was preferred. The method appears to lack the normal accuracy attained by good spectrophotometric methods.

For the range 4–16 ppm, anthranilic acid can be used subsequent to the distillation of the octavalent oxide into a solution of hydrogen peroxide and hydrobromic acid.

Majumdar and Sen Gupta[66] recorded the procedure, which involves measurements at 620 mμ of the green complex formed by sodium anthranilate in a pH range of 5·2–6. The sensitivity is 0·024 μg/cm^2 and the solution obeys Beer's Law over the range 1–20 ppm. Development of colour is not sensitive to excess reagent and reaches a stable maximum in about 20 min when heated on the steam bath. Platinum metals interfere when present in the proportions usually encountered in natural deposits.

Stoner[67] used the greenish-yellow colour of potassium perruthenate for concentration ranges of 0·1–12 mg in a final volume of 100 ml. The octavalent oxide is distilled from a mixture of perchloric acid, phosphoric acid, sodium bismuthate and a trace of chloride into a solution of potassium hydroxide. Measurements are made at 380 mμ. The proposed procedure has been applied successfully to uranium alloys containing neodymium, zirconium and molybdenum. Larsen and Ross[68] found that distillation into 13*M* sodium hydroxide containing no hypochlorite gave solutions in which 100% of the ruthenium was in the sexivalent state; while distillations into 1*M* sodium hydroxide and 0·05*M* sodium hypochlorite gave solutions in which more than 99% of the ruthenium was in the septivalent state. Between these concentrations unstable mixtures of both states were obtained.

The importance of the composition of the collecting liquid is emphasised by the fact that ruthenium metal can be dissolved and the octavalent oxide volatilised by heating in a caustic solution to which chlorine is added.[69] Larsen and Ross[68] used a slurry of sodium bismuthate in 6*N* sulphuric acid but fumed strongly with the acid before oxidation. These authors considered bromate and permanganate inferior as oxidants to bismuthate, periodate and cerium(IV) salts.

An adaptation of the ruthenate method was used by Anderson and Del Grosso.[70] The procedure involved a carbon tetrachloride extraction of the oxide from a mixture in a Carius tube. The extract was added to a beaker containing 2*M* potassium hydroxide and the mixture warmed at 70°–75° until the organic layer was clear. The aqueous layer was then separated, heated and made up to a specific volume with 2*M* potassium hydroxide. Contrary to previous reports, the authors found only an initial instability which was attributed to new glassware. When the latter was treated with ruthenate–potassium hydroxide solution the stability increases from 0·5 hr to several days.

Perruthenate ion was used for the spectrophotometric determination of ruthenium by Il'inskaya and Solntsev.[71] Maximum absorbance occurred at 380 mμ. Procedures were provided for 0·1–12 mg of ruthenium. In contrast to perruthenate ions the ruthenate ion was unstable.

A modification of the ruthenate and perruthenate methods for the determination of ruthenium was used by Woodhead and Fletcher.[72] These authors compared the conflicting values reported for the molar absorptivities of ruthenate and perruthenate at 460, 385 and 317 mμ. The redetermined coefficients were, respectively, for ruthenate 1710, 831 and 301; for perruthenate: 278, 2173 and 2302. The authors proposed to determine ruthenium by oxidation with ammonium peroxydisulphate in a 2*M* potassium hydroxide solution. The absorbing species were accepted as ruthenate and perruthenate. From standards prepared by various methods the authors found an isosbestic point at 415 mμ with a molar absorptivity of 1047. There was a second isosbestic point at 273 mμ for which the molar absorptivity was 1005. The constancy of absorbance at the isosbestic points, 273 and 455 mμ, was taken as evidence that ruthenate and perruthenate were the only absorbing species. The value 1047 at 415 mμ

remained constant in concentrations of alkali from 0·2 to 2*M* and over the concentration range 0·01–0·20 mg of ruthenium/ml of solution.

For concentrations of approximately 1 ppm Guebely[73] measured the absorbance at 410 $m\mu$ of solutions of iodine produced by the reaction of ruthenium(IV) with potassium iodide. The 4*N* sulphuric acid solution of ruthenium was treated with chlorine, the latter was removed by heat and potassium iodide was added. The absorbance of the liberated iodine was compared to a blank containing ruthenium(III) and potassium iodide.

TABLE III.—SPECTROPHOTOMETRIC REAGENTS FOR RUTHENIUM

No.	Reagent	Range of concentration, *ppm*
1.	Catalytic[46] $As^{3+} + Ce^{4+} \rightarrow As^{5+} + Ce^{3+}$	0·001–0·1
2.	1,10-Phenanthroline[47,75]	0·1–1·5
3.	*p*-Nitrosodimethylaniline[76]	0·31–3·1
4.	5-Methylphenanthroline[47,77]	0·3–2
5.	Acetylacetone[48]	0·4–20
6.	1,4-Diphenylthiosemicarbazide;[49]	0·5–15
	other semicarbazide derivatives;[11,50–52]	
	2,4-diphenylthiosemicarbazide[53,69]	8–30
7.	1-Naphthylamino-3,5,7-trisulphonic acid[54]	0·5–14
8.	Dithio-oxamide[82,55,77–81]	0·6–5·0
9.	*N,N′*-Bis-(3-dimethylaminopropyl)-dithio-oxamide[81]	0·27–9·52
10.	Catalytic[82] $KIO_3 + KI$	0·7–6
11.	Thiocyanate[56–58]	1–15 B.L.
12.	2-Nitroso-1-naphthol[59–61]	1–10 B.L.
13.	Thiourea[62–64, 83–85]	2–15
14.	Oxalic acid[65]	2–36
15.	Anthranilic acid[66]	4–16
16.	5-Hydroxyquinoline-8-carboxylic acid[86]	2·1–21
17.	*S*-Diphenylthiourea[52]	6–18
18.	K_2RuO_4[67–72]	10–40
	$KRuO_4$	200–400
19.	Potassium iodide[73]	0·1–12 mg/100 ml (about 1 ppm)
20.	Dithiophthalimide[74]	

Dithiophthalimide has been used for the determination of ruthenium as the hexachlororuthenate. The yellow complex is extracted by chloroform to produce a blue solution whose maximum absorbance is 660 $m\mu$.[74]

OSMIUM

New procedures for the trace determination of osmium by applying its catalytic effect on specific redox reactions have been proposed. For the concentration range 1–60 μg/5 ml of solution Bognár and Sepos[88] applied the catalytic effect of octavalent osmium tetroxide on the luminescence reaction of hydrogen peroxide on lucigenin. The time required to complete the fading reaction for osmium tetroxide concentrations varying from 0–60 μg/5 ml altered from 260 to 0·5 min. Solutions of known and unknown osmium content containing hydrogen peroxide and lucigenin were treated simultaneously with sodium hydroxide solution to initiate the reaction. No data were provided to indicate the degree of interference from associated noble metals. Interference from copper and nickel could be masked by EDTA. Silver, chromium, cobalt and iron interfered.

A variety of catalytic methods for determining osmium was recorded by Bognár and Sárosi.[89] Hydroquinone, orcinol and 1,3-naphthalenediol can be oxidised by hydrogen peroxide with octavalent osmium oxide as the catalyst. The respective optimum pH is 10·5, 10·3 and 12·4. The sensitivity of the reactions is 0·001 μg of osmium tetroxide/5 ml of solution.

Other determinations of osmium based on catalytic properties were proposed by Bognár *et al.*[90] Potassium chlorate oxidises apomorphine at pH 1·7 in the presence of osmium tetroxide. With a photometer it is possible to detect 0·001 μg. Similarly, osmium tetroxide will catalyse the reaction between chlorate and *p*-phenylenediamine at pH 2·3; 0·005 μg of the tetroxide can be detected.

For the range 0·1–8 ppm of osmium, 1-naphthylamine-4,6,8-trisulphonic acid was used by Steele and Yoe[91] to produce a water-soluble purple complex which changes to violet at pH 1, light blue at pH 6 and pale green at pH 8. Maximum absorbance at 555 mμ is attained at a pH between 1·0 and 1·5. The sensitivity of the reaction is 0·0068 μg/cm^2. At room temperature, the colour is stable for weeks, excess reagent is without measurable effect, but there is some decomposition and a resultant absorbance change after standing for 1 month. Maximum colour development requires about 1 hr at 35°. Because the associated platinum and base metals interfere, a separation is required and osmium tetroxide is distilled from a nitric acid medium and collected in a solution of potassium hydroxide.

Sodium *p*-aminosalicylate forms a complex with osmium which obeys Beer's Law over the range 0·25–4·15 ppm.[92] The optimum pH is 7–8; constant absorbance is reached in 15 min and measured at 496 mμ.

For the range 0·3–1 ppm Goldstein[93] used 1,5-diphenylcarbohydrazide to produce with octavalent osmium in aqueous media a blue-violet compound, with a maximum absorbance at 560 mμ. The complex could be extracted with chloroform, the extract of which showed an enhanced colour intensity. A second method involves the previous extraction by chloroform of the octavalent oxide, followed by the addition of the reagent.[94] The aqueous method involves the addition of the solution of osmium tetroxide to a solution of perchloric acid, glacial acetic acid and reagent, heating to 65° for 5 min, cooling to room temperature and extracting with chloroform. Development of colour is dependent upon temperature, time of standing in the aqueous phase, period between extraction of the complex into chloroform and subsequent absorbance measurement, concentrations of perchloric acid, colour reagent and its solvent, and order of addition of reagents. There is interference from associated platinum metals and base metals. Conceivably, much of the interference could be avoided by the isolation of osmium. However, the available data do not provide information concerning the efficiency of the oxidation and subsequent extraction procedures for the removal of base-metal interference. There is little to recommend the above two methods in their present form except the high sensitivity of 0·00127 μg/cm^2 for the aqueous method.[93] As one would expect, the latter involves a greater degree of interference.

Among the proposed new spectrophotometric reagents for osmium, *p*-(morpholino)-*N*-(4′-hydroxy-3′-methoxy)-benzylidine-aniline (Anil) was proposed by Ayres and McDonald.[95] Because the reagent is not available the authors provided a recipe for its preparation. The wide range of interferences makes necessary a previous isolation of osmium which is accomplished by an oxidation by nitric acid, receiving the octavalent oxide in hydrochloric acid. The range of application is at the relatively low level of 1–4 ppm with a 1-cm light path. Molar absorptivity of the blue constituent is $3{\cdot}49 \times 10^4$. Two complexes have been identified, one, a red species, occurring with an excess of osmium over Anil and the other, a blue constituent, with the reverse proportions. The former is converted to the latter on standing in solution. With the red species the mole ratio of osmium to Anil is 1:1 and with the blue species 1:2. Maximum absorbance of the red dissolved constituent occurs at 466 mμ and of the blue constituent at 650 mμ. The acidity of the solution is a critical factor and a buffer of pH 3·5 is used to achieve an acidity in the pH range 4·3–4·7. Absorbance at 615 mμ is measured after standing for 1 hr at room temperature against a blank containing all reagents. The colour remains stable for at least 6 hr and is relatively insensitive to excess reagent. A minimum of 27 moles of Anil to 1 atomic weight of osmium is required. The formation of a blue precipitate is prevented by the addition of ethanol in which media the colour develops more rapidly and remains more stable.

This method has a useful and sensitive range of application, but in common with most spectrophotometric methods for osmium it is sensitive to the impurities associated with the volatility of the octavalent oxides. One cannot assume that the reported tolerance for sulphate and nitrate ions will apply to solutions prepared from solids by the usual processes for dissolution. The required pH range is adversely narrow and occurs at an acidity which will encourage precipitation of a hydrated oxide of osmium. Thus, one must expect the necessity of a rather rigid adherance to the prescribed conditions of colour development, such as order of additions, *etc.*

Three triazine derivatives with an —SH group attached to the ring produce colours of low stability.[96] 3,5-Dihydroxy-6-mercapto-1,2,4-triazine, 3-mercapto-5-hydroxy-6-methyl-1,2,4-triazine and 3-mercapto-5-hydroxy-6,6-dimethyl-1,6-dihydroxy-1,2,4-triazine are used for the respective ranges of 1·2–24·6; 1·0–24·9; and 1·0–8·3 μg of osmium/ml. In general, the procedures involve addition of sulphuric acid, reagent solution and dilution to 10 ml with ethanol. Presumably, the above three reagents can be applied directly to a distillate of octavalent osmium oxide in sodium hydroxide. This should possibility receive further attention.

Either menthionine or acetylmenthionine may be used as osmium reagents applied to solutions of the octavalent oxide. The optimum pH is 3·8–4·1. Colour appears in 10 min and remains stable for 24 hr. The menthionine colour complex obeys Beer's Law over the range 1–16 ppm, and the acetyl complex over the range 3·5–35 ppm.[92]

For concentrations of osmium in the ranges of about 1 to 40 μg/ml a number of new organic reagents have been proposed.[96] The two thiourea derivatives, α-thiosemicarbazidobutyric acid and the butyronitrile derivative, as 0·1% solutions in 1% sodium hydroxide, can be used for the respective ranges of 1·2–9·8 and 2·1–41·4 ppm of osmium.

Anthranilic acid[97] has been used for the range 2–6 ppm of osmium. The sensitivity is 0·008 μg/cm^2. In the quadri-, sexa- and octavalent states and at a pH between 5·5 and 6·5 the reagent forms a stable dark violet 1:1 mole complex with a maximum absorbance at 460 mμ. With quadrivalent osmium the colour develops on heating in less than 10 min, but with sexavalent and octavalent osmium a sufficiently stable colour is attained in the cold after 1 hr. Difficulties can be experienced on the addition of the buffer if excesses of osmium are present with a deficiency of reagent. This problem is associated with methods in which colour development requires near neutral solutions. Associated platinum and base metals interfere, but EDTA serves to mask some of the interference.

For the range 2–8 μg/ml the following reagents are available: sulphanilic acid,[97] *m*-aminobenzoic acid,[98] *o*-aminophenol-*p*-sulphonic acid and 1-amino-8-naphthol-3, 6-disulphonic acid.[99]

Procedures for each of these reagents have been recorded by Majumdar and Sen Gupta. Sulphanilic acid[97] forms a stable dark violet complex with sexa and octavalent osmium, the composition of which is 1 mole of osmium to 2 of reagent. The optimum pH range is 1·8–3·5 and maximum absorbance occurs at 490 mμ. The optimum concentration range for osmium(VIII) is 2–8 ppm and for osmium(VI), 4–16 ppm. The sensitivity of the former is 0·01 μg/cm² and 0·02 μg/cm² for the latter. The colour is not sensitive to excess of reagent. It develops in weak sulphuric acid or alkaline solutions, and reaches a maximum intensity on standing 2 hr at room temperatures. There is interference from associated metals and a nitric acid distillation is usually required. The reported procedure did not incorporate this distillation but was adapted to solutions prepared by dissolving "osmic acid" in dilute alkali and for osmium(VI) the caustic solution was reduced by ethanol.

m-Aminobenzoic acid,[98] like the ortho derivative (anthranilic acid), reacts with osmium(VIII) and osmium(VI) at pH 4·5–6·0 to form a purple complex with maximum absorption at 500 mμ. With osmium(VIII) the optimum range is 3–8 ppm, the sensitivity is 0·012 μg/cm² and the molar osmium-reagent ratio is 1: 5. With osmium (VI) the optimum range is 2–8 ppm, the sensitivity is 0·018 μg/cm² and the osmium-reagent ratio is 1: 3. With osmium(IV) the colour development is relatively slow requiring heating for 10 min on the steam bath; longer periods result in the appearance of insoluble hydrated osmium oxides. In general, there is interference from the associated platinum and base metals with some toleration for palladium, rhodium and iridium. The method was not applied to caustic distillates.

o-Aminophenol-*p*-sulphonic acid[99] reacts with osmium(VI) and osmium(VIII) at pH 2·5–4 to give an intense dark brown colour with an absorbance maximum at 440 mμ. Maximum colour is developed in 30 min at room temperatures. The optimum range is 2–8 ppm and the sensitivity is 0·01 μg/cm². Associated platinum and base metals interfere. 1-Amino-8-naphthol-3,6-disulphonic acid[99] may be used in much the same way as *o*-aminophenol-*p*-sulphonic acid. The colour is developed in the pH range 4·5–6 and requires a period of 2 hr at room temperature. The sensitivity is 0·01 μg/cm² and maximum absorption occurs at 480 mμ.

Diantipyrylpropylmethane was used by Busev and Akimov[100] for the spectrophotometric determination of osmium in the presence of ruthenium. The applicable range for osmium was 2–23 μg of osmium/ml and 2–20 μg of osmium could be determined in the presence of 40 mg of ruthenium. Absorbance was measured at 346 and 378 mμ against a blank prepared according to the full procedure. Iridium and rhodium did not interfere but platinum and palladium must be absent. The method required osmium in the form of $OsCl_6^{2-}$ ions. In the case of osmium tetroxide, distilled by chromic acid into 6*M* hydrochloric acid, the required form could be obtained by treating the distillate with hydrazine hydrochloride or sulphate. The osmium solution in hydrochloric acid in a separatory funnel was extracted by shaking with a 0·1% solution of diantipyrylpropylmethane in dichlorethane. The extract was filtered directly into the cell. Quadrivalent ruthenium also formed an extractable complex with the reagent whose maximum absorbance occurred at 400 and 490 mμ, but the completeness of extraction depended upon the acidity and an excess of reagent of about 150-fold. Tervalent ruthenium formed a complex which was extractable to a much smaller extent although the degree of extraction increased with acidity, with its concentration and with excess of reagent. These factors combined to allow a separatory procedure based on the relatively high degree of extraction of osmium with a moderate excess of reagent in the presence of a hydrazine salt to ensure reduction of ruthenium to the tervalent state. This method will find application to distillates from solutions of the platinum metals treated with perchloric acid to isolate simultaneously the octavalent oxides of osmium and ruthenium. The addition of a hydrazine salt to the receiving liquid would ensure a complete retention of the oxides.

A potentially useful spectrophotometric method for the determination of osmium and ruthenium without a previous separation was described by Pilipenko and Sereda.[101] The reagent, seleno-urea, forms a complex with ruthenium whose ratio of constituents is 1 atomic weight of metal to 3 formula weights of reagent. Maximum light absorbance occurs at 760 mμ. The complex formed with osmium shows a maximum light absorbance at 600 mμ. Absorbance of ruthenium at 600 mμ is very weak and there is no significant absorbance at 760 mμ in the case of osmium. Thus, the method is based on measuring the absorbance of the ruthenium complex at 760 mμ at the favourable acid strength of 6*N*. Subsequently, in 1*N* acid, favourable for osmium, the total absorbance of the complexes of both osmium and ruthenium is measured at 600 mμ; knowing the ruthenium content from the standard curves, the absorbance corresponding to ruthenium at 600 mμ is subtracted from the total absorbance to find the osmium content. Therefore, the method involves the preparation of three standard curves. Urea is added to the metal solution in hydrochloric acid before the addition of the seleno-urea. The mixed colour constituents are stable for 45 min. A complete determination can be made in 45–60 min and the method permits determinations of 2–60 μg of ruthenium/ml and 2–60 μg of osmium/ml. The data obtained by the authors indicate an error of −4% for about 170 μg of ruthenium in the absence of osmium; no values are recorded for osmium alone; unfortunately, the authors provided no data concerning the identity of the osmium salt used for standards and only indirectly the composition of the ruthenium salt. In the light of the vagaries of the thiourea–osmium reaction one cannot conclude that the seleno-urea reaction can be applied over the range of identities of the usual dissolved osmium constituents encountered in analytical work. It must also be noted that one can only accept the stated range of application with reservations, *e.g.*, the determination of osmium at the low range of 2–60 parts of ruthenium, obtained as it is by difference from a total absorbance, may be of little value.

In any case this method ought to be examined with a view to its practical applications to receiving solutions containing both osmium and ruthenium.

The composition and stability of the complexes of osmium and seleno-urea were studied by Pilipenko and Sereda.[102] Seleno-urea first reduces osmium to the tervalent state, then forms an intensely coloured blue-green complex. The complex has an osmium-seleno-urea ratio of 1: 8. The colour appears when the eighth molecule of the seleno-urea has been added. The intermediate product of the osmium reduction is also intensely coloured and absorbs in the ultraviolet and visible regions.

The reaction of thiourea-osmium was also examined and as in the case of the seleno-urea complex the colour was associated with the last (or sixth) molecule of reagent.

TABLE IV.—SPECTROPHOTOMETRIC REAGENTS FOR OSMIUM

No.	Reagent	Range of concentration, *ppm*
1.	Catalytic[108]	0·01–0·2
	Catalytic[89]	Sensitivity = 0·001 μg/5 ml
	hydroquinone + H_2O_2	
	orcinol + H_2O_2	
	1,3-naphthalenediol + H_2O_2	
	3,3′-dimethylnaphthidine + $KClO_3$	
	Catalytic[109]	
	$Ce(SO_4)_2 + As_2O_3$	0·01–0·06
	$KClO_3$ + KI	0·02–0·2
	Phen. Diam. + H_2O_2	0·04–0·2
	$KMnO_4 + As_2O_3$	0·08–0·38
	Catalytic[88]	
	lucigenin + H_2O_2[88]	0·2–12
	$KClO_3$ + apomorphine[90]	Sensitivity = 0·001 μg/ml
	$KClO_3$ + *p*-phenylenediamine[90]	Sensitivity = 0·005 μg/ml
2.	1-Naphthylamine-4,6,8-trisulphonic acid[91]	0·1–8
3.	Sodium *p*-aminosalicylate[92]	0·25–4·15
4.	Tetraphenylphosphonium chloride[110]	0·3–1·5 (2-cm path)
5.	1,5-Diphenylcarbohydrazide[93,94]	0·3–1 1·2–4
6.	*p*-(Morpholino)-*N*-(4′-hydroxy-3′-methoxy)-benzylidene-aniline (Anil)[95]	1–4
7.	3,5-Dihydroxy-6-mercapto-1,2,4-triazine;[96]	1·2–24·6
	3-mercapto-5-hydroxy-6-methyl-1,2,4-triazine;[96]	1·0–24·9
	3-mercapto-5-hydroxy-6,6-dimethyl-1,6-dihydroxy-1,2,4-triazine[96]	1·0–8·3
8.	1-Naphthylamine-3,5,7-trisulphonic acid[111]	1·5–5·5
9.	Menthionine;[92]	1–16 B.L.
	acetylmenthionine[92]	3·5–30 B.L.
10.	α-Thiosemicarbazidobutyric acid	1·2–9·8
	and butyronitrile derivative[96]	2·1–41·4
11.	Anthranilic acid[97]	2–6
12.	Sulphanilic acid[97]	2–8 Os(VIII) 4–16 Os(VI)
13.	*m*-Aminobenzoic acid[98]	3–8 Os(VIII) 2–8 Os(VI)
14.	*o*-Aminophenol-*p*-sulphonic acid[99]	2–8
15.	1-Amino-8-naphthol-3-6-disulphonic acid[99]	2–8
16.	Diantipyrylpropylmethane[100]	2–23
17.	Seleno-urea[101,102]	2–60
18.	Quinisatin oxime (2,4-dihydroxy-3-nitrosoquinoline)[103]	3–10
19.	Thiourea[112–116]	5–50
20.	Dithio-oxamide (rubeanic acid)[104]	6–15
21.	Disodium 1,2-dihydroxybenzene-3,5-disulphonate (Tiron)[105]	8–24
22.	Ultraviolet with OsO_4[106,107]	16–132

2,4-Dihydroxy-3-nitrosoquinoline (quinisatin oxime) reacts with osmium(VIII) solutions to form a stable complex with a 1:2 mole ratio of metal to reagent.[103] The oxime was dissolved in a solution made up to contain 30% of *N*,*N*-dimethylformamide and 70% methanol by volume. The latter solvent was required to attain full colour development. Maximum colour was attained with at least four times the molar concentration of reagent to osmium. The reaction requires a solution of pH 5 and heating to near boiling for 1·5 hr. Absorbance was measured at 515 mμ against a reagent blank. The optimum range of application is 3–10 ppm of osmium. Associated base and platinum metals interfere in proportions greater than the upper optimum range of osmium concentrations. It is unfortunate that the method was not applied to caustic receiving solutions of octavalent oxide distillates.

Dithio-oxamide (rubeanic acid) was applied by Wawrzyczek and Majkowska[104] to determine osmium in the range 6–15 ppm of osmium, as the octavalent oxide. The optimum pH was 6–7 and full colour development was achieved after standing for 1 hr. Measurements were made with a red filter No. 6 and a Pulfrich colorimeter. Again, one may hope that this method will be applied to a receiving solution of the octavalent oxide.

For the range 8–24 ppm of osmium, Majumdar and Savariar[105] used Tiron, the disodium salt of 1,2-hydroxybenzene-3,5-disulphonate. The reagent produces a reddish-violet coloured constituent with a 1:1 mole ratio of osmium to reagent and with a sensitivity of 0·033 μg/cm^2. Full colour, stable for several hours, is achieved with heating for 15 min at pH 4·9–5·5. Maximum absorbance occurs at 470 mμ. There is interference from associated platinum and base metals.

Goldstein *et al.*[106] recorded an ultraviolet spectrophotometric method for the determination of milligram quantities of osmium in solutions of uranyl sulphate containing copper, nickel, iron and chromium as minor constituents. The osmium is first converted to the octavalent form and extracted by chloroform as described by Sandell[11] and Sauerbrunn and Sandell.[107] The chloroform extracts showed absorption bands centered at 282, 289, 297, 304 and 312 mμ. The respective optimum ranges of concentration in mg of osmium/25 ml of solution were 0·4–1·8, 0·4–1·9, 0·5–2·0, 0·5–2·4 and 0·7–3·3. There is no interference from the uranyl ion nor from the minor constituents normally present. As would be expected, ruthenium is the only interfering element of the platinum metals. Chloride interferes through its resistance to the oxidation and extraction of the chloride–osmium complexes.

GOLD

In a previous review the author recorded the spectrophotometric methods for gold published up to August 1960. The following report deals with methods recorded in chemical abstracts up to June 1964.

The high sensitivity of tolidine, whose range of application is 0·04–0·4 ppm of gold, has encouraged the development of derivatives for which an improved sensitivity is claimed. *N*,*N'*-Tetramethyl-*o*-tolidine (Tetron) was used by Daiev and Jordanov[117] with a claim for a sensitivity of 0·004 μg/cm^2. Variations of the method were applied to determine gold in solutions containing copper and iron; lead and solutions of anode copper. For the anode copper, gold was removed by the anion exchanger Dowex 11, 310-mesh in the chloride form. With other solutions the gold was coprecipitated with tellurium subsequent to the addition of potassium tellurite and tin(II) chloride. Following the ignition of the mixed precipitate and its dissolution, gold was selectively extracted with ether. The organic layer was evaporated, the residue dissolved by *aqua regia*, the solution evaporated and Tetron then added with subsequent dilution to 10, 20 or 50 ml, depending upon the gold concentrations. Presumably, the range of application for the various methods was 0·1–0·8 ppm. The orange-yellow colour develops to a maximum in about 4 min and the absorbance, measured with a blue filter, remains stable for 20–25 min. It would seem that the new reagent provides no real advantage over the well-tried tolidine.

Useful progress has been made in the methods of separating microgram and submicrogram amounts of gold from a variety of specified materials. In one instance Mizuike[118] isolated 0·1–6 μg of gold from 1 g or less of copper alloy by dissolution in nitric acid, followed by hydrochloric acid, then adding excess ammonia solution. Purified mercury was added and intimate mixing was ensured by a magnetic stirrer. The solution was then decanted and the washed mercury dried by filter paper and transferred to a silica boat from which it was volatilised in the presence of nitrogen. The gold residue was dissolved by one of two methods depending upon whether the gold present was more or less than 0·5 μg, and similarly two modifications of the *p*-dimethylaminobenzylidenerhodanine method[119] were applied, depending also upon the quantity of gold present. Absorbance was measured in a 1- or 2-cm cell at 562 mμ against water. Presumably Beer's Law is followed to at least 0·6 ppm of gold. There was no interference from 100 ppm each of copper, iron, mercury and 5 ppm of platinum and 2 ppm of silver. Palladium interferes.

The rate and efficiency of the gold collection by mercury was determined by the use of gold-188 as a tracer: 5 μg of gold in 50 ml of solution required 1 hr; 0·24 μg of gold in 500 ml of solution required 4 hr. Significantly, when copper was absent the recovery was greatly retarded and the results were low. The accuracy obtained was 5% over the range of 1–100 ppm and 10% at about 0·5 ppm.

p-Dimethylaminobenzylidenerhodanine was used by Thilliez[120] for the determination of gold in minerals poor in gold. Subsequent to dissolution by acids the gold was extracted with dithizone in chloroform. The latter was volatilised and finally gold was determined colorimetrically.

The tin(II) chloride-tellurium reaction was used by Hirano and Ujihira[121] to determine traces of gold in copper. The metal was converted to a solution in hydrochloric acid and gold was collected by the usual carrier precipitation with tellurium. The mixture was dissolved, nitric acid removed and the hydrochloric acid solution treated with sodium chloride and fluoride and *p*-dimethylaminobenzylidenerhodanine. Absorbance was measured at 562 mμ and Beer's Law is obeyed over the range 0–6 μg of gold/ml. Less than 1 ppm of gold in copper could be determined in 1–2 hr with ±5 to 10% error.

A bromaurate method for the determination of gold was reported by McBryde and Yoe.[27] The method was not affected adversely by salt content or by trace quantities of many ions, including all of the platinum metals except osmium. Absorbance was measured at 380 mμ and the applicable range is 0–40 ppm. The procedure involved the preparation of bromaurate which was first extracted by isopropyl ether, then returned to an aqueous phase. Applied by various operators in different laboratories the method failed to provide consistent results. Chow and Beamish[122] found that the extraction both by isopropyl ether and by water reduced the colour intensity, which could not be restored by the usual treatment. The fact that only 50% of the gold was extracted by the ether from the acid solution while the subsequent extraction from the ether by water was complete suggested the failure to retain completely the extractable aurobromate species. Similar experiments with ethyl acetate as an extractant indicated that while the acetate contained the total weight of gold, the intensity measurements indicated approximately 50% of the gold as the required coloured species.

Based on the fact that the ethyl acetate contained the gold quantitatively, Chow and Beamish[122] developed a modified procedure which involved an evaporation of the acetate layer, treatment with *aqua regia*, conversion to bromide and measurement of the absorbance at 350 mμ. In the absence of platinum metals an extraction is not required and this direct bromaurate procedure is the simplest colorimetric method available for the determination of gold. It is applicable to amounts of 15 μg or more; it is insensitive to variations in technique, to salt, hydrochloric and hydrobromic acids, and to many trace ions. When extractions and good accuracy are required the modified method is not recommended for amounts of gold less than 25 μg.

The work by Chow and Beamish[122] indicated that at least a portion of the error, associated with the extraction procedure, arose from impurities in the isopropyl ether. All effort to identify the interfering constituent or to improve the purity of the ether failed. The method is of sufficient importance to justify further efforts to provide an alternative extractant or a method of purifying the ether.

A similar extraction method was proposed by Ziegler and Matsche[123] which avoided the interference of copper and iron associated with the ether extraction of the bromaurate. The proposed method accomplished the formation of a stable, polyethylene bromaurate(III) complex, soluble in methylene chloride. The solution is buffered to a pH of 0·9–1·4 with a solution of disodium hydrogen phosphate in phosphoric acid and following extraction, the absorbance is measured at 394 mμ. The polyethylene reagent should be colourless and free from aldehyde or phenol. The method tolerates large proportions of copper, iron, nickel, cobalt and lead and proportions of platinum of the order of about 6: 1 of gold. Palladium produces a similar bromide which is simultaneously extracted.

Ammonium thiocyanate, pyridine and chloramine-T react with gold to produce a colour with minimum transmittance at 430 mμ. The method is applicable over the range 0·5–5 ppm of gold.[124]

The tranquilising reagent chloropromazine was used by Lee[125] for the determination of 15–200 μg of gold in a 25-ml volume. Beer's Law is obeyed over the range 0·5–8·0 μg of gold/ml. It would seem that the working range could be appreciably lowered if that was necessary. The absorbance is measured at 530 mμ. The fact that the gold can be dissolved in *aqua regia* without the subsequent removal of nitric acid is of some advantage. The nitric acid concentration should not exceed 15%. The procedure requires the addition of phosphoric acid and excess of reagent. The optimum volume concentration of the former is 20% and of the latter, 5 mg of the chloropromazine hydrochloride/ml. As one would expect in the case of a reagent which is dependent upon the oxidation potential of gold(III), there is a wide variety of interferences. Both platinum and palladium form interfering complexes. The proposed method has little to recommend it.

The Rhodamine-B method for gold developed by MacNulty and Woollard[126] was re-examined by Onishi[127] and applied to the wet determination of gold in ores. The sample should contain 1–10 μg of gold in 80 ml, and should be about $3M$ in hydrochloric acid. Onishi was able to use benzene as an extractant by centrifugation of the benzene layer at 2000 rpm for 5 min. The hydrochloric acid concentration was kept at $0{\cdot}75M$ and the ammonium chloride concentration at $1{\cdot}4M$. Contrary to the findings of MacNulty and Woollard, platinum introduced no interference.

Polyethyleneglycol was applied by Ziegler to produce a spectrophotometric procedure.[128] The gold solution was treated with nitric acid, sodium saccharinate, a phosphate buffer in the presence of large amounts of iron, then with polyethyleneglycol. The soluble complex of polyethyleneglycol–gold(III) saccharinate was extracted with methylene chloride, the organic phase filtered and finally the absorbance measured at 315 mμ. The method is usefully free of interference from lead, copper, cobalt, nickel, iron and palladium.

For the range 2·5–30 μg of gold/ml Ziegler[129] used polyethyleneglycol and extracted with methylene chloride from strong solutions of hydrochloric acid. Absorbance was measured at 320 mμ against a reagent blank. Beer's Law is followed for 25–300 μg of gold/10 ml of solution. The method is reasonably free of interference from iron, nickel, manganese, palladium, platinum and rhodium.

Anthranilic acid reacts with gold in an acidic medium and can be applied for the spectrophotometric determination of gold over the range of about 7–82 ppm. Absorbance is measured at 533 mμ.[130]

Tetraphenylarsonium chloride forms a precipitate with the chloride complex of gold, whose composition is probably the ion pair $[(C_6H_5)_4As^+AuCl^-]$.[131] The precipitate can be extracted by chloroform and the absorbance measured at 323 mμ against a chloroform extraction of the reagents as the reference solution. There is the advantage that the extraction may be accomplished without the complete removal of nitric acid. The method is applicable over a gold concentration range of 7–30 ppm. The chloroform extractant must be freed from any ethanol to encourage colour stability; pretreatment of the chloroform by alkaline permanganate provides stability over 24 hr or more. The hydrochloric acid concentration before extraction should range from 0·3 to $0{\cdot}5M$.

In determining the interfering constituents the authors showed caution in adding foreign metal constituents in the oxidised form expected from the usual dissolution process for gold. Further improvement would be achieved by preparing the contaminated solution by an evaporation, and submitting the residue to the usual *aqua regia, etc.*, treatments. There was little interference from copper, nickel, tellurium rhodium and ruthenium; however, there was interference from silver, osmium, platinum, palladium and iridium. The serious interference from iron was avoided by the addition of ammonium fluoride, the amount required being predetermined by the addition, to a measured aliquot of the gold solution, of thiocyanate followed by a solution of the fluoride measured to the disappearance of the red iron complex. This method provides a simple technique and of some importance is the fact that traces of nitrate do not interfere. The optimum range of gold concentrations and the tolerance for amounts of silver ion residual from a silver chloride precipitation suggest useful applications to the determination of gold in silver assay beads.

Woods reagent {2-hydroxymethyl-6-(2′-hydroxymethyl-5′-hydroxy-4′-pyrone-6′)-pyranyl[3,2-b]-pyran-4,8-dione} was used by Wilson and Lester[132] to produce a wine coloured complex soluble in an acetic acid medium and with an optimum absorbance at 535 mμ. Based on calculations from somewhat confusing data the working range of the method seems to be approximately 8–40 ppm with a sensitivity of 0·066 μg/ml. The addition of acetic acid had a marked effect on the sensitivity and the stability of the coloured constituent, its presence preventing the formation of a gold colloid. The platinum metals interfered.

For amounts of gold over the range 0·90–13·40 μg of gold/ml Popa *et al.*[133] added 2-amino-4,6-dinitrophenol (picramic acid) to a hydrochloric acid solution of gold to produce a yellow colour with absorbance measured at 482 mμ or with an S42 filter. Platinum was tolerated up to a ratio of 1: 22 and copper at a ratio of 1: 105. The method has little to recommend it.

A potentially useful solvent-extraction method for separating gold from some commonly associated base and noble metals was described by Senise and Pitombo.[134] Separations of gold, iron, silver, platinum, copper and palladium from solutions of alloys could be accomplished.

The alloy was dissolved by *aqua regia* and nitric acid removed by the usual evaporations with hydrochloric acid with a final dilution to a pH of 0–1. If silver was present sufficient hydrochloric acid was added to effect dissolution. Solutions of triphenylisopropyl chloride and sodium thiocyanate were added followed by benzene or toluene. Gold forms an orange colour in the organic layer which was removed; extractions were continued to remove the gold quantitatively. This technique was continued with the removal of iron by extraction with tri-n-butyl phosphate to form a red layer, then silver with extraction by 2-methylcyclohexanol to form a colourless layer, then platinum whose dissolution required a previous heating to 65–70° followed by extraction to form a yellow layer with tri-n-butyl phosphate. Following the removal of platinum, the copper complex was formed and extracted with methyl isobutyl ketone to form a wine red colour. Finally, the palladium phosphonium–cyanate complex was removed with cyclohexanone to form a yellow solution. Undoubtedly, a variety of sequential separations could be devised in the case of a more limited number of metals. In any case, one may hope that further separations of this type may be investigated quantitatively. The integration of suitable spectrophotometric methods applied to the extraction solvents would provide useful procedures for the analysis of such alloys as silver-noble metal assay alloys.

Methyl Violet was used by Tsai, Li and Ta[135] for the colorimetric determination of gold in raw materials and copper metallurgical products. The sample was treated with acids to effect the dissolution of gold. The filtered solution, converted to bromates, was treated with ether to extract the gold. The evaporated extract was treated with sulphuric and hydrochloric acids and sodium nitrite. Finally, an extraction of the Methyl Violet–gold solution was made with toluene. Measurements were made at 520 mμ, with adherence to Beer's Law for <5 μg of gold/ml.

An extraction photometric determination of gold in ores was described by Blyum and Vl'yanova.[136] The ore was treated by the usual *aqua regia* extraction. To the filtered solution were added tellurium, filter paper pulp and hydrazine, the mixture was boiled and tin(IV) chloride added to form a colloidal mass. The latter was dissolved in *aqua regia* and the evaporated residue treated with acids, iron(III) chloride and hydrogen peroxide. To the solution in a separatory funnel were added Crystal Violet and toluene. Gold was determined in the coloured layer.

TABLE V.—SPECTROPHOTOMETRIC REAGENTS FOR GOLD

No.	Reagent	Range of concentration, *ppm*
1.	*o*-Tolidine or 3,3′-dimethylbenzidine;[139–141]	0·04–0·4
	N,*N*′-tetramethyl-*o*-tolidine (Tetron)[117,142,143]	0·1–0·8
2.	*p*-Dimethylaminobenzylidenerhodanine[11,118–120,144–149]	0·3–0·7 0·03–0·3 (extracted with isoamyl acetate)
3.	Tin(II) chloride[11,121,150–154]	0·4–4 0–6 B.L.
4.	Bromaurate;[27,122,155]	0·5–4
	polyethylene bromaurate[123]	0–40
5.	Ammonium thiocyanate[124]	0·5–5
6.	Chloropromazine[125]	0·5–8·0 B.L.
7.	Rhodamine-B[126,127,156]	0–30
8.	α-Naphthylamine hydrochloride[163,164]	Limit of detection 1·0 μg
9.	Leuco compound of Malachite Green[165]	About 0·3 μg
10.	Brilliant Green[166]	
11.	Dithizone[157–161]	2–5
12.	Oxonium salt of polyethyleneglycol[128,129]	2·5–3·0 B.L.
13.	Phenyl α-pyridyl ketoxime[162]	4–10
14.	*o*-Dianisidine[167]	5–300 5–30
15.	*o*-Aminobenzene arsonic acid[168]	7 μg
16.	Anthranilic acid[130]	6·84–82·12
17.	Tetraphenylarsonium chloride[131]	7–30
18.	2-Hydroxymethyl-6-(2′-hydroxymethyl-5′-hydroxy-4′-pyrone-6′)-pyranyl-(3,2-b)-pyran-4,8-dione (Woods Reagent)[132]	8–40
19.	2-Amino-4,6-dinitrophenol (picramic acid)[133]	
20.	Triphenylisopropylphosphonium chloride and sodium thiocyanate[134]	
21.	Crystal Violet[136]	
22.	Methyl Violet[135]	
23.	Thio-Michler's Ketone [4,4′-bis-(dimethylamino)-thiobenzophenone][137]	
24.	Kojic acid (5-hydroxy-2-hydromethyl-1,4-pyrone)[138]	
25.	Phenol[169]	
	pyrocatechol	
	resorcinol	
	hydroquinone	
	pyrogallol	
	phloroglucinol	
	1-naphthol	
	2-naphthol	
	thymol	
26.	Amino acid[170]	
27.	Benzidine[173,174]	
28.	Formaldehyde[171,175]	
29.	Hydrogen peroxide[176]	
30.	Mercury(II) chloride[11,177]	

Thio-Michler's Ketone [4,4′-bis-(dimethylamino)-thiobenzophenone was used by Cheng and Lott[137] to determine gold at pH 3. The reagent in isoamyl alcohol was shaken with the gold solution for 1 min and the absorbance of the filtered extract measured at 545 mμ. The sensitivity is 0·0013 μg/cm^2.

Kojic acid (5-hydroxy-2-hydroxymethyl-1,4-pyrone) has been used by Murata and Ujihara[138] to produce with gold in a neutral or slightly acidic solution an intense blue-green fluorescence in ultraviolet radiation. Optimum intensity is obtained at pH 5·7–6·8 in the presence of dissolved sodium chloride. The fluorescence is developed over 30 min in a dark box and the intensity is measured at 470 mμ *vs.* a solution of sodium fluorescein. The gold determination tolerates the presence of tellurium which allows the use of the latter as a coprecipitant. This method may find application in the determination of gold in ores, *etc.*

Zusammenfassung—Es wird eine kritische Übersicht über die nach 1958 veröffentlichten spektralphotometrischen Bestimmungsmethoden für Rhodium, Iridium, Ruthenium, Osmium und Gold gegeben. Zusammen mit den Beschreibungen des Verhaltens der Metalle wird eine Tabelle vorgelegt, die vor 1958 beschriebene Reagentien mit den einschlägigen Literaturzitaten registriert.

Résumé—On passe en revue, de façon critique, les méthodes spectrophotométriques de dosage du rhodium, de l'iridium, du ruthénium, de l'osmium et de l'or publiées postérieurement à 1958. A la description de chaque métal est joint un tableau identifiant les réactifs mentionnés avant 1958 avec les références correspondantes.

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THEORY OF COMPLEXOMETRIC TITRATIONS BASED ON EXTRACTIVE END-POINT DETECTION

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Summary—The theory of complexometric titrations, which employ extractive end-point detection, is presented. If dithizone is used as an indicator in the complexometric titrations of zinc, lead and cadmium, high sensitivities can be attained because of the intense colour and low metal-ion concentrations at the colour transition points. It should be possible to titrate metals in very dilute solutions where many other indicators are not sensitive enough, particularly in the pH range around the neutral point.

THE theory of complexometric titrations, in which end-points are detected by extraction, has not been fully expounded, although such titrations have been widely used.

Bovalini and Casini[1] determined lead and cadmium by back-titration of excess EDTA with zinc, at pH 5·3, after adding dithizone in carbon tetrachloride to the system. The end-point was indicated by a colour change in the organic phase. When Minami and Sato[6] attempted to determine micro amounts of lead by direct titration with EDTA in the presence of dithizone and chloroform, they found that the end-point did not coincide with the equivalence point. This is perhaps a result of slow attainment of equilibrium.

Cameron and Gibson[3,4] determined cobalt, copper, nickel, iron, chromium and vanadium by back-titration of excess EDTA with a standard cobalt solution; the end-point was taken to coincide with the appearance of a blue colour, in the organic layer, from the complex formed by triphenylmethylarsonium, cobalt and thiocyanate ions, $[Ph_3MeAs]_2[Co(SCN)_4]$. The extraction of the iron(III)–thiocyanate complex into organic solvents has also been employed for end-point detection in complexometric titrations.[2,5]

Extraction indicators are employed either as acid-base or as metal indicators. The theory of these two cases will now be discussed, taking dithizone (HDz) as an example.

Acid-base indicators

Dithizone functions as an acid-base indicator in aqueous solution, but because the compound is sparingly soluble in water, a water–alcohol mixture is usually employed. The pH at the mid-point of the colour transition, pH_{trans}, is equal to the $\log_{10}$ of the stability constant of the proton complex of dithizone, K_{HDz}, and is 4·5.

When an organic solvent immiscible with water, *e.g.*, chloroform or carbon tetrachloride, is added to the system, the dithizone will be extracted into the organic phase, which will then assume a dark green colour. The colour transition now occurs at a higher pH. The mid-point of the colour transition interval may be taken to be attained when half of the amount of indicator is in the organic phase and the other half is present as the yellow anion in the aqueous phase. If one assumes the following equilibria to prevail in the system (charges omitted):

$$H + Dz \rightleftharpoons HDz \qquad K_{HDz} = \frac{[HDz]}{[H][Dz]} \tag{1}$$

$$HDz \rightleftharpoons HDz\,(org) \qquad D_{HDz} = \frac{[HDz]_{org}}{[HDz]} \tag{2}$$

the pH at the mid-point of the colour transition interval is given by

$$pH_{trans} = \log K_{HDz} + \log D_{HDz} + \log \frac{V_{org}}{V_{aq}} \tag{3}$$

where V_{org} and V_{aq} denote the volumes of the organic and aqueous phases, respectively, and D_{HDz} is the distribution coefficient of the proton complex of dithizone (log $D_{HDz} = 4{\cdot}0$ for carbon tetrachloride and 5·7 for chloroform).

If $V_{org} = V_{aq}$, the last term in the equation will be zero and the mid-points of the colour transitions when carbon tetrachloride and chloroform are the organic solvents will be attained when the pH of the aqueous phases are 8·5 and 10·2, respectively.

The phase-transfer equilibria are reached very slowly, so that extraction indicators offer very little advantage compared with other acid-base indicators which function satisfactorily in homogeneous systems. Extraction indicators are, however, of greater value as metal indicators in complexometric titrations.

Metal indicators

The advantages of extraction indicators as metal indicators in complexometric titrations are two-fold.

Firstly, the indicators have high absorptivities and hence very low concentrations of the indicators are sufficient to impart a colour to the organic phase. The sensitivity can be further increased by altering the ratio, $V_{org}:V_{aq}$, of the volumes of the organic and aqueous phases.

Secondly, the pH of the aqueous phase is higher when the colour transition occurs and hence the conditional constant of the complex formed by a metal and a complexing agent will have a higher value. This means that very dilute solutions of metals can be titrated. Moreover, metal extraction indicators can often be used in the pH range around the neutral point, where there is a need for more metal indicators.

Consider the titration of zinc with EDTA (H_4Y) when dithizone is the indicator and carbon tetrachloride is the organic phase. The following equilibria are involved:

$$Zn + Y \rightleftharpoons ZnY \qquad \log K_{ZnY} = 16{\cdot}5 \tag{4}$$

$$Zn + 2HDz(org) \rightleftharpoons ZnDz_2(org) + 2H \qquad \log E_{ZnDz_2} = 2{\cdot}3 \tag{5}$$

When half of the indicator present in the organic phase has reacted with zinc, *i.e.*, at the mid-point of the colour transition interval,

$$[ZnDz_2]_{org} = \tfrac{1}{2}[HDz]_{org} \tag{6}$$

The equilibrium at this point is defined by the equation

$$\frac{[H]^2}{[Zn][HDz]_{org}} = 10^{2\cdot 6} \tag{7}$$

If one denotes by C_{HDz} the concentration of unbound indicator, all of which is assumed to be in the organic phase, the value of the α-coefficient[7] of dithizone which represents the extent to which dithizone has been transformed into other forms and transferred to another phase, is given by[7,8]

$$\alpha_{HDz} = \frac{C_{HDz}}{[HDz]_{org}} = \frac{[HDz]_{org} + \frac{V_{aq}}{V_{org}}([HDz] + [Dz])}{[HDz]_{org}} \tag{8}$$

The term [HDz], which is $10^{-4}[HDz]_{org}$, can be neglected, and it follows that

$$\alpha_{HDz} = 1 + \frac{V_{aq}}{V_{org}D_{HDz}K_{HDz}[H]} = 1 + \frac{V_{aq}\,10^{-8\cdot 5}}{V_{org}[H]} \tag{9}$$

The hydrogen ion concentration, pH_{trans}, when the indicator is equally distributed between the two phases is $10^{-8\cdot 5}$. When the ratio $V_{aq}:V_{org}$ is 10:1

$$[HDz]_{org} = \frac{C_{HDz}}{1 + 10^{-7\cdot 5+pH}} \tag{10}$$

Values of pZn and pZn_{trans}, at the mid-point of the colour change [from equation (7)] and at the equivalence point are given for various pH in Table I. The indicator concentration C_{HDz} has been assumed to be $10^{-5}M$ and the total zinc concentrations 10^{-3} and $10^{-5}M$.

The value of pZn at the equivalence point is given by

$$[Zn']_{eq} = [Y']_{eq} = \sqrt{\frac{[ZnY]}{K_{Zn'Y'}}} \tag{11}$$

where $K_{Zn'Y'}$ is the value of the conditional constant[7] of the Zn-EDTA complex at the pH in question.

Values of pZn at the mid-points of the colour transition, when the solvent is a water–alcohol mixture and no organic phase is present, are also included in Table 1.[9] These values have been computed on the assumption that the dithizone concentration is $10^{-5}M$ and $\log K_{ZnDz_2} = 10\cdot 8$.

Values of pZn referring to a two-phase solvent system composed of chloroform and water have been calculated on the assumption that $\log E_{ZnDz_2} = 0\cdot 7$ and they are also given in Table 1.

The values of pZn_{trans} and pZn_{eq} are plotted against pH in Fig. 1.

It will be seen that pZn_{trans} may be very high in value when the experimental conditions are appropriately chosen. This means that the curves plotting pZn_{trans} and pZn_{eq} will intersect at very low total concentrations of the metal. It should be theoretically possible, therefore, to titrate very dilute zinc ion solutions.

TABLE I.—VALUES OF pZn_{trans} AND pZn_{eq} UNDER VARIOUS CONDITIONS

pH	pZn_{trans}			pZn_{eq}	
	CCl_4/water	$CHCl_3$/water	C_2H_5OH-water	$[ZnY] = 10^{-3}M$	$[ZnY] = 10^{-5}M$
3·0	3·6	2·0	2·6	4·5	5·5
4·0	5·6	4·0	4·4	5·5	6·5
5·0	7·6	6·0	5·5	6·5	7·5
6·0	9·6	8·0	5·8	7·4	8·4
7·0	11·5	10·0	5·8	8·1	9·1
8·0	13·0	12·0	5·8	8·6	9·6
9·0		13·8		9·1	10·1

Curves computed analogously for titrations of lead and cadmium are plotted in Figs. 2 and 3. The following values of the necessary constants were employed:[7]

$$\log K_{PbY} = 18{\cdot}0 \qquad \log K_{CdY} = 16{\cdot}5$$

$$\log E_{PbDz_2} = 0{\cdot}7\ (CCl_4) \qquad \log E_{CdDz_2} = 1{\cdot}8\ (CCl_4)$$

$$= 0{\cdot}0\ (CHCl_3) \qquad = 0{\cdot}7\ (CHCl_3)$$

Comparison with Eriochrome Black T

The advantage offered by dithizone for the titration of zinc in a pH range where other metallochromic indicators often are not sufficiently sensitive will be shown by an example.

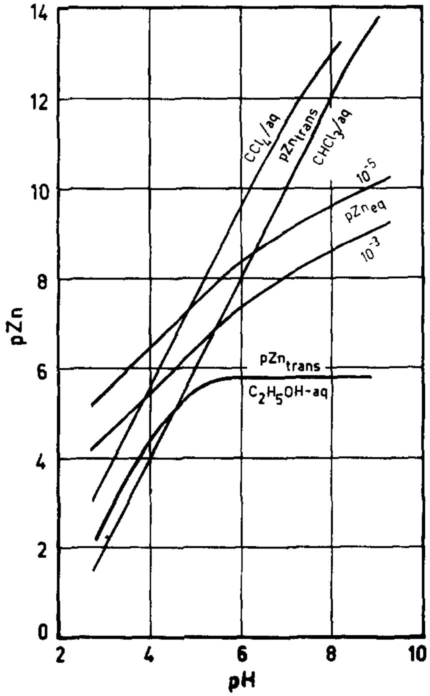

FIG. 1.—pZn_{trans} and pZn_{eq} as functions of pH ($C_{HDz} = 10^{-5}M$; $V_{aq}:V_{org} = 10:1$).

One may ask what accuracy is attainable with

(a) Eriochrome Black T (HI),

and (b) dithizone in carbon tetrachloride($C_{\mathrm{HDz}} = 2 \times 10^{-6}M$; $V_{aq}:V_{org} = 10:1$) when a solution containing about $10^{-5}M$ in zinc is buffered to pH 8 by a secondary complexing agent with $\log \alpha_{\mathrm{Zn}} = 4$ (*e.g.*, aqueous ammonia or citrate) and titrated with EDTA.

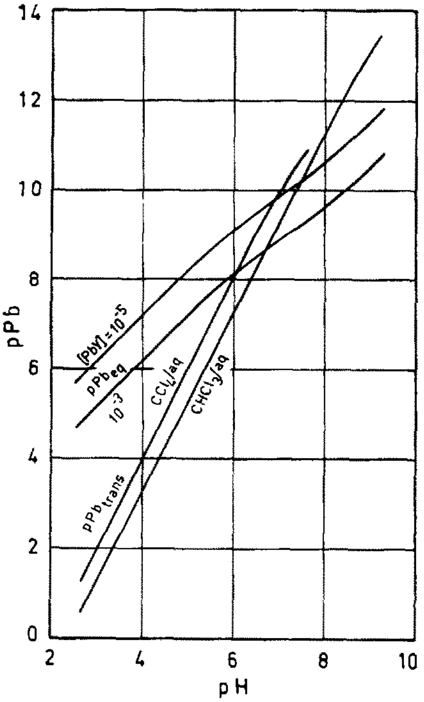

FIG. 2.—$\mathrm{pPb_{trans}}$ and $\mathrm{pPb_{eq}}$ as functions of pH ($C_{\mathrm{HDz}} = 10^{-5}M$; $V_{aq}:V_{org} = 10:1$).

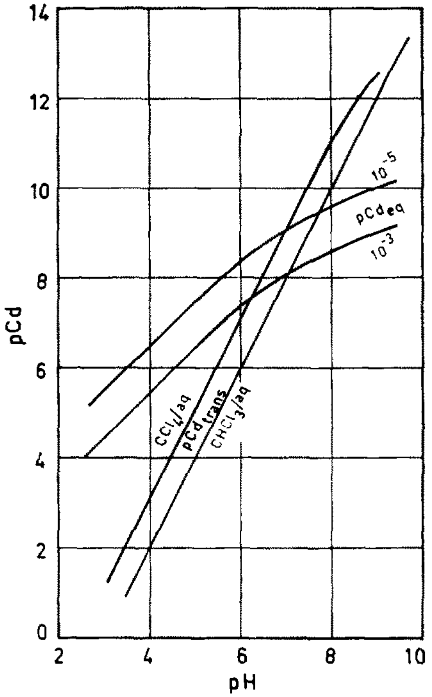

FIG. 3.—$\mathrm{pCd_{trans}}$ and $\mathrm{pCd_{eq}}$ as functions of pH ($C_{\mathrm{HDz}} = 10^{-5}M$; $V_{aq}:V_{org} = 10:1$).

The conditional constants are:[7] $\log K_{\mathrm{Zn'Y'}} = 10{\cdot}2$, and $\log K_{\mathrm{Zn'I'}}$, $= 5{\cdot}3$. $\mathrm{pZn_{eq}}' = 7{\cdot}6$. Consequently,

(a) $\mathrm{pZn'_{trans}} = 5{\cdot}3$, $\Delta\mathrm{pZn}' = -2{\cdot}3$, error[7] *ca.* -50%.

(b) $\mathrm{pZn_{trans}} = 12{\cdot}3$, $\mathrm{pZn'_{trans}} = 8{\cdot}3$, $\Delta\mathrm{pZn}' = 0{\cdot}7$, error *ca.* $1{\cdot}2\%$.

The advantages of an extraction indicator are thus obvious.

Dithizone is also an excellent indicator at pH 6 ($\log \alpha_{\mathrm{Zn}} = 0$; $\log K_{\mathrm{ZnY'}} = 11{\cdot}7$; $\mathrm{pZn_{eq}} = 8{\cdot}35$; $\mathrm{pZn_{trans}} = 8{\cdot}9$ in CCl_4; $\Delta\mathrm{pZn} = 0{\cdot}55$; error *ca.* $0{\cdot}15\%$). Eriochrome Black T cannot be used at this pH.

EXPERIMENTAL

The above theoretical deductions were checked by titrating EDTA solutions with metal salt solutions. This procedure was chosen because the reactions attained equilibrium very slowly when EDTA solutions were added to metal salt solutions.

The visual titrations were performed in daylight. In the photometric titrations a Beckman B spectrophotometer was used.

All solutions were prepared from reagent-grade chemicals and were standardised by titration with EDTA using Eriochrome Black T as indicator. The solvents were redistilled and the water was passed through a column of a cation-exchanger in the hydrogen form to remove all copper.

Results from some titrations are presented in Table II.

TABLE II.—TITRATIONS OF METAL IONS USING DITHIZONE AS AN EXTRACTION INDICATOR

Metal	End-point detection	Organic phase	$V_{org}:V_{aq}$, *ml:ml*	pH	EDTA taken, *mmole*	EDTA found, *mmole*	Error, %
Zn	Visual	CCl_4	10:50	6·0	$1{\cdot}92 \times 10^{-1}$	$1{\cdot}92 \times 10^{-1}$	0·0
	Visual	CCl_4	10:50	6·2	$9{\cdot}60 \times 10^{-2}$	$9{\cdot}64 \times 10^{-2}$	+0·4
	Visual	CCl_4	10:50	6·9	$4{\cdot}80 \times 10^{-2}$	$4{\cdot}84 \times 10^{-2}$	+0·8
	Visual	CCl_4	10:50	6·0	$5{\cdot}12 \times 10^{-3}$	$5{\cdot}13 \times 10^{-3}$	+0·2
	Photometric	$CHCl_3$	50:10	6·7	$4{\cdot}80 \times 10^{-4}$	$4{\cdot}82 \times 10^{-4}$	+0·4
	Photometric	$CHCl_3$	50:10	7·0	$1{\cdot}92 \times 10^{-4}$	$1{\cdot}87 \times 10^{-4}$	−2·6
	Photometric	$CHCl_3$	50:10	6·7	$0{\cdot}96 \times 10^{-4}$	$\sim 0{\cdot}98 \times 10^{-4}$	~2·1
Cd	Photometric	$CHCl_3$	50:10	6·5	$9{\cdot}60 \times 10^{-2}$	$9{\cdot}60 \times 10^{-2}$	0·0
Pb	Photometric	$CHCl_3$	50:10	7·0	$9{\cdot}60 \times 10^{-2}$	$9{\cdot}61 \times 10^{-2}$	+0·1

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Zusammenfassung—Die Theorie komplexometrischer Titrationen mit extraktiver Endpunktsanzeige wird vorgelegt. Mit Dithizon als Indikator lassen sich bei komplexometrischen Titrationen von Zink, Blei und Cadmium wegen der intensiven Farbe und der geringen Metallionenkonzentration bei den Farbumschlagspunkten hohe Empfindlichkeiten erzielen. Man sollte Metalle in sehr verdünnten Lösungen titrieren können, wo viele andere Indikatoren nicht empfindlich genug sind, besonders in pH-Bereich um den Neutralpunkt herum.

Résumé—On présente la théorie des dosages complexométriques qui utilisent la technique de détection par extraction du point de virage. En employant la dithizone comme indicateur pour les dosages complexométriques du zinc, du plomb et du cadmium, on peut atteindre des sensibilités élevées par suite de l'intense coloration et des faibles concentrations en ion métallique au point de virage de la coloration. Il devrait être possible de doser des métaux en solutions très diluées, là où de nombreux autres indicateurs ne sont pas suffisamment sensibles, en particulier dans le domaine de pH avoisinant la neutralité.

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SEPARATION OF TRACES OF METALS FROM URANIUM BY CHROMATOGRAPHY ON CELLULOSE COLUMN*

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Summary—Submicrogram amounts of thirteen metals have been separated from 50 g of uranyl nitrate by adsorption chromatography on cellulose column. The adsorbed metals have been eluted by solutions of potassium thiocyanate and hydrochloric acid in organic solvents. The quantitative recovery of metals has been verified by using radioisotopes and gamma-ray spectrometry.

MANY methods have been used to separate trace impurities from uranium. These methods (ion-exchange chromatography, solvent extraction, *etc.*) have been designed to separate one element or a group of similar elements.

From studies concerned with the separation of rare earths from uranium and their adsorption on cellulose,[1–3] it has been inferred that other cations could also be adsorbed by the acid groups of cellulose, if the cellulose is in a suitable solvent or has been treated with special reagents.[4] In fact, cadmium, at a concentration of 5 ppb, as well as ytterbium and scandium at a concentration of 0·5 ppb, and dysprosium, erbium, europium and yttrium at a concentration of 2 ppb, have all been determined in uranium by passing a solution of uranyl nitrate in ethyl ether through cellulose and carrying out emission spectrography on the ashed cellulose column.[5]

The present study demonstrates that effective separations of trace impurities from reactor-grade uranium can be realised by adsorption chromatography with organic solvents. Moreover, suitable choice of reagents and solvents enables these impurities to be quantitatively separated from each other by the chromatographic elution of very small amounts of these adsorbed metals from the cellulose. Radioisotopes have been used to follow the separations, even during the course of the adsorption or elution.

EXPERIMENTAL

Reagents and apparatus

Reagent-grade chemicals and solvents were used for the preparation of all solutions.

Eluting solutions. (a) Fifty g of uranyl nitrate and 5 ml of concentrated nitric acid dissolved in 95 ml of ethyl ether.

(b) Five ml of concentrated nitric acid dissolved in 95 ml of ethyl ether.
(c) Forty mg of potassium thiocyanate dissolved in 40 ml of methanol plus 60 ml of ethyl ether.
(d) Forty mg of potassium thiocyanate dissolved in 100 ml of acetone.
(e) Thirty ml of concentrated hydrochloric acid dissolved in 70 ml of acetone.
(f) Ten ml of concentrated hydrochloric acid in 90 ml of acetone.

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Column. Whatman cellulose powder Chromedia CF II, ashless, standard grade n.l.

Radioisotopes. The high specific activity radioisotopes were obtained from the Oak Ridge National Laboratory Isotopes Division.

Radioactivity measurements. The presence or absence of radioactivity in the eluted fractions and in the cellulose column was measured by a 200-channel gamma-ray spectrometer, electronically coupled to a NaI(Tl) activated crystal.

Trace elements preparation. In, Zn, Co, Cu, Cr, Mn, Ba, Fe, Ag, Cd, Sr, Sb and Cs were used because they are representative of the trace element contaminants found in uranium and have appreciable neutron activation cross-sections. A weighed amount of the element was dissolved in nitric acid or converted to the nitrate and diluted to a known volume after the radioisotope was added. An aliquot was taken to simulate the normal levels of the impurity found in uranium.

Preparation of cellulose column. A 50 ml burette (1-cm diameter) was filled with 95% ether-5% HNO_3 solvent and cellulose added slowly, to form an air-free column. The cellulose pad was pressed down to a height of 25 cm by compressed air. The prepared cellulose column was kept wet with ether–nitric acid solvent. A new column was prepared for each separation immediately before use.

Preparation of uranium solution and chromatographic procedure

About 50 g of fine crystalline and dried uranyl nitrate were dissolved in 95 ml of ethyl ether and transferred to a beaker containing the radiotracer dissolved in 5 ml of concentrated nitric acid. This solution, (a), was introduced into the burette, and the flow rate of 7 ml min was attained by keeping the column under air pressure. Uranium passed through the column as the nitrate complex.

TABLE I.—METALS SEPARATED FROM URANIUM BY CHROMATOGRAPHY

Radio-isotope	Element present, μg	Metal in uranium, ppb	Band colour	Eluant*	Adsorption, %	Elution, %
^{114m}In	0·075	2·5	Red	c	100	100
^{65}Zn	0·378	12·6	Pink	c	100	100
^{60}Co	0·050	1·7	Pink	c	100	100
^{64}Cu	0·400	13·3	Red	c	100	100
^{51}Cr	0·032	1·1	Red	c	100	100
^{54}Mn	0·080	2·7	Yellow	c	100	100
^{133}Ba	0·028	0·9	Colourless	c	100	50
^{59}Fe	0·012	0·4	Red	c	100	100
^{110}Ag	2·900	96·6	Red	c	100	100
^{115m}Cd	4·000	133	Colourless	d	100	100
^{85}Sr	0·100	3·3	Colourless	d	100	100
^{124}Sb	0·034	1·1	Red	e	100	100
^{137}Cs	Carrier free	—	Colourless	e	100	100

* Letters refer to solutions given under *Reagents and Apparatus.*

The column was washed with 100 ml of ether–nitric acid solution, (b), introduced in small fractions to elute the remaining uranium. A few drops of methanol were added to the last 10 ml of ether–nitric acid, to avoid precipitation of potassium thiocyanate from the following eluting solution.

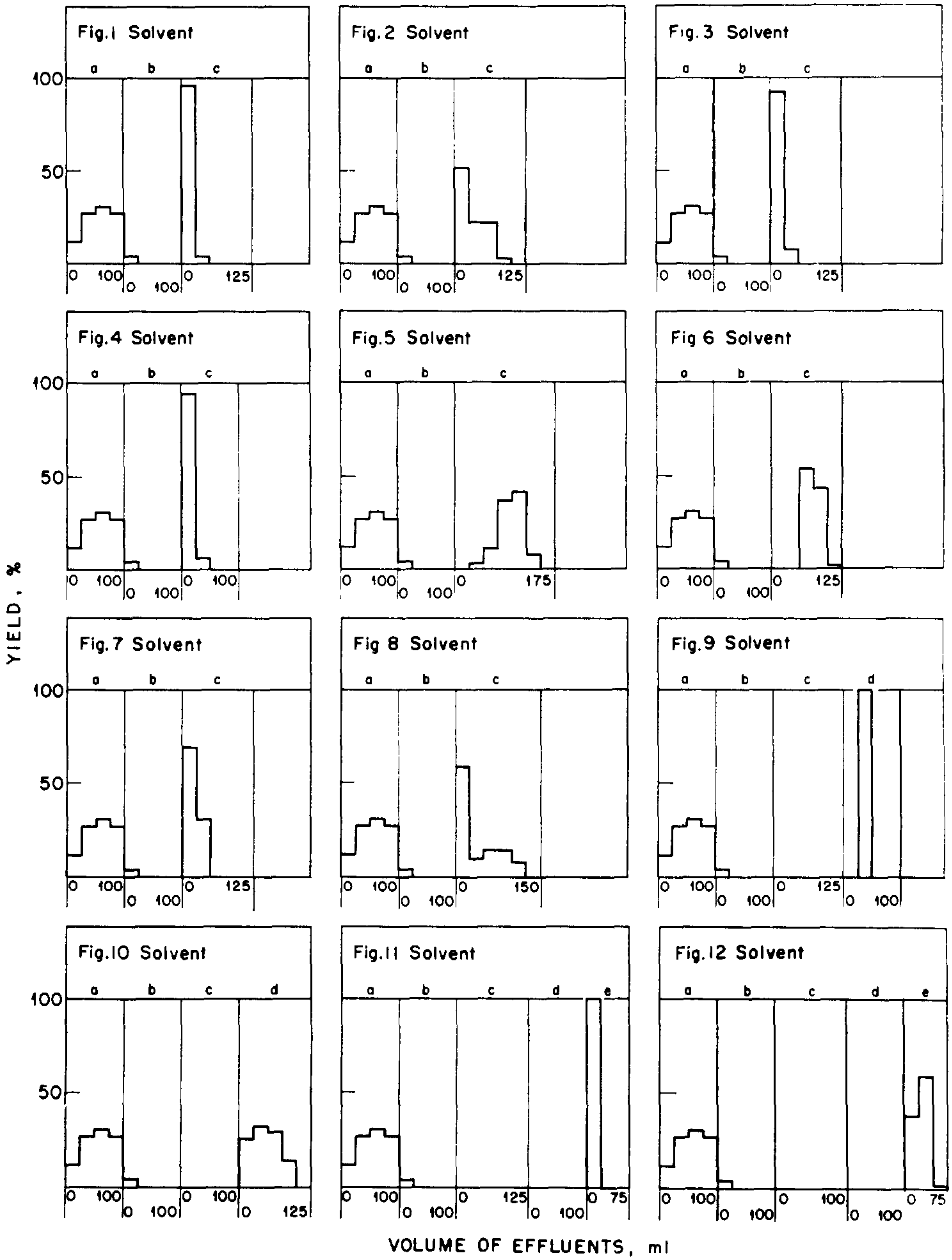
The first eluting solution, (c), was 40 mg of potassium thiocyanate in 100 ml of 60% ether-40% methanol. Immediately after the potassium thiocyanate eluent was added, coloured complexes of several metal ions were formed (Table I).

These coloured bands and the associated radioactivity were rapidly eluted from the column. Each fraction, a column volume, of 25 ml was collected separately, for radioactivity measurement, for each eluent.

The amount of radioactive isotope added varied from 1·10 × 10^5 to 1·10 × 10^7 dpm; the total element concentration associated with each nuclide added is given in the second column of Table I.

The second eluting solution, (d), 40 mg potassium thiocyanate in 100 ml of acetone, was passed through the column, removing cadmium and strontium. The third eluting solution, (e), 30 ml of concentrated hydrochloric acid in 70 ml of acetone, removed antimony and caesium from the cellulose column.

The above procedure was applied first to the separation of each element individually from uranium. Later, different mixtures of radio-elements were separated from uranium. To determine the extent of recovery, the radioactivity of each fraction of effluent was compared with a radioactive standard containing the same amount of radio-element used in the separation.



FIGS. 1-12.—Separation and elution of individual metal ions from uranium:

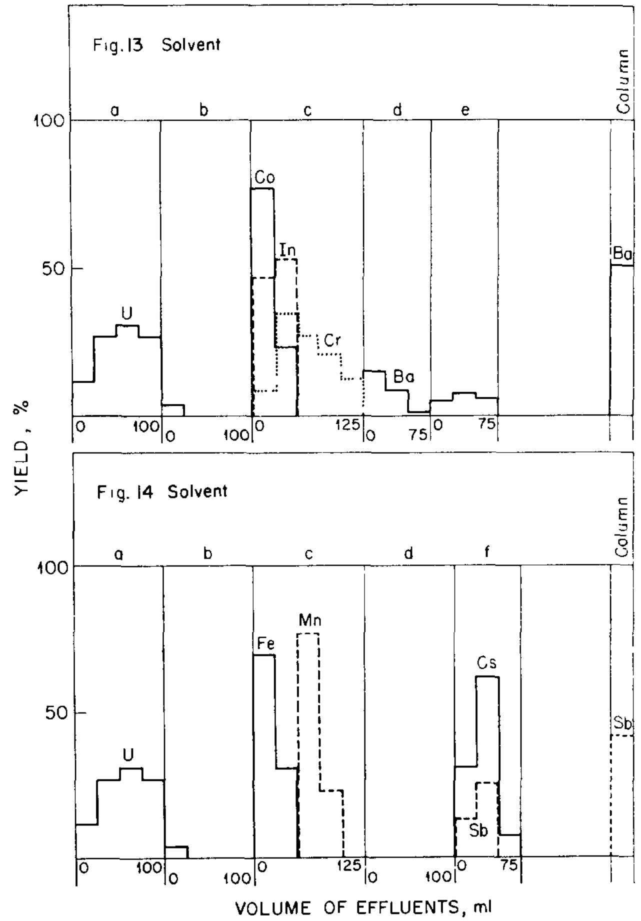
1. In, 2. Zn, 3. Co, 4. Cu, 5. Cr, 6. Mn,
7. Fe, 8. Ag, 9. Cd, 10. Sr, 11. Sb, 12. Cs.

The complete separation of the trace elements from uranium takes 2 hr, including the preparation of solutions and column. Fresh solutions (a) and (b) are made each time to prevent the formation of peroxides, which are hazardous and have been known to explode.

The uranium can be recovered from the ether-HNO_3 mixture. Place the mixture in an evaporating dish, add 100 ml of water and then blow air over the dish to remove the ether. Heat the aqueous solution gently until crystallisation occurs. This operation takes 1 hr.

RESULTS AND DISCUSSION

When the solution of uranyl nitrate in ether was passed through the column, uranium was not retained at all, and it moved at the same speed as the solution. Only 25 ml of solution (b) would have been necessary to wash the column, but 100 ml were used to ensure a complete separation of uranium from the trace metal ions. No radioactivity was detected in these ether fractions.



FIGS. 13 and 14.—Separation and elution of mixtures of metal ions from uranium.

Traces of metals were retained by the acid groups of cellulose on the column at different levels, as shown by the coloured bands appearing after the introduction of solvent (c).

Uranium was removed from the thirteen elements studied and the effluent solution containing uranium could be concentrated. Very pure uranyl nitrate could be crystallised from the concentrate. The trace elements collected on the column were eluted with organic solvents containing complexing agents.

The elution of the thiocyanate complexes of several metals in ether-methanol are represented in Figs. 1–8. The elution curves for thiocyanate complexes of cadmium and strontium in acetone are in Figs. 9 and 10. Antimony and caesium did not form thiocyanate complexes under these conditions, but they were removed by acetone-hydrochloric acid (Figs. 11 and 12), because the eluent attacked the cellulose to such an extent that a more dilute eluent, (f), was prepared (Fig. 14). Figs. 13 and 14 show typical elution curves for two uranium solutions containing trace elements. From these, it can be seen that uranium may be completely separated from these elements and also that a partial separation of these trace elements can be made. (The examination of the γ-ray spectra of manganese and iron in the eluent indicates that these two elements are completely separated.) These elements are completely eluted, except barium and antimony, which partially remain on the cellulose column.

Earlier workers have used at least 40 g[1–3] or 20 g[5] of cellulose for one column. For the present work, the amount of cellulose powder has been reduced to a few grams only.

It has been demonstrated that trace amounts of thirteen different elements can be quantitatively separated from uranium by adsorption and elution from a cellulose column treated with 95% ether-5% nitric acid. The efficiency of the separations was tested by a radioactive-tracer technique.

For analytical applications, the method could be used to separate trace quantities of elements present in uranium with the final elemental determination being made by physico-chemical measurements or neutron-activation analysis.

Future studies might well include evaluation of other complexing agents in different solvents for additional trace element determinations.

Acknowledgments—R. A. A. Muzzarelli expresses his appreciation to the Consiglio Nazionale delle Ricerche, Rome, Italy, which supported his studies at the Oak Ridge National Laboratory.

Zusammenfassung—Submikrogrammengen von dreizehn Metallen wurden aus 50 g Uranylnitrat durch Adsorptionschromatographie an einer Cellulosesäule abgetrennt. Die adsorbierten Metalle wurden eluiert durch Lösungen von Kaliumrhodanid und Salzsäure in organischen Lösungsmitteln. Daß die Metalle quantitativ wiedergefunden werden, ließ sich mit Hilfe von Radioisotopen und Gammastrahlspektrometrie nachweisen.

Résumé—On a séparé des quantités inférieures au microgramme de treize métaux à partir de 50 g de nitrate d'uranyle, par chromatographie d'adsorption sur une colonne de cellulose. On a élué les métaux adsorbés par des solutions de sulfocyanure de potassium et d'acide chlorhydrique en solvants organiques. On a contrôlé la récupération quantitative des métaux au moyen de radioisotopes et de la spectrométrie aux rayons gamma.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF GOLD BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A highly selective, rapid, one-step radiochemical separation procedure for gold has been developed. It is based on the solvent extraction of gold diethyldithiocarbamate from a 0·01–10*N* sulphuric or hydrochloric acid medium using a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of gold by neutron-activation analysis in high-purity lead, the rock W-1, gold-doped semiconductor-grade silicon and a biological material (kale). Amounts of gold down to 2×10^{-10} g have been determined.

NEUTRON-ACTIVATION analysis is well suited to the determination of traces of gold in various materials, especially for the high sensitivity which can be reached by this method. Gold is a mono-isotopic element and by its activation with thermal neutrons the following nuclear reaction occurs:[1]

$$^{197}\mathrm{Au}(n, \gamma)^{198}\mathrm{Au}$$

($t_{\frac{1}{2}} = 2{\cdot}7$ days; $\sigma = 96$ barns; $\beta^- = 0{\cdot}96$ MeV; $\gamma = 0{\cdot}41$ MeV). From the above data it follows that under suitable conditions (irradiation in a flux of 10^{12} neutrons. $\mathrm{cm}^{-2}.\mathrm{sec}^{-1}$ to saturation activity, followed by radiochemical separation) it is theoretically possible to determine down to 10^{-11} g of gold. The following possible nuclear interference reactions

$$^{198}\mathrm{Hg}(n, p)^{198}\mathrm{Au}$$

$$^{198}\mathrm{Pt}(n, \gamma)^{199}\mathrm{Pt} \rightarrow {}^{199}\mathrm{Au}$$

must be considered in the case of a mercury or platinum matrix. Also, the reaction[32]

$$^{198}\mathrm{Au}(n, \gamma)^{199}\mathrm{Au}$$

($t_{\frac{1}{2}} = 3{\cdot}1$ days; $\sigma = 26{,}000$ barns; $\beta^- = 0{\cdot}30$, $0{\cdot}25$, $0{\cdot}46$ MeV; $\gamma = 0{\cdot}16$, $0{\cdot}21$, $0{\cdot}05$ MeV) must be taken into account, especially in the case of prolonged irradiation.

Neutron-activation analysis has been used for the determination of traces of gold in such industrially important materials as semiconductors,[2] high-purity metals,[3,4] lithium compounds,[5,25] petrochemicals,[6] as well as in sea water,[7] meteorites,[8,9] rocks,[10] minerals,[9,11,13] biological materials,[14–16] *etc.* These methods necessitate the use of radiochemical separation procedures by means of which the radio-gold is separated in a radiochemically pure form suitable for chemical yield determination. The monograph by Emery and Leddicotte[17] contains several separation procedures for gold which well illustrate the complicated and time-consuming nature of these standard methods.

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The purpose of the present paper was to develop a substoichiometric separation procedure for gold, which, from its generally higher selectivity and the avoidance of determining the chemical yield,[18] would permit a considerable simplification over the radiochemical procedures commonly used. During recent years such substoichiometric procedures have been successfully applied to the determination of various trace metals by neutron-activation analysis. From the theory of substoichiometry,[18] it follows that a reproducible substoichiometric separation can be developed only when the metal under consideration forms a very stable, readily extractable chelate with the reagent employed. Moreover, the chelating agent itself must not be easily decomposed by light, oxidising agents, *etc.*

The selectivity of the separation of gold is affected by the extractability of the chelate formed. Dithizone seems to be particularly suitable for the substoichiometric determination of gold because the extractability of metal dithizonates decreases in the following order:[19] Pd(II), Au(III), Hg(II), Ag(I), Cu(II), Bi(III), Pt(II), In(III), Zn(II), Cd(II), Co(II), Pb(II), Ni(II), Sn(II) and Tl(I) and dithizone solutions in organic solvents are sufficiently stable against decomposition. However, our attempts to use this reagent for the substoichiometric separation of gold were unsuccessful. The main reason is that two types of dithizonate, AuHDz and Au_2Dz (where H_2Dz represents dithizone itself), are formed, the ratio of which depends on pH, excess of dithizone used and chloride ion concentration.[20] For this reason a reproducible substoichiometric separation of gold by dithizone can only be achieved by a strict control of the conditions. It is preferable to maintain the chloride ion concentration at the lowest possible level, which, from a practical point of view, is not very convenient.

Attention was, therefore, turned to other chelating agents containing the reactive —SH group, such as dialkyldithiophosphates and dithiocarbamates. The relative order[21] of extraction of metal chelates with di-n-butyl phosphorodithioic acid [Pd(II), Au(III), Cu(I), Hg(II), Ag(I), Cu(II), Sb(III), Bi, Pb, Cd, Ni and Zn] does not differ very much from that of the dithizonates. A similar conclusion is reached in the case of the metal diethyldithiocarbamates on the basis of the systematic study of Bode and Neumann[22]—with one significant exception—the extraction of gold diethyldithiocarbamate. Using diethyldithiocarbamate as a chelating agent and carbon tetrachloride as the organic solvent, gold was found[22] to be extracted only partially (*ca.* 30%) above pH 1, while Pd, Pt, Cu, Hg, Ag, *etc.*, are extracted even from 10*N* sulphuric acid. This observation unexpectedly places gold amongst the least extractable metals with this particular chelating agent. From our experiments it follows that this is because of the low solubility of gold diethyldithiocarbamate in carbon tetrachloride; with chloroform as solvent, however, this chelate can be extracted quantitatively even from very strong mineral acid solutions. It is impossible to use sodium diethyldithiocarbamate or diethylammonium diethyldithiocarbamate for the substoichiometric separation because both reagents are rapidly decomposed. Of various metallic salts of the parent reagent which offer a greater stability, copper diethyldithiocarbamate has been found extremely suitable in the present case. Its solution ($4{\cdot}83 \times 10^{-4}M$ in chloroform) can be kept without significant change in strength for at least 2 months. Moreover, in acid solutions, gold replaces the copper in the chelate very quickly and the colour of the organic extract changes from dark brown to golden yellow. For these reasons an extractive titration can be used for checking the concentration of gold or of the extractant. It can also be expected that the procedure will be highly selective, because the extraction of copper diethyldithiocarbamate (which is evidently a weaker complex than that of gold) is well known to be one of the most selective methods for the determination of copper.

EXPERIMENTAL

Apparatus

Scintillation counter. The detector used was a 1·75 in. diameter × 2 in. NaI(Tl) well-type crystal: well volume 5 ml. This was associated with a single channel gamma-ray spectrometer. In all experiments a setting of discriminator voltage corresponding to 0·07 MeV was used. This ensured only low selectivity, but higher sensitivity of counting the ^{198}Au activity.

Reagents

All reagents were prepared from analytical reagent grade chemicals.

Gold carrier solution (2·06 mg/ml; 1·05 × 10^{-2}*M*). Prepared from a weighed amount of metallic gold (metal leaves *ca.* 0·0001 mm, General Chemical Co., Division of Fisons Scientific Apparatus Ltd., Loughborough, England) by dissolution in *aqua regia*. The resulting solution was evaporated almost to dryness, then diluted to a standard volume with 1*N* hydrochloric acid.

Copper diethyldithiocarbamate solution (4·83 × 10^{-4}*M*). Prepared by mixing 250 ml of an aqueous solution of sodium diethyldithiocarbamate (0·2253 g; B.D.H. Ltd., Poole, England) with 25 ml of copper sulphate solution (2·5 g of pentahydrate), the precipitate thus formed being extracted by two 250-ml portions of chloroform and the combined extracts diluted to 1000 ml with the same solvent. The concentration of the resulting solution was checked by absorbance measurement at 436 mμ. Assuming that the molar extraction coefficient is the same in chloroform as in carbon tetrachloride (1·3 × 10^4),[19] the concentration of the prepared solution was 4·83 × 10^{-4}*M*, which was in good agreement with the amount of sodium diethyldithiocarbamate weighed originally. By extractive titration in a medium of 1*N* hydrochloric acid (the end-point being a change in colour from golden yellow to dark brown), 1·00 ml of gold was equivalent to 10 ml of copper diethyldithiocarbamate, which indicates that a 1:1 chelate of gold with diethyldithiocarbamate is formed.

Radiotracer solutions. Used for direct interference studies and prepared by irradiation of the corresponding elements (or their chlorides or sulphates) in a flux of 6 × 10^{11} neutrons.cm^{-2}.sec^{-1} for 6 hr (Universities of Manchester and Liverpool Research Reactor).

Irradiation

The test samples were weighed (see Table IV), sealed in quartz ampoules (rocks) or wrapped in spectrographically-tested analytical reagent grade aluminium foil (lead, kale and silicon) and irradiated in a reactor simultaneously with an appropriate amount of gold standard. The time of irradiation (24 hr to 5 days), reactor flux (6 × 10^{11} to 6 × 10^{12} neutrons.cm^{-2}. sec^{-1}) and time of cooling (usually *ca.* 1 day) were chosen according to the content of gold expected. For irradiation the Harwell reactors BEPO and DIDO and the Universities of Manchester and Liverpool Research Reactor were used.

Development of Method

All preliminary experiments were carried out using 1·05 × 10^{-2} *M* gold carrier solution and 4·83 × 10^{-4} *M* copper diethyldithiocarbamate solution in chloroform. With the exception of the direct interference studies, the solution of gold carrier was labelled with ^{198}Au which contained a negligible amount of isotopic carrier.

Reproducibility

The optimum acidity for the substoichiometric separation of gold was first investigated. To a series of 100-ml separatory funnels, containing 25 ml of different concentrations of sulphuric or hydrochloric acids or of water alone, 0·5 ml of labelled gold carrier solution was added; the pH of the resulting solutions was adjusted by adding dilute aqueous ammonia and/or small amounts of 0·1*M* acetate or borate buffer solutions to reach different values in the pH range 0–8·5. After adding 3·0 ml of copper diethyldithiocarbamate solution, the extraction was carried out for 3 min. The activities of equal volumes (2·0 ml) of the chloroform layer were measured in the scintillation counter and plotted against the acidity of the extracted solution. From the curve obtained (Fig. 1) it can be seen that a reproducible substoichiometric separation can be achieved over a very wide range of acidity (0·01–10*N* hydrochloric or sulphuric acid). For all further experiments a medium of 1·5 ± 1*N* hydrochloric acid was chosen.

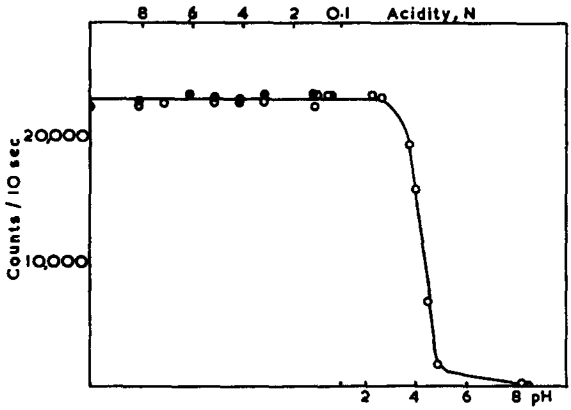

Fig. 1.—Influence of acidity on the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform (60% stoichiometry):
●—hydrochloric acid,
○—sulphuric acid.

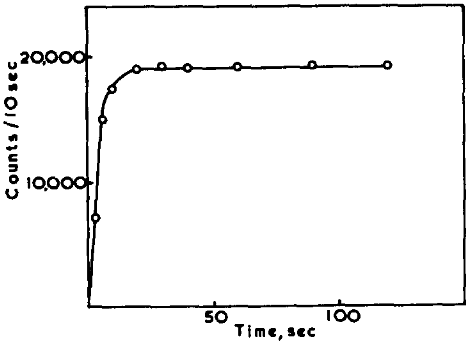

Fig. 2.—Time necessary for reaching extraction equilibrium in the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform (1·5 ± 1*N* hydrochloric acid; 80% substoichiometry).

The time necessary for reaching extraction equilibrium, which also ensures the reproducibility of the substoichiometric separation, was ascertained by extraction of gold for different times from 25 ml of 1·5 ± 1*N* hydrochloric acid, containing 0·5 ml of labelled gold carrier solution, using 4·0 ml of copper diethyldithiocarbamate solution as the extractant. From Fig. 2, where the activities of the obtained extracts are plotted *vs.* time of shaking, it can be seen that extraction equilibrium is reached within 20 sec and that the extract is unaffected by prolonged shaking. For all further experiments an extraction time of about 1 min was chosen.

Finally, the reproducibility of the substoichiometric separation was tested in the following way. A series of solutions of 1·5 ± 1*N* hydrochloric acid, containing precisely known, increasing amounts of labelled gold carrier solution, were simultaneously extracted with 4·0 ml of copper diethyldithiocarbamate solution for about 1 min. The activity of the extracts was measured as before and plotted against the amount of gold originally present in the aqueous phase. From the graph obtained (Fig. 3) it can be seen that after reaching the equivalence point very good reproducibility of the substoichiometric separation was achieved.

Selectivity

The selectivity of the substoichiometric separation was studied using direct and indirect methods. In both cases only the influence of those metals the extractability of which is higher or similar[19,21] to that of copper diethyldithiocarbamate were tested. The investigation of metals which do not form extractable diethyldithiocarbamates (Na, K, Ca, Sr, rare earths, *etc.*) or form chelates of very low extractability (Zn, Ga, Tl, Mn, Fe, *etc.*) is unnecessary.

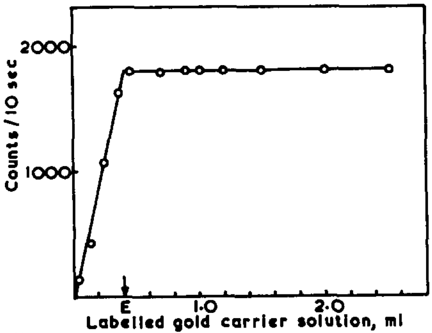

FIG. 3.—Reproducibility of the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform (E denotes the equivalance point).

TABLE I.—INTERFERENCE WITH THE EXTRACTION* OF GOLD BY COPPER DIETHYLDITHIOCARBAMATE IN CHLOROFORM CAUSED BY THE ADDITION OF INACTIVE ELEMENTS OR OTHER SPECIES.

Element of other species added	Activity of extract,† *counts*/10 *sec*
—‡	23118
Platinum(IV) (2 mg)	23184
Tin(II) (2 mg)‡	300
Tin(IV) (1 mg)	24424
Indium(III) (2 mg)	23345
Antimony(III) (2 mg)	22475
Antimony(V) (1 mg)	24904
Arsenic(III) (2 mg)	24108
Arsenic(V) (1 mg)	24424
Molybdenum(VI) (4 mg)	24108
Palladium(II) (1 mg)	19720
Palladium(II) (2 mg)	12390
Lead(II) (3 g in 1*N* HNO_3)	23830
0·1 ml of 5 vol. H_2O_2	23178
1·0 ml of 5 vol. H_2O_2	23315
1·5*N* HNO_3 (no HCl present)	22835
1 ml of 40% HF	22950
0·5 ml of 70% $HClO_4$	22410
1 ml of 70% $HClO_4$	22740

* All extractions made from 1·5 ± 1*N* HCl unless otherwise stated.

† All activities corrected for background and decay.

‡ No H_2O_2 present

The indirect interference studies were based on the detection of any depression of the gold activity extracted as diethyldithiocarbamate, caused by the presence of various other metal ions in the original aqueous solution. In these experiments labelled gold carrier solution was mixed with the corresponding (by weight) amounts of foreign metal ions or other species (Table I) in 1·5 ± 1*N* hydrochloric acid with the addition of 1 ml of 5 vol. hydrogen peroxide solution. From the activities of the extracts obtained it can be seen that the method proposed is very selective: only palladium and tin(II) interfere. The interference of the latter is caused by reduction of the gold to the metallic state, which can easily be avoided by adding hydrogen peroxide. Comparatively large amounts of nitric acid, hydrofluoric acid, perchloric acid or hydrogen peroxide do not destroy the extractant and so can be tolerated. This is important because these species may of necessity be present in the aqueous phase obtained when dissolving test matrices.

The direct interference studies were based on using microgram or submicrogram amounts of radioisotopes of the foreign ions. These radiotracers were mixed with a non-active isotopic gold carrier solution and substoichiometric extractions carried out. The selectivity of separation, carried out from 1·5 ± 1*N* hydrochloric acid in the presence of 5 vol. hydrogen peroxide solution, is very high (Table II) and the results obtained in this way are in good agreement with indirect interference studies.

TABLE II.—INTERFERENCE WITH THE EXTRACTION OF GOLD BY COPPER DIETHYLDITHIOCARBAMATE IN CHLOROFORM CAUSED BY THE ADDITION OF RADIOACTIVE TRACERS*

Radioisotope added	^{110}Ag	^{76}As	$^{122+124}$Sb	^{64}Cu	^{197}Pt	^{99}Mo	^{203}Hg	^{109}Pd
Total activity added, *counts*/10 *sec*	41,394	159,465	228,330	312,576	1,170,162	1,441,261	226,314	225,700†
Activity of substoichiometric extract, *counts*/10 *sec*	14	29	313	32	272,720	292	127	19,027‡
Radioisotope extracted, %	0·03	0·02	0·14	0·01	23·3	0·02	0·06	8·4

* 2 mg of gold carrier present; interfering elements present in microgram amounts.

† One-twentieth of stated activity actually measured. Solution evaporated to dryness on standard aluminium planchet and counted on end-window Geiger-Müller counter.

‡ One-sixth of stated activity actually measured (see †).

Although platinum(IV) was not found to depress the extracted gold activity in the indirect interference studies (Table I), interference was obtained using labelled platinum(IV). This means that this metal must be extracted by another mechanism than that for gold; this conclusion was confirmed by an experiment in which, instead of using copper diethyldithiocarbamate in chloroform as the extractant, pure solvent (chloroform) was used alone. The same amount of radioactive platinum (*ca.* 23%) was still extracted. It will be shown later that, for nuclear reasons, the interference of platinum (and palladium) need only be considered if this metal is present in great excess compared to gold.

Dissolution procedures

To determine the losses of gold which can occur during dissolution of test samples,[23] the dissolution procedures detailed below were investigated using a non-irradiated matrix and a known amount of active gold (Table III).

Before their dissolution, any surface contamination was removed from the irradiated lead samples by careful leaching with dilute nitric acid and from the silicon samples with hydrofluoric and nitric acids.

Silicon and rocks. To the test matrix, placed in a 50-ml Teflon beaker, 1·00 ml of gold carrier solution was added and the matrix dissolved in a mixture of concentrated hydrofluoric (10 ml), hydrochloric (2 ml) and nitric (10 ml) acids. After the silicon had been fumed off, two evaporations were carried out with 5-ml portions of hydrochloric acid to a volume of about 1–2 ml in order to remove oxides of nitrogen.

Lead. To the test matrix, placed in a 500-ml conical flask, 1·00 ml of gold carrier solution was added and the matrix dissolved in a mixture of glacial acetic acid (5 ml) and 100 vol. hydrogen peroxide (*ca.* 15 ml, added in 0·5-ml portions with gentle warming between the additions). The resulting solution was evaporated almost to dryness and the evaporation repeated with 15 ml of 50% v/v hydrochloric acid plus 2 drops of concentrated nitric acid, then with 15 ml of 50% v/v hydrochloric acid alone. The residue was dissolved in the minimum volume of hot concentrated hydrochloric acid (3 g of lead requires *ca.* 150 ml of acid) to obtain a perfectly clear solution. This solution was diluted to twice its volume with water and allowed to stand in an ice-bath, whereupon

TABLE III.—INVESTIGATION OF DISSOLUTION PROCEDURES

Matrix	Weight, *g*	Activity of Au added, *counts*/10 *sec*	Activity of Au recovered, *counts*/10 *sec*	Recovery, %
Silicon	1	64373	60876	94
Lead	3	16287	15696	96*
Kale	1	30154	19232	64

* After extraction with diethyl ether.

lead chloride precipitated. The supernatant liquid was decanted into a 500-ml separatory funnel, the lead chloride being washed with two 10-ml portions of 25% v/v hydrochloric acid and the washings also added to the separatory funnel. The gold was then extracted, as the chloride, by two 50-ml portions of diethyl ether. Finally, the combined ether extracts were evaporated to dryness and the residue dissolved in 20–30 ml of 1·5 ± 1*N* hydrochloric acid.

Biological material (kale).[14] To the test matrix, placed in a 250-ml beaker, 1·00 ml of gold carrier solution was added, followed by 2 ml of 100 vol. hydrogen peroxide. The beaker was covered with a clock glass and 5 ml of concentrated sulphuric acid carefully added *via* the beaker lip, then the beaker contents swirled gently until effervescence ceased. Next 5 ml of concentrated nitric acid were added, the beaker again swirled gently, and finally 2 ml of 70% perchloric acid added. The covered beaker was heated until white fumes appeared, then allowed to cool appreciably before adding 20 ml of *aqua regia*. Heating was resumed and evaporation continued to the appearance of white fumes of sulphuric acid. The resulting clear solution, after cooling, was diluted to about 30 ml with 1·5 ± 1*N* hydrochloric acid.

Extraction procedures

The dissolved samples were diluted to 20–50 ml with water or acid so as to obtain a medium of 1·5 ± 1*N* hydrochloric acid, then transferred to 100-ml separatory funnels. After adding 0·5 ml of 5 vol. hydrogen peroxide, extraction was carried out with 7·0 ml of copper diethyldithiocarbamate solution for about 1 min. In the case of the biological material (kale), where only 64% recovery of gold was obtained after dissolution (Table III), a volume of 5·0 ml of extractant was used so as to be below the stoichiometric requirement. To the appropriate amount of irradiated gold standard (y_s), 1·00 ml of gold carrier solution was added and the gold extracted in exactly the same way as described above for the test solutions. In the case of the samples of rock W-1 (or other very impure test materials) the organic extract obtained must be washed with 1*N* hydrochloric acid and filtered to remove the last traces of aqueous phase. The activities of exactly the same volumes of separated organic extracts from the test (a) and standard (a_s) samples were measured using the scintillation counter; the amount of gold present in the test sample (y) was then calculated from the equation

$$y = y_s \frac{a}{a_s}.$$

RESULTS

The results obtained for the various test materials are summarised in Table IV. The reproducibility in the case of the silicon, lead and kale is good. The results for the analysis of the rock W-1 differ rather more, but the difference cannot be explained by the presence of radionuclides other than that of gold in the extracts; the decay measurements of these extracts confirmed their radiochemical purity (Fig. 4). In any case, the mean value of the present experiments is in good agreement with the results of other workers on the rock W-1.

The gold concentration of the gold-doped semiconductor-grade silicon, calculated on the basis of the equilibrium segregation coefficient for gold in silicon, is *ca.* 4 × 10^{-2} ppm. If this estimate were to be corrected for the Burton-Slichter layer,[33] because of the rather high crystal pulling speed employed in the preparation of this particular crystal of silicon, then a figure around that found by neutron-activation analysis would be obtained. There is little doubt that the latter figure is the more precise.

As expected, the gold content of the biological material (kale) is very low; the results are in excellent agreement with those of Morris and Gupte,[12] also obtained by neutron-activation analysis. From the close agreement of our results with the figure obtained by Hoste,[24] it seems that the dissolution procedure for the high-purity lead developed by us is fully satisfactory and isotopic exchange between carrier and radiogold formed by neutron activation has been completed.

DISCUSSION

The selectivity of the substoichiometric separation of gold using copper diethyl dithiocarbamate is very high. This fact, to be expected from theoretical considerations

TABLE IV

Sample	Gold-doped semiconductor-grade silicon (1153)*				
Weight, *g*	0·4472	0·5904	0·8949	1·0984	1·1429
Gold standard, *μg*	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	14613	14613	14613	14613	14613
Activity‡‡ from gold sample (*counts*/10 *sec*)	6149	9297	10985	14016	14625
Gold found, *μg*	$4·4 \times 10^{-2}$	$6·6 \times 10^{-2}$	$7·8 \times 10^{-2}$	$9·9 \times 10^{-2}$	$10·4 \times 10^{-2}$
ppm	$9·6 \times 10^{-2}$	$11·0 \times 10^{-2}$	$8·7 \times 10^{-2}$	$9·1 \times 10^{-2}$	$9·1 \times 10^{-2}$
Mean value, *ppm*			$9·5 \times 10^{-2}$		
Results of other authors, *ppm*			—		

Sample	High-purity lead (VM$_3$)†				
Weight, *g*	1·6350	2·0500	2·5120	3·2270	3·6130
Gold standard, *μg*	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	6932	6932	6932	6932	6932
Activity‡‡ from gold sample (*counts*/10 *sec*)	680	773	1315	1093	1673
Gold found, *μg*	$2·0 \times 10^{-3}$	$2·3 \times 10^{-3}$	$4·0 \times 10^{-3}$	$3·3 \times 10^{-3}$	$5·0 \times 10^{-3}$
ppm	$1·3 \times 10^{-3}$	$1·1 \times 10^{-3}$	$1·6 \times 10^{-3}$	$1·0 \times 10^{-3}$	$1·4 \times 10^{-3}$
Mean value, *ppm*			$1·3 \times 10^{-3}$		
Results of other authors, *ppm*			$1·0 \pm 0·4 \times 10^{-3}$ (ref. 24)		

Sample	Rock W-1‡			Dried leaves of kale (*Brassica oleracea*)¶‡‡‡		
Weight, *g*	1·0000	0·5000**	0·5000**	0·2000††	1·0006	1·0023
Gold standard, *μg*	$4·0 \times 10^{-2}$	$4·0 \times 10^{-2}$	$4·0 \times 10^{-2}$	$4·2 \times 10^{-2}$	$4·2 \times 10^{-2}$	$4·2 \times 10^{-2}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	15237	15237	15237	15237	11609	11609
Activity‡‡ from gold sample (*counts*/10 *sec*)	1940	3269	3288	82	720	794
Gold found, *μg*	$5·1 \times 10^{-3}$	$8·6 \times 10^{-3}$	$8·6 \times 10^{-3}$	$2·1 \times 10^{-4}$	$2·5 \times 10^{-3}$	$2·7 \times 10^{-3}$
ppm	$0·5 \times 10^{-2}$	$1·7 \times 10^{-2}$	$1·7 \times 10^{-2}$	$1·1 \times 10^{-3}$	$2·5 \times 10^{-3}$	$2·7 \times 10^{-3}$
Mean value, *ppm*		$1·1 \times 10^{-2}$***			$2·1 \times 10^{-3}$	
Results of other authors, *ppm*	$1·1 \times 10^{-2}$ (ref. 26)	$8·4 \times 10^{-3}$ (ref. 9)	$4·9 \times 10^{-3}$ (ref. 28)		$2·2 \times 10^{-3}$††† (ref. 12)	

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* Provided by Mullard Southampton Works, Southampton, England.

† Provided by Professor Dr. J. Hoste, University of Ghent, Ghent, Belgium.

‡ Provided by U.S. Geological Survey, Washington, D.C., U.S.A.

¶ Provided by Dr. H. J. M. Bowen, The University, Reading, England.

** Two equal aliquots from a l-g sample after dissolution.

†† This constituted a preliminary test. The sample was irradiated in a quartz ampoule and, apart from the gold carrier solution, half quantities of the reagents detailed in the dissolution procedure (p. 7) were used. The final evaporation was taken nearly to dryness and the residue taken up in 2 ml of concentrated hydrochloric acid plus 10 ml of water. A 59% recovery of gold was obtained under these conditions (*cf.* Table III).

‡‡ All samples were counted for a period sufficient to obtain a total of at least 10,000 counts.

¶¶ The stated activities are the mean of two standards.

*** Obtained by averaging the results from the two 0·5-g "samples," then averaging this figure with the result from the l-g sample.

††† Average of $2·1 \times 10^{-3}$, $2·0 \times 10^{-3}$, $2·4 \times 10^{-3}$, $2·4 \times 10^{-3}$ ppm (ref. 12). Samples heated at 80° for *ca.* 4 hr before being weighed for analysis.

‡‡‡ Samples weighed without drying; material reported to have water content of 3–5%.

(see p. 830), has been confirmed not only by the preliminary studies (Tables I and II) but also by checking the radiochemical purity of the organic extracts obtained from the various test samples (Fig. 4). Furthermore, the high-purity lead is known to contain Ag, As, Cu, Hg, Sb and Tl in trace amounts (determined by neutron-activation analysis)[24] and the rock W-1 to contain Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, F, Ga, Ge, In, La, Li, Mo, Nb, Nd, Ni, Pb, Pd (0·02 ppm), Rb, Re, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, U, V, W, Y, Yb, Zn and Zr at trace levels (0·001 to 300 ppm) and large amounts of Fe, Mg, Ca, Na, K, Ti, P and Mn, the main constituents being SiO_2 and Al_2O_3.[29]

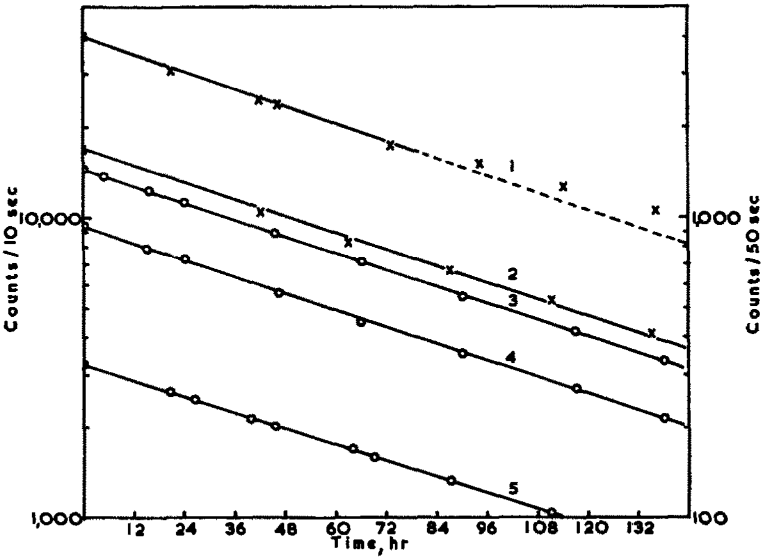

Fig. 4.—Typical decay curves of the chloroform extracts of gold diethyldithiocarbamate obtained from various irradiated materials (samples 1 and 2 refer to the right-hand vertical scale; samples 3–5 refer to the left-hand vertical scale; all extracts were measured for a period sufficient to obtain a total of at least 5,000 counts):

1—biological material (kale),
2—high-purity lead,
3—gold-doped semiconductor-grade silicon,
4—gold standard,
5—rock W-1.

It would appear from curve 1 that there is a long-lived component associated with the separated ^{198}Au activity. The nature of this component is (at this time) unknown, but we believe it will make very little difference to the results calculated for gold in kale.

As was mentioned above, platinum and palladium are extracted simultaneously with gold, but these elements are activated by thermal neutrons to a much lesser extent than is gold[7] and the half-lives of their radioisotopes formed by (n, γ) reactions are shorter than that of ^{198}Au (Table V). Moreover, by setting the discriminator level of the scintillation counter to the value corresponding to 0·25 MeV, allowing the activity to decay sufficiently for the ^{199}Pt to have disappeared, and still counting all the radiation above this level, the sensitivity of determination of gold is only slightly reduced and interference from platinum is almost completely avoided. (There will be a very small contribution from the 0·28 MeV γ-ray of 20 hr ^{197}Pt.) This precaution is only necessary in the case of a platinum matrix. Also, a method proposed by Morris and Killick[27] or its combination with the present method can be recommended with this matrix.

TABLE V[32]

Stable isotope	Product of (n, γ) reaction	Half-life	Principal γ-energies, *MeV*
$^{196}\mathrm{Pt}$	$^{197m}\mathrm{Pt}$	80 min	0·337
$^{196}\mathrm{Pt}$	$^{197}\mathrm{Pt}$	20 hr	0·077 (19%) 0·19 (2·5%) 0·28 (0·6%)
$^{198}\mathrm{Pt}$	$^{199}\mathrm{Pt}$	30 min	0·074 0·197 0·318 0·540
$^{108}\mathrm{Pd}$	$^{109}\mathrm{Pd}$	13·5 hr	—
$^{110}\mathrm{Pd}$	$^{111m}\mathrm{Pd}$	5·5 hr	0·17
$^{110}\mathrm{Pd}$	$^{111}\mathrm{Pd}$	22 min	—

Recently, a very simple substoichiometric radiochemical procedure for determination of gold by neutron-activation analysis has been published by Alimarin and Perezhogin.[30] This method, based on the extraction of gold chloride using tetraphenylarsonium chloride in chloroform solution, is especially interesting because it is the first substoichiometric separation to employ an extractable ion-association compound. Disadvantages of Alimarin and Perezhogin's method compared to that proposed in the present paper are that the separation is more affected by the presence of chloride ions (more than 0·5*N* hydrochloric acid cannot be used) and the volume of aqueous solution from which the extractions are made is relatively small (10 ml). Various high-purity metals (copper, zinc, lead, bismuth) were analysed by Alimarin and Perezhogin, but no interference studies were carried out.

CONCLUSION

Metallic salts of diethyldithiocarbamic acid in chloroform solution are very suitable for substoichiometric separations. Using these reagents it has been possible to develop substoichiometric methods for arsenic[31] and now gold; these separations are far simpler than previously published radiochemical procedures for the two elements. Unfortunately, quantitative extraction data (extraction constants) of metal diethyldithiocarbamates are still not available and for this reason it is not possible to calculate the theoretical optimum conditions for the separation and selectivity of the method now proposed for gold and to compare them with those conditions found experimentally. For the same reason, conditions for the substoichiometric determination of platinum, silver, mercury, thallium and tin by neutron-activation analysis cannot be predicted, although the extraction of these metals in the form of their diethyldithiocarbamates seems to be suitable for this purpose.

Our future work will be directed towards applying the solvent extraction of gold, using a substoichiometric amount of a metallic salt of diethyldithiocarbamate in an organic solvent, to the determination of trace amounts of gold by isotope dilution. This type of separation would also seem to have potentialities as a basis for the radiometric titration or spectrophotometric determination of gold.

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Zusammenfassung—Eine hochselektive, schnelle, einstufige radiochemische Abtrennmethode für Gold wurde entwickelt. Sie beruht auf flüssig-flüssig-Extraktion von Gold-diäthyldithiocarbamat aus 0,01 bis 10 N Schwefel- oder Salzsäure mit einer unterstöchiometrischen Menge Kupfer-diäthyldithiocarbamat in Chloroform. Die Abtrennung wurde auf die Bestimmung von Goldspuren durch Neutronenaktivierungsanalyse in hochreinem Blei, im Gestein W-1, in Gold-dotiertem Halbleitersilicium und in einer Probe von biologischem Material (Grünkohl) angewandt. Goldmengen bis herunter zu $2 \cdot 10^{-10}$ g wurden bestimmt.

Résumé—On a élaboré une technique de séparation radiochimique de l'or en un seul stade, hautement sélective et rapide. Elle est basée sur l'extraction par solvant du diéthyldithiocarbamate d'or à partir d'un milieu 0,01–10*N* en acide sulfurique ou chlorhydrique, en utilisant une quantité substoechiométrique de diéthyldithiocarbamate de cuivre en chloroforme. On a appliqué la séparation au dosage de traces d'or par analyse par activation de neutrons dans le plomb hautement pur, la roche W-1, le silicium qualité semi-conducteur dopé â l'or, et un produit biologique (chou vert). On a dosé des quantités d'or ne dépassant pas 2×10^{-10} g.

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DETERMINATION OF NITROGEN IN URANIUM-PLUTONIUM DIOXIDES

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Summary—Both mass spectrometric and chemical procedures have been used to determine the nitrogen in uranium-plutonium dioxides. An improved chemical procedure, involving dissolution of the oxide in sulphuric-phosphoric acid mixture, distillation of the ammonia in the presence of Devarda's alloy and spectrophotometric determination of the distilled ammonia, has been developed in this work.

INTRODUCTION

NUCLEAR fuels, based on mixtures or solid solutions of the dioxides of uranium and plutonium, are being proposed for use in fast reactors.[1] Very high fuel temperatures are encountered in these reactors and traces of nitrides, present in the fuels, may decompose to yield gaseous nitrogen. Such nitrogen may be deleterious, leading to fuel can pressurisation or nitriding of the canning material with the subsequent deterioration of its mechanical properties.[2] It is essential, therefore, that close control should be kept over the nitrogen content of fuel material.

Two approaches to the measurement of nitrogen in uranium-plutonium dioxides have been made. The first involves heating the oxide to high temperatures and then measuring the amount of nitrogen released; the second involves the determination of nitrogen by chemical procedures.

PRELIMINARY EXPERIMENTS

Samples of oxide materials (about 1 g) were heated in a mullite tube using a wire-wound furnace. The tube was connected to the inlet of an A.E.I. MS3 mass spectrometer and the evolution of gas was followed by mass spectrometry. During the determination, the temperature of the sample was raised to about 1350° over a period of about 3 hr. The gases detected and measured included hydrogen, carbon dioxide, carbon monoxide and argon as well as the nitrogen.

The chemical determination of nitrogen was based on the classical Kjeldahl procedure. The samples of oxide were first dissolved in acid, any nitrogen present being converted to ammonia in the process. The ammonia was separated by distillation from an alkaline solution of the dissolved oxide. The ammonia in the distillate was determined by spectrophotometry using the phenol-hypochlorite reagent procedure.[3]

RESULTS AND DISCUSSION

Mass spectrometry work

Several different samples of uranium-plutonium dioxides were outgassed, as described above. The principal gases released were nitrogen and hydrogen (Fig. 1). The nitrogen released would consist of gaseous nitrogen absorbed or trapped in the oxide material plus the nitrogen released by decomposition of nitrides. The evolution of nitrogen appeared to start at about 900–1,000° and be complete by about 1,300–1,400°. Chemical analyses showed that the residual nitrogen content of the oxide material was very low, indicating that over 90% of the nitrogen in the fuel was released by this heat treatment. Further heat treatment of the sample failed to release any more nitrogen, thus agreeing with the chemical values.

The complete release of nitrogen is, at first sight, unexpected because the mononitride of uranium is relatively stable in vacuum at these temperatures and higher nitrides release nitrogen to form the mononitride.[4] Experiments have shown, however, that when samples of uranium-plutonium dioxide containing nitrogen are heated at 1400° for 3 hr at pressures of less than 5×10^{-3} torr, the oxygen-to-metal ratio falls from 2·00 to about 1·96 whilst the nitrogen falls from about 700 ppm to less than 20 ppm. Thus, it appears that oxidation of the nitride is occurring and that this is accomplished at the expense of the oxygen of the dioxide which is thus reduced to a hypostoichiometric compound.

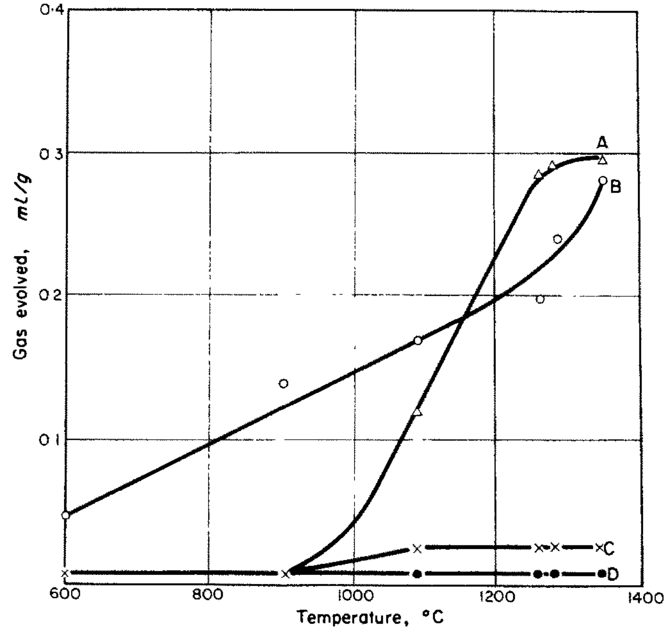

FIG. 1.—Gases evolved from mixed plutonium/uranium dioxides: A—nitrogen; B—hydrogen; C—carbon monoxide; D—hydrocarbons.

A comparison was made between the results obtained for nitrogen by vacuum treatment and nitrogen by the chemical procedure (Table I).

TABLE I.—NITROGEN CONTENT OF FUEL

Sample	Nitrogen, *ppm* (*w*/*w*) Vacuum extraction	Nitrogen, *ppm* (*w*/*w*) Chemical method
A	380	320
B	14	20
C	10	20
D	360	280
E	350	290

The agreement between the mass spectrometric results and the chemical values is reasonably good. It is noticeable that the mass spectrometric figures are invariably higher; this possibly represents nitrogen which is present in the fuel material as gaseous nitrogen and which would not be measured by the chemical procedure. Because the difference between the mass spectrometric and the chemical results are not thought significant, in terms of the risk of fuel cladding damage, it was considered that, for routine measurements, use should be made of the chemical procedure and the mass spectrometric procedure was not developed further.

Chemical determination

Initial work on the chemical determination of nitrogen in uranium-plutonium dioxides involved dissolving the sample in hydrochloric acid in the presence of copper selenate and hydrofluosilicic acid, as recommended by Lathouse *et al.* for uranium dioxide.[5] After dissolution, the ammonia was separated by distillation, from an alkaline solution of the dissolved sample, and determined in the distillate by the phenol-hypochlorite method.[3] It was found that the dissolution stage was lengthy, and low recoveries (60–80%) were obtained with synthetic samples of uranium-plutonium dioxide containing the higher nitrides of uranium.

TABLE II.—EFFECTS OF COPPER SELENATE ON RECOVERY OF NITROGEN FROM SULPHURIC/PHOSPHORIC ACID MIXTURE

Duration of heating,* *min*	Recovery of nitrogen,† %	
	Copper selenate (200 mg) present	No copper selenate present
1	99	100
10	88	100
20	50	99
30	5	100

* The temperature was such that white acid fumes were just being evolved.

† The recoveries obtained by adding 250 μg of nitrogen, as ammonium chloride, to each experiment.

The absolute values of the nitrogen levels in the standards were determined (a) by calculation from the thermogravimetric weighings made during the preparation of the nitrides and (b) from measurements on the nitrides by the Dumas procedure.

It was considered that the low recovery may have been the result of incomplete conversion of nitrogen to ammonia during the dissolution stage. The addition of Devarda's alloy to the alkaline solution of sample just before the ammonia distillation was incorporated into the procedure and increased the recovery of nitrogen to between 70 and 90%. Attempts to speed the dissolution rates of the oxides by adding various substances such as peroxides, *etc.*, were only marginally successful.

An alternative acidic solvent, consisting of equal quantities of concentrated phosphoric acid and 9*M* sulphuric acid, dissolved the samples much more rapidly; the time required was 5–45 min compared with up to 4 hr for the Lathouse procedure. A limited number of checks showed that while the addition of copper selenate to the hydrochloric acid improved the recovery of nitrogen, it effected little or no improvement on the recovery from phosphoric-sulphuric acid mixtures. Prolonged heating of the phosphoric-sulphuric mixtures at high temperatures with copper selenate present was found to be detrimental (Table II) and this loss of nitrogen due to selenium, noted by other workers,[6,7] may have contributed to the low recoveries experienced with the hydrochloric acid dissolution procedure. Under optimum conditions, with no copper selenate present, the recoveries were always greater than 95% of the theoretical value for samples containing the mono, sesqui and dinitrides of uranium.

Experiments showed that the addition of Devarda's alloy before the distillation stage was still essential if the maximum recovery of nitrogen was to be effected.

An improved chemical procedure was developed for the measurement of the nitrogen in solid solutions of uranium-plutonium dioxides; this is given below.

EXPERIMENTAL

Reagents

Sulphuric-phosphoric acid. Add 500 ml of concentrated (s.g. 1·75) phosphoric acid (analytical reagent grade) to 250 ml of ammonia-free water. To this mixture add 250 ml of concentrated (sp.gr. 1·84) sulphuric acid (analytical reagent grade).

Sodium hydroxide. 25% w/w aqueous solution (analytical reagent grade).

Sodium hypochlorite solution. 1% available chlorine.

Devarda's alloy. Finely powdered.

Sodium phenate solution. To 220 ml of an aqueous phenol solution (60 g of phenol/l.) add 25% sodium hydroxide solution until a pH between 11·9 and 12·1 is attained. Add 5 ml of acetone and dilute the solution to 250 ml with water. Store in a dark bottle. Prepare fresh reagent daily.

Hydrochloric acid. Approximately 0·004M aqueous solution.

Procedure for determination of nitrogen in uranium-plutonium dioxides

Weigh out accurately about 1 g of the oxide sample into a 150-ml flask. Add 10 ml of sulphuric-phosphoric acid mixture. Heat the flask until the sample has dissolved (5 to 45 min). Transfer the sample to a 10-ml volumetric flask, dilute to 10 ml with water and mix.

Add 50 ml of sodium hydroxide solution to the distillation flask of a Kjeldahl nitrogen distillation apparatus, add 0·1–0·2 g of Devarda's alloy into the tap funnel and wash it into the flask with 40–50 ml of the water. Distil until 40 ml of distillate has been collected and apply the colour development procedure as below. If more than negligible amounts of ammonia are found, add 50-ml aliquot(s) of water and repeat distillation(s) until there are negligible amounts of ammonia in the distillate. Add an aliquot ($\not>$5 ml) of the sample solution, which should contain approximately 200 μg of nitrogen, to the tap funnel (*Note* 1). Run it into the distillation flask, washing it in with 10–15 ml of water, taking care to ensure that any liberated ammonia does not escape from the apparatus. Add 0·3–0·5 g of Devarda's alloy to the distillation flask, *via* the tap funnel, and wash it in with 30–40 ml of water, again taking care that ammonia does not escape. Distil the contents of the flask into a receiver containing 5 ml of 0·004M hydrochloric until about 50 ml of distillate have been collected. Add 50 ml of water to the distillation flask and continue the distillation until the volume of the distillate is about 95 ml. Dilute the distillate to 100 ml and mix thoroughly.

Pipette a 10·0-ml aliquot into a 25-ml flask. Add 10·0 ml of sodium phenate; mix and then add 3·0 ml of sodium hypochlorite solution, dilute to 25 ml with water and mix again. Wait for between 20 and 40 min to allow the blue colour to develop fully. Measure the absorbance of the resultant solution using a Spekker absorptiometer equipped with Kodak No. 7 filters and 2-cm cells (*Note* 2).

Determine the reagent "blank" by carrying out the whole procedure with the sample omitted. This is typically 1 μg of nitrogen in 10 ml of distillate, *i.e.*, equivalent to 20 μg of nitrogen/g of sample.

Calibrate the Spekker absorptiometer by applying the colour development procedure directly to a standard ammonium chloride solution.

Note 1. The sample should not exceed 5 ml to ensure that when the sodium hydroxide is added for the ammonia distillation it does, in fact, represent a substantial excess of alkali.

Note 2. For the amounts taken, a 2-cm cell is better than 1-cm or 4-cm cells. Unit absorbance corresponds to about 33 μg of nitrogen.

Sensitivity and precision

Both the coefficient of variation and the bias of the results by the chemical method are less than 10% when the recommended amount of nitrogen is taken. The limit of detection is about 20 μg of nitrogen gram of sample. This is adequate for the intended application but it is thought that both the sensitivity and precision could be improved if necessary.

Zusammenfassung—Massenspektrometrische und chemische Verfahren wurden zur Stickstoffbestimmung in Dioxyden von Uran und Plutonium verwendet. Eine verbesserte chemische Arbeitsvorschrift mit Lösen des Oxyds in Schwefelsäure-Phosphorsäure, Destillation des Ammoniaks in Gegenwart von Devardascher Legierung und spektralphotometrische Bestimmung des abdestillierten Ammoniaks, wurde in dieser Arbeit entwickelt.

Résumé—On a utilisé la spectrométrie de masse et des méthodes chimiques pour doser l'asote dans des bioxydes d'uranium-plutonium. On a développé, au cours de ce travail, une méthode chimique améliorée comprenant la dissolution de l'oxyde dans un mélange acide sulfurique-acide phosphorique, la distillation de l'ammoniac en présence d'alliage de Devarda et le dosage spectrophotométrique de l'ammoniac distillé.

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DETERMINATION SEMIMICROVOLUMETRIQUE DES BASES ORGANIQUES AU MOYEN DU LAURYLSULFATE DE SODIUM

INFLUENCE DES GROUPEMENTS FONCTIONNELS

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Résumé—La formation de laurylsulfates de bases organiques azotées extractibles par un solvent organique non miscible au milieu aqueux réactionnel a permis de fonder un procédé de dosage applicable à un grand nombre d'amines et d'ammoniums quaternaires. L'étude systématique met en évidence l'influence de divers facteurs qui limitent le domaine d'application de la méthode: poids moléculaire de la base qui doit être au moins égal à 200 et présence dans la molécule d'autres groupements fonctionnels; parmi ceux-ci, la présence d'une deuxième fonction basique ou bien de fonctions à caractère hydrophile et notamment hydroxylées ne permet pas d'appliquer le procédé. L'ensemble des résultats obtenus permet de délimiter le domaine d'application de la méthode et de prévoir les possibilités d'extension à d'autres composés.

De nombreuses bases organiques et certains colorants basiques forment avec l'anion laurylsulfate des sels extractibles par un solvant organique non miscible au milieu aqueux réactionnel. Cette propriété a été mise à profit pour la détermination semimicrovolumétrique des bases organiques par de nombreux auteurs, au particulier Aoki et Iwayama,[1] Barr, Oliver et Stubbings,[2] Carkhuff et Boyd,[3] Epton,[4] Harper, Elliker et Moseley,[5] Igawa et Kimura,[6] Yoda et Coll.[7] La mise au point d'un procédé et son application systématique à divers types de bases organiques, isolées ou présentes dans des mélanges pharmaceutiques ont été rapportées par Pellerin, Gautier et Demay.[8–10] Demay[11] a de plus étudié le mécanisme de la réaction et précisé la nature saline des laurylsulfates de bases organiques ou de colorants formés.

Le principe des méthodes réside dans la formation du laurylsulfate de base organique.

$$\underset{\text{Solvant}}{[\text{Base organique}]^+} + \underset{H_2O}{[\text{Laurylsulfate}]^-} \rightarrow \underset{CHCl_3}{\text{Laurylsulfate de base organique.}}$$

Lorsque les deux antagonistes ont réagi en proportion stoechiométrique, la formation d'un sel entre le colorant et un léger excès d'anion laurylsulfate se traduit par un changement de teinte dans la phase chloroformique. Il s'établit, au cours du titrage, une compétition entre la base et le colorant pour l'anion laurylsulfate. Lorsque la formation du laurylsulfate de base précède celle du colorant, le virage de celui-ci coincide avec l'atteinte du point d'équivalence. La méthode est alors directement applicable. L'étude systématique d'environ 150 bases organiques a montré qu'il n'en va pas toujours ainsi. On observe en effet avec certaines bases organiques un virage prématuré de l'indicateur ne correspondant pas à la formation stoechiométrique du sel; parfois même, l'anion laurylsulfurique se combine directement avec le colorant, provoquant ainsi le virage dès la première affusion de solution anionique titrante et rendant ainsi la méthode inapplicable.

Le présent mémoire a pout objet de préciser les causes des échecs enregistrés. Parmi les nombreux facteurs susceptibles d'intervenir il était légitime d'attribuer une part de responsabilité à la basicité propre des composés essayés et à leur poids moléculaire; l'aptitude à la formation de sel extractible est en effet d'autant plus prononcée que le poids moléculaire de la base salifiante est plus élevé;[8,11] de même Johnson et King[12] ont élargi le domaine d'application du procédé en opérant en milieu tamponné et en choisissant un anion salifiant plus lourd. L'expérience a toutefois montré que ces facteurs ne sont pas les seuls à intervenir. La nature des groupements fonctionnels présents en plus de la fonction basique dans la molécule est le plus souvent à l'origine des échecs de la méthode; en particulier, les groupements fonctionnels hydrophiles ou la présence de deux ou plusieurs fonctions basiques diminuent ou empêchent à des degrés divers le passage du sel dans la phase chloroformique. Le laurylsulfate de colorant est extrait le premier par le solvant organique ce qui provoque le virage; la formation du laurylsulfate de base organique n'est pas pour autant exclue; Demay[11] a en effet isolé quelques-uns d'entre eux par d'autres voies. Les résultats obtenus mettent en lumière la nature et l'influence plus ou moins forte des fonctions inhibitrices; ils permettent de plus d'édicter quelques règles expérimentales simples et de prévoir les possibilités d'application de la méthode en fonction des bases organiques à doser.

PARTIE EXPERIMENTALE

Reactifs

Solution aqueuse 0,01*M de laurylsulfate de sodium.* Cette solution renferme 2,883 g de laurylsulfate de sodium pur pour analyses pour un litre. Si l'on ne dispose pas d'un échantillon de pureté garantie, l'étalonnage de la solution peut être effectué au moyen d'une base organique de pureté garantie (par exemple, chlorure de benzéthonium, papavérine).

Solution acido-alcoolique de jaune de méthyle (p-*diméthylaminoazobenzène*). Solution de jaune de méthyle à 0,01 pour cent dans l'éthanol à 95° . . . 10 ml

† Solution d'acide sulfurique au dixième (v/v) . . . 40 ml

Bases organiques de qualité pure pour analyses ou de qualité courante. Dans tous les cas, la teneur en base organique des échantillons utilisés a été contrôlée par une méthode de référence (protométrie dans l'acide acétique anhydre notamment).

N.B. La dénomination commune internationale préconisée par l'O.M.S. a été adoptée pour les bases organiques d'intérêt pharmaceutique.

Mode operatoire

Dans une fiole conique de 150 ml, introduire une prise d'essai p mg exactement pesée correspondant à 0.1 mequiv. Dissoudre dans 20 ml d'eau distillée ou de chloroforme selon la solubilité. Ajouter 20 ml de solvant (eau ou $CHCl_3$) non utilisé pour la dissolution et 5 ml de solution de colorant. Agiter jusqu'à ce que la phâse aqueuse devienne incolore et la phase chloroformique jaune. Titrer au moyen de la solution de laurylsulfate de sodium en agitant vigoureusement après chaque affusion jusqu'à obtention de la teinte rose orangée de virage.

RESULTATS

Lorsque le virage de l'indicateur coïncide avec la formation du laurlysulfate de base organique en proportion stoechiométrique, les résultats sont notés par + dans les différents tableaux; les divers composés sont titrables dans les conditions de la méthode. Dans le cas d'un virage prématuré de l'indicateur avant atteinte du point d'équivalence, le résultat est exprimé en pourcentage de formation du sel

$$\left\{\frac{\text{mequiv de laurylsulfate}}{\text{mequiv de base}} \times 100\right\}.$$

Le plus souvent le virage est étiré et les valeurs portées dans les tableaux correspondent à l'évolution de la teinte du milieu entre les deux limites. Parfois, pour un pourcentage de salification, inférieur à la théorie, le virage est net et reproductible; dans ce cas, le procédé est applicable au dosage à la condition toutefois d'effectuer parallèlement un étalonnage de la solution par rapport à un échantillon de référence. Enfin, lorsque le virage de l'indicateur se produit dès la première affusion de solution titrante les résultats ont été notés par O dans les tableaux. La comparaison des valeurs obtenues pour des composés voisins permet de mettre en évidence l'influence des divers facteurs qui conditionnent l'aptitude des bases organiques à former dans les conditions expérimentales de la méthode des laurylsulfates extractibles.

Ammoniums quaternaires

De nombreux cations organiques à fonction ammonium quaternaire forment avec l'anion laurylsulfate des sels quantitativement extractibles; le virage de l'indicateur est très net et correspond à la formation du sel attendu. Toutefois, le domaine d'application de la méthode à ces composés est limité par deux conditions:

—Poids moléculaire suffisamment élevé.

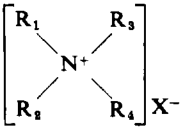
—Une seule fonction ammonium quaternaire dans la molécule à l'exclusion de toute autre fonction basique.

Poids moleculaire

Dans le cas des ammoniums *quaternaires aliphatiques* (tableau I) la méthode est applicable lorsquel'azote quaternaire est lié:

—Soit à 4 radicaux alcoyles identiques d'au moins 4 atomes de carbone.

TABLEAU I.—AMMONIUMS QUATERNAIRES ALIPHATIQUES



			Résultat
$R_1R_2R_3R_4$	$—CH_3$	Tétraméthylammonium	0 pour cent
	$—C_2H_5$	Tétraéthylammonium	0 pour cent
	$—C_3H_7$	Tétrapropylammonium	10–25 pour cent
	$—C_4H_9$	Tétrabutylammonium	+
$R_1R_2R_3$	$—CH_3$	Acétylcholine	0 pour cent
R_4	$—CH_2—CH_2—COOCH_3$		
$R_1R_2R_3$	$—CH_3$	Cétrimium	+
R_4	$—C_{16}H_{33}$		
R_1, R_2	CH_3	Dodécyldiméthyl carbetoxyméthyl ammonium	+
R_3	$—CH_2—(CH_2)_{10}—CH_3$		
R_4	$CH_2—COO—C_2H_5$		
$R_1R_2R_3$	CH_3	Triméthylstéaryl	+
R_4	$—CH_2—(CH_2)_{16}—CH_3$		

—Soit à 3 radicaux alcoyles identiques ou non, avec un ou plusieurs atomes de carbone et une longue chaîne.

C'est ainsi que les cations tétraméthyl et tétraéthylammonium ne consomment pas d'agent anionique, tandis que l'ion tétrapropyl en consomme une certaine quantité. Les ions tétrabutyl et laurylsulfate se combinent à environ 97 pour cent mais le virage de l'indicateur est étiré. L'atome d'azote de l'acétylcholine qui porte trois groupements méthyle et une chaîne en C_4 ne consomme pas d'agent anionique, alors que des molécules dont l'atome d'azote quaternaire est lié à 3 méthyle et une longue chaîne sont aisément dosées.

L'examen des résultats obtenus avec *les cations ammoniums quaternaires carbocycliques et hétérocycliques* met aussi en évidence l'influence du poids moléculaire (tableau II).

TABLEAU II.—AMMONIUMS QUATERNAIRES CARBOCYCLIQUES ET HETEROCYCLIQUES

Triméthylphénylammonium		0 pour cent
Thiazinamium	(triméthylammonio-2 propyl)10 phénothiazine	70 à 90 pour cent
Oxyphénonium	(cyclohexyl-2 hydroxy-2 phényl-2 acétoxy)-2 éthyl diéthyl méthylammonium	75 à 90 pour cent
Laurylpyridinium	Dodécyl-1 pyridinium	+
Cétyl pyridinium	Hexadécyl-1 pyridinium	+
Céthéxonium	(Hydroxy-2 cyclohexyl) hexadécyldiméthyl-ammonium	+
Propanthéline	Xanthène carboxylate-9 de (diisopropyl méthyl ammonio)-2 éthyle	+
Benzalkonium	Alcoylbenzyldiméthylammonium	+
Benzododécinium	Benzyldiméthyl dodécylammonium	+

Ainsi le triméthyl phénylammonium ne consomme pas de réactif titrant; la fixation sur l'atome d'azote quaternaire de chaînes plus longues ou de noyaux alourdissant suffisamment la molécule, se traduit par une augmentation de la consommation de réactif titrant nécessaire à l'obtention du virage. Par exemple, le thiazinamium et l'oxyphénonium consomment de 70 à 90 pour cent d'agent anionique et la propanthéline forme un sel quantitativement extractible.

Les ammoniums quaternaires à longue chaîne tels que le benzalkonium, le benzododécinium, le céthéxonium, les lauryl et cétylpyridinium etc. . . sont aisément titrables.

Composés a deux ou plusieurs fonctions basiques

La présence dans la molécule d'une deuxième fonction ammonium quaternaire ou d'une fonction amine constitue dans tous les cas un facteur d'échec de la méthode. C'est ainsi que les cations penta et hexaméthonium ne consomment pas de réactif titrant.

Pentaméthonium: $n = 5$

$$(CH_3)_3{\equiv}\overset{+}{N}{-}(CH_2)_n{-}\overset{+}{N}{\equiv}(CH_3)_3$$

Hexaméthonium: $n = 6$

D'après les résultats, il s'avère donc que le champ d'application de la méthode s'étend à tous les composés à fonction ammonium quaternaire—en particulier à tous les détergents cationiques—à la condition qu'ils ne renferment qu'une seule fonction ammonium quaternaire à l'exclusion de toute autre fonction basique et que le poids moléculaire soit suffisant.

Amines

En règle générale, les amines primaires et secondaires aliphatiques ou aromatiques ne peuvent être dosées au moyen du laurylsulfate dans les conditions expérimentales de la méthode; la consommation de réactif titrant est pratiquement nulle; il se produit tout au plus un virage très étiré de l'indicateur, qui ne permet pas de saisir le point d'équivalence et ne correspond pas à la salification de la base.

	Consommation de réactif titrant
Amphétamine	0·5 pour cent
Méphétédrine	50 á 70 pour cent
Benzocaïne	0 pour cent

Seules sont susceptibles d'être dosées les amines tertiaires à condition toutefois de répondre à certaines conditions que l'étude systématique de ces composés a permis de préciser: influence du poids moléculaire et des groupements fonctionnels présents dans la molécule. Le procédé a été à environ 120 composés le plus souvent d'intérêt pharmaceutique appartenant à diverses séries.

Influence du poids moleculaire

Nous n'insisterons pas sur le fait expérimental; aucune base organique de poids moléculaire inférieur à 200 ne peut être dosés même en l'absence d'autres groupements fonctionnels, tant en série aliphatique qu'aromatique ou hétérocyclique. Ainsi, la pyridine (P.M. = 79·1) ne consomme pas de réactif titrant, la triéthylamine (P.M. = 101,2) en consomme 1 à 4 pour cent et la diméthylaniline (P.M. = 121,2) 10 à 20 pour cent de la quantité théorique.

Dans le cas de la tributylamine (P.M. = 185,35) le virage de l'indicateur est reproductible mais ne correspond pas à la salification molécule à molécule.

Influence des groupements fonctionnels

L'aptitude à la formation de sel quantitativement extractible en phase organique entre l'anion laurylsulfurique et les amines tertiaires est souvent modifiée par certains groupements fonctionnels. La présence de ces fonctions perturbatrices dans des molécules de structure identique ou voisine, se traduit expérimentalement par une réduction ou une annulation de la consommation de réactif titrant.

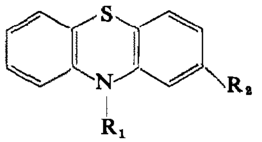
Fonctions amines. Deux cas peuvent être considérés selon que la deuxième fonction azotée, s'ajoutant à la fonction amine tertiaire, est ou non basique. La présence d'un atome d'azote non basique n'affecte pas la stoechiométrie de la réaction. Tel est le cas de l'azote du noyau phénothiazine; tous les dérivés de la phénothiazine renfermant une seule fonction amine tertiaire sont titrables et le point d'équivalence correspond à la réaction molécule à molécule de l'anion laurylsulfate avec la base considérée (tableau III).

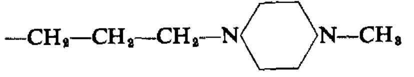
Il en va de même d'un composé tel que la réserpine dont l'atome d'azote du noyau indolique présente un caractère acide.

En revanche, la présence d'une deuxième fonction amine tertiaire perturbe la formation du sel extractible. Aucune exception à cette règle n'a été observée même lorsque les deux fonctions basiques sont sensiblement de même force.

Ainsi, dans le cas des dérivés de la phénothiazine, l'aminopromazine et la prochlorperazine consomment seulement environ 20 pour cent de réactif titrant, alors qu'avec les autres dérivés, le virage de l'indicateur correspond à la formation du sel. D'autres exemples illustrent l'influence perturbatrice d'une deuxième fonction amine tertiaire; quel que soit l'éloignement des deux fonctions basiques, quelle que soit la nature des fonctions amines tertiaires, aliphatiques, aromatiques ou hétérocycliques, la consommation de réactif titrant est nulle ou inférieure à la théorie (tableau IV). Lorsque la deuxième fonction basique est une amine primaire ou secondaire, le procédé tombe en défaut par exemple procaïne, butacaïne, tétrahydrazoline. A plus forte raison, on aboutit à des résultats identiques avec les polyamines telles que chloroquine, mépyramine, thiamine, strychnine ou la quinine. Demay a néanmoins[11] isolé le laurylsulfate neutre de quinine, formé d'une molécule de quinine et de deux molécules d'acide laurylsulfurique.

Tableau III.—Derives de la phenothiazine



	R_1	R_2	Résultat
Prométhazine	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-N-(CH_3)_2$		+
Promazine	$-CH_2-CH_2-CH_2-N(CH_3)_2$		+
Diéthazine	$-CH_2-CH_2-N(C_2H_5)_2$		+
Isothiazine	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-N(C_2H_5)_2$		+
Chlorpromazine	$-CH_2-CH_2-CH_2-N(CH_3)_2$	Cl	+
Acépromazine	$-CH_2-CH_2-CH_2-N(CH_3)_2$	$-\underset{\underset{\displaystyle O}{\Vert}}{C}-CH_3$	+
Levomepromazine	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-N(CH_3)_2$	$-O-CH_3$	+
Propiomazine	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-N(CH_3)_2$	$-\underset{\underset{\displaystyle O}{\Vert}}{C}-C_2H_5$	+
Alimemazine	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-N(CH_3)_2$		+
Aminopromazine	$-CH_2-\underset{\displaystyle N-(CH_3)_2}{\underset{\vert}{CH}}-CH_2-N(CH_3)_2$		20 pour cent
Prochlorpérazine		Cl	20 pour cent

En règle générale, parmi les autres fonctions azotées, la fonction amide ne modifie pas la réaction (benzoquinamide); il en va de même de la fonction nitrile (diphénoxylate).

TABLEAU IV.—COMPOSES POLYAMINES

Diméthylamino-2 diéthylamino éthoxy cyclohexane		1 pour cent
N phényl *N* benzyl diméthylaminopropanol		2 à 5 pour cent
N benzyl *N' N'* diméthyl *N* phényl éthylène diamine		20 à 25 pour cent
Amino-4 benzoate de diéthylaminoéthyle	Procaïne	0 pour cent
Amino-4 benzoate de dibutylaminopropyle	Butacaïne	5 à 10 pour cent
(Tétrahydro 1–2–3–4 naphtyl-1)-2 imidazoline-2	Tétrahydrozoline	4 à 6 pour cent
Chloro-7 (diéthylamino-4 méthyl 1 butylamino)$_4$ quinoléine	Chloroquine	5 à 10 pour cent
Np méthoxy benzyl *N'*, *N'* diméthyl *N*-(pyridyl-2) éthylènediamine	Mépyramine	5 à 10 pour cent
	Thiamine	0 pour cent
	Quinine	10 à 20 pour cent
	Strychnine	40 à 50 pour cent

Groupement fonctionnel hydroxylé. Le caractère hydrophile des fonctions phénol et alcool perturbe, à des degrés divers, l'extraction par la phase organique des laurylsulfates de bases organiques renfermant ces groupements fonctionnels. Avec les phénols notamment la consommation de réactif titrant est le plus souvent nulle.

	Consommation de réactif titrant
Hydroxy-8 quinoléine	0 pour cent
Hordénine	0,05 à 0,1 pour cent
Boldine	10 à 20 pour cent
Pyridoxine	0 pour cent

La fonction alcool est également gênante mais à un degré moindre que la fonction phénol; en effet, il subsiste toujours, pour des composés de poids moléculaire suffisant ne renfermant pas d'autres fonctions génantes que l'OH alcoolique, une consommation plus ou moins importante de réactif titrant.

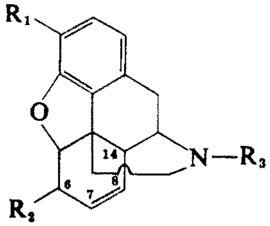
Dans le cas de la pyridoxine, la consommation nulle de réactif titrant est due essentiellement à la présence des trois fonctions hydroxylées: alcools et phénol.

Le cas des alcaloïdes du groupe de la morphine est particulièrement démonstratif de l'influence des fonctions phénol et alcool (tableau V). La morphine, la nalorphine et la dihydrone, dont les fonctions hydroxylées sont libres ne consomment pas ou peu de réactif titrant. Avec le remplacement de l'OH phénolique de la morphine par un méthoxy dans la codéine ou un éthoxy dans la codéthyline, la consommation de réactif titrant est de l'ordre de 10 à 30 pour cent. La thébaïne (diméthoxymorphine) qui ne renferme pas de fonction hydroxylée libre, forme un laurylsulfate quantitativement extractible et le virage de l'indicateur correspond à la formation du sel.

Dans la même série, la codéinone et l'hydrocodone consomment respectivement 25 à 40 pour cent et 40 à 55 pour cent de laurylsulfate en raison de leur énolisation en solution. En effet, si l'on forme le bromacétal de codéinone rendant ainsi l'énolisation impossible, on constate que la consommation de réactif correspond à la formation du sel.

Parmi les alcaloïdes à noyau isoquinoléique (tableau VI), la narcotine est titrable; en revanche, un de ses produits de dégradation, la cotarnine, consomme seulement 10 à 15 pour cent de réactif titrant; ce composé est en effet en solution sous différentes formes: hydrate d'amine, alcool et aldéhyde.

TABLEAU V.—ALCALOÏDES DU GROUPE DE LA MORPHINE



	R_1	R_2	R_3	
Morphine	—OH	—OH	$—CH_3$	0 pour cent
Nalorphine	—OH	—OH	$—CH_2—CH{=}CH_2$	0 pour cent
Codéine	$—OCH_3$	—OH	$—CH_3$	8 à 15 pour cent
Ethylmorphine	$—OC_2H_5$	—OH	$—CH_3$	20 à 30 pour cent
Thébaïne	$—OCH_3$	$—OCH_3$	$—CH_3$ doubles liaisons en 6–7, 8–14	+
Diamorphine	$CH_3COO—$	$CH_3COO—$	$—CH_3$	+
Codéinone	$—OCH_3$	=O	$—CH_3$	25 à 40
Bromacétal de	$—OCH_3$	$(OCH_3)_2$	$—CH_3$ saturé en 7–8 Br en 8	+
Dihydrone (oxycodone)	$—OCH_3$	=O	$—CH_3$ saturé en 7–8	8 à 15 pour cent
Hydrocodone	$—OCH_3$	=O	$—CH_3$ saturé en 7-8	40 à 55 pour cent

TABLEAU VI.—BASES ORGANIQUES DIVERSES

Noscapine		+
Narcotine		+
Cotarnine		10 à 15 pour cent
Atropine		25 à 40 pour cent
Tropanol		0,5 à 1 pour cent
Ephédrine		0,5 pour cent
Captodiamine (covatine) diméthylamino 2-éthylsulfure de *p* butylthiodiphénylméthyle		+
Benactyzine	Benzilate de diéthylamino-2 éthyle	+
Procyclidine	Cyclohexyl-1 phényl-1 (pyrrolidinyl-1)-3 propanol-1	+

Dans le groupe des alcaloïdes des dérivés ou voisins du tropanol, l'atropine renfermant la fonction alcool primaire libre de l'acide tropique consomme 25 à 40 pour cent de réactif titrant; le tropanol dont la fonction alcool secondaire est libre en consomme seulement 0,5 à 1 pour cent.

La comparaison des formules de l'éphédrine et de la méphétédrine de structure sensiblement identique et de poids moléculaires voisins met en évidence l'influence perturbatrice de la fonction alcool secondaire de l'éphédrine (0,5 pour cent de laurylsulfate employé au lieu de 50 à 70 dans le cas de la méphétédrine).

Enfin, d'après les proportions de laurylsulfate employé pour obtenir le virage, il semble que l'action perturbatrice de la fonction alcool tertiaire est plus faible que celle des fonctions alcools secondaire ou primaire; c'est ainsi que la bénactyzine et la procyclidine sont dosables avec toutefois pour la première un léger étirement du virage au point d'équivalence. Ceci constitue toutefois une exception et il nous semble raisonnable d'admettre que l'hydroxyle alcoolique est le plus souvent inhibiteur alors que l'hydroxyle phénolique l'est systématiquement.

Groupements fonctionnels méthoxy et éthoxy. Ces groupements fonctionnels n'exercent pas d'influence perturbatrice. Ce fait a déjà été mis en évidence précédement avec les bases organiques du groupe de la morphine ou de la narcotine. L'échec de la méthode dans le cas de la boldine est à rapporter aux fonctions phénols.

Groupement fonctionnel carbonylé. La fonction cétone ne paraît pas gênante dans la mesure ou il ne se produit pas d'énolisation (cas de la codéinone cité précédemment). Le paradiméthylaminobenzaldéhyde ne consomme pas de réactif titrant alors que la diméthylaniline qui ne diffère du précédent que par l'absence du groupement—CHO consomme 10 à 20 pour cent de laurylsulfate; il semble donc que la fonction aldéhyde inhibe le passage du sel en phase organique.

Fonction ester. En règle génerale, la fonction ester n'est pas gênante. Un grand nombre d'amines tertiaires renfermant ce groupement fonctionnel dans leur molécule sont dosables et le virage de l'indicateur correspond à la formation du laurylsulfate de base organique en proportion stoechiométrique; quelques résultats empruntés à diverses séries chimiques sont indiqués dans le tableau VII.

TABLEAU VII.—BASES ORGANIQUES A FONCTION ESTER

Pethidine	Méthyl-1 phényl-4 pipéridinecarboxylate-4 d'éthyle	+
Amyléine	Benzoate de (diméthylaminométhyl)-1 méthyl-1 propyle	+
Paréthoxycaïne	Ethoxy-4 benzoate de diéthylamino-2 éthyle	+
	Propylphénylacétate de diéthyleaminoéthyle	+
Caramiphène	(diéthylamino-2 éthyl) phényl-1 cyclopentanecarboxylate 1	+
Adiphenine	diphénylacétate de diéthylamino-2 éthyle	+
Dicyclovérine	cyclohexyl-1 cyclohexane carboxylate-1 de diéthylamino-2 éthyle	+
Diphénoxylate	(cyano-3 diphényl-3,3 propyl)-1 phényl-4 pipéridinecarboxylate d'éthyle	
Cocaïne		25 à 40 pour cent
Benzquinamide (nom déposé)	acetoxy-2*N*,*N* diéthylcarbamyl-3 diméthoxy-9,10 hexahydro 1,2,3,4,6,7–ose bH-benzo(a) quinolisine	+ +

L'échec enregistré dans le cas de la cocaïne ne parait pas attribuable à la présence de deux fonctions esters. En effet, la diacétylmorphine qui renferme aussi ces deux fonctions se combine avec la laurylsulfate dans la proportion de 88 pour cent du résultat attendu avec un virage très net de l'indicateur.

En résumé, les principaux facteurs qui limitent le champ d'application du procédé semimicrovolumétrique de dosage des bases organiques au moyen du laurylsulfate de sodium sont le poids moléculaire et parmi les groupements fonctionnels: la présence d'une deuxième fonction basique ou d'un groupement fonctionnel à caractère hydrophile. Quelle que soit la base organique, le poids moléculaire doit être au moins éqal à 200.

Dans le cas des ammoniums quaternaires, la présence d'une deuxième fonction azotée rend la méthode inapplicable; les groupements fonctionnels à caractère hydrophile ne paraissent pas avoir d'incidence si une longue chaîne est présente dans la molécule. Dans le cas des amines, seules les amines tertiaires rentrent dans le cadre de l'application de la méthode; l'influence perturbatrice des fonctions hydrophiles-et notamment de la fonction hydroxyle-est particulièremment nette.

Par ailleurs, parmi les autres facteurs susceptibles d'intervenir, il convient de noter que l'influence de la basicité de la molécule est faible. En effet, des bases organiques de pK_b voisins sont titrables ou non.

D'autre part, lorsque la base organique à doser est à l'état de sel. (chlorhydrate, bromhydrate, nitrate, sulfates, maléate....) l'anion salifiant n'exerce aucune influence perturbatrice. Il en va de même, lorsque la base est salifiée par un acide alcool (citrate, tartrate, maléate), un acide aminé ou un composé azoté à caractère acide tel que la théophylline. L'effet inhibiteur des groupements fonctionnels ne s'exerce que s'ils sont fixés sur la molécule de base à doser.

Zusammenfassung—Auf Grund der Bildung von Laurylsulfaten organischer Stickstoffbasen, die sich durch ein mit Wasser nicht mischbares organisches Lösungsmittel aus wäßriger Lösung extrahieren lassen, wurde eine Arbeitsvorschrift zur Bestimmung einer großen Anzahl von Aminen und Ammoniumverbindungen entwickelt. Eine systematische Untersuchung erhellte den Einfluß verschiedener Faktoren, die den Anwendungsbereich der Methode begrenzen: das Molekulargewicht der Base sollte wenigstens 200 betragen; andere funktionelle Gruppen im Molekül müssen berücksichtigt werden; eine zweite basische Gruppe oder hydrophile, speziell Hydroxylgruppen, schließen die Anwendung der Methode aus. Die Ergebnisse zeigen die Grenzen des Anwendungsbereiches der Methode und Möglichkeiten zur Ausdehnung auf andere Verbindungen.

Summary—The formation of lauryl sulphates of nitrogenous organic bases extractable from aqueous solution by a non-miscible organic solvent has given the basis of a procedure for the determination of a large number of amines and ammonium compounds. A systematic study has revealed the influence of several factors which limit the field of application of the method: the molecular weight of the base which should be at least 200, and the presence in the molecule of other functional groups; amongst the latter the presence of a second basic function or of functions of a hydrophilic nature, particularly hydroxyl, precludes the application of the method. The body of results obtained allows the limits of application of the method to be indicated and suggests possibilities for its extension to other compounds.

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SHORT COMMUNICATIONS

Investigation of cation-exchange behaviour of molybdenum (VI) in aqueous and ethanolic solutions of hydrochloric acid

(*Received* 4 *November* 1964. *Accepted* 21 *February* 1965)

THERE are a small number of papers treating the sorption of ions from mixtures of water and some organic solvents.[1–10] It was found by certain authors[8] that the use of such mixed media increases the sorption and often the degree of ion separation.

The aim of the present study was to investigate the ion-exchange behaviour of molybdenum in aqueous and ethanolic solutions of hydrochloric acid with the cation-exchanger Ku-2 × 8.

EXPERIMENTAL

Reagents

Ion-exchange resin. The strongly acidic cation-exchanger Ku-2 × 8 in the acid form is used. Remove iron by washing with 2*M* hydrochorlic acid, wash out excess acid and air dry.

Molybdenum solution. Dissolve sodium molybdate dihydrate "pro analysi", to give 1 mg/ml of molybdenum.

Rhodamine B

Ethyl alcohol. Absolute alcohol "pro analysi".

Apparatus

Spectrophotometer. Φ3K-M spectrophotometer with a blue light filter is used.

Determination of distribution coefficient

Place 0·2 g of the resin in a flask and add 20 ml of solution containing 1 mg of molybdenum, hydrochloric acid (between 0·01 and 4*M*) and ethanol (between 20 and 80%). Shake mechanically until equilibrium is established; this usually takes about 3 hr. Take an aliquot part of the solution and determine the unadsorbed molybdenum by the rhodamine B method. The difference between the initial quantity of molybdenum and the quantity found in the solution after the establishment of equilibrium, gives the quantity of molybdenum adsorbed by the resin under the given conditions. Thus, it is possible to compute the distribution coefficient (Kd).

TABLE I.—THE SORPTION OF MOLYBDENUM(VI) ON Ku-2 × 8 FROM MIXED MEDIA (HCl-WATER-ETHANOL)

HCl, *M*	0·01	0·05	0·1	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0
EtOH, %	Sorption, %										
None	31·43	28·00	20·00	2·5	5·0	5·0	15·0	22·5	40·0	45·0	52·5
20	54·29	38·00	30·00	2·5	5·0	5·0	15·0	20·0	52·5	65·0	77·5
40	62·86	48·00	32·00	2·5	10·0	15·0	30·0	37·5	60·0	48·0	57·5
60	60·72	48·00	32·00	2·5	12·5	2·5	20·0	20·0	65·0	45·0	67·5
80	62·86	50·00	40·00	2·5	15·0	22·5	30·0	—	—	—	—

RESULTS AND DISCUSSION

From Table I it can be seen that with increasing concentration of the hydrochloric acid from 0·01 to 0·5*M*, in the absence of ethyl alcohol, sorption decreases, but when the acid concentration is further increased from 0·5 to 4·0*M*, an increase in the sorption of molybdenum is observed. This behaviour can be explained by the change of anionic molybdenum to a cationic form with acidity according to the equation

$$MoO_4^{2-} + 4H^+ \rightleftharpoons MoO_2^{2+} + 2H_2O.$$

Between 3 and 4*M* hydrochloric acid, an average of 45% of MoO_2^{2+} is sorbed.

The next experiments were carried out under the same conditions, with the difference that a gradually increasing quantity of ethyl alcohol was added to the system, in order to investigate its influence. It was found (Table I) that the variation of sorption with acidity was similar to that from aqueous solutions, but that at a given acidity the adsorption generally increased with the percentage of ethanol.

This phenomenon can be explained in the following way. The dielectric constant of the solvent decreases as the percentage of ethanol increases, so the resin will swell to a lesser degree. The distortion of the resin is less and the selectivity greater. In this case also, water molecules in the hydration shell of the ions are displaced by ethanol and this leads to increased sorption.

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Summary—The sorption of molybdenum(VI) onto Ku-2 × 8 cation-exchange resin in the hydrogen form from hydrochloric acid (0.01–4*M*) in the presence and absence of ethanol (20–80%) has been investigated.

Zusammenfassung—Es wurde die Zusammenwirkung unter dem Molybdän (VI) und dem Kationaustauscher Ku-2 × 8 mit H-Kation in Zusammenhang mit der HCl-Konzentration (von 0,01–4*N*) in Ab- und Anwesenheit von Äthylalkohol in der Konzentrationsgrenze 20–80%, untersucht.

Résumé—L'auteur examine l'attitude du molibdène (VI) dans les échangeurs de cations Ku-2 × 8 en forme H, par rapport à la concentration de l'acide chlorhydrique (de 0,01 à 4*N*) en absence et en présence de l'alcohol éthylique dans les limites de 20 à 80%.

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Potentiometric titration of quaternary ammonium iodide salts

(*Received* 26 *April* 1965. *Accepted* 12 *June* 1965)

BECAUSE of the importance of some quaternary ammonium iodide esters, such as the choline or thiocholine iodide esters, as substrates for cholinesterase, there developed a need in these laboratories for a simple, rapid method of accurately determining the purity of such compounds.

RESULTS AND DISCUSSION

From Table I it can be seen that with increasing concentration of the hydrochloric acid from 0·01 to 0·5*M*, in the absence of ethyl alcohol, sorption decreases, but when the acid concentration is further increased from 0·5 to 4·0*M*, an increase in the sorption of molybdenum is observed. This behaviour can be explained by the change of anionic molybdenum to a cationic form with acidity according to the equation

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This phenomenon can be explained in the following way. The dielectric constant of the solvent decreases as the percentage of ethanol increases, so the resin will swell to a lesser degree. The distortion of the resin is less and the selectivity greater. In this case also, water molecules in the hydration shell of the ions are displaced by ethanol and this leads to increased sorption.

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Because of the importance of some quaternary ammonium iodide esters, such as the choline or thiocholine iodide esters, as substrates for cholinesterase, there developed a need in these laboratories for a simple, rapid method of accurately determining the purity of such compounds.

Very little has been reported in the literature on the titration of quaternary ammonium halide salts. Pifer and Wollish[1] described the potentiometric titration of the bromide and chloride salts of quaternary ammonium compounds in acetic acid with perchloric acid as titrant. The reaction was based on the conversion of the halide salt of the quaternary compounds to the corresponding acetate, using mercury(II) acetate in acetic acid. The acetate of the organic base was then titrated with 0·1*M* perchloric acid in dioxan. No iodide salts were tried by these authors.

Izmailov and Vail[2] reported the titration of mixtures of an inorganic iodide salt, such as ammonium iodide or potassium iodide, and an organic iodide salt, tetramethylammonium iodide, with silver nitrate in acetone or acetonitrile. Sharp inflection points were observed, but large deviations were obtained in the case of tetramethylammonium iodide.

Attempts to use the method of Pifer and Wollish for the titration of iodide compounds yielded low results (1–2% deviation), because of the oxidation of iodide to iodine during heating of the sample for dissolution in acetic acid. Preliminary experiments indicated that the sample could be easily dissolved in methanol first, followed by addition of acetic acid and mercury(II) acetate, and finally titrated with perchloric acid. Various organic iodides, such as tetrabutylammonium iodide, triethylmethylammonium iodide and tetrapropylammonium iodide (0·02–0·20 g) were analysed with a relative standard deviation of about 0·2%, with an accuracy (compared to results obtained using the Kolthoff modification of the Winkler method[3] or the Liepert procedure[4]) of better than 0·17%. However, the thiocholine iodide esters could not be determined because of large drifts in potential. These drifts are caused by hydrolysis, by the acids used, of the esters to the thiols and the corresponding acid. In the titration of acetylcholine iodide, spot tests with the reagent bis-dithionitrobenzoate[5] indicated the presence of thiol. It was found, however, that these compounds could be titrated with silver nitrate in aqueous solution, using a silver indicating electrode with deviations of about 0·2%. Using this technique, 2–20 mg of propionyl choline iodide, butyryl thiocholine iodide, 2-(*N*,*N*,*N*-diethylmethylammonium) ethyl butyrate iodide, 2-(*N*,*N*,*N*-diethylmethylammonium) ethyl benzoate iodide, tetrabutylammonium iodide, and the pyridinium iodide, 4-amino-1-methylpyridinium iodide, were analysed with an accuracy of about 0·2%.

The procedure that was used in the potentiometric titrations with perchloric acid was as follows: a sample of the salt, containing 0·2–2·0 mg, is dissolved in 2 ml of anhydrous methanol. Five ml of acetic acid are added, followed by 2 ml of the mercury(II) acetate reagent, then the resulting solution is titrated with 0·1*M* perchloric acid-dioxan solution from a 5·0-ml microburette, using the mV-scale of the potentiometric instrument.

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Summary—A potentiometric titration is described for quaternary ammonium iodide compounds based on a modification of the method of Pifer and Wollish. By this technique, 0·2–2·0 mg of these compounds can be titrated with a deviation of 0·2% and an accuracy of 0·17%. Thiocholine iodide esters cannot be titrated because of hydrolysis by the titrant, but they can be determined by titration with silver nitrate with a deviation and accuracy of 0·2%.

Zusammenfassung—Eine potentiometrische Titration für quartäre Ammoniumjodide wird beschrieben, die auf einer Modifikation der Methode von Pifer und Wollish beruht. Mit dieser Methode können 0,2–2,0 mg dieser Verbindungen mit einer Abweichung von 0,2% und einer Richtigkeit von 0,17% titriert werden. Thiocholinjodid-Ester können nicht titriert werden, da der Titrant hydrolysiert wird, aber sie lassen sich durch Titration mit Silbernitrat mit einer Abweichung und Richtigkeit von 0,2% bestimmen.

Résumé—On décrit un dosage potentiométrique d'iodures de composés ammonium quaternaires, basé sur une modification de la méthode de Pifer et Wollish. Par cette technique, on peut doser 0,2–2,0 mg de ces composés, avec un écart de 0,2% et une précision de 0,17%. Les esters de l'iodure de thiocholine ne peuvent être dosés par suite de l'hydrolyse par l'agent de dosage, mais on peut les titrer au moyen de nitrate d'argent, avec un écart et une précision de 0,2%.

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A phosphorimetric investigation of several representative alkaloids of the isoquinoline, morphine and indole groups

(*Received* 17 *May* 1965. *Accepted* 12 *June* 1965)

THE quantitative determination of the alkaloid content of crude drugs, plants and biological fluids is important for many legal and medical reasons. Since its first suggested use as a means of chemical analysis by Keirs, Britt and Wentworth,[1] phosphorimetry has been applied successfully in a number of areas[2-5] and shown to be a powerful method when coupled with proper separation methods.[4-6] In this study, the phosphorescence emission and excitation peaks of a number of alkaloids in neutral, basic and acidic ethanol at 77°K are given. In addition, the phosphorescence decay times and approximate limits of detection in μg/ml of ethanol are given for the same alkaloids. Because of the great sensitivity of phosphorimetry for many of the alkaloids, phosphorimetry as a measurement technique should have use in the analysis of trace concentrations of these alkaloids in a variety of materials.

EXPERIMENTAL

Apparatus

A spectrophotofluorimeter (Aminco-Bowman No. 4-8202, American Instrument Co., Inc., Silver Spring, Md., U.S.A.) with a phosphoroscope (Aminco-Keirs No. C27-62140, American Instrument Co., Inc., U.S.A.), a potted RCA 1P28 photomultiplier tube, a 200-W mercury-xenon arc lamp and with an X-Y recorder (No. 1620-814, American Instrument Co., Inc., U.S.A.) was employed for all measurements. All studies were performed at constant slit width (slit arrangement #4).[7]

Reagents

The solvent used was distilled technical grade ethanol.[5] The acidic and basic ethanolic solutions were prepared by adding 2 drops of concentrated hydrochloric acid and concentrated sodium hydroxide, respectively, to 10 ml of the ethanolic solution containing the sample. Stock neutral, acidic and basic ethanolic solutions, containing a concentration of 1 mg of each of the following alkaloids/ml of solvent, were prepared: papaverine hydrochloride, morphine alkaloid, morphine sulphate, strychnine phosphate, brucine alkaloid, yohimbine hydrochloride, codeine alkaloid, narcotine alkaloid, apomorphine hydrochloride, narceine alkaloid and thebaine alkaloid. All drugs used in this investigation were U.S.P. grade. All volumetric glassware was cleaned thoroughly according to directions specified by the manufacturer.[8]

Procedure

Dilute solutions of each alkaloid were prepared by successive dilution of the stock solution to give ethanolic solutions having concentrations from 1 mg/ml to 0.1 pg/ml. Excitation and emission spectra and decay curves were recorded with the X-Y recorder. The relative intensity (meter reading in percentage transmittance times the coarse meter multiplier with fine sensitivity remaining constant for all measurements) of each of the ethanolic solutions was measured on the photomultiplier microphotometer. The limit of detection was taken as that concentration which produced a signal on the meter of 5 units above the background phosphorescence signal if the meter multiplier was adjusted to give the maximum background signal. The decay time was the time for the emitted light to fall to 1/e of its initial intensity. The limits of detection of all compounds except morphine sulphate and narcotine alkaloid were measured in neutral ethanol. Because morphine sulphate and narcotine alkaloid were only slightly soluble in neutral ethanol, their limits of detection were measured in acidic ethanol. Ethanol was used as the solvent because it froze to a clear glass at liquid nitrogen temperatures with less than 5% of water[9] and it was a good polar solvent. All the alkaloids studied were

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A phosphorimetric investigation of several representative alkaloids of the isoquinoline, morphine and indole groups

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THE quantitative determination of the alkaloid content of crude drugs, plants and biological fluids is important for many legal and medical reasons. Since its first suggested use as a means of chemical analysis by Keirs, Britt and Wentworth,[1] phosphorimetry has been applied successfully in a number of areas[2-5] and shown to be a powerful method when coupled with proper separation methods.[4-6] In this study, the phosphorescence emission and excitation peaks of a number of alkaloids in neutral, basic and acidic ethanol at 77°K are given. In addition, the phosphorescence decay times and approximate limits of detection in μg/ml of ethanol are given for the same alkaloids. Because of the great sensitivity of phosphorimetry for many of the alkaloids, phosphorimetry as a measurement technique should have use in the analysis of trace concentrations of these alkaloids in a variety of materials.

EXPERIMENTAL

Apparatus

A spectrophotofluorimeter (Aminco-Bowman No. 4-8202, American Instrument Co., Inc., Silver Spring, Md., U.S.A.) with a phosphoroscope (Aminco-Keirs No. C27-62140, American Instrument Co., Inc., U.S.A.), a potted RCA 1P28 photomultiplier tube, a 200-W mercury-xenon arc lamp and with an X-Y recorder (No. 1620-814, American Instrument Co., Inc., U.S.A.) was employed for all measurements. All studies were performed at constant slit width (slit arrangement #4).[7]

Reagents

The solvent used was distilled technical grade ethanol.[5] The acidic and basic ethanolic solutions were prepared by adding 2 drops of concentrated hydrochloric acid and concentrated sodium hydroxide, respectively, to 10 ml of the ethanolic solution containing the sample. Stock neutral, acidic and basic ethanolic solutions, containing a concentration of 1 mg of each of the following alkaloids/ml of solvent, were prepared: papaverine hydrochloride, morphine alkaloid, morphine sulphate, strychnine phosphate, brucine alkaloid, yohimbine hydrochloride, codeine alkaloid, narcotine alkaloid, apomorphine hydrochloride, narceine alkaloid and thebaine alkaloid. All drugs used in this investigation were U.S.P. grade. All volumetric glassware was cleaned thoroughly according to directions specified by the manufacturer.[8]

Procedure

Dilute solutions of each alkaloid were prepared by successive dilution of the stock solution to give ethanolic solutions having concentrations from 1 mg/ml to 0.1 pg/ml. Excitation and emission spectra and decay curves were recorded with the X-Y recorder. The relative intensity (meter reading in percentage transmittance times the coarse meter multiplier with fine sensitivity remaining constant for all measurements) of each of the ethanolic solutions was measured on the photomultiplier microphotometer. The limit of detection was taken as that concentration which produced a signal on the meter of 5 units above the background phosphorescence signal if the meter multiplier was adjusted to give the maximum background signal. The decay time was the time for the emitted light to fall to 1/e of its initial intensity. The limits of detection of all compounds except morphine sulphate and narcotine alkaloid were measured in neutral ethanol. Because morphine sulphate and narcotine alkaloid were only slightly soluble in neutral ethanol, their limits of detection were measured in acidic ethanol. Ethanol was used as the solvent because it froze to a clear glass at liquid nitrogen temperatures with less than 5% of water[9] and it was a good polar solvent. All the alkaloids studied were

TABLE I—PHOSPHORESCENCE PARAMETERS OF SEVERAL ALKALOIDS: WAVELENGTHS OF EMISSION AND EXCITATION PEAKS,*† DECAY TIMES AND LIMITS OF DETECTION

	Neutral ethanol		Acidic ethanol		Basic ethanol			
Alkaloid	Exc., *mμ*	Emis., *mμ*	Exc., *mμ*	Emis., *mμ*	Exc., *mμ*	Emis., *mμ*	Decay time, *sec*	Limit of detection, *μg/ml*
Codeine alkaloid	275	505	240, 275(m)	495	245, 275(m)	500	0·30	0·01
Morphine alkaloid	285	500	285	500	290	500	0·25	0·01
Morphine sulphate			265	460			0·75	10
Papaverine hydrochloride	245, 305(m) 360	455, 480(m)			350	455(m), 485	1·5	0·0005
Yohimbine hydrochloride	290	410(m)			290	410, 440(m)	7·4	0·01
Narcotine alkaloid			315	440			0·5	0·01
Apomorphine hydrochloride	320	440, 470(m)	320	440, 470(m)	290, 330(m)	465	3·1	0·001
Narceine alkaloid	290	440	290	440	290	440	0·5	0·1
Thebaine alkaloid	315	500	240, 275(m) 325	450	335(m), 265	450	1·0	1
Brucine alkaloid	305	435			305	435	0·88	0·1
Strychnine phosphate	220, 290(m)	325, 440(m)	260	410			1·2	50

* All wavelengths are uncorrected for instrumental characteristics.

† (m) indicates the most intense peak.

either soluble in ethanol or could be dissolved by making the ethanol slightly acidic or basic. If the alkaloids were soluble (0.5 mg/ml or greater) in acidic, basic and neutral ethanolic solution, then excitation and emission peaks were recorded for those solutions. Otherwise, only the excitation and emission peaks were recorded for the ethanolic solutions in which the alkaloids were soluble.

RESULTS AND DISCUSSION

Table I gives the wavelengths for the uncorrected phosphorescence excitation and emission peaks when using the experimental setup and conditions described above. No spectra are given here because they would be characteristic of the instrumentation used.[4] Although several methods of correcting spectra for experimental factors are available,[10,11] it is felt that corrected spectral peaks would not yield any more useful data than those listed in the table. In any analysis, the analyst must select the optimum wavelengths of excitation and emission for his own instrumental setup for the compounds of interest. However, for an experimental setup and conditions similar to those above, the optimum wavelengths should not vary a great deal from those given in Table I.

The phosphorescence decay times were essentially the same within experimental accuracy for each compound in the various ethanolic solutions. The phosphorescence decay times in seconds for the alkaloids studied are given in Table I and range from 0.25 sec for morphine alkaloid to 7.4 sec for yohimbine hydrochloride.

Acidic solutions of the alkaloids which were soluble in both neutral and acidic ethanol, gave slightly lower intensities for equivalent concentrations. The cause of the quenching is not known. Thebaine and codeine exhibited the greatest changes as was evident from the shifts in excitation and emission peaks and the appearance of several new peaks as can be seen in Table I. Basic solutions of the alkaloids also showed considerable quenching. An additional disadvantage resulted when basic ethanolic solutions were used. The solutions cracked or produced snows about 30% of the time at liquid nitrogen temperatures.

In every case which could be compared, the intensity of phosphorescence is greater in neutral ethanol than either acidic or basic solution. The sensitivity is as much as 10-fold greater for morphine alkaloid and 100-fold greater for papaverine. Therefore, all limits of detection are measured in neutral solutions with the exception of morphine sulphate and narcotine. Papaverine hydrochloride displays an unexpected change in its excitation curve with decrease in concentration. At a concentration of 0.05 mg/ml there are two main peaks [245 mμ and 305 mμ (maximum)]. The intensity of the 305-mμ peak is about 2.5 times that of the 245-mμ peak. When the concentration is reduced to 5 μg/ml the intensities are almost equal, while at a concentration of 0.5 μg/ml the intensity of the 245-mμ peak is the strongest. The emission curve remains unchanged in character as the concentration changes.

Because many of the alkaloids phosphoresce, phosphorimetry appears to offer drug chemists a very powerful, sensitive tool for the analysis of alkaloids. Because the excitation and emission bands are broad and will overlap for a mixture of several of the alkaloids, it would be best to use a separation method, such as thin-layer chromatography, to separate first the individual alkaloid of a complex mixture before the phosphorimetric measurement. By suitable selection of excitation and emission wavelengths and phosphoroscope speed, it should be possible to resolve instrumentally some alkaloid mixtures. For best results the form of the alkaloid should be either the pure alkaloid or a salt that is readily soluble in neutral ethanolic solution. Of course, if there is appreciable phosphorescence background interference at the wavelength settings for maximum alkaloid emission, the peak phosphorescence of the alkaloid might be shifted beyond that of the interfering substance by using acidic or basic ethanolic solution.

Acknowledgements—This research was carried out as part of a study on the phosphorimetric analysis of drugs in blood and urine, supported by a grant from the U.S. Public Health Service (GM 11373-02). We also wish to thank Dr. P. A. Foote, Dean of the College of Pharmacy, University of Florida, who furnished a number of alkaloids used in this study.

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Summary—The phosphorescence emission and excitation peaks of several representative alkaloids of the isoquinoline, morphine and indole groups in neutral, basic and acidic ethanol at 77°K are given. In addition, the phosphorescence decay times and approximate limits of detection in μg/ml of ethanol are given for the same alkaloids.

Zusammenfassung—Die Maxima der Phosphoreszenzemissions- und -anregungsspektren verschiedener Vertreter der Gruppen der Isochinolin-, Morphin- und Indolalkaloide in neutralem, basischem und saurem Äthanol bei 77°K werden angegeben. Zusätzlich werden die Phosphoreszenz-Abklingzeiten und die ungefähren Nachweisgrenzen in μg/ml Ethanol für die selben Alkaloide aufgeführt.

Résumé—On donne les maximums d'émission de phosphorescence et d'excitation de divers alcaloïdes types des groupes de l'isoquinoléine, de la morphine et de l'indole, en éthanol neutre, basique et acide à 77°K. En outre, on donne, pour les mêmes alcaloïdes, les temps de persistance de la phosphorescence et les limites approximatives de détection en μg par ml d'éthanol.

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INVESTIGATION OF ION-EXCHANGE BEHAVIOUR OF TUNGSTEN(VI) AND MOLYBDENUM(VI) FROM FORMIC ACID SOLUTIONS

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Summary—A study has been made of the ion-exchange behaviour of tungsten(VI) and molybdenum(VI), in formic acid solutions, with the cation exchangers KU-1, KU-2 and Wofatite CN in the H-, Na- and NH_4-forms and with the anion exchangers EDE-10 and EDE-10p in the formate form. At pH 1 and a formic acid concentration of $0{\cdot}1M$ the cation exchangers adsorb approximately 30% of the tungsten and 10% of the molybdenum, and the anion exchangers adsorb approximately 70% of the tungsten and 90% of the molybdenum. The sequence of greatest adsorption for tungsten is KU-2 > Wofatite CN > KU-1; EDE-10 > EDE-10p and for molybdenum it is Wofatite CN > KU-1 > KU-2; EDE-10 > EDE-10p.

Recently, ion-exchange methods have been applied to the study of the properties of tungsten and molybdenum in the presence of complex-forming substances and for their separation from accompanying elements.[1-7]

The aim of this investigation was to study the ion-exchange behaviour of tungsten and molybdenum in formic acid solutions. For this purpose we used representative weak and strong cation and anion ion-exchange resins.

EXPERIMENTAL

Reagents

*Cation-exchange resins.** KU-1, with sulphonic acid and phenol groups as active sites; KU-2, with sulphonic acid groups as active sites; Wofatite CN with carboxylic acid active groups. The grain sizes are between 0·1 and 0·5 mm. Treat with $1M$ solutions of hydrochloric acid, sodium chloride and ammonium chloride to give the acid-, sodium- and ammonium-forms.

*Anion-exchange resins.** EDE-10, with trimethylammonium groups as active sites; EDE-10p, with $\equiv$N and $=$NH groups as active sites. The grain sizes are between 0·1 and 0·5 mm. Convert to the formate form by washing with $1M$ formic acid followed by water until the washings are neutral.

Molybdenum and tungsten solutions. Prepared from sodium molybdate and sodium tungstate of *pro analysi* grade.

Rhodamine-B

Apparatus

Photometer. An FEK-M photometer was used.

Procedure

Place a 50-ml sample, containing 0·1 mg of molybdenum or tungsten, formic acid of varying molarity ($0{\cdot}005$–$0{\cdot}1M$) and the solution at pH 1, in a 100-ml flask. Add 0·2 g of a resin and shake mechanically until equilibrium is attained (usually within 3 hr). Determine the metal concentration in the aqueous phase photometrically with rhodamine-B.

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* KU-1, KU-2, EDE-10 and EDE-10p resins available from Scientific Research Institute for Plastics, Moscow, U.S.S.R.; Wofatite CN available from Wolfen Fabric, Bitterfeld, German Democratic Republic.

RESULTS AND DISCUSSION

The reaction between tungsten(VI) and molybdenum(VI) and formic acid in aqueous solutions has not been reported. It could be expected that complexes are formed because, in the presence of even a very small amount of formic acid, molybdenum does not precipitate with the reagents used in qualitative analysis. Tungsten(VI) would be expected to react in the same way.

The capacity of formate ions to form complex compounds with ions of different metals in various organic solvents[7,8] is well known. Earlier we[3] pointed out the important role of hydrogen ions in complex formation:

$$(MO_4)^{2-} + 4COOH^- + 4H^+ \rightarrow [(MO_2(COOH)_4]^{2-} \quad \text{where } M = \text{Mo or W.}$$

We found that pH 1 is the optimum pH for complex formation. In more acid solutions heteropolyacids are formed and at higher pH hydrolysis occurs. The process is also dependent on the concentration of the complexing agent.

Consequently, at various concentrations of formic acid a series of complexes is found: a positively charged ion $[MO_2(HCOO)]^+$, a neutral complex $[MO_2(HCOO)_2]^0$ and two negatively charged ions $[MO_2(HCOO)_3]^-$ and $(MO_2(HCOO)_4]^{2-}$. The positively charged complex is adsorbed to a different degree by the cation exchangers, depending of the nature of the resins, their functional groups and on their form. This is reflected by the results obtained. The negatively charged complexes, formed with further increase of formic acid concentration, are absorbed by the anion exchangers to different degrees (Figs. 1 and 8).

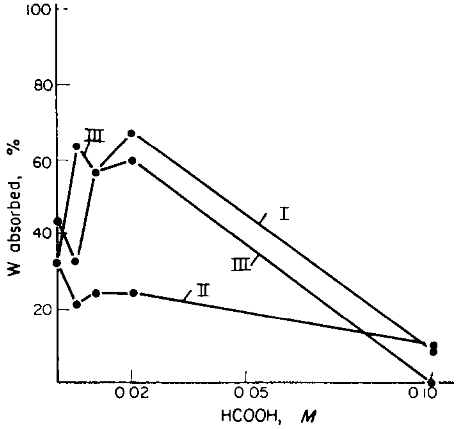

FIG. 1.—Adsorption of tungsten onto the cation exchanger KU-1 in a solution of formic acid of different concentrations, at pH 1: I—H-form; II—Na-form; III—NH_4-form.

Tungsten adsorption

In the tungsten system, with increase of formic acid concentration, all other conditions being constant, a gradual decrease of tungsten adsorption is observed with all the resins in their different forms. Generally, the positively charged complexes are most strongly adsorbed on the cation exchangers in the hydrogen form, then in the ammonium form and least of all by resins in the sodium form.

When the formic acid concentration is 0·02*M*, the adsorption curves of all three forms of the cation exchanger KU-1 reach their maximum (Fig. 1). Hence, in this case the greatest amounts of positively charged and neutral complexes exist. The positively charged complexes are adsorbed to different degrees by the different forms of the resins. With further increase of formic acid concentration the adsorption drops sharply. When the concentration of formic acid is 0·1*M* the adsorption is reduced almost to zero.

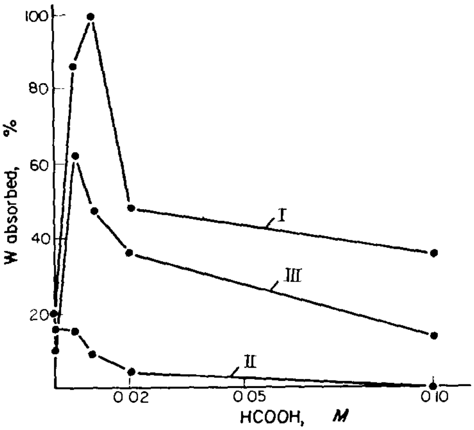

FIG. 2.—Adsorption of tungsten onto the cation exchanger KU-2 in a solution of formic acid at different concentrations, at pH 1: I—H-form; II—Na-form; III—NH_4-form.

The adsorption curves in the case of the resin KU-2, in its different forms, also have their maximum when the formic acid concentration is less than 0·02*M* (Fig. 2).

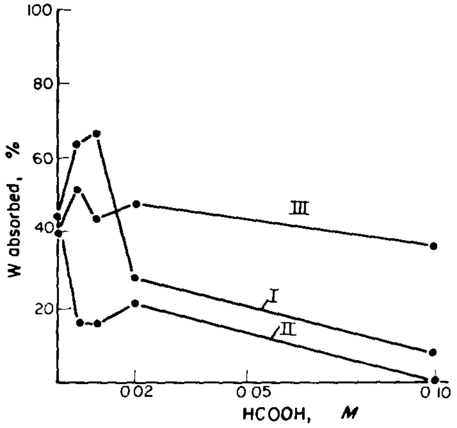

FIG. 3.—Adsorption of tungsten onto the cation exchanger Wofatite CN in a solution of formic acid at different concentrations, at pH 1: 1—H-form; II—Na-form; III—NH_4-form.

The positively charged complex ions of tungsten, which are formed, are most strongly adsorbed when the resin is in the hydrogen form and least of all when in the sodium form. At greater formic acid concentration the adsorption drops sharply, reaching a minimum at 0·1*M*.

The weak-acid cation exchanger Wofatite CN behaves similarly (Fig. 3). When the formic acid concentration is 0·1M, however, the adsorption is greatest onto the resin in the ammonium form.

All the cation exchangers, in their three forms, adsorbed an average of about 30% of the complexes at a formic acid concentration of 0·1M. Under the same conditions tungsten is not adsorbed by the anion exchangers (Fig. 4). This shows that the complex-forming processes discussed above take place under these conditions.

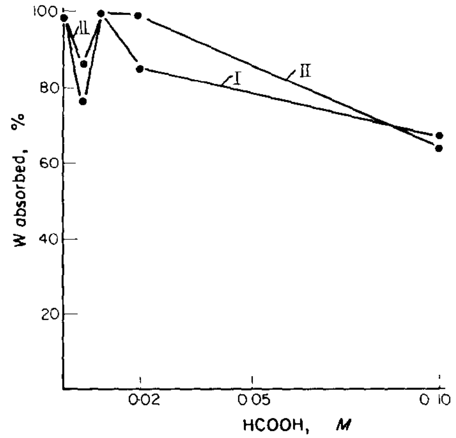

Fig. 4.—Adsorption of tungsten onto the anion exchangers EDE-10 and EDE-10p in the formate form in solutions of formic acid at different concentrations, at pH 1: I—EDE-10; II—EDE-10p.

Molybdenum adsorption

In the molybdenum system, with increase of formic acid concentration, a decrease of the molybdenum adsorption onto the cation exchangers examined, in all their forms, was observed. The curves (Figs. 5, 6 and 7) are seen to have three parts. Up to a formic acid concentration of 0·01M, a sharp decrease in molybdenum adsorption can be observed, with the exception of Curves I and II of Fig. 6. Probably, a negatively charged complex, $[MoO_2(HCOO)_4]^{2-}$ is formed. When the acid concentration is 0·01 to 0·02M, a sharp increase in molybdenum adsorption is obtained, which can probably be explained by hydrolysis of the complex formation. For this reason, there cannot be seen any molybdenum adsorption by the cation exchangers in this region. With a further increase of the formic acid concentration, the adsorption of the molybdenum decreases and at an acid concentration of 0·1M it approaches its minimum, because of the formation of a negatively charged ion. This proves that, with a gradual increase of formic acid concentration, a variety of complexes is formed in this system.

Molybdenum is adsorbed by anion exchangers to a greater degree. Initially, a decrease in the adsorption of molybdenum with increase of formic acid concentration is observed with the anion exchangers EDE-10 and EDE-10p in the formate form (Fig. 8). Then, when the formic acid concentration is increased to 0·1M, a sharp increase in molybdenum adsorption is observed. Positively charged, neutral and negatively charged complexes exist simultaneously in some parts of the system and so the behaviour of cation- and anion-exchangers complement each other. An adsorption of

20–50 % is observed in the first section of the cation exchangers, 50–80 % with the anion exchangers; when the concentration of formic acid is 0·1*M* that part of the complexes which is not adsorbed by the cation exchangers is adsorbed by the anion exchangers.

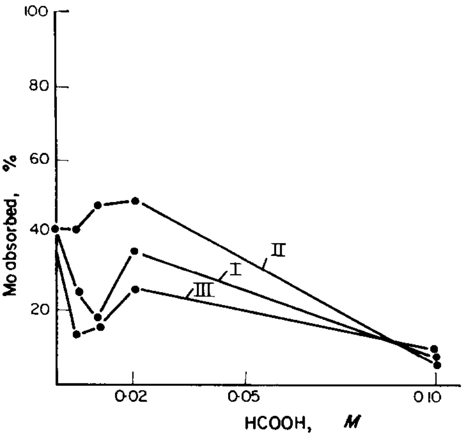

FIG. 5.—Adsorption of molybdenum onto the cation exchange KU-1 in solutions of formic acid at different concentrations, at pH 1: I—H-form; II—Na-form; III—NH_4-form.

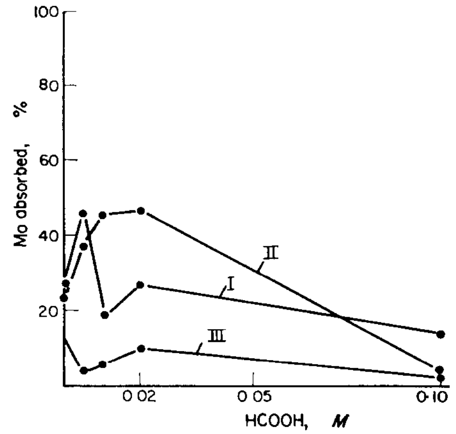

FIG. 6.—Adsorption of molybdenum onto the cation exchanger KU-2 in solutions of formic acid at different concentrations, at pH 1: I—H-form; II—Na-form; III—NH_4-form.

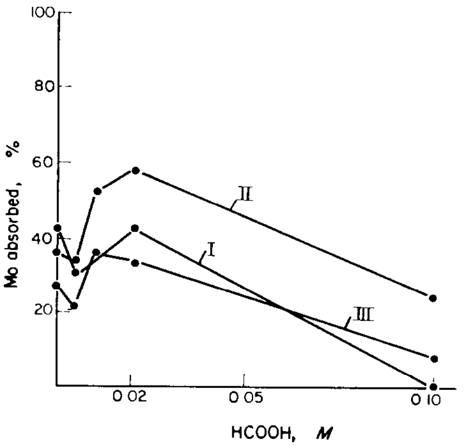

FIG. 7.—Adsorption of molybdenum onto the cation exchanger Wofatite CN in solutions of formic acid at different concentrations, at pH 1: I—H-form; II—Na-form; III—NH_4-form.

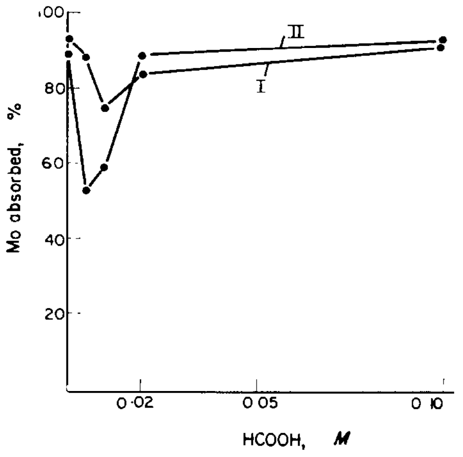

FIG. 8.—Adsorption of molybdenum onto the anion exchangers EDE-10 and EDE-10p in the formate form in solutions of formic acid at different concentrations, at pH 1: I—EDE-10; II—EDE-10p.

When the formic acid concentration is 0·1*M* or greater, the equilibrium shifts in the direction of a formate complex and the possibility of mixed complexes existing within this system decreases. These complexes are readily absorbed by the anion exchangers. At these acid concentrations 98–99 % of the molybdenum is adsorbed. The results show that the ease of replacing the ion on the cation exchangers follows the sequence

$Na^+ > H^+ > NH_4^+$. Further, the relatively weakly acidic cation exchanger Wofatite CN, in all its three forms, had the greatest sorption capacity. KU-1 has a greater capacity than KU-2. The anion exchanger EDE-10p has a greater selective capacity towards the negatively charged formate complex of molybdenum than EDE-10, but the difference in their sorption capacity is insignificant.

CONCLUSION

A study has been made of the ion-exchange behaviour of tungsten and molybdenum with the cation exchangers KU-1, KU-2 and Wofatite CN in the H-, Na- and NH_4-forms and the anion exchangers EDE-10 and EDE-10p in the formate form, at different formic acid concentrations; the formic acid was used as a complexing agent. It was found that at a formic acid concentration of $0{\cdot}1M$, when the pH was 1, the cation exchangers, in all forms, adsorb on the average about 30% of tungsten and 10% of molybdenum, whereas the anion exchangers adsorb about 70% of tungsten and 90% of molybdenum on the average. This confirms that relatively stable and negatively charged formate complexes of tungsten are formed.

Tungsten is adsorbed onto the cation exchangers in the following sequence KU-2 > Wofatite CN > KU-1 whereas for molybdenum the sequence is Wofatite CN > KU-1 > KU-2. Both tungsten and molybdenum are preferentially adsorbed by EDE–10 compared with EDE–10p.

Zusammenfassung—Das Ionenaustauschverhalten von Wolfram(VI) und Molybdän(VI) wurde in ameisensauren Lösungen an den Kationenaustauschern KU-1, KU-2 und Wofatit CN in den H-, Na- und NH_4-Formen sowie den Anionenaustauschern EDE-10 und EDE-10p in der Formiatform untersucht. Bei pH 1 und einer Ameisensäurekonzentration von 0,1 M adsorbieren die Kationenaustauscher das angebotene Wolfram etwa zu 30%, Molybdän zu 10%; die Anionenaustauscher nehmen etwa 70% vom Wolfram und 90% vom Molybdän auf. Die Reihenfolge der adsorbierten Mengen ist bei Wolfram KU-2 > Wofatit CN > KU-1; EDE-10 > EDE-10p, bei Molydbän Wofatit CN > KU-1 > KU-2; EDE-10 > EDE-10p.

Résumé—On a effectué une étude sur le comportement, au point de vue échange ionique, du tungstène (VI) et du molybdène (VI) en solutions formiques, avec les échangeurs de cations KU-1, KU-2 et Wofatite CN à l'état H, Na et NH_4 et avec les échangeurs d'anions EDE-10 et EDE-10p à l'etat formiate. A pH 1 et pour une concentration $0{,}1M$ en acide formique les échangeurs de cations absorbent approximativement 30% du tungstène et 10% du molybdène, et les échangeurs d'anions absorbent approximativement 70% du tungstène et 90% du molybdène. Pour le tungstène, l'ordre d'adsorption décroissante est: KU 2 > Wofatite CN > KU 1; EDE 10 > EDE-10p et pour le molybdène, il est: Wofatite CN > KU-1 > KU-2; EDE-10 > EDE-10p.

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QUANTITATIVE ANALYSE VON LEGIERUNGEN UND VERBINDUNGEN HOCHSCHMELZENDER METALLE, VON HARTMETALLEN UND HARTSTOFFEN MITTELS RÖNTGENFLUORESZENZ

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Zusammenfassung—Es wird über die Erfahrungen bei der Analyse von Legierungen und Verbindungen hochschmelzender Metalle, von Hartmetallen und Hartstoffen mittels Röntgenfluoreszenz berichtet. Für die Analyse auf verschiedene Bestandteile dieser Materialien wurden Analysenverfahren entwickelt. Die Vorbereitung der Proben und die experimentellen Analysenbedingungen werden mitgeteilt. Die Reproduzierbarkeit der Ergebnisse entspricht im wesentlichen dem durch die Quantenstatistik bedingten Zählfehler. Es werden Gleichungen zur Berechnung der Standardabweichung und der unteren Bestimmungsgrenze der einzelnen Verfahren aus den Analysenparametern angegeben.

Die naßchemische Untersuchung von hochschmelzenden Metallen und ihren Legierungen, von Verbindungen dieser Metalle, von Hartmetallen und Hartstoffen gestaltet sich meist sehr schwierig und ist mit einem erheblichen Zeitaufwand verbunden. Die Genauigkeit der dabei erhaltenen Ergebnisse ist vielfach unbefriedigend. Hier bietet die Anwendung der Röntgenfluoreszenzanalyse wegen ihrer Einfachheit und ihres geringen Zeitbedarfs bedeutende Vorteile[5–7]. Die rasche Durchführbarkeit der Analysen ist insbesondere für die Betriebskontrolle von großem Wert. Aber auch hinsichtlich der Analysengenauigkeit (Richtigkeit und Reproduzierbarkeit) ist die Röntgenfluoreszenzanalyse bei der Untersuchung der oben angeführten Stoffe den naßchemischen Methoden überlegen.

Wir haben die Analyse dieser Substanzen mittels Röntgenfluoreszenz eingehend untersucht und dafür besondere Arbeitsvorschriften entwickelt. Diese haben wir bereits seit längerem im Routinebetrieb erprobt. Im folgenden wollen wir über unsere diesbezüglichen Erfahrungen berichten und eine Reihe von bewährten Vorschriften mitteilen.

Bei der pulvermetallurgischen Verarbeitung und Herstellung hochschmelzender Stoffe fällt der größte Teil der zu untersuchunden Proben in Pulverform an; oft handelt es sich um Pulvergemische. Bekanntlich birgt die direkte Untersuchung von Pulvern mittels Röntgenfluoreszenz eine Reihe von Fehlerquellen in sich, da die Korngröße, die Kornverteilung und lokale Inhomogenitäten die Intensität der sekundären Röntgenstrahlung beeinflussen. Auch das Verpressen von Pulvern zu Tabletten, wie es vielfach empfohlen wird, ist aus den genannten Gründen nicht immer zweckmäßig. Bei Pulvergemischen, wie z.B. Wolfram-Kupfer, deren Komponenten stark unterschiedliche Dichte und Duktilität aufweisen, kann im Verlauf der Herstellung eines Preßlings Entmischung eintreten, während beim Pressen selbst die weichere Komponente über die härtere verschmiert werden kann. Letztere Erscheinung täuscht zu hohe Kupferwerte vor.

Daraus ergibt sich die allgemein gültige Schlußfolgerung, daß die günstigste Form der zu messenden Probe die Lösung ist, weil hier die Forderung nach Homogenität erfüllt ist. Ein weiterer wesentlicher Vorteil der Lösungsmethoden ist, daß sich Matrixeffekte der Probe durch entsprechendes Verdünnen beseitigen lassen. In der Fachliteratur findet man zwei Möglichkeiten zum Lösen von Proben für die nachfolgende Röntgenfluoreszenzanalyse:

1. Lösen der Probe durch Schmelzaufschluß
2. Überführen der Probe in eine wässrige Lösung.

Am verbreitetsten ist das Aufschmelzen mit Borax. Der erhaltene Schmelzkuchen kann entweder gepulvert werden, wobei anschließend aus dem Pulver eine Tablette gepreßt wird, oder unter gewissen Voraussetzungen direkt analysiert werden. Bei Preßlingen aus gepulverten Schmelzen können die bereits erwähnten Einflüsse der Korngröße zu Fehlergebnissen führen. Für die *direkte* Untersuchung muß der Schmelzkuchen sorgfältig gegossen und oft sogar poliert werden. Nicht selten zerbricht die Schmelze beim Erstarren oder beim Polieren. Die Bildung von Blasen an der Oberfläche, bzw. von Entmischungen kann häufig beobachtet werden. Alle diese Argumente sprechen gegen die *allgemein* anzuwendende direkte Analyse von Schmelzen, wiewohl sie in einigen speziellen Fällen von Vorteil sein mag.

Ein weiterer Nachteil der Aufschlußmethoden ist folgender: Wenn man die Temperatur und die Zeit des Aufschlusses nicht konstant halten kann, kommt es beispielsweise bei Pyrosulfatschmelzen zum Verdampfen wechselnder Mengen des Aufschlußmittels und damit zu einer unkontrollierbaren Verfälschung der Konzentration der Probe in der Schmelze.

Für die Analyse von metallischen Proben, wie z.B. W- oder Mo-Pulvern, scheiden Aufschlußmethoden ohnehin von vornherein aus, da sie ja eine vorangehende Überführung dieser Metalle in ihre Oxide erfordern würden.

Aus dem Gesagten ergibt sich ganz allgemein, daß die günstigste Art der Probenvorbereitung das Überführen in eine wässrige Lösung ist. Hier ist besonders zu beachten, daß die Untersuchungslösungen so weit verdünnt sein müssen, daß Matrixeffekte aus den Lösungschemikalien weitestgehend eliminiert werden. Dies soll an einem Beispiel erläutert werden:

Zur Erstellung einer Eichkurve für reines Tantal wurden 100 bis 800 mg Ta_2O_5 in 10 g $K_2S_2O_7$ aufgeschmolzen, die kalte Schmelze wurde mit 10 ml HF und 10 ml H_2SO_4 (1:1) unter Zusatz von 3 ml H_2O_2 aufgenommen und auf 100 ml aufgefüllt. Die resultierende Eichkurve wich von einer Geraden beträchtlich ab und hatte konvexe Form. Wurden aber nur 5 g $K_2S_2O_7$ zum Aufschluß verwendet und die erhaltene Schmelze auf 200 ml Lösung verdünnt, so wurde eine strenge Gerade erhalten.

An einem weiteren Beispiel soll gezeigt werden, wie sich durch entsprechendes Verdünnen der Maßlösung Matrixeffekte des Probenmaterials ausschalten lassen:

Man kennt verschiedene Hartmetallsorten, angefangen von reinen WC-Co-Sorten bis zu Quälitaten in denen das WC teilweise durch TiC, TaC und NbC ersetzt ist. Wir haben eine Reihe synthetischer Mischungen mit konstantem Co-Gehalt untersucht, wobei der Carbidgehalt von wechselnder Zusammensetzung war. Die Verdünnung betrug 1 g Probe auf 100 ml Meßlösung. Die Zusammensetzung der Proben geht aus Tabelle I hervor. Die gemessene Intensität der CoK_α-Linie war ungeachtet der sehr unterschiedlichen Matrix, in jedem Fall gleich groß. Dies zeigt deutlich, daß unter den von uns gewählten Analysenbedingungen die Massenabsorptionskoeffizienten der Matrixelemente keinen Einfluß mehr haben und nur der Massenabsorptionskoeffizient von Wasserstoff und Sauerstoff (Wasser) für den Hintergrund bestimmend ist.

TABELLE I.—PROBENZUSAMMENSETZUNG SYNTHETISCHER HARTMETALL-LÖSUNGEN

Co, %	WC, %	TiC, %	TaC + NbC, % (Nb:Ta = 7:1)
8	92	—	—
8	82	10	—
8	82	—	10
8	72	10	10

Die Ausschaltung von Matrixeffekten allein durch Verdünnen der Analysenlösung gelingt natürlich nur in gewissen Grenzen. Theoretisch verschwinden die Matrixeffekte zur Gänze erst bei sehr großer Verdünnung; praktisch darf man aber die Verdünnung nur so weit treiben, daß man bei der Messung stets ein vernünftiges Verhältnis von Signal zu Hintergrund erhält.

Bezüglich der Auswertung der Meßergebnisse haben wir festgestellt, daß die Verwendung von Eichkurven über einen längeren Zeitraum nicht empfehlenswert ist. Hervorgerufen durch die *Alterung der Röntgenröhre* beobachtet man bei gleichen Anregungsbedingungen eine allmähliche Abnahme der Strahlungsintensität mit der Zeit. Dies würde aber eine wiederholte und daher zeitraubende Korrektur der Eichkurven erfordern. Aus diesen Gründen hat es sich als vorteilhaft erwiesen, die Eichung für jedes Probengut täglich gesondert durchzuführen, indem gleichzeitig mit den Analysenproben eine Standardprobe mitgemessen wird.

Die Verwendung eines Eichstandards bietet einen weiteren Vorteil: Fehler, die durch eine geringfügige Verschiebung des Goniometers entstehen können, werden dadurch ausgeschaltet. Es genügt nicht, daß die Vergleichsstandardlösung eine bekannte Menge der zu bestimmenden Elemente enthält, sie muß vielmehr (Untergrund!) ähnlich wie in der optischen Photometrie sämtliche Chemikalien enthalten, genau wie die Analysenlösung. Die Bestimmung des Untergrundes führen wir so durch, daß eine Blindlösung, die sämtliche Chemikalien und bei der Analyse auf Nebenbestandteile auch die Hauptelemente der Probe enthält, genau auf der Analysenlinie gemessen wird.

Unter diesen Voraussetzungen erhält man innerhalb der interessierenden Konzentrationsbereiche eine lineare Abhängigkeit zwischen Zählrate und Konzentration, so daß die Berechnung des Analysenergebnisses durch eine einfache Proportion möglich wird.

In Fällen, wo eine Gruppe von Elementen in Proben von stark variierender Zusammensetzung bestimmt werden soll, wäre eine größere Anzahl von verschieden bereiteten Standardlösungen (wegen der verschiedenen Lösungsbedingungen und der variierenden Elemente) erforderlich. Ein *einziger* Standard genügt aber, wenn man die zu bestimmenden Elemente durch eine *grobe* chemische Vortrennung von den übrigen isoliert, wobei man bereits bei der Einwaage den wechselnden Gehalt der Proben an zu bestimmenden Elementen berücksichtigt. Als Beispiel hierzu sei auf die weiter unten beschriebene Bestimmung von Titan, Niob und Tantal in Hartmetallen verwiesen.

Im folgenden werden die von uns entwickelten Arbeitsvorschriften für die Analyse von Wolframlegierungen, Hartmetallen, Niob-Tantal-Carbid, Tantalpulver, Tantal-Abfällen, Tantal-Wolfram-Legierungen, Molybdänlegierungen, Molybdänoxid und Hartstoffen auf TiC-oder TiB_2-Basis ausführlich beschrieben.

EXPERIMENTELLER TEIL

Apparatur

Philips-Einrichtung zur Röntgenfluoreszenzanalyse bestehend aus: Generator PW 1010, Großwinkelgoniometer PW 1050 mit Universalvakuumspektrograph sowie Zähl- und Regeleinrichtung PW 1051.

Meßvorgang und Berechnung der Ergebnisse

10 ml der gemäß der jeweiligen Arbeitsvorschrift hergestellten Probelösung werden mittels Pipette in säurefeste Probenbehälter (Polyvinylchlorid) gegeben, in deren Boden sich ein Mylar-Fenster befindet. Molybdän- und Tantaloxid werden in Tablettenform in Al-Behältern mit Mylar-Fenster gemessen. Die Einstellungen am Gerät werden, wie in Tabelle II zusammengefaßt, vorgenommen.

Das Goniometer wird auf den Winkel der betreffenden Analysenlinie eingestellt und die Zählrate der Probe wird dreimal gemessen. Analog verfährt man mit Standard- und Blindlösung. Zur Berechnung des Ergebnisses verwendet man das arithmetische Mittel der abgelesenen Zählraten. Man könnte natürlich, anstatt jede Messung dreimal durchzuführen, einfach die Meßzeit verdreifachen. Die dreifache Messung ist aber sicherer, weil man hier gelegentliche Ausreisser, die durch Induktionsstöße hervorgerufen werden, erkennen und ausscheiden kann. Der Probenanteil des gesuchten Elements in der Probe ergibt sich aus folgender Formel:

$$P = P' \frac{\bar{Z}_P - \bar{Z}_B}{\bar{Z}_S - \bar{Z}_B} \tag{1}$$

Hierin bedeuten: Z_P ... die Zählrate der Probe (Mittel)
Z_S ... die Zählrate des Standards (Mittel)
Z_B ... die Zählrate der Blindlösung (Mittel)
P ... den Prozentgehalt in der Probe
P' ... den Prozentgehalt im Standard

Voraussetzung zur Anwendbarkeit von Formel (1) ist strikte Proportionalität zwischen Konzentration und Impulsrate. Innerhalb des in Tabelle II angegebenen Konzentrationsbereiches ist diese Forderung erfüllt, wenn bei der Analyse die nachstehenden Arbeitsvorschriften befolgt werden.

Arbeitsvorschriften:

Tabelle II enthält zusammengefaßt die Anregungs- und Meßbedingungen für eine Reihe von Elementen in den eingangs aufgezählten Materialien. Die ausführlichen Vorschriften zur Vorbereitung der Proben, sowie der Standard- und Blindlösungen finden sich anschließend unter jener Ziffer, die in der dritten Spalte von Tabelle II angegeben ist. Für jeden einzelnen Fall haben wir die *Richtigkeit* der erzielten Ergebnisse anhand von Lösungen mit bekanntem Gehalt überprüft. Die *Reproduzierbarkeit* geben wir bei jedem Verfahren für einen bestimmten Konzentrationsbereich an. Die angegebenen Standardabweichungen haben wir aus Einzelwerten von Parallelbestimmungen nach folgender Formel[1] berechnet:

$$s = \pm\sqrt{\frac{\Sigma(x_i' - x_i'')^2}{2M}} \tag{2}$$

Darin bedeuten: x_i' und x_i'' ... zusammengehörige Wertpaare einer Parallelbestimmung
M ... Anzahl von Parallelbestimmungen

Vorschrift 1:

Cu, Ni und Fe in W-Cu-Ni-Fe-Legierungen.

Probenvorbereitung. 2 g in 5 ml HF und 3 ml HNO_3 (konz.) lösen. 10 ml Weinsäure (40% ig), 10 ml Borsäure (4% ig) und 10 ml Ammoniak (konz.) zugeben und auf 100 ml auffüllen.

Blindlösung. 18,4 g W-Pulver in 50 ml HF und 30 ml HNO_3 (konz.) lösen. 100 ml Weinsäure (40% ig), 100 ml Borsäure (4% ig) und 100 ml Ammoniak (konz.) zugeben und auf 1000 ml auffüllen.

Standardlösung (5% Ni, 3% Cu, 2% Fe). 18,0 g W-Pulver, 1,0 g Ni-Metall, 0,6 g Cu-Metall und 0,4 g Fe-Metall wie oben lösen und weiterbehandeln.

Die experimentell ermittelten Standardabweichungen betragen:

Cu im Bereich von 0,5–3% ... ± 0,025%
Ni im Bereich von 0,5–6% ... ± 0,027%
Fe im Bereich von 0,2–3% ... ± 0,010%

TABELLE II

Material	Element	Vorschrift Nr.	Meßlinie	Röhre	Anregung *kV*	Anregung *mA*	Kristall	Zählrohr	Diskriminator	Meßzeit	Abschwächung	Untersuchter Konzentr.-Bereich
W–Cu–Ni–Fe	Cu	1	Kα I	W	30	20	LiF	Szint.	ohne	32	8	0,1–3,0%
W–Cu–Ni–Fe	Ni	1	Kα I	W	30	20	LiF	Szint.	ohne	32	16	0,2–8,0%
W–Cu–Ni–Fe	Fe	1	Kα I	W	30	20	LiF	Szint.	ohne	32	8	0,1–4,0%
W–Cu–Tränklegierung	Cu	2	Kα I	W	30	20	LiF	Szint.	ohne	32	32	5–50%
W–Cu–Tränklegierung	Ni	2	Kα I	W	30	20	LiF	Szint.	ohne	32	32	0,2–1,0%
W–Mo–Legierung	Mo	3	Kα I	W	30	20	LiF	Szint.	ohne	32	16	0,05–1,00/1–20%
W–Re–Legierung	Re	4	Lα I	W	20	36	LiF	Szint.	ohne	64	16	1–30%
W–Ag–Tränklegierung	Ag	5	$K\alpha_1$ II	W	50	10	LiF	Szint.	mit	32	16	5–30%
Hartmetalle	Co	6	Kα I	W	30	20	LiF	Szint.	ohne	32	16	0,5–30%
Hartmetalle	Fe	6	Kα I	W	30	20	LiF	Szint.	ohne	64	8	0,05–2,0%
Hartmetalle	Ti	7	Kα I	W	30	30	LiF	Durchfluß-Vakuum	mit	64	4	8–80 mg/100 ml
Hartmetalle	Nb	7	Kα I	W	30	10	LiF	Szint.	mit	32	16	1–10 mg/100 ml
Hartmetalle	Ta	7	Lα I	W	30	20	LiF	Szint.	mit	32	8	8–70 mg/100 ml
Ta–Nb–Leg. Carbide	Nb	8	Kα I	W	30	30	LiF	Szint.	ohne	32	16	1,0–15%
Ta–W–Legierungen	W	9	Lα I	Au	30	20	LiF	Szint.	ohne	32	16	5–20%
Ta–Abfälle	Ta	10	Lα I	W	30	20	LiF	Szint.	mit	128	16	50–400 mg Ta_2O_5 100 ml
Ta–Pulver	Nb	11	Kα I	W	30	30	LiF	Szint.	ohne	32	8	0,01–0,6%
Ta–Pulver	Fe	11	Kα I	W	30	30	LiF	Szint.	ohne	32	4	0,005–0,12%
Mo–Re–Legierungen	Re	12	Lα I	W	20	36	LiF	Szint.	ohne	64	16	1,0–30%
Mo–W–Re–Legierungen	Re	12	Lα I	W	20	36	LiF	Szint.	ohne	64	16	1,0–30%
MoO_3	W	13	Lα I	Au	30	20	LiF	Szint.	mit	64	16	0,05–4%
Mo–Ti–Legierungen	Ti	14	Kα I	W	30	30	LiF	Durchfluß-Vakuum	mit	64	4	0,05–1%
Mo–Ti–Zr–Legierungen	Ti	14	Kα I	W	30	30	LiF	Durchfluß-Vakuum	mit	64	4	0,05–1%
Mo–Ti–Zr–Legierungen	Zr	14	Kα I	W	30	20	LiF	Szint.	ohne	32	16	0,01–0,2%
Hartstoffe TiC, TiB_2	Co	15	Kα I	W	30	20	LiF	Szint.	ohne	32	16	0,01–5%
Hartstoffe TiC, TiB_2	Fe	15	Kα I	W	30	20	LiF	Szint.	ohne	64	8	0,05–2%

Vorschrift 2:

Cu und Ni in W-Cu-Tränklegierungen.

Probenvorbereitung. 1 g in 5 ml HF und 3 ml HNO_3 (konz.) lösen. Mit 10 ml Weinsäure (40% ig), 10 ml Borsäure (4% ig) und 10 ml Ammoniak (konz.) versetzen und auf 100 ml auffüllen.

Blindlösung. 7,5 g W-Pulver in 50 ml HF und 30 ml HNO_3 (konz.) lösen. 100 ml Weinsäure (40% ig). 100 ml Borsäure (4% ig) und 100 ml Ammoniak (konz.) zugeben und auf 1000 ml auffüllen.

Standardlösung (25% Cu, 1% Ni). 7,5 g W-Pulver, 2,5 g Cu-Metall und 0,1 g Ni-Metall wie oben lösen und weiterbehandeln.

Vorschrift 3:

Mo in W-Mo-Legierungen.

Probenvorbereitung. 10 g in HF und HNO_3 lösen und zur Trockene eindampfen. Rückstand mit 20 g $KNaCO_3$ aufschließen, in H_2O lösen und auf 1000 ml auffüllen. Einen Teil der Lösung filtrieren und zur Messung verwenden.

Blindlösung. 12,6 g WO_3 mit 20 g $KNaCO_3$ aufschließen, in Wasser lösen und auf 1000 ml auffüllen,

Standardlösung I (10% Mo). 11,36 g WO_3 und 1,500 g MoO_3 wie oben behandeln.

Standardlösung II (0,5% Mo). 12,51 g WO_3 und 0,075 g MoO_3 wie oben behandeln.

Vorschrift 4:

Re in W-Re-Legierungen.

Probenvorbereitung. 2 g werden in 5 ml HF und 10 ml HNO_3 (konz.) gelöst. Mit 5 ml H_2O_2 (10% ig), 10 ml Weinsäure (40% ig), 10 ml Borsäure (4% ig) und 10 ml Ammoniak (konz.) versetzen und auf 100 ml auffüllen.

Blindlösung. 1,90 g W-Pulver werden wie oben behandelt.

Standardlösung. 1,9 g W-Pulver und 100 bzw. 200 mg Re-Pulver, je nach zu bestimmender Konzentration, werden wie oben behandelt. Standard ist *täglich frisch* zu bereiten.

Vorschrift 5:

Ag in W-Ag-Legierungen.

Probenvorbereitung. 1 g Probe wird mit 10 ml HNO_3 (konz.) und nach Erwärmen mit 5 ml HF versetzt. Sodann setzt man 10 ml Weinsäure (40% ig), 10 ml Borsäure (4% ig) und 25 ml Ammoniak (konz.) zu und füllt auf 100 ml auf.

Blindlösung. 1,6 g W-Pulver mit der doppelten Menge obiger Reagenzien behandeln und auf 200 ml auffüllen.

Standardlösung. 1,6 g W-Pulver und 0,4 g Ag-Metall wie oben behandeln.

Vorschrift 6:

Co und Fe in Hartmetallen.

Probenvorbereitung. 1 g Probe in 10 ml HF und 10 ml HNO_3 (konz.) lösen. 10 ml H_2O, 5 g Zitronensäure, 5 ml H_2O_2 (10%) und 6 g Borsäure zusetzen; bis zur vollständigen Klärung erhitzen und auf 100 ml auffüllen. Ist die Lösung durch Graphit getrübt, wird vor der Messung durch ein trockenes Filter filtriert.

Blindlösung. 0,8 g W-Pulver wird wie oben behandelt (*täglich* zu bereiten).

Standardlösung. 0,8 g W-Pulver und eine 50,0 mg Co enthaltende Menge an Co-Standardlösung werden wie oben behandelt (*täglich frisch* zu bereiten).

Die experimentell ermittelten Standardabweichungen betragen:

Co im Bereich von etwa 5%... ± 0,021%
Fe im Bereich von etwa 0,2%... ± 0,017%

Vorschrift 7:

Ti, Nb und Ta in Hartmetallen.

Probenvorbereitung. Je nach erwartetem Gehalt an Ti, Nb und Ta werden folgende Probenmengen eingewogen:

TiC-Gehalt:	NbC + TaC-Gehalt	Einwaage, *g*
8-20%	7-15%	0,5
4- 8%	4- 7%	1,0
1- 4%	1- 4%	2,0
< 1%	< 1%	10,0

Man löst in HF und HNO_3, setzt 5 ml H_2SO_4 konz. zu und raucht bis zum Auftreten von SO_3-Nebeln ab. Nach Verdünnen mit Wasser auf mindestens 100 ml gießt man in ein Gemisch von 100 ml NH_3 (konz.) + 100 ml H_2O + 10 g NH_4Cl und 1, 2, 4, bzw. 10 g ÄDTA, je nach der

Einwaage. Bis zum Sieden erhitzen und absitzen lassen. Filtrieren und waschen. Filter samt Niederschlag in Pt-Schale bringen. Ohne das Filter zu zerstören mit 10 ml HF, 1 ml HNO_3 (konz.) 10 ml Weinsäure (40% ig), 5 ml H_2O_2 (10% ig) und 6 g H_3BO_3 versetzen und bis zur vollständigen Klärung erhitzen. Lösung in 100-ml-Meßkolben nachspülen. Auf 100 ml auffüllen.

Blindlösung. 100 ml HF, 10 ml HNO_3 (konz.), 100 ml Weinsäure (40% ig), 50 ml H_2O_2 (10% ig) und 60 g H_3BO_3 bis zur Klärung erhitzen und auf 1000 ml auffüllen.

Standardlösung. 200,0 mg Ti-Metall, 200,0 mg Ta-Metall, 25,0 mg Nb-Metall mit 50 ml HF und 5 ml HNO_3 (konz.) lösen. Mit 50 ml Weinsäure (40% ig), 25 ml H_2O_2 (10% ig) und 30 g H_3BO_3 versetzen, bis zur Klärung erhitzen und auf 500 ml auffüllen. Die experimentell ermittelten Standardabweichungen betragen:

Ti im Bereich von 0,1–3,5%... ± 0,015%
Nb im Bereich von 0,02–0,6%... ± 0,006%
Ta im Bereich von 0,2–4,0%... ± 0,011%

Vorschrift 8:

Nb in Ta-Nb-Legierungen und -Carbiden.

Probenvorbereitung. 1 g Probe wird wie bei Vorschrift 6 behandelt.

Blindlösung. 0,9 g Ta-Pulver wird wie oben behandelt.

Standardlösung (10% Nb). 0,9 g Ta-Pulver und 0,100 g Nb-Metall werden wie oben behandelt.

Vorschrift 9:

W in Ta-W-Legierungen.

Probenvorbereitung. 1 g in 10 ml HF und 3 ml HNO_3 (konz.) lösen. 10 ml H_2O, 10 ml Weinsäure (40% ig), 5 ml H_2O_2 (10% ig) und 6 g Borsäure zugeben und auf 100 ml auffüllen.

Blindlösung. 0,9 g Ta-Pulver wie oben behandeln.

Standardlösung (10% W). 0,9 g Ta-Pulver und 0,100 g W-Metall wie oben behandeln.

Vorschrift 10:

Ta in Ta-Abfällen.

Probenvorbereitung. 200 mg Probe werden durch Glühen zu Ta_2O_5 oxidiert und im Pt-Tiegel mit 5 g $K_2S_2O_7$ bei *niederer* Temperatur aufgeschlossen. Sobald alles Oxid gelöst ist, läßt man erstarren, setzt 0,5 ml H_2SO_4 (konz.) zu und schmilzt nochmals auf. Der Schmelzkuchen wird in einer Pt-Schale mit 10 ml HF, 10 ml H_2SO_4 (1:1) und etwas Wasser in Lösung gebracht. Gegen Ende gibt man 3 ml H_2O_2 (10% ig) zu und füllt im Meßkolben auf 200 ml auf. Sofort nach dem Auffüllen und Mischen in ein Plastikgefäß überführen, damit der Kolben nicht zu stark geätzt wird.

Blindlösung. 5 g $K_2S_2O_7$ werden wie oben behandelt.

Standardlösung. 100,0 mg spektralreines, geglühtes Ta_2O_5 werden wie oben behandelt.

Vorschrift 11:

Fe und Nb in Ta.

Probenvorbereitung. 10,00 g Probe im Porzellantiegel bei 900° 3 Stunden glühen. In einer Reibschale gut pulvern und mit 5 ml ätherischer Paraffinlösung (10 g Paraffin mit Äther auf 100 ml) innig verreiben. Aus dem gesamten Pulver eine Tablette pressen.

Blindprobe. 12,200 g Ta_2O_5, spektralrein, wie oben behandeln.

Standardprobe (0,3% Nb, 0,05% Fe). 12,170 g Ta_2O_5 (spektralrein), 42,9 mg Nb_2O_5 (spektralrein) und 7,15 mg Fe_2O_3 (p.a.) *sehr innig* mischen, mit 5 ml Paraffinlösung versetzen, wie oben weiterbehandeln.

Die experimentell ermittelten Standardabweichungen betragen:

Fe im Bereich von 0,005–0,2%... ± 0,0008%
Nb im Bereich von 0,01– 0,1%... ± 0,0033%

Vorschrift 12:

Re in Mo-Re- und Mo-W-Re-Legierungen.

Probenvorbereitung. 2,000 g werden in 5 ml HF und 10 ml HNO_3 (konz.) gelöst. Mit 5 ml H_2O_2 (10% ig), 10 ml Weinsäure (40% ig), 10 ml Borsäure (4% ig) und 10 ml Ammoniak (konz.) versetzen und auf 100 ml auffüllen.

Blindlösung. 0,950 g Mo-Pulver und 0,950 g W-Pulver werden wie oben behandelt.

Standardlösungen (5 und 10%). 0,95 g Mo-Pulver, 0,95 g W-Pulver und 100,0 bzw. 200,0 mg Re werden wie oben behandelt.

Vorschrift 13:

W in MoO_3.

Probenvorbereitung. 10,00 g MoO_3 in Porzellanreibschale pulvern. Mit 5 ml ätherischer Paraffinlösung (10% ig) gut verreiben und zu einer Tablette pressen.

Liegt metallisches Material vor, so werden 10 g in HNO_3 und HCl gelöst, zur Trockene eingedampft und bei 450° geglüht. 10,00 g dieses Glührückstandes werden wie oben weiterbehandelt.

Blindprobe. 10 g MoO_3 (hergestellt aus spektralreinem Ammoniumparamolybdat durch Glühen bei 450°) werden wie oben behandelt.

Standardprobe (1% WO_3). 9,90 g MoO_3 aus Ammoniumparamolybdat) und 0,100 g WO_3 sehr innig miteinander vermischen und wie oben weiterbehandeln.

Vorschrift 14:

Ti und Zr in Mo-Ti und Mo-Ti-Zr-Legierungen.

Probenvorbereitung. 10,00 g in HNO_3 und HCl lösen und anschließend ammoniakalisch machen. Niederschlag abfiltrieren und mit ammoniakhaltigem Wasser waschen. Filter samt Niederschlag im Pt-Tiegel veraschen. Mit 2 g $K_2S_2O_7$ aufschließen. Schmelze mit 10 ml H_2SO_4 (konz.) lösen und mit Wasser auf 50 ml auffüllen.

Blindlösung. 10,0 g $K_2S_2O_7$ mit 50 ml H_2SO_4 (konz.) lösen und mit Wasser auf 250 ml auffüllen.

Standardlösung (0,5% Ti; 0,1% Zr). 416,5 mg TiO_2 (p.a.) und 67,5 mg ZrO_2 (p.a.) mit 10,0 g $K_2S_2O_7$ aufschließen, mit 50 ml H_2SO_4 (konz.) lösen und mit Wasser auf 250 ml auffüllen.

Vorschrift 15:

Co und Fe in Ti-haltigen Hartstoffen (TiC, TiB_2).

Probenvorbereitung. Wie bei der Co-Bestimmung in Hartmetallen, Vorschrift 6.

Blindlösung. 4 g Ti-Schwamm in 50 ml HF und 50 ml HNO_3 (konz.) lösen. 50 ml H_2O, 25 g Zitronensäure, 25 ml H_2O_2 (10% ig) und 30 g Borsäure zusetzen und bis zur vollständigen Klärung erhitzen. In Meßkolben auf 500 ml auffüllen.

Standardlösung (1% Co, 1% Fe). 4 g Ti-Schwamm, 50,0 mg Co-Metall und 50,0 mg Fe-Metall werden wie oben behandelt.

BERECHNUNG DER REPRODUZIERBARKEIT EINES VERFAHRENS UND SEINER UNTEREN BESTIMMUNGSGRENZE AUS DEN ANALYSENPARAMETERN

Im nachfolgenden werden folgende Symbole verwendet:

$Z_{P,S,B}$	Mittlere Zählerablesung am Gerät für Probe, Standard oder Blindlösung (unter Analysenbedingungen)
N	Anzahl der Messungen an Probe, Standard und Blindlösung
a	Abschwächungsfaktor
P	Prozentgehalt der Probe
P′	Prozentgehalt des Standards
s	Standardabweichung einer Einzelbestimmung an der Probe
s′	Standardabweichung einer Einzelbestimmung am Standard

Reproduzierbarkeit eines Verfahrens

Es wird vorausgesetzt, daß der Meßfehler nur von der Zählstatistik[2] und von der Exaktheit der Standardbereitung abhängig ist. Wie bereits erwähnt, ergibt sich der Gehalt der Probe gemäß

$$P = P' \frac{Z_P - Z_B}{Z_S - Z_B} \tag{1}$$

Sowohl P′, als auch Z_P, Z_S und Z_B sind fehlerbehaftete Größen. Der Fehler für eine Zählrate beträgt unter Berücksichtigung des Abschwächungsfaktors a und des Umstandes, daß jede Messung N-mal durchgeführt wurde

$$s_Z = \pm\sqrt{\frac{Z \cdot a}{N}} \tag{3}$$

Unter der Voraussetzung, daß N und a für Probe, Standard und Blindwert gleich sind, ergibt sich die *Reproduzierbarkeit einer Einzelbestimmung* aus (1) und (3) unter Berücksichtigung des Fehlerfortpflanzungsgesetzes[3]

$$s = \pm P' \frac{Z_P - Z_B}{Z_S - Z_B} \sqrt{\left\{\frac{s'^2}{P'^2}\right\} + \left\{\frac{1}{aN}\right\} \left[\left\{\frac{Z_P + Z_B}{(Z_P - Z_B)^2}\right\} + \left\{\frac{Z_S + Z_B}{(Z_S - Z_B)^2}\right\}\right]} \qquad (4)$$

Es ist vorteilhaft, bei Neuentwicklung eines Analysenverfahrens die experimentell aus den erhaltenen Resultaten ermittelte Standardabweichung mit der nach obiger Gleichung berechneten zu vergleichen. Liegt die experimentell ermittelte wesentlich höher, so weist dies auf irgendwelche Fehlerquellen hin, die außerhalb der Quantenstatistik liegen, und es ist dann notwendig, das Verfahren einer näheren Überprüfung zu unterziehen. Gelegentlich pflegt man die Standardabweichung auf das Resultat zu beziehen, wodurch man den Variationskoeffizienten v in Relativprozent erhält:

$$v = \pm \frac{s \cdot 100}{P}$$

Für die Bewertung eines Analysenverfahrens im allgemeinen ist unseres Erachtens der absolute Analysenfehler wichtiger; bei extrem niedrigen Gehalten nimmt der Analytiker oft und gerne einen relativen Fehler von ±10% und darüber in Kauf.

Aus Gleichung (4) geht hervor, daß die Ergebnisse umso geringer streuen werden, je genauer der Eichstandard bestimmt worden ist. Wo immer es möglich ist, sollte der Eichstandard unter Verwendung einer Metallösung bereitet werden, die durch Auflösen einer *gewogenen* Menge Metallblech oder -draht bzw. Metalloxid hergestellt worden ist. Ferner sieht man, daß die Reproduzierbarkeit mit zunehmender Anzahl der Messungen besser wird. Für die Praxis genügt es, jede Messung dreimal durchzuführen.

Wie man aus Gleichung (4) ersieht, ist die Standardabweichung eine Funktion der gesuchten Menge $P = P' \cdot \frac{Z_P - Z_B}{Z_S - Z_B}$ und *nicht*, wie bei den klassischen Analysenverfahren der Gravimetrie und Titrimetrie, unabhängig von der vorgelegten Menge an Analysensubstanz.

Untere Grenze eines Verfahrens

Es ist einzusehen, daß die untere Grenze der Anwendbarkeit einer Analysenmethode dann erreicht ist, wenn sich das Signal nicht mehr mit hinreichender Sicherheit vom Untergrund unterscheiden läßt.

In einer eingehenden Behandlung statistischer Methoden gibt Doerffel[4] zur Ermittlung der Bestimmungsgrenze einer beliebigen Analysenmethode folgende Gleichung an:

$$\bar{X}_u = \bar{X}_B + \frac{t(P,n) \cdot s_B}{\sqrt{N_f}} \qquad (6)$$

Dies besagt, daß sich der kleinste, mit P% Sicherheit feststellbare mittlere Meßwert $\bar{X}_u$ vom mittleren Blindwert $\bar{X}_B$ um den Betrag $\frac{t(P,n) \cdot s_B}{\sqrt{N_f}}$ abheben muß. Hierin bedeuten N_j die Anzahl der Parallelbestimmungen des Meßwertes, s_B die Standardabweichung des Blindwertes und t einen Faktor, der von der geforderten statistischen Sicherheit P und der Anzahl der Freiheitsgrade n des Blindwerts abhängig ist.

Auf unsere Problemstellung angewandt heißt dies, die mittlere Impulszahl der Probe $a \cdot Z_P$ muß um den Betrag $\frac{t(P,n) \cdot s_B}{\sqrt{N_j}}$ größer sein, als das Untergrundsignal aZ_B:

$$aZ_P \geqq aZ_B + \frac{t(P,n) \cdot s_B}{\sqrt{N_j}} \tag{7}$$

oder

$$a(Z_P - Z_B)_{\lim} = t(P,n) \cdot \frac{s_B}{\sqrt{N_j}} \tag{8}$$

Für eine geforderte statistische Sicherheit von P = 99 % und unter der Voraussetzung, daß für Z_B noch eine Normalverteilung angenommen werden kann, beträgt der Wert für t(P, n) = 2,58.[1] Da dem Wert für Z_P drei Parallelmessungen zugrunde liegen, ist $N_j = 3$ und es ergibt sich

$$a(Z_P - Z_B)_{\lim} = 2{,}58 \cdot \frac{s_B}{\sqrt{3}} = 1{,}49 \cdot s_B \tag{9}$$

Setzt man (9) unter Berücksichtigung von (3) in (1) ein, so erhält man den geringsten Prozentanteil an gesuchtem Element, der mit 99%iger statistischer Sicherheit in einer Probe noch bestimmbar ist.

$$P_{\lim} = P' \cdot \frac{1{,}49 \cdot \sqrt{a \cdot Z_B}}{a \cdot (Z_S - Z_B)} \tag{10}$$

In dieser Gleichung sind P′ und $(Z_S - Z_B)$ fehlerbehaftet und sie gilt daher nur angenähert. Eine genauere Überprüfung zeigt aber, daß ein anzubringendes Korrekturglied dann vernachläßigt werden kann, wenn $\frac{s'^2}{P'^2}$ sehr gering und $Z_S \gg Z_B$ ist.

Summary—Experience in the analysis of alloys and compounds of high-melting metals, hard metals and hard materials by X-ray fluorescence is reported. Analytical procedures have been developed for various components of these materials. Preparation of samples and experimental conditions are detailed. Reproducibility of results corresponds, in the main, to the errors occasioned by quantum statistics. Equations for calculating the standard deviation and the lower limit of determination of the individual procedures from the analytical parameters are given.

Résumé—On décrit la pratique de l'analyse d'alliages et de composés de métaux à haut point de fusion, de métaux durs et de matériaux durs par fluorescence aux rayons X. On a élaboré des techniques analytiques pour divers constituants de ces matériaux. On décrit en détail la préparation des échantillons et les conditions expérimentales. La reproductibilité des résultats correspond, essentiellement, aux erreurs occasionnées par les statistiques quantiques. On donne les équations de calcul de l'écart type et de la limite inférieure de dosage pour les techniques individuelles à partir des paramètres analytiques.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL-GRADE REAGENTS—III*

RUBIDIUM SALTS

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Summary—The most common rubidium salts have been investigated by the method of derivatography, their weight change, rate of weight change and enthalpy change being measured as a function of temperature. On the basis of these experiments, those temperatures at which the salts can be dried without danger of decomposition are deduced. The results can be interpreted by the acid-base theory of high temperatures.

In our former communications[1,2] we reported on the thermoanalytical properties of some important ammonium and caesium salts. In the present paper our results for rubidium compounds are discussed.

EXPERIMENTAL

Our experiments were carried out with an F. Paulik-J. Paulik-L. Erdey ORION-GYEM 676 Type derivatograph.[3,4]

About 500 mg of sample were weighed into a platinum crucible and the rate of heating was 10°/min. Most of the substances examined were analytical grade or purissimum reagents which were made available by E. Merck, Darmstadt, German Federal Republic.

RESULTS

Rubidium chloride

The derivatogram of rubidium chloride (Fig. 1), of sodium chloride lattice type, shows that the crystals have constant weight up to the melting point and that there is no enthalpy change. Its polymorphous modification exists only at high pressure. The melting point appears on the differential thermoanalytical (DTA) curve as an endothermic peak at 720°. We have previously found that the melting point is 10° higher; the discrepancy is probably the result of different experimental conditions. Decrease of weight, from evaporation, could be observed only above the melting point. This contradicts another finding, which gives 605° as the upper limit of constant weight.[5] Under the given experimental conditions, the loss of weight is about 10% up to 1000°.

Rubidium bromide

The derivatogram shows that the sample of rubidium bromide (Chemapol, Czechoslovakia) contained 1·8% of volatile material (Fig. 2). Peaks with associated decrease in weight can be observed on the thermogravimetric (TG) and derivative

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* Part II: see reference 2.

thermogravimetric (DTG) curves at 80, 120, 240 and 500°. The DTA curve indicates enthalpy changes at these temperatures and a further change, unaccompanied by weight change at 600°, which is probably caused by various impurities in the substance. The melting point of rubidium bromide was found to be 680°. Above the melting point a decrease in weight, from evaporation, is observed which reaches 12% at 1000° under the given experimental conditions.

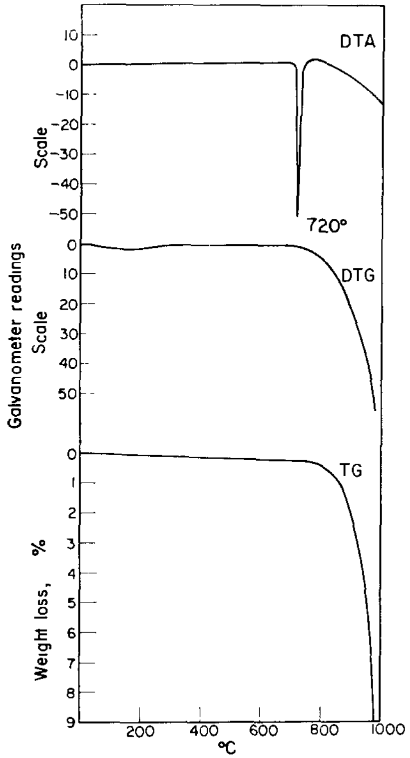

FIG. 1.—Rubidium chloride.

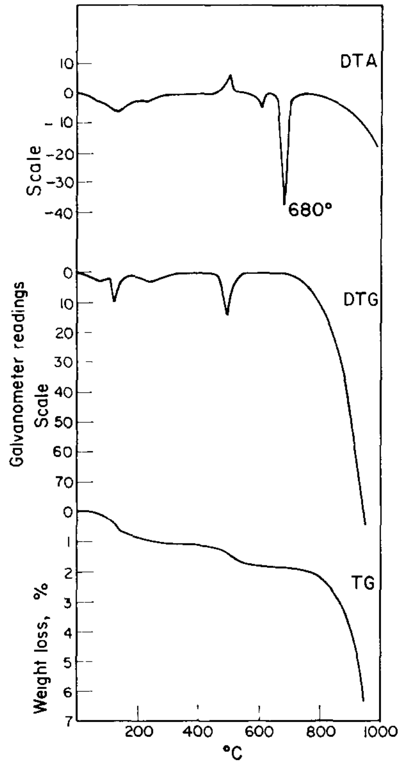

FIG. 2.—Rubidium bromide.

Rubidium iodide

The sodium chloride lattice-type crystals of rubidium iodide do not show any change of modification with increasing temperature. The caesium chloride lattice-type polymorphous modification of rubidium iodide is known only at high pressure. It can be established, on the basis of the TG and DTG curves (Fig. 3), that the sample contained some moisture, which was only removed completely at 300°. The melting point of the substance was found to be 640° from the DTA curve. Above the melting point the weight of the sample decreases rapidly and about 20% of the substance evaporates at 1000°.

Rubidium sulphate

The thermal decomposition of the rhombic dipyramidal crystals of analytical-grade rubidium sulphate is shown in Fig. 4. Rubidium sulphate does not contain waters of crystallisation, but the sample contained 2 % of moisture whose removal was indicated by a DTG maximum at 100°.

A sharp exothermic peak appeared at 630°. A rhombic hexagonal polymorphous transformation at 649° has been reported,[6] and the process is enantiotropic. It is known that a marked dilatation occurs at the transformation. The derivatographic studies gave a transformation temperature lower than that reported and, on cooling, curve reversion of the crystal did not appear, *i.e.*, the process is monotropic. We found, also, that this modification change proceeded so quickly that the substance formed at the transformation always splashed out of the crucible, causing a decrease in weight of variable amount. The melting point of rubidium sulphate is above 1000°, but above 900° a small decrease in weight is observed; this agrees well with other literature values.[5] Therefore, it is expedient to carry out drying of rubidium sulphate below 520° in order to avoid possible weight losses.

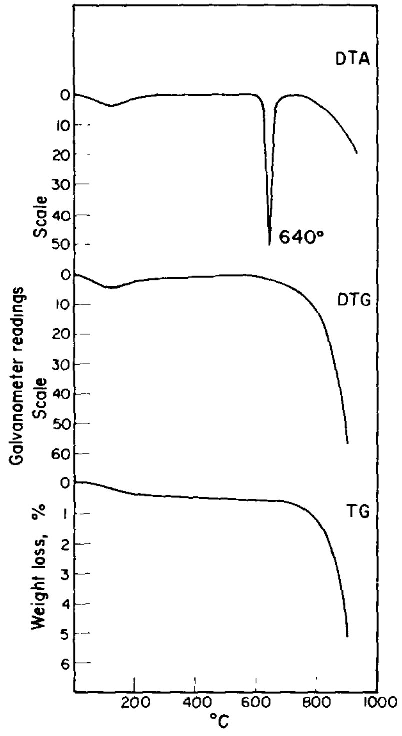

FIG. 3.—Rubidium iodide.

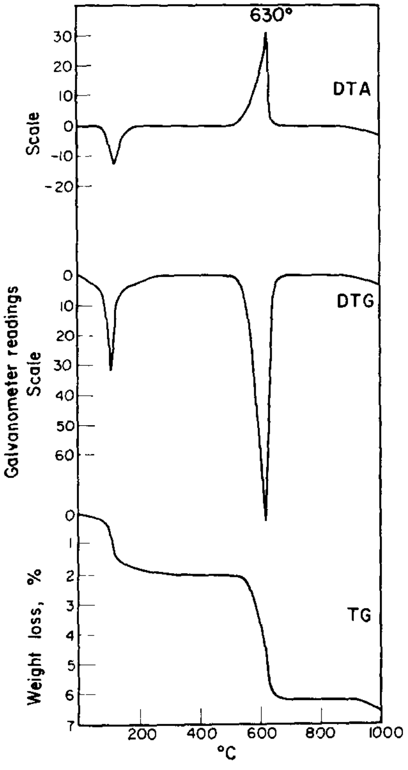

FIG. 4.—Rubidium sulphate.

Rubidium aluminium sulphate dodecahydrate

The water of crystallisation of rubidium aluminium sulphate dodecahydrate, produced in this laboratory, leaves in three steps, as with the potassium[7] and caesium aluminium sulphates.[2] Three peaks of the derivative thermogravimetric curve (Fig. 5) show that the water molecules are bound by bonds of three different strengths. By projecting the minima of the DTG curve to the TG curve it can be established that in the first step (up to 90°) 4 moles of water leave, in the second step (up to 190°) 6 moles leave and in the third step (up to 260°) 2 moles leave. The DTA curve shows the three processes, but the first and second peaks overlap and only a point of inflection appears on the curve.

Above 260° the anhydrous form is of constant weight up to 680°. At this point sulphur trioxide starts to leave; initially that belonging to aluminium oxide goes off. This process lasts up to 1000° and decomposition of rubidium sulphate can only be observed above 1000° because the decomposition of the aluminium sulphate masks the slight decomposition of rubidium sulphate that takes place below 1000° (Fig. 4). Stable compounds of stoichiometric composition are found; up to 50° the product has 12 moles of crystal water, and between 260 and 680° the product is anhydrous rubidium aluminium sulphate.

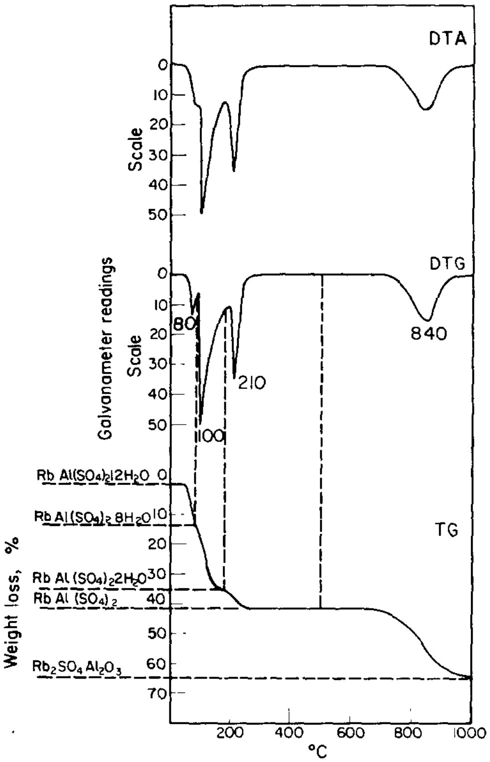

FIG. 5.—Rubidium aluminium sulphate dodecahydrate.

Rubidium carbonate

According to the derivatogram (Fig. 6), the strongly hygroscopic rubidium carbonate contained about 4% of moisture. In spite of its hygroscopic nature, water was removed by 200° and this water was released in one step.

If the sample is exposed to air for a short time it adds 2 moles of water.

Decomposition of this hydrate shows some similarity to the results of Reisman.[8] We found that in this sample the loss of 2 moles of water actually proceeds in four steps (dotted line), at a heating rate of 3°/min, and above 250° rubidium carbonate is of constant weight. From this temperature up to 800° no weight change was observed, and the small endothermic peak observed by Reisman[9] at 303° was not found.

It has been stated that rubidium carbonate is very volatile at red-heat[10] and that it melted at this temperature without decomposition.[11] We established 870° as the melting point, which is in contradiction with older values.[12] According to our experiments, decomposition and loss of weight of the sample starts at 800°. At the melting point it was observed, especially from the DTG curve, that the rate of loss of weight temporarily increases. Above the melting point, raising the temperature increases the degree of decomposition.

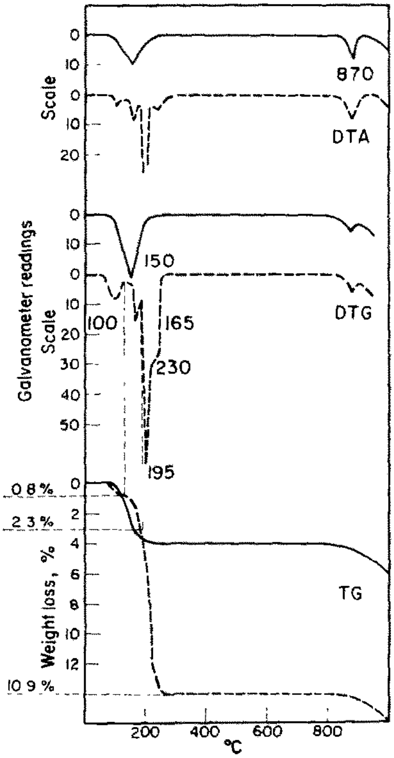

FIG. 6.—Rubidium carbonate.

Rubidium chromate

Our rubidium chromate sample contained water, adsorbed on the surface, which left at a DTG maximum at 60° (Fig. 7). Between 400 and 500° a weight change of about 0·7%, caused by some contaminant, was observed.

On the DTA curve at 740° a reversible change of modification appears, which is similar to that of caesium chromate.[2] It was also established from the DTA curve that the melting point of the substance was 980°.

The weight curve shows that, as in the case of rubidium carbonate, a weight decrease begins below the melting point, at 850°.

Rubidium bichromate

The rubidium bichromate (Chemapol sample) is practically of constant weight up to 650°, according to the derivatogram (Fig. 8). Two endothermic peaks appear on the DTA curve. The first one at 330° is irreversible and indicates a change of modification. Formerly, two modifications of rubidium bichromate, crystallised from solution, have been reported.[13,14] We are reporting elsewhere the conditions and demonstration of thermal decomposition.[15]

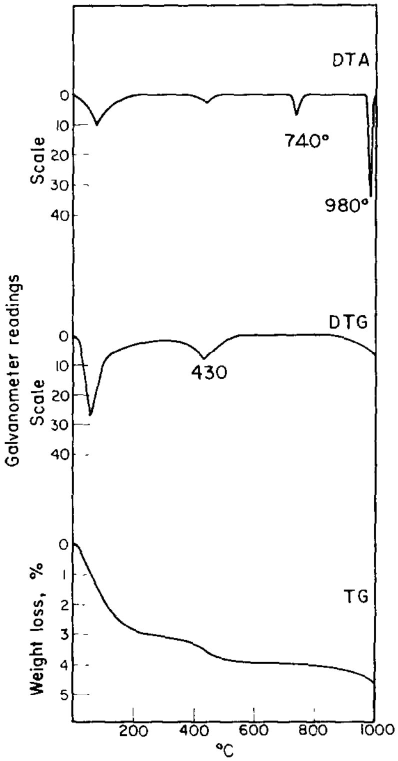

Fig. 7.—Rubidium chromate.

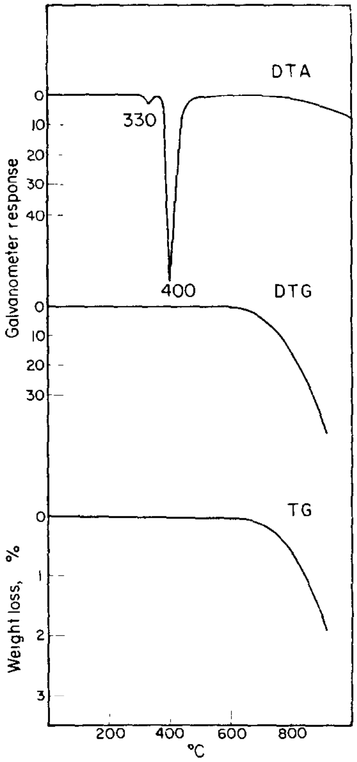

Fig. 8.—Rubidium bichromate.

The other endothermic peak was at the melting point of rubidium bichromate, *i.e.*, 400°. The substance is of constant weight even at a temperature 250° higher than the melting point, and the weight of the sample begins to decrease only above 650°.

Rubidium nitrate

It can be established from the thermoanalytical curves of rubidium nitrate (Fig. 9) that it is practically of constant weight up to 600°. Four endothermic peaks were found on the curve showing the enthalpy change; it was shown by the cooling curve that all of them were reversible.

The first three of the four peaks are caused by a change of modification. The rhombohedral form, stable at room temperature, changes into a cubic lattice at 165°. This cubic lattice transforms into hexagonal lattice at 220°, which transforms into a crystal form of unknown structure at 290°. The fourth peak at 320° corresponds to the melting point.

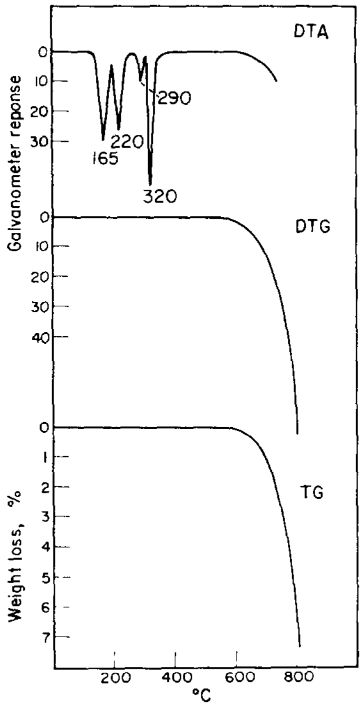

Fig. 9.—Rubidium nitrate.

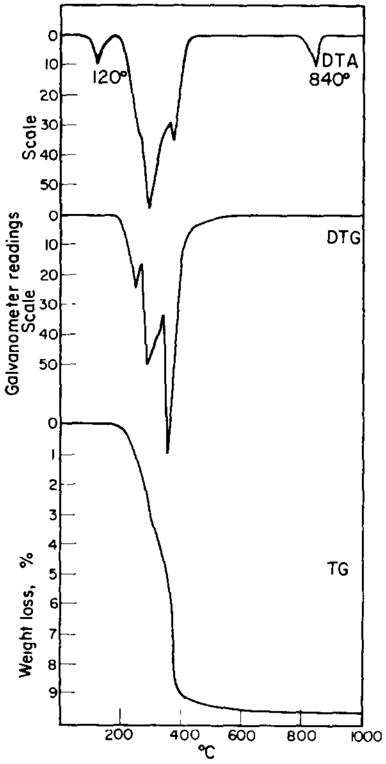

Fig. 10.—Rubidium dihydrogen phosphate.

Rubidium nitrate, as was caesium nitrate,[2] is stable up to 600° and decomposition starts only above this temperature.

Rubidium dihydrogen phosphate

It can be established from the derivatogram (Fig. 10) that the sample does not contain waters of crystallisation and is of constant weight up to 180°. There is an endothermic peak on the DTA curve at 120°, which is irreversible, and indicates recrystallisation of the sample. Water is lost from the sample, on heating, according to the equation:

$$RbH_2PO_4 \rightarrow RbPO_3 + H_2O.$$

The loss of the water proceeds, according to the DTG and DTA curves, in three stages. Rubidium metaphosphate is of constant weight from 550° and melts at 840°, according to the DTA curve.

These results are summarised in Table I, in which the peaks from loss of surface water have been omitted.

TABLE I.—SUMMARY OF DERIVATOGRAPHIC RESULTS

Figure	Rubidium salt	Formula	DTA peaks,* °*C*	M.p., °*C*	DTG peaks,* °*C*	Temperature of drying, °*C*
1	Chloride	$RbCl$		720		<650
2	Bromide	$RbBr$	(80, 120, 240, 500, 600)	680	(80, 120, 240, 500)	<650
3	Iodide	RbI		640		<600
4	Sulphate	Rb_2SO_4	630 exothermic, irreversible	1074†		<520
5	Aluminium sulphate	$RbAl(SO_4)_2 \cdot 12H_2O$	80, 100, 210 endothermic		80, 100, 210, 840	Room temperature‡
6	Carbonate	Rb_2CO_3		870		<800
7	Chromate	Rb_2CrO_4	(430), 740 endothermic, irreversible	980	(430)	<850
8	Bichromate	$Rb_2Cr_2O_7$	330 endothermic, irreversible	400		<650
9	Nitrate	$RbNO_3$	165, 220, 290 endothermic, reversible	320		<280
10	Dihydrogen phosphate	RbH_2PO_4	120 endothermic, irreversible 250, 290, 360 endothermic		 250, 290, 360	<150
	Metaphosphate	$RbPO_3$		840		<800

* Peaks given in brackets are caused by small amounts of contaminants.

† Literature value.

‡ Anhydrous rubidium sulphate can be heated between 260 and 680° without decomposition.

DISCUSSION

The results gained by derivatographic methods can be interpreted very satisfactorily by the theory of high temperature systems worked out by Erdey and his coworkers.[16,17] Because the acidic cation was the same in all cases, the influence of the basic anion on the thermal properties of the substances was examined.

The melting point of the halides decreases with decreasing electronegativity (*i.e.*, with increase of polarisability and diameter). It was also established that the halides did not have polymorphous modifications.

Lewis acid cations (C^{4+}, N^{5+}, S^{6+}, Cr^{6+}) on the right-hand side of the Periodic Table, are not stable by themselves, but always occur in a form neutralised with O^{2-} ions. As in the case of the caesium salts of these ions, the rubidium salts also show a relatively high stability and high melting point.

Pauling's electronegativity values of the acid cations studied and the melting points are inversely proportional. An exception is the Cr^{6+} acid cation, whose melting point should be higher than the observed value. This is surprising, because properties of salts of alkali metals generally pass through a maximum going downwards in the Periodic Table, and the change of melting points (and if any, modification-change points) of chromates also shows a tendency to increase. The findings for potassium[18] and sodium salts[19] will be published shortly.

It was also found with rubidium chromate that the substitution of an O^{2-} ion of CrO_4^{2+} ion by another CrO_4^{2-} ion, which is less basic than O^{2-}, decreased the bond strength so that the melting point appears at a lower temperature: 400° compared with 980°.

The reason for the loss of water in three steps from rubidium aluminium sulphate dodecahydrate, similar to the analogous potassium and caesium compounds,[3,13] is that the water molecules are bound by different strengths to the rubidium, aluminium and sulphate ions.

The high-temperature acid-base theory explains why aluminium sulphate decomposes first in rubidium aluminium sulphate. The aluminium ion is a stronger acid cation and, therefore, rubidium sulphate decomposes at a higher temperature.

Rubidium carbonate, similar to caesium carbonate,[2] loses water of crystallisation in several separate steps, and the amounts of water lost are not in a stoichiometric ratio of whole numbers. This can be explained by the presence of water molecules bound by different strengths and situated at different points of the lattice.

It is also of interest that rubidium nitrate is of constant weight up to a temperature more than 250° higher than the melting point and decomposition begins only above this value.

Acknowledgement—Most of the samples were made available to us by E. Merck, Darmstadt, German Federal Republic, to whom we express our thanks.

Zusammenfassung—Die häufiger vorkommenden Rubidiumsalze wurden der Derivatographie unterworfen, wobei ihre Gewichtsänderung und deren Geschwindigkeit und die Enthalpieänderung als Temperaturfunktionen gemessen wurden. Aus diesen Versuchen wurden die Temperaturen erschlossen, bei denen die Salze ohne Zersetzungsgefahr getrocknet werden können. Die Ergebnisse lassen sich durch die Säure-Basen-Theorie hoher Temperaturen deuten.

Résumé—On a étudié par dérivatographie les sels de rubidium les plus communs et measuré leur variation de poids, la vitesse de variation de poids et la variation d'enthalpie en fonction de la température. Sur la base de ces expériences, on déduit les températures auxquelles les sels peuvent être séchés sans danger de décomposition. On peut interpréter les résultats par la théorie acide-base aux températures élevées.

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A REVIEW OF ORGANIC COMPOUNDS CONTAINING P=S AND P(S)SH GROUPS AS SEPARATORY AND ANALYTICAL REAGENTS*

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Summary—A review of separations with, and analytical applications of organic compounds with P=S and P(S)SH groups is presented.

ORGANOPHOSPHORUS compounds containing the phosphoryl group (P=O) are widely used as extractants for inorganic metal salts. Diamond and Tuck[1] noted the lack of studies with the corresponding sulphur analogues containing the thiophosphoryl group (P=S). Since this observation, a number of papers have appeared on the application to separations and analytical chemistry of organic compounds containing the thiophosphoryl group. The purpose of the present paper is to present a review of these studies.

It was realised early that the solvating powers of extractants containing the phosphoryl group was due to the ionic character or shift from P=O to $P^+—O^-$ configuration. Correspondingly, the solvating powers of compounds containing the P=S bond will also depend, in part, on the ionic character or shift from P=S to $P^+—S^-$ configuration. The difference in the electronegativities of P and O is 1·4 according to Pauling;[2] therefore, the ionic character of the P=O bond is about 80%, in the absence of electrophilic substituents. The difference in the electronegativities of P and S is 0·4, so that the ionic character of the P=S bond will be about 8% in the absence of electrophilic substituents. The above values of ionic character are only an approximation, and the character of additional substituents will most certainly affect the P=O and P=S bond; however, the numerical values are helpful in understanding reactions of compounds containing P=O and P=S bonds. The possibility of increasing the ionic character of compounds with the P=S group by proper substituents, and hence the extractive properties, is greater for P=S bonds than the corresponding P=O bonds. For organophosphorus compounds whose only structural difference is the P=O and P=S, the compound with the P=O bond will have greater electron-donating ability and consequently greater extraction powers for most metal salts.

Trialkyl Thiophosphates

Wendlandt and Bryant[3] compared the solvating powers of tributyl phosphate (TBP) with tributyl thiophosphate (TBTP) for thorium, uranium and copper nitrates.

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They reported TBP to be by far the better solvent. Wendlandt and Bryant concluded that because the dielectric constants for the two solvents are similar,[4] the difference in solvability must be due to the difference in bonding between the metal salts and organic molecules. Earlier Pishchimuksa[5] reported that trialkyl thiophosphates were poor solvents for metal salts. Handley and Dean[7] also reported tri-iso-octyl thiophosphate to be a poor extractant for thorium and copper. However, compounds with the P=S bond should bond with a different class of inorganic metal salts as compared to compounds with P=O bonds. The phosphoryl group donates chiefly to class "a" or border region acceptors.[6] The thiophosphoryl group would be expected to donate to class "b" acceptors which are good sulphur co-ordinators.

Before the studies at the Oak Ridge National Laboratory, organophosphorus reagents containing the P=S bond had not been systematically studied. Handley and Dean[7] were the first to utilise the low solvating power of trialkyl thiophosphates for most metal ions to develop a highly selective solvent extraction method for the separation of silver and mercury from 35 other elements studied. From an aqueous $6M$ nitric acid phase, 10^{-3} to 10 mg of silver and mercury were quantitatively extracted in one equilibration by an carbon tetrachloride phase $0{\cdot}67M$ in tri-iso-octyl thiophosphate (TOTP). The effects of $[\text{TOTP}]_o$, [Hg], [Ag] and $[HNO_3]$ on the distribution ratio, D, of mercury and silver were also studied by Handley and Dean. The complex was established as an ion-association type. D is defined as the total concentration of metal in the organic phase divided by the total concentration of metal in the aqueous phase at equilibrium. They also reported the effect of temperature, salting agents, various anions and acids on D_{Ag} and D_{Hg}. The bond between TOTP and the metal salt is not strong. A mole ratio of TOTP to silver of at least 25 is necessary for quantitative extraction, and an aqueous phase $\geq 6M$ in nitrate is also necessary. Silver is stripped from the organic phase by washing with water. It should be possible to apply the separation to many types of sample. They applied the extraction to the successful separation and radiochemical determination of silver in "young" fission product mixtures.

Wish and Foti[8] have also applied a solvent-extraction step with tri-iso-octyl thiophosphate to the sequential procedure[9] for the radiochemical separation of tracer silver from fission products. In the procedure, the metals forming anionic complexes in concentrated hydrochloric acid are absorbed on an anion-exchange column. Silver, cadmium and rhodium are among the elements remaining in solution, and are absorbed on a second anion column from $0{\cdot}1M$ hydrochloric acid. Rhodium is eluted with $2M$ hydrochloric acid, silver with $6M$ hydrochloric acid and cadmium with $12M$ hydrochloric acid. Rhodium elution is slow and there is considerable tailing. Consequently, silver, which was eluted with $6M$ hydrochloric acid, was contaminated with rhodium. The silver fraction was freed from rhodium contamination by conversion to a solution $8M$ in nitric acid and extracted with a 30% TOTP-carbon tetrachloride solution. Wish and Foti reported the $D_{\text{Ag}} = 1900$, $D_{\text{Cd}} = 10^{-3}$ and $D_{\text{Rh}} = 10^{-4}$.

Nelson and Michelson[10] have used TOTP and ion-exchange techniques to separate tracer rhodium and silver. The TOTP was absorbed on microporous polyethylene beads. The absorbant bed, 0·28 cm² by 1·0 cm, was heated to 50° and a $6M$ nitric acid solution containing rhodium and silver added to the bed. The rhodium was eluted with $6M$ nitric acid, then the silver was eluted with $1M$ nitric acid. Excellent separation from barium, sodium, magnesium, beryllium, copper, nickel, manganese, chromium, aluminum, yttrium and indium was reported.

Lewis[11] has used a TOTP-hexane solution to separate ^{109}Cd and ^{110m}Ag. Following neutron bombardment, the silver target was dissolved in $8M$ nitric acid and contacted with a 30 w/v % TOTP-hexane solution. The theoretical separation coefficient was reported to be 6×10^{15}; however, practical consideration of individual techniques was found to give a somewhat lower separation coefficient. Ability to perform the ^{110m}Ag–^{109}Cd separation remotely was considered to be an advantage, and the entire procedure required much less than 1 day to complete.

Parker[12] has reported using TOTP to separate and determine radioactive mercury in thallium radioisotopes. The mercury activities were extracted from an aqueous $6M$ nitric acid phase by 30 w/v % TOTP in carbon tetrachloride. One equilibration was usually sufficient to give an excellent separation of thallium and mercury radioactivities.

In the application of TOTP to extraction techniques, it should be remembered that aqueous 6–$8M$ nitric acid solutions cause hydrolysis of trialkyl thiophosphates. However, during a 5 to 10 min extraction period the extraction properties of TOTP are not appreciably affected by the aqueous nitric acid, but longer contact periods should be avoided. If the mercury or silver is to be back extracted into the aqueous phase for subsequent analytical steps, the back extraction should be performed immediately. It is probable that the hydrolysis products prevent quantitative back extraction into the aqueous phase. Back extraction is easily accomplished by washing the organic phase with water, aqueous ammonia or hydrochloric acid. Applications of trialkyl thiophosphates have been limited to separation of radioactivities. Practical applications to separation of mercury and silver from a mixture containing large amounts of other metal ions followed by subsequent analytical steps have been limited. During a study of the flame emission characteristics of silver, Dean and Stubblefield[13] used a 30 w/v % solution of TOTP dissolved in various solvents as an extractant for silver from an aqueous nitric acid phase.

Trialkylphosphine Sulphide

A survey of tributylphosphine sulphide (TBPS)[14] as an extractant has been reported. TBPS is the sulphur analogue of trialkylphosphine oxides such as trioctylphosphine oxide (TOPO). The selectivity for silver and mercury agrees with results reported for trialkyl thiophosphates as extractants. No analytical applications have been reported for TBPS. Selective extraction of mercury and silver from aqueous acid solutions appears to be a characteristic of organophosphorus compounds containing a P=S bond.

Elliott and Banks[15] studied the use of trioctylphosphine sulphide (TOPS), the sulphur analogue of trioctylphosphine oxide (TOPO), as an organic extractant and as the stationary phase in the reversed-phase partition paper chromatography of inorganic metal salts. Silver(I), mercury(II) and palladium(II) were selectively extracted from aqueous nitric acid solutions. D for these metals decreased with increased aqueous phase nitric acid concentration. This result contrasts sharply with the reported increase in D_{Hg} and D_{Ag} with increasing nitric acid concentration when TOTP was used as extractant.[4] The increased basicity of TOPS over TOTP with resultant greater competition of nitric acid for the donor sites of TOPS as compared to TOTP probably explains the contrasting results. The reported difficulty of back extracting mercury from the organic phase containing TOPS is also indicative of a stronger complex as compared to TOTP. The difference in extraction properties of TOPS and TOTP are in agreement with corresponding differences in extractive properties of similar organophosphorus compounds containing the phosphoryl group P═O, namely TOPO and TBP. Elliott and Banks also reported extraction of gold(III) and mercury(II) from aqueous hydrochloric acid solutions. D_{Au} increased and D_{Hg} decreased with an increase in hydrochloric acid concentration. Palladium was only partially extracted and D_{Pd} decreased with increasing hydrochloric acid concentration. Reversed-phase partition paper chromatography results were in agreement with extraction results with the exception of the retention of uranium and thorium. No explanation for this exception was offered. With nitric acid as the mobile phase only mercury(II), silver(I) and palladium(III) were completely retained, while uranium(VI), thorium(IV) and molybdenum(VI) had low R_f values. With hydrochloric acid as the mobile phase mercury(II), palladium(II), platinum(IV) and gold(III) were completely retained.

Trialkyl- and Hexa-alkylphosphorothioic Triamides

Handley[16] has studied the trialkyl- and hexa-alkylphosphorothioic triamides as extractants for metal ions. The *N*-alkyl and *N*-aryl substituted derivatives of $(NH_2)_3PS$ are the nitrogen analogues of the esters of phosphorothioic acid. The extraction results indicate that substitution of a nitrogen atom for an oxygen atom between carbon and phosphorus caused the P═S group to co-ordinate more strongly to the metal ions, in comparison to TOTP as extractant. However, the P═S group remains as a selective co-ordinator for mercury(II), silver(I), copper(I), palladium(II) and gold(III). The trialkyl phosphorothioic triamides permit quantitative extraction from a wider range of acid concentration and from acids other than nitric as compared to the trialkyl thiophosphates. However, substitution of a nitrogen atom for an oxygen atom did not expand the number of inorganic metal salts extracted. Substitution of alkyl groups for all the hydrogen atoms in the parent $(NH_2)_3PS$ causes the compound to be less effective as an extractant. This is attributed to steric hinderance.

The effects of aqueous phase mineral acid, inorganic salt and metal ion concentration, organic solvent, size of substituent group and concentration of extractant in the organic phase were studied by Handley. The complex is a co-ordination type and the species extracted is of the type $[(RNH)_3PS]_2HgSO_4$ or some multiple thereof. Trihexylphosphorothioic triamide is a very selective extractant for copper(I). Because copper(II) is not extracted, it is separated from mercury(II), silver(I), palladium(II) and gold(III) by first extracting these metals followed by reduction of copper(II) to copper(I), which is then extracted.

The organophosphorus compounds containing the thiophosphoryl group under normal conditions are relatively unreactive. However, they are subject to hydrolysis at elevated temperatures and on prolonged exposure to both strongly acidic and basic conditions. Strong oxidising agents cause substitution of an oxygen atom for the sulphur atom. Those compounds containing longer chained alkyl groups are more resistant to chemical change as compared to compounds with short chained alkyl groups.

Acute oral toxicological studies show the trialkyl phosphorthioates to be relatively non-toxic with the toxicity decreasing as the molecular weight increases.[17] The toxic properties of corresponding phosphine and triamide derivatives are probably not significantly different.

Dialkyl Phosphorodithioates and -thioates

The use of diethyl phosphorodithioic acid as an analytical reagent was suggested by Busev[18] in 1949. Since that time dialkyl phosphorodithioates have been investigated by a number of people, but only limited general use has developed. It is the purpose of this paper to review the literature and stimulate further development of these versatile reagents.

Although dialkyl phosphorodithioic acids and their metal complexes are unavailable in reagent grades, large quantities are produced commercially. Generally, these products are mixtures and are used as additives in lubricating oils and flotation agents. They are synthesised by the straightforward reaction of alcohols with phosphorus pentasulphide.[19] The raw materials are abundant and cheap; therefore, the final product is not costly. Short-chain (through butyl) derivatives can be purified by vacuum distillation. Purification is also achieved by conversion to alkali or ammonium salts and recrystallisation from an organic solvent. The dialkyl phosphorodithioic acids are strong acids,[20,21] and titration curves are indistinguishable from a completely dissociated monobasic acid. Bode and Arnswald[22] made a study of diethyl phosphorodithioic acid (diethyl-DTPH) and compared its properties to diethyldithiocarbamate. They reported a half-life period of 250 hr for diethyl-DTPH in 1*M* hydrochloric acid, and for equal normal sulphuric acid solutions a longer period. Diethyldithiocarbamic acid has a half-life period of only a few seconds for corresponding conditions. Thus, diethyl-DTPH has an advantage over dithiocarbamic and xanthoic acids when one works in mineral acid solutions. Therefore, diethyl-DTPH can be used for gravimetric as well as solvent extraction methods. In an extraction system wherein the diethyl-DTPH is dissolved in an organic solvent in which mineral acids have a low solubility, stability would be considerably increased. Kabachnik and coworkers[23] report an ionisation constant of diethyl-DTPH in an aqueous solution containing 7%, by volume, of ethanol to be $2{\cdot}4 \times 10^{-2}$, while Bode reports the dissociation constant to be greater than $2{\cdot}4 \times 10^{-2}$ in aqueous solutions. Diethyl-DTPH was also reported to be significantly extracted by carbon tetrachloride from aqueous hydrochloric acid solutions $\geq 0{\cdot}05M$, while pH 4 is necessary for the extraction of diethyldithiocarbamic acid. Increasing the alkyl chain causes only small changes in dissociation constants[21] and only small changes in the reaction of $(RO)_2P(S)SH$ with metal ions. However, the distribution ratio increases significantly. Also, the reductive action of $(RO)_2P(S)SH$ on certain metal ions [copper(II), gold(III), *etc.*] takes place chiefly in the aqueous phase,[24] and dibutyl-DTPH when used as extractant will extract a greater number of metal ions than diethyl-DTPH. For these reasons dibutyl-DTPH or a longer chained derivative has a distinct advantage when performing solvent extractions. However, diethyl-DTPH, because of its water solubility, has an advantage when used for gravimetric, titimetric and other methods in which water solubility is important.

Three papers have appeared,[25–27] two of which are extensive surveys and the third a partial review of dialkyl phosphorodithioic acids as extractants. Bode and Arnswald[26] used the diethyl derivative dissolved in carbon tetrachloride to study the extraction of

25 metal ions. The extractions were conducted from 0·1–10*M* hydrochloric acid and 0·05–7·5*M* sulphuric acid solutions. They concluded that the high stability of diethyl-DTPH dissolved in carbon tetrachloride offers advantages when compared to disubstituted dithiocarbonic acids. A carbon tetrachloride solution of diethyl-DTPH contacted for 100 hr by 10*M* hydrochloric acid still retained 94% of the reagent. In general, those metals that form insoluble sulphides are extracted. Spectrophotometric determinations are possible in many cases.

TABLE I.—PERCENTAGE EXTRACTION OF METAL IONS WITH A SOLUTION OF DIBUTYL PHOSPHORODITHIOIC ACID IN CARBON TETRACHLORIDE

	Acid, *N*					
	HCl			H_2SO_4		
Element	0·1	1·0	6·0	0·1	1·0	6·0
Fe(III)	88	51	11	91	66	18
Co(II)	58	1	>0·01	67	<0·01	>0·01
Ni(II)	>99	48	>0·01	>99	51	>0·01
Cu(II)	100	100	100	100	100	100
Zn(II)	>99	58	<0·01	>99	52	10
Ga(III)	3	<0·01	<0·01	5	<0·01	<0·01
As(III)	94	95	96	40	65	90
Se(IV)	>99	>99	>99	>99	>99	>99
Mo(VI)	95	>99	4	93	95	54
Pd(II)	100	100	100	>99	>99	>99
Ag(I)	100	100	100	100	100	>99
Cd(II)	100	100	31	>99	>99	95
In(III)	100	97	5	100	>99	97
Sn(II)	>99	92	29	>99	96	87
Sb(III)	98	98	27	>99	98	96
Te(IV)	<0·01	2	20	>99	97	94
Re(VII)	<0·01	<0·01	12			
Au(I)	100	100	100	100	100	100
Hg(II)	100	100	100	100	100	100
Tl(I)	>99	94	30			
Pb(II)	100	100	100	>99	>99	>99
Bi(III)	100	100	100	100	100	99

Organic phase: 0·207*M* $(C_4H_9O)_2P(S)SH$ in CCl_4
Aqueous phase: Acid shown, 0·5 mg of metal ion/ml, electrolyte ≥0·3*M* (NaCl or Na_2SO_4)

Handley[25,27] surveyed the extraction of metal ions using a carbon tetrachloride solution of dibutyl phosphorodithioic acid. The extractions were conducted from 0·01–10*M* hydrochloric and sulphuric acid solutions. Radioactive isotopes were used to determine the distribution ratio of the metal ions. Of 42 elements studied, a significant *D* was found for 22 elements. Table I is a summary for those metals that were extracted. There are advantages in extractions from acid solutions; however, use of masking reagents to aid in separations is limited. It was shown[25] that several metal ions are quantitatively extracted at pH 8, a condition wherein many masking compounds are effective. Handley also reported the effect of the alkyl group, organic solvent and diverse salts on the distribution ratio. The relative displacement of one metal by another was reported to be palladium(II) > gold(III) > copper(I) > mercury(II) > silver(I) > copper(II) > antimony(III) > bismuth(III) > lead(II) > cadmium(II) > nickel(II) > zinc(II). If the lead(II) complex is used as an extractant, those metals below lead(II) in the order of extraction will not be extracted. Such a technique will increase the selectivity. However, certain metal ions are extracted in an amount greater than that represented by a hydrogen-atom-replacement reaction.[28] Thus, the metal complexes of mercury(II), silver(I) or palladium(II) cannot be used to improve the selectivity. This result agrees with the reported[26] difficulty of determining diethyl-DTPH as Pd(diethyl-DTP)$_2$ upon addition of palladium(II) in excess. Handley[27,29] surveyed the use of dibutyl phosphorothioic acid as an extractant for metal ions. In this compound one of the sulphur atoms has been replaced by oxygen. Dibutyl phosphorothioic acid is somewhat more selective and forms fewer coloured species when compared to the dithioic derivative. Cobalt(II) and nickel(II) are not extracted, whereas with the dithioic derivative they are extracted. Of the metals studied, 18 were extracted in significant amounts. The influence of dibutyl phosphorothioic acid concentration, organic solvents, mineral acid concentration and limits of extraction were studied by Handley. As with the dithioic derivative, those metal ions forming insoluble sulphides were found to be extractable; although not all metal ions forming insoluble sulphides were extracted. Those forming strong inorganic complexes with anions present could not be extracted. The effect of dibutyl phosphorothioic acid, mineral acid, metal ion concentrations and solvent were studied by Handley. For both the dithioic and thioic derivatives and for low aqueous acid concentrations ($\leq 0{\cdot}25M$) the electrolyte, *e.g.*, sodium chloride, sodium perchlorate, must be $\geq 0{\cdot}25M$ in order to obtain a maximum D. When the thioic derivative was used as an extractant the same order of displacement was found as that for the dithioic derivative. However, the thioic derivative was found to react in every instance by displacement of hydrogen atoms by a metal atom. The difficulty experienced in extracting more than the stoichiometric amounts of metal ions with the dithioic derivative is not observed with the thioic derivative. Consequently, a selective isotopic-exchange method for mercury was developed by Handley.[30] A carbon tetrachloride solution of mercury(II) dibutyl phosphorothioate was equilibrated with an acid aqueous phase containing an unknown quantity of mercury. Measurement of D_{Hg} by use of mercury-203 tracer affords a simple and easy method of mercury determination from 10^{-7} to 10^{-2} g. Only palladium(II) and gold(III) are known to interfere.

The extraction of certain metal ions [zinc(II), indium(III) and nickel(II)] is dependent on the organic phase concentration of dibutyl phosphorodithioic or dibutyl phosphorothioic acid raised to the power of the charge on the metal ion and also inversely dependent on the aqueous phase hydrogen ion concentration raised to the power of the charge on the metal ion. Obviously, for these metal ions the extractant concentration of the organic phase and acidity of the aqueous phase must be carefully controlled for quantitative extraction. The initial concentration of metal ion in the aqueous phase must also be low relative to the concentration of extractant in the organic phase. Certain other metal ions [silver(I), mercury(II), palladium(II), copper(II) and bismuth(III)] only require a small excess of extractant over the stoichiometric amount for quantitative extraction. Because these metals are only slightly dependent on the acidity of the aqueous phase as long as the electrolyte concentration is $>0{\cdot}25M$, less control of acidity is required. Handley and coworkers[31] have studied the properties of zinc dibutyl phosphorodithioate as related to a solvent-extraction system. They concluded that the dibutyl or longer-chained derivatives have advantages as compared to the ethyl derivative when applied to a solvent-extraction system. The solubility and acidity of the diethyl, di-isopropyl, dibutyl and di-isobutyl esters of phosphorodithioic acid in water and distribution into organic solvents have been studied.[32]

The greatest number of applications of the dialkyl- and diaryl phosphorodithioic acids to analytical problems have been made by Busev and coworkers. They have used dialkyl phosphorodithioic acids and their salts in the potentiometric determination of copper;[33] gravimetric, titrimetric and photometric determination of palladium;[34] gravimetric and titrimetric methods for cadmium;[35] amperometric and visual titration of lead;[36] gravimetric, titrimetric and photometric methods for bismuth[37] and photometric determination of copper.[38] In a summation Busev[39] gives detailed information on the precipitation reactions, photometric properties and analytical applications of diethyl phosphorodithioates of copper, silver, cadmium, mercury, indium, thallium, tin, lead, arsenic, antimony, bismuth, molybdenum, selenium, tellurium, iron, nickel, cobalt, ruthenium, rhodium, palladium, platinum, osmium and iridium. Comparisons are made to corresponding sulphides and xanthates. All the complexes listed above are insoluble in strong mineral acids and most are usually soluble in organic solvents. Selectivity is improved by the use of masking agents and pH adjustments. The dialkyl phosphorodithioates can be widely used for the detection, separation and determination of many elements by gravimetric, titrimetric and photometric methods.

Forster and coworkers[24] have determined copper colorimetrically with zinc di-isopropyl phosphorodithioate. A number of procedures have been published on the use of the copper complex to determine the dialkyl phosphorodithioates or certain pesticides which are first decomposed to the dialkyl phosphorodithioate,[40] then reacted with copper. Rhenium[41] has also been determined photometrically with diethyl phosphorodithioic acid.

CONCLUSION

Although a considerable body of information has been added to the literature concerning organic compounds with P=S and P(S)SH groups, many problems for investigation still exist. For example, the effect on compound reactivity brought about by changes in the attached R group or in its structure, needs additional study.

Translation of the specific chemical information concerning these compounds to practical applied methods of separation or analysis has only just begun; additional useful analytical adaptations could be made from data already accumulated.

This paper is not intended to be a complete review of these compounds and their uses, particularly in the citation of Russian references, which are selective rather than exhaustive. Instead, it is the author's hope that this review will stimulate other chemists to further evaluation and development of these versatile reagents.

Zusammenfassung—Es wird eine Übersicht über Trennungen mit und analytische Anwendungen von organischen Verbindungen mit P=S- und P(S)SH-Gruppen gegeben.

Résumé—On présente une revue sur les séparations au moyen de composés organiques possédant des groupes P=S et P(S)SH et sur leurs applications analytiques.

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SIMULTANEOUS DETERMINATION OF $^{65}_{30}$Zn AND $^{32}_{15}$P IN SHELLFISH BY RADIOCHEMICAL TECHNIQUES

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Summary—A radiochemical procedure for the simultaneous determination of $^{65}_{30}$Zn and $^{32}_{15}$P in shellfish has been devised. Shellfish samples have been analysed for these two nuclides over a period of 8 months. The values obtained by the radiochemical procedure agree with the $^{65}_{30}$Zn and $^{32}_{15}$P values of other investigators.

INTRODUCTION

BOTH $^{65}_{30}$Zn and $^{32}_{15}$P are created by neutron activation in single-pass water-cooled reactors. The usual procedure in such reactors involves the circulation of the river water after removal of suspended materials by water treatment around and through the reactor for cooling purposes, and after several hours, returning the heated water to the river.

$^{65}_{30}$Zn is produced by the bombardment of stable $^{64}_{30}$Zn with thermal neutrons. $^{64}_{30}$Zn is 48·89% abundant and has a thermal neutron cross-section of 0·47 barn.[1] The radioactive $^{65}_{30}$Zn, produced according to equation (1), decays 98·5% of the time by electron capture and 1·5% by positron emission.

$$^{64}_{30}\text{Zn} + ^{1}_{0}\text{n} \rightarrow ^{65}_{30}\text{Zn} + \gamma \tag{1}$$

In the decay of $^{65}_{30}$Zn by electron capture, a gamma ray, which is 44% abundant with an energy of 1·119 MeV, is produced. The half-life of $^{65}_{30}$Zn is 245 days.

$^{32}_{15}$P is produced by the neutron activation of $^{31}_{15}$P and $^{32}_{16}$S. $^{31}_{15}$P, which exists as dissolved phosphates, is 100% abundant and has a thermal neutron cross-section of 0·20 barn.[1] The production of $^{32}_{15}$P is

$$^{31}_{15}\text{P} + ^{1}_{0}\text{n} \rightarrow ^{32}_{15}\text{P} + \gamma \tag{2}$$

$^{32}_{15}$P is also produced by the neutron activation of $^{32}_{16}$S, which is present in the cooling water as naturally-existing dissolved sulphates or is added in the form of aluminium sulphate in the water treatment process. It is 95% abundant and has an over-all cross-section for slow and fast neutrons of 0·065 barn.[2] The neutron interaction with $^{32}_{16}$S is

$$^{32}_{16}\text{S} + ^{1}_{0}\text{n} \rightarrow ^{32}_{15}\text{P} + ^{1}_{1}\text{H} \tag{3}$$

$^{32}_{15}$P decays 100% of the time by beta emission. The radionuclide, which has a half-life of 14·3 days, emits several beta particles among which the maximum energy is 1·707 MeV.

The radionuclides, $^{65}_{30}$Zn and $^{32}_{15}$P, entering a river by way of returned reactor cooling water, may follow three pathways. First, they may be removed to some extent by reaction with other chemical ions or sedimentation materials. Second, they may be partially taken up in the metabolic processes of aquatic environmental species. Third, they may continue to exist as chemical ions in the water.

Various researchers have indicated that shellfish, in particular, tend to concentrate ${}^{65}_{30}$Zn.[3–5] Rice, Baptist and Price[6] have also studied the removal of ${}^{32}_{15}$P-tagged phytoplankton from sea water by clams, *Mercenaria mercenaria*. Because it has been shown that various environmental media, particularly shellfish, highly concentrate ${}^{65}_{30}$Zn and ${}^{32}_{15}$P, a number of analytical procedures have been developed for their determinations.

There are several techniques which can be used to determine the concentration of ${}^{65}_{30}$Zn and ${}^{32}_{15}$P in shellfish. Generally, these techniques involve a separate analysis for each nuclide. A common method of determining ${}^{65}_{30}$Zn is by gamma spectroscopy in which either "matrix" or "spectrum stripping" methods are employed.

The "matrix" method consists of qualitatively analysing the gamma spectrum of a bulk sample in order to determine the specific radionuclides that are present. After the existing radionuclides have been identified, a mathematical matrix is prepared from experimental data by using concentrations of the nuclides known to be present. The "spectrum stripping" technique consists of subtracting the interfering components from a gross gamma-ray spectrum. Both methods are highly sensitive and exact, but there are disadvantages associated with the use of each technique. In using the matrix method, a qualitative analysis must be made for each sample unless one makes the assumption that the radionuclide composition does not differ among samples. In instances where the spectrum stripping technique is to be used, considerable time is necessary for the preparation of a catalogue of standard spectra. A specific disadvantage associated with the preparation of a catalogue is the procurement of radionuclides with accurately known composition. This was shown by Kolde and Karches[7] in their research on standards.

Probably the largest disadvantage associated with the use of both techniques is the need for expensive equipment, such as a multichannel analyser, its associated readout devices, massive shield and perhaps a computer. The total cost for this equipment is in the range $20,000–50,000.

Because ${}^{32}_{15}$P is a beta emitter, samples cannot be analysed for this radionuclide by gamma spectroscopy. Of course, beta spectroscopy might be employed, but this is still regarded as being in the experimental stage of development.

A relatively small number of samples can be analysed for ${}^{65}_{30}$Zn and ${}^{32}_{15}$P economically with regard to time and cost, by using radiochemical procedures. Chemical procedures have been formulated by analysts for the individual determinations of zinc and phosphorus in a variety of materials.[8–10] This information suggests that it is possible to devise a radiochemical procedure for the simultaneous determination of ${}^{65}_{30}$Zn and ${}^{32}_{15}$P in a single aliquot. The advantages of a procedure of this type are several. First, a radiochemical procedure is a great deal less expensive than those methods previously described because a single channel analyser can be used to count the purified gamma emitter when a multichannel analyser is not available. Second, a radiochemical procedure is particularly adaptable to a small number of samples. Third, the incorporation of a specific procedure for each nuclide into one simultaneous procedure for both ${}^{65}_{30}$Zn and ${}^{32}_{15}$P reduces the time of sample preparation and eliminates a number of chemical steps.

EXPERIMENTAL

The generalised radiochemical procedure consists of: 1. wet ashing the shellfish flesh with concentrated nitric acid and hydrogen peroxide; 2. separation of $^{65}_{30}$Zn from $^{32}_{15}$P by an ion-exchange procedure; 3. selective precipitation of the zinc in the zinc fraction and 4. selective purification and precipitation of the phosphorus in the phosphorus fraction. A completion of the procedure involves the gamma counting of $^{65}_{30}$Zn and beta counting of $^{32}_{15}$P. Experience has shown that 5–7 samples can be handled conveniently in applying the procedure.

Reagents

Distilled water is used for all of the work.

Zinc carrier solution. Dissolve 41·8 g of anhydrous zinc chloride in enough water to make 1 litre of solution. Standardise with zinc reagent solution.

Zinc reagent solution. Dissolve 128 g of ammonium thiocyanate plus 108 g of mercury(II) chloride in enough water to make 1 litre of solution. Store in a brown bottle.

2*M Hydrochloric acid solution.* Mix 6,667 ml of water with 1,333 ml of concentrated hydrochloric acid (36·5% HCl).

1*M Nitric acid solution.* Mix 7,467 ml of water with 533 ml of concentrated nitric acid (69% HNO_3).

Perchloric acid. Place 30 ml of concentrated perchloric acid (70% $HClO_4$) in a dropper bottle.

Alcohol. 95% ethanol in a plastic wash bottle.

Concentrated nitric acid (69% HNO_3)

Ice cubes frozen from distilled water

30% *Hydrogen peroxide solution*

Citric acid solution. Dissolve 50 g of citric acid in enough water to make 1 litre of solution.

Ammonium molybdate solution. Dissolve 100 g of ammonium molybdate in enough water to make 1 litre of solution.

Magnesia mixture. Dissolve 50 g of magnesium chloride and 100 g of ammonium chloride in enough water to make 1 litre of solution.

Ammonia solution. Mix 500 ml of concentrated aqueous ammonia (28% NH_3) with 500 ml of water.

6*M Nitric acid solution.* Mix 400 ml concentrated nitric acid (69% HNO_3) with enough water to make 1 litre of solution.

5% *Ammonium nitrate solution.* Dissolve 50 g of ammonium nitrate per litre of water.

Dissolution of sample

A. Place a weighed portion of fish flesh in a 1,500-ml beaker (usually 50 g of wet flesh is sufficient, if that much is available). Add 5·00 ml of zinc carrier solution to the beaker containing the sample.

B. Add 20 ml of 30% hydrogen peroxide solution and 150 ml of concentrated nitric acid to the sample. Stir with a stirring rod to disperse as much flesh throughout the acid as possible.

C. Warm the beaker gradually on a hot plate. Stir frequently. A white foam will appear and slowly rise up the beaker walls. When this occurs, stir vigorously and add a small amount of water if necessary. Watch the sample until all the flesh is in solution.

D. When it appears that all the flesh is in solution, increase the heat slowly and evaporate the solution to about 5 ml over a period of 2 hr. If, after evaporation, there appears to be some organic material, add 20 ml of concentrated nitric acid and again evaporate to 5 ml.

E. Cool the sample solution to room temperature and add 100 ml of 2*M* hydrochloric acid solution. If any fatty acids are formed upon addition of the hydrochloric acid, filter the solution, using Whatman No. 42 filter paper. Previous determinations have shown that no $^{65}_{30}$Zn is retained in the residue. Collect the filtrate in a quantitative manner.

Ion-exchange separation of $^{65}_{30}$Zn *from* $^{32}_{15}$P

A. Pretreat a Dowex-21K resin bed (50–100 mesh, 6″ × 1″) by passing 200 ml of 2*M* hydrochloric acid solution through the bed (flow rate: 1 drop/sec). Stop the flow of acid when the last of the hydrochloric acid solution is about 3 inches above the *top* of the resin bed.

B. Add the sample solution to the column. Use the same flow rate of 1 drop/sec. Retain the solution that goes through the column for the $^{32}_{15}$P analysis. Again, stop the solution about 3 inches above the top of the resin bed. Wash the resin bed with 100 ml of 2*M* hydrochloric acid solution. When the solution approaches the top of the resin bed, wash down the inside of the column with 2*M* hydrochloric acid solution (about 15–20 ml). Allow the solution just to reach the top of the resin bed, then stop the column flow. Retain all of the liquid, combined in a single aliquot for the $^{32}_{15}$P analysis.

C. The column is now ready for the zinc elution procedure. This is accomplished by placing 125 ml of $1M$ nitric acid solution in the reservoir. Open the stopcock on the reservoir and allow 30 ml of the nitric acid solution to stand on top of the resin bed. Place the reservoir in position and open the stopcock on the column. Allow 50 ml of eluant to flow through the column. Discard this portion. Refill the reservoir to 125 ml and allow this to run through the column. Stop the column when the level of the liquid is at the top of the resin bed.

Precipitation of zinc

A. Add 4 (1 inch) ice cubes to the eluate from the column. Stir for 2–5 min. Add 5 drops of perchloric acid and stir until the temperature reaches 2–5°.

B. Add 20 ml of zinc reagent solution, with stirring, to the cold solution containing the zinc. Continue to stir for a few minutes after the zinc reagent solution has been added. Allow the white precipitate to settle for 30 min (*do not allow the precipitate to sit for a long period of time before filtering.*)

Filtration of zinc precipitate

A. Set up a 2-inch membrane filter chimney apparatus, using a circle of tared Whatman No. 42 filter paper (predried at 100° for 24 hr). Check the apparatus with water, for leakage before pouring in solution containing the precipitate.

B. Pour all of the solution and precipitate into the filter chimney. Wash the beaker with water and add this to the filtration apparatus. When *all* the mother liquor has gone through the filter paper, wash down the sides of the chimney with 95% ethanol. Wash out the beaker with 95% ethanol and add this to the filtration apparatus.

C. Carefully remove the filter chimney and wash off the bottom with 95% ethanol, allowing the solution to go through the filter paper.

D. Place the paper containing the precipitate on a watchglass and dry it in an oven at 100° for 24 hr.

E. At the end of the drying period remove the filter paper containing the precipitate and weigh on an analytical balance.

F. Place the paper and precipitate in the centre of a stiff card about 2·5″ × 2·5″. Attach the paper and precipitate to the card by strips of transparent tape.

Phosphorus purification and precipitation

A. Evaporate the combined phosphorus fractions from the ion-exchange step to a volume of 5 ml. Add 10 ml of concentrated nitric acid and again evaporate to 5 ml.

B. After the solution has cooled to room temperature, add 50 ml of $6M$ nitric acid solution with stirring. Add 10 ml of citric acid solution.

C. Heat the solution to 45°.

D. Precipitate the phosphorus by adding 100 ml of ammonium molybdate solution with stirring. Allow the solution, containing the precipitate, to stand at 45° for 30 min.

E. Transfer the precipitate and solution to a 250-ml centrifuge cone and centrifuge at a normal speed of about 1000 rpm (the actual speed will depend on the type of centrifuge) for about 10 min. Decant the supernatant liquid and wash the precipitate with 50 ml of 5% ammonium nitrate solution. Centrifuge and decant the liquid.

F. Add 30 ml of 1:1 aqueous ammonia and cool in an ice bath for 20 min. After cooling in the ice bath, add 50 ml of magnesia mixture with vigorous stirring. The phosphorus is precipitated as magnesium ammonium phosphate. Centrifuge and decant the liquid.

G. Redissolve the precipitate in 30 ml of $6M$ nitric acid solution and adjust the pH to 9 with aqueous ammonia and precipitate the phosphorus as magnesium ammonium phosphate by again adding 50 ml of magnesia mixture. Stir and allow the precipitate to settle.

H. Filter the precipitate, using a 1-inch circle of Whatman No. 42 filter paper, in a filter chimney apparatus.

J. Dry the precipitate at 110° in an oven overnight. Remove and weigh on an analytical balance.

K. Mount the precipitate for counting by placing the paper and precipitate on a 7/8″ nylon disc; place a 2-inch square of thin mylar film over the precipitate; carefully force a nylon ring over the paper and disc; trim the edges of the mylar film. The sample is now ready for counting.

Counting considerations

A. A multichannel gamma analyser coupled to a 4″ × 4″ NaI(Tl) crystal is used to count the $^{65}_{30}$Zn. (The counting could be carried out with a single channel analyser.) The concentration of $^{65}_{30}$Zn is determined by counting for 100 min, then summing under the 1·119 MeV gamma-ray photopeak. Corrections are applied for background, chemical recovery, analyser efficiency, decay time, gamma abundance and sample weight. The final value for the concentration of $^{65}_{30}$Zn is reported in picocuries/g of live weight (pc/g l.wt.).

The $^{32}_{15}$P is counted in a low background beta-counting system with anticoincidence circuitry. Counting could also be carried out with a proportional counter if the activity is high enough. Corrections are made for background (less than 1 cpm), over-all efficiency of counting, decay time and sample weight. As in the case of $^{65}_{30}$Zn, the $^{32}_{15}$P values are reported in terms of picocuries/g of live weight.

RESULTS AND DISCUSSION

Various researchers have used ion-exchange resins to separate zinc quantitatively from several contaminants.[10,11] However, a description of an anion-exchange system specifically to separate zinc from phosphorus in a simultaneous procedure has not appeared in the literature.

The anion-exchange resin used in this work was Dowex-21K (50–100 mesh). It is a strong-base anion-exchange resin which incorporates a quaternary ammonium functionality. The four substituents on the nitrogen atom are a polymeric benzyl and three methyl groups. After pretreatment with 2*M* hydrochloric acid the resin is in the chloride form. The zinc complex, $ZnCl_4^{2-}$, absorbs on the resin whereas orthophosphate is not adsorbed because of a short contact time and the lower probability of PO_4^{3-} for Cl^- exchange. $ZnCl_4^{2-}$ has a maximum distribution coefficient at a solution concentration of 2*M* in hydrochloric acid. This serves as a particular advantage because it allows for a separation from $CoCl_4^{2-}$, which has a maximum distribution coefficient at a solution concentration of 9*M* in hydrochloric acid and which coprecipitates with zinc if present. The anion-exchange step was checked thoroughly on both known and unknown samples with $^{65}_{30}$Zn and $^{32}_{15}$P tracers. The results indicated that, under the specific conditions of the procedure, $^{65}_{30}$Zn adsorbed on the anion-exchange column in a quantitative manner whereas $^{32}_{15}$P was not adsorbed. The quantitative zinc adsorption and its elution are conclusive as is shown by the chemical recovery factor. The average chemical recovery for 30 analyses was 95·6 % based upon the addition of zinc carrier; the range of chemical recoveries was 85·1–99·7 %.

Shellfish samples were obtained each month from an independent State health department laboratory. Portions of the shellfish samples were taken for analysis by the independent laboratory and analysed for several nuclides, including $^{65}_{30}$Zn. Upon our receipt of the samples they were further divided into portions for $^{65}_{30}$Zn analysis by a "matrix method" in which $^{65}_{30}$Zn was determined by applying a matrix model for $^{65}_{30}$Zn, $^{40}_{19}$K, $^{60}_{27}$Co and $^{46}_{21}$Sc. An aliquot of the portion used in the matrix determination was used for the radiochemical determination of $^{65}_{30}$Zn and $^{32}_{15}$P.

The chemical analysis of the phosphorus fraction is carried out in the same manner as described by Hillebrand, Lundell, Bright and Hoffman.[13] In analysing shellfish for $^{32}_{15}$P one disadvantage exists in not being able to add phosphorus carrier at the beginning of the procedure (the fish flesh contains phosphorus). Thus, a chemical recovery cannot be calculated on the basis of added carrier. Several simultaneous determinations for $^{32}_{15}$P were made on different samples. An aliquot of a sample was analysed for its $^{23}_{15}$P content. A second aliquot of the same aliquot was spiked with a known amount of $^{32}_{15}$P activity and the sample analysed. Results of several analyses showed that the chemical recovery of phosphorus was greater than 95 %.

In addition to chemical recovery, another factor that can be used to test an analytical procedure is the minimum sensitivity. Minimum sensitivity is the activity concentration which is detectable under specific conditions of sample volume, background, counting time, chemical yield and counting efficiency. The minimum sensitivity can be calculated by using the following expression:

$$\text{M.S.} = \frac{\text{M.D.A.}}{(\text{eff.})(\text{chem. yield})(2{\cdot}22\ \text{dpm/pc})(\text{sample size})}$$

M.D.A. = minimum detectable activity given by

$$2\sqrt{\frac{\text{count rate of bkg.}}{\text{time of bkg.}}}$$

at the 95% confidence level

where chem. yield = chemical recovery factor given by the total amount of zinc or phosphorus carrier recovered, divided by the amount added at the beginning of the procedure,

sample size = weight of fish flesh used for an aliquot in the procedure (expressed in g),

2·22 dpm/pc = conversion factor from activity units of disintegration per minute to picocuries.

Minimum sensitivities of 0·3 pc/g l. wt. for ${}^{65}_{30}$Zn and 0·005 pc/g l. wt. for ${}^{32}_{15}$P were calculated.

Precision tests were made for the determination of both ${}^{65}_{30}$Zn and ${}^{32}_{15}$P in shellfish. Special duplicate samples were prepared in order to eliminate any problems dealing with non-homogeneous sampling. Shellfish samples which had previously been analysed for ${}^{65}_{30}$Zn and ${}^{32}_{15}$P were spiked with known quantities of ${}^{65}_{30}$Zn and ${}^{32}_{15}$P. The results are shown in Table I.

TABLE I.—${}^{65}_{30}$Zn AND ${}^{32}_{15}$P PRECISION TESTS

Sample number	Activity added, *pc*		Activity recovered, *pc*	
	${}^{65}_{30}$Zn	${}^{32}_{15}$P	${}^{65}_{30}$Zn	${}^{32}_{15}$P
1	989·7	563·4	984·3	563·1
2	989·7	563·4	986·8	563·3
3	601·3	315·8	597·3	315·8
4	601·3	315·8	600·9	315·6
5	263·6	97·4	261·0	97·3
6	263·6	97·4	261·3	97·3
7	100·4	25·8	99·6	25·7
8	100·4	25·8	100·1	25·5
9	56·1	15·3	54·6	15·1
10	56·1	15·3	55·7	14·9

After the radiochemical procedure was developed and tested with shellfish samples, experiments were conducted to determine possible interferences. Results indicate that the simultaneous procedure for ${}^{65}_{30}$Zn and ${}^{32}_{15}$P specifically separates the two radionuclides from ${}^{51}_{24}$Cr, ${}^{59}_{26}$Fe, ${}^{60}_{27}$Co, ${}^{40}_{19}$K, ${}^{203}_{80}$Hg, ${}^{103}_{44}$Ru, ${}^{106}_{44}$Ru, ${}^{90}_{38}$Sr, ${}^{89}_{38}$Sr, ${}^{144}_{58}$Ce, ${}^{95}_{40}$Zr, ${}^{95}_{41}$Nb, ${}^{54}_{25}$Mn, ${}^{76}_{33}$As, ${}^{90}_{39}$Y and ${}^{22}_{11}$Na. These nuclides exist as contaminants in environmental materials.

A comparison of the results of three separate determinations of ${}^{65}_{30}$Zn in shellfish is presented in Table II. For most of the samples the $^{65}_{30}$Zn values of the three determinations compare reasonably well. In making this comparison there are several factors that must be considered. First, the radiochemical results are compared with values obtained by two matrix methods of determination. Although one cannot conclusively say that the matrix results are biased because of the use of a particular matrix, the tendency for bias is still present. Secondly, probably the most important cause of deviation among the three sets of data occurred in the processing of the samples. Shellfish have a large amount of liquid associated with their flesh. This is particularly true in the case of oysters and clams. Crabs have somewhat less moisture. Therefore, non-homogenous sampling in processing of the shellfish by the three groups is a distinct possibility. One can see this tendency in the data. There appears to be a slightly closer correlation for the $^{65}_{30}$Zn values in the crab samples, whereas this is not the case in the oyster samples. Third, there is one difference in the method of reporting values. The Oregon State Health Laboratory reported their values in pc/g of drained weight while the $^{65}_{30}$Zn values obtained by use of our matrix method and radiochemical method are reported in pc/g l. wt. The live weight is designated as being the flesh plus body liquids.

Table II.—Comparison of $^{65}_{30}$Zn values for shellfish (pc/g l.wt.)

	Clams (Tillamook Bay)			Oysters (Tillamook Bay)		
Month	Matrix method	Rad. method	Oregon State Health Department	Matrix method	Rad. method	Oregon State Health Department
March	2·4	3·0	1·2	15·4	12·8	11·8
April	1·5	1·5	1·2	13·9	14·1	11·3
May	1·6	1·6	1·3	14·8	14·8	9·6
June	1·6	2·7	1·6	19·6	22·5	18·3
July	2·0	2·0	2·1	19·3	24·1	16·4
August	—	—	—	—	29·0	—
September	1·9	3·4	—	19·7	—	—
October	1·8	1·7	—	29·7	29·4	—

	Crab Meat (Tillamook Bay)			Crab Meat (Astoria Bay)		
Month	Matrix method	Rad. method	Oregon State Health Department	Matrix method	Rad. method	Oregon State Health Department
March	12·9	14·9	10·9	19·2	19·0	16·4
April	11·5	12·3	9·4	17·9	17·6	16·1
May	10·7	10·7	10·6	21·0	20·6	15·7
June	13·3	14·3	12·6	16·9	19·9	14·5
July	16·6	18·0	16·1	21·2	21·4	17·9
August	13·9	17·6	—	—	—	—
September	16·7	21·0	—	—	—	—
October	14·3	17·9	—	—	—	—

In all cases the matrix values for $^{65}_{30}$Zn in shellfish obtained by the Oregon laboratory are lower than the radiochemical values. In comparing the radiochemical $^{65}_{30}$Zn values with our SEC matrix values, the results are random. In a few cases, duplicate results were obtained.

The $^{32}_{15}P$ values (Table III) were not obtained by another method in our laboratories because the classical procedure which is employed is the same as the procedure incorporated into the over-all simultaneous procedure. Several researchers have already extensively applied the phosphorus procedure to various samples.[12–14] This information, plus the information obtained in testing the simultaneous procedure, lead us to believe very strongly that the $^{32}_{15}P$ values obtained in shellfish are true values.

TABLE III.—$^{32}_{15}P$ IN SHELLFISH (pc/g l.wt.)

	Tillamook Bay	Tillamook Bay	Tillamook Bay	Astoria Bay
Months	Ostrea Gigas (oysters)	Mya (clams)	Cancer Magister (crabs)	Cancer Magister (crabs)
March	1·207	5·689	0·433	0·186
April	0·605	2·632	0·369	0·235
May	0·872	2·564	0·384	0·219

CONCLUSION

A radiochemical procedure has been devised for a rapid determination of $^{65}_{30}Zn$ in shellfish. Because of the interest in both $^{65}_{30}Zn$ and $^{32}_{15}P$, the procedure was combined with a classical phosphorus procedure and made compatible with the simultaneous determination of the two nuclides. It has the main feature of being far less expensive than matrix or spectrum stripping methods of determination. The procedure has been applied to both pure samples consisting only of $^{65}_{30}Zn$ and $^{32}_{15}P$ and unknown samples consisting of a complex organic matrix. Sensitivity, precision and accuracy tests indicate that the procedure has direct application to the determination of the two nuclides in shellfish. Reasonably good agreement was obtained in comparing the radiochemical values with the values obtained by two separate matrix methods.

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Zusammenfassung—Eine radiochemische Arbeitsvorschrift zur gleichzeitigen Bestimmung von $^{65}_{30}Zn$ und $^{32}_{15}P$ in Schellfisch wurde entworfen; Schellfischproben wurden über 8 Monate hinweg auf diese beiden Nuklide analysiert. Die radiochemisch erhaltenen Werte stimmen mit den von anderen Autoren gefundenen $^{65}_{30}Zn$- und $^{32}_{15}P$-Werten überein.

Résumé—On a établi une technique radiochimique pour le dosage simultané de $^{65}_{30}Zn$ et $^{32}_{15}P$ dans les crustacés. On a analysé des échantillons de crustacés pour ces deux nucléides pendant une période de 8 mois. Les valeurs obtenues par la technique radiochimique sont en accord avec celles données pour $^{65}_{30}Zn$ et $^{32}_{15}P$ par d'autres chercheurs.

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PHOTOMETRIC TITRATIONS—XI*

CONSTRUCTION AND EVALUATION OF A SEMI-IMMERSION PHOTOTITRATOR

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Summary—The principal differences in the requirements of a photometer and a phototitrator are discussed and it is shown that an instrument specifically designed for photometric titrations is more versatile than a modified photometer. The prime requirements for a phototitrator are operation with the vessel in ambient light, freedom from the need for special cuvettes and the possibility of adjusting the light path length by some means other than changing vessels. A simple, yet versatile phototitrator which meets these requirements is described.

INTRODUCTION

HIGHLY sophisticated automatic photometric titrators are commercially available. However, the application of a photometric end-point to many methods of analytical interest requires the production of a titration curve, either manually or with the aid of a recorder and constant flow burette. Most of the instruments which allow this have been either modifications of commercial photometers or special designs intended for specific types of photometric titration. Even where versatile and well-designed phototitrators are available, it seems to the present authors that there is still considerable room for improvement.

The object of this investigation has, therefore, been the development of a versatile, yet simple and inexpensive photometric titrator. Because the available instruments have recently been reviewed,[1,2] only papers of immediate interest will be cited.

At first, it is desirable to consider the properties of an ideal, general-purpose instrument which would be applicable to any and all non-automatic photometric titrations. The characteristics of such an instrument are discussed below; the order of listing does not reflect on the relative importance.

General. A photometric titrator should be highly stable, rugged, inexpensive and as simple as possible. Reasons of expense and simplicity will restrict the consideration to a single beam instrument.

Light source. In a single beam instrument, high stability of the light source is mandatory. Some means of adjusting the light intensity is desirable.

Titration vessel. The titration vessel should be as simple as possible, preferably a piece of common laboratory glassware, such as a beaker. A selection of capacities is desirable. With a given vessel, it should be possible to change the length of the light path.

Monochromator. A reasonable degree of monochromacy is required. Interference filters are usually satisfactory but a means of continuously varying the wavelength is desirable.

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* Part X: see *Talanta*, 1964, **11**, 1651.

Photodetector. The photoreceptor should be sensitive, stable and capable of operation over the entire spectral region of interest. Linear response and absence of fatigue effects are required. The characteristics of the photodetector should not be affected by strong illumination, self heating or moderate changes in ambient temperature.

Electrical circuit. The circuitry should be as simple as possible and should be insensitive to ambient temperature changes and stray magnetic or electrical fields. Provision for scale expansion is mandatory with highly absorbing samples and in cases where the absorbance changes only slightly during the titration.

Photometric titrations are most frequently performed using a general purpose colorimeter, photometer or spectrophotometer for the photometric measurements on the titration solution. It should be realised, however, that the requirements for a photometric titrator and a photometer, although similar, differ in several important respects.

Fluctuations in the readings cannot be tolerated in either instrument. Long term stability of the light source and electrical circuitry are important in a photometer but even more so in a phototitrator. Most photometers offer a means to recheck the 100% T setting. During a photometric titration, such checking is usually not possible; very often, for instance, the titration solution itself, in its initial state, is used to set 100% T. Consequently, in a photometric titrator, the 100% setting must remain constant for at least the duration of one titration. A well-designed double beam instrument will compensate for changes in light intensity, of course, but the complexity and expense of such an instrument can hardly be justified for titration purposes.

For a photometric determination, exact location of the zero *and* 100% T points is necessary; for a titration, the precise location of the 100% T point is unimportant so long as this location does not change during a titration.

In a photometer, the path length must be exactly reproducible from cell to cell and, frequently, the path length must be accurately known. On the other hand, the exact path length is never of interest in a photometric titrator and the only requirement is constancy during a given titration.

More differences could be easily listed, but the items mentioned should serve to illustrate the contention that, in some respects, a photometer is inadequate for photometric titration purposes while, in other respects, a general-purpose photometer is too good an instrument to be diverted from its primary purpose and limited to service as a phototitrator.

To perform titrations conveniently with a photometer, it is nearly always necessary to modify the instrument. In most cases the first problem is the accommodation of the titration vessel, which is commonly much larger than the cuvettes for which the photometer has been designed. With the cell compartment modified or replaced, it is important to take care that the light beam is not defocussed by the new vessel. Light-tight introduction of the burette tip is necessary. The same holds for the stirrer or provision must be made beneath the cell compartment for a magnetic stirrer. Some workers have preferred to avoid major modifications by titrating outside the instrument and circulating the solution through a flow cell in the photometer.[3,4] The large minimum solution volume and the fixed path-length of the cell are disadvantages of the method.

Further, few photometers have provision for scale expansion and any modification necessary to allow such an expansion is complicated, if possible at all. Perhaps the greatest disadvantage to the use of a modified photometer for titration purposes is the necessity for a light-tight cell compartment because such a compartment prevents direct observation of the solution for colour changes, turbidity, positioning of the stirrer, bubbles, splashing, *etc.*

Many workers have successfully performed photometric titrations in modified commercial photometers.[5,6] It is clear, however, that the adaptation of a photometer for titration purposes will hardly ever result in a fully adequate general-purpose photometric titrator. The construction of an instrument specifically designed for photometric titrations is the only solution.

To permit easy operation and minimum restriction of vessel size and shape, the first consideration of the design is operation in ambient light. There are two principle approaches which permit such operation. The first is the use of chopped light to create a.c. signal at the detector. This signal is electrically separated from the d.c. component from ambient light reaching the detector. The a.c. signal can be amplified readily and, in fact, usually must be because low level rectification is difficult. The circuitry required is usually quite involved and prohibitively expensive for a simple titrator.

The second approach is based on the use of a relatively intense light beam which, after passing through the solution, is attenuated before striking the detector. This weakening of the light beam is accomplished by locating the monochromator between the sample and detector and, often, by the addition of a grey filter, grey wedge or diaphragm. The light is attenuated by a large factor as is any ambient light which enters the detector housing. With appropriate design, the amount of ambient light then reaching the detector is negligible. Disadvantages of this approach are the difficulty of obtaining a stable, high power supply for the exciter lamp and, in some cases, heating of the sample solution. The approach is often useful in automatic titrators, however, where long term stability is commonly not important because only large and/or sudden absorbance changes are utilised to trigger the relay mechanism.

A modification of this second approach has been employed by Flaschka and Sawyer.[7] In their instrument, a rather weak, nearly parallel light beam passes through the solution and enters the detector compartment through an interference filter. The beam is then focussed on an extremely small photodetector without being additionally weakened. Only the light entering within a rather small angle can strike the photodetector and this angle is considerably less than that subtended by the light housing. Thus, only the ambient light which has been reflected by the titration vessel or scattered by the vessel or solution into this small angle need be considered. Further, the ambient light is white and only the small fraction which is passed by the filter strikes the photoreceptor; the amount of such light is negligible. This device has been used for several years and has been found to be quite satisfactory. It is limited, however, in that no means of path length adjustment is available, other than the changing of titration vessels, and that only titration vessels with fairly flat and parallel sides can be used.

Consideration of, and experimentation with a number of possible designs for photometric titrators have convinced the authors that the most versatile construction would be a complete departure from the usual practice. Instead of bringing the solution into the titrator, the instrument, or at least a part of it, would be brought into the solution. In principle, the light would enter the titration solution through a tube or light guide, pass through a length of solution, be reversed by a prism or mirrors, and leave the solution through a second tube which would lead to the detector. The combination of the two tubes and the prism (or mirrors) might be termed a photoprobe. By raising or lowering the prism, the light path length through the solution could be varied continuously. Application of one of the principles discussed above should provide insensitivity to ambient light.

Experimentation has shown, however, that it is difficult to construct a small photoprobe which is sufficiently rugged and unaffected by vibration; a completely satisfactory model has not yet been built. Agazzi and Bond[8] and Lacy[9] have constructed instruments whose designs point in this general direction. In both devices the ends of two tubes are immersed in the titration solution. A lamp is located near the immersed end of one tube; the light passes through the side of the tube and a short length of solution before falling upon the photoreceptor which is positioned behind a filter in the second tube. Neither model has provision for changing the path length although redesigning the tube mountings should make that possible within limits. However, changing of the filters is quite difficult and the titration of small volumes of liquids is impossible.

While work on an "ideal", full-immersion phototitrator is in progress, the authors have temporarily settled on a compromise design for a simple, easily constructed semi-immersion instrument which is, nonetheless, quite versatile. In this design, the light enters the titration solution from above, through a tube whose immersed end is closed with a flat, transparent disc. The light then passes through a length of solution, leaves the solution through the bottom of the titration vessel, and enters the detector compartment. The tube through which the light enters the solution can be moved up and down to vary the path length. The principle of precise focussing on a small detector is again applied to exclude the influence of ambient light. In this design, freedom from the need for special cuvettes, operation in ambient light, and adjustability of the light path length are combined in a simple, inexpensive instrument. It is of interest to note that the principle of this design goes back to the well known Duboscq colorimeter and to the first really practical photometric titrator, built in 1928 by Muller and Partridge.[10] In the latter device, a light bulb was suspended over a beaker containing the sample solution and the beaker was located immediately above the photodetector. Because the instrument was used for automatic titrations, there was little need for path length adjustment and ripples on the surface of the solution were not troublesome.

CONSTRUCTION

The general features of the photometric titrator are shown in Fig. 1. The exciter lamp is a flashlight bulb (GE #222 or equivalent), operating at 3–4 V and less than 0·5A, and powered by a lead accumulator. This bulb has a small lens incorporated in the glass envelope. The bulb is mounted with this lens downward. A focussing lens (17·3 mm diameter, 12·5 mm focal length) is mounted on a rack and pinion to allow easy focusing. Both lamp and focussing lens are located inside the $1\frac{5}{8} \times 2\frac{1}{8} \times 3\frac{3}{4}$ in. housing (Catalogue #CU-3001A, Bud Manufacturing Co.) shown in Figs. 1 and 2. The light beam passes downwards into a glass or plastic tube which dips into the solution. The tube is blackened inside and closed at its lower end by a round plate cut from a glass microscope slide. The upper end of the tube is glued into a threaded brass fitting which screws into a tapped brass block glued into the bottom of the light housing. Tubes of different size and length are available and may be interchanged in a matter of a few seconds. A manually operated shutter is located in the lamp housing. This shutter provides a means of blocking the light beam when setting zero per cent transmission.

A vertical 0·5 in. aluminium rod extends above the body of the titrator housing. Three brass fittings (denoted I, II and III in Fig. 1) are bored to give a sliding fit over the rod and are designed to permit the fixing of the location of the lamp housing. Fitting I is used for height (*i.e.*, path length)

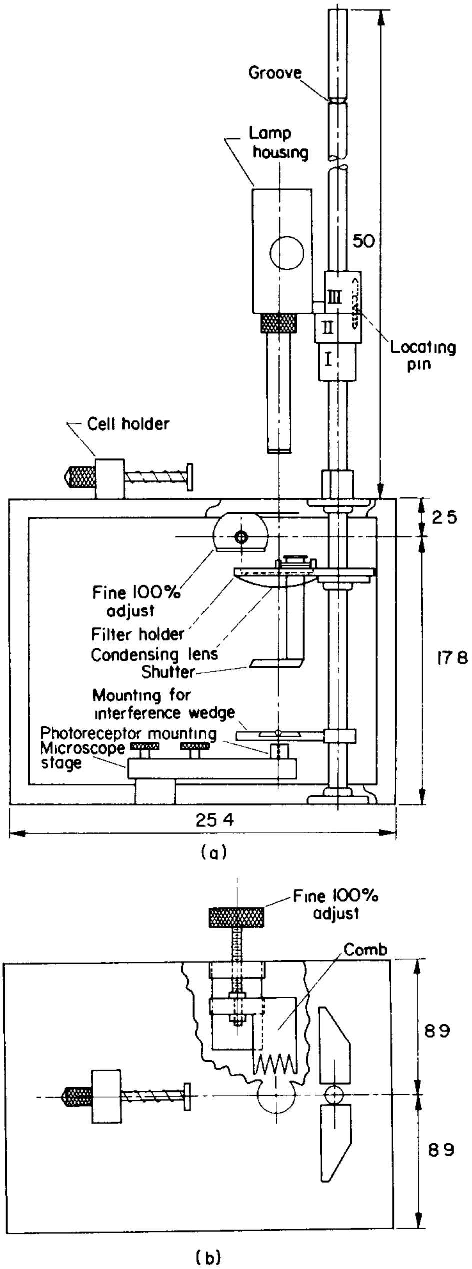

FIG. 1.—General view of assembled phototitrator (dimensions in cm):
A. Side view with door removed.
B. Top view with an opening drawn to permit view of comb assembly.

adjustment and is fixed in place by tightening a thumbscrew against the rod. Fitting II can then be rotated about the rod to permit aligning of the light path; this fitting is subsequently locked in place by a second thumbscrew. The lamp housing is attached to fitting III. A locating pin in fitting II fits snugly into a hole in fitting III to fix the position of the housing. A spring loaded pin in fitting III snaps into a groove near the top of the aluminium rod; this arrangement holds the lamp housing and tube out of the way while the titration vessel is being emptied and refilled.

The titration vessel can be a beaker; if a non-standard size is desired, an appropriate container can easily be fabricated. A glass or plastic cylinder is glued (epoxy) to one side of a 10 × 10 cm glass or plastic plate and small plastic runners are glued to two parallel edges of the opposite side to prevent scratching of the plate. The spring-loaded cell holder presses the titration vessel against the brass blocks flanking the aluminium rod (see Fig. 1). If the titration vessel is a beaker, a wood block with a "V" shaped notch is placed between the beaker and the cell holder to prevent sidewise motion of the beaker.

Stirring is accomplished by a small, glass propeller, dipping into the solution beside the light tube and driven by a miniature 6-V motor (the stirring motor *must not* be powered by the lamp battery). The stirring assembly is mounted on a separate stand. If titration vessels of small diameter are used, stirring is effected by bubbling a stream of nitrogen through the solution near one side of the vessel.

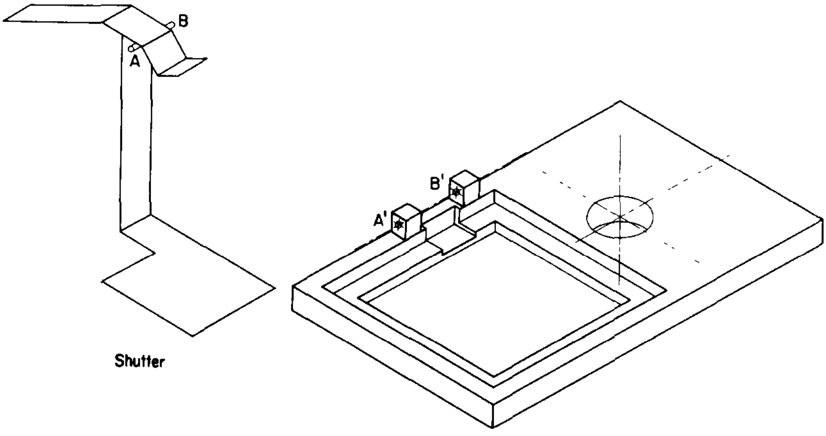

FIG. 2.—Filter holder and shutter.

The body of the instrument is a black, 7 × 8 × 10 in. steel box (Catalogue #CU-879B, Bud Manufacturing Co.) having two removable sides. For ease of access, one side is provided with a piano hinge and a latch. This box serves as the base for the vertical rod and as the enclosure for the filter, the photoreceptor and most of the circuitry. The rod is fixed to the top and bottom of the box with Fisher "Flexaframe" feet. The light beam enters the box through a 0·75 in. hole located directly under the light housing.

The instrument has been built to receive interference filters as well as an interference wedge; either provides sufficient monochromacy, but the continuous wavelength adjustment, possible with the wedge, offers greater flexibility.

The filter holder shown in Figs. 1 and 2 is milled from $\frac{3}{16}$ in. brass plate and is mounted on a "Flexaframe" foot to allow positioning on the rod. The filter rests in a 2 in. square recess in the holder and the light passes through a 1·75 in. square hole which is centred in the recess. A gravity operated shutter is located on the filter holder and is arranged to block the light beam when the filter is removed. A plano-convex condensing lens (60 mm diameter; 79 mm focal length) is attached to the bottom of the filter holder with epoxy glue.

In the alternative arrangement, a Bausch and Lomb interference wedge[11] is mounted in a holder similar to that of Safford and Westneat.[12] The wedge is about 75 mm long and has a dispersion of 5·3 nm/mm. The peak transmittance is about 30% and the half peak width (1 mm slit) is about 10 nm. The wedge holder has an adjustable slit (a fixed, one millimeter slit would be sufficient) and is mounted on the vertical rod inside the instrument case. The slit is located in the smallest portion of the light beam, *i.e.*, as near the photoreceptor as possible.

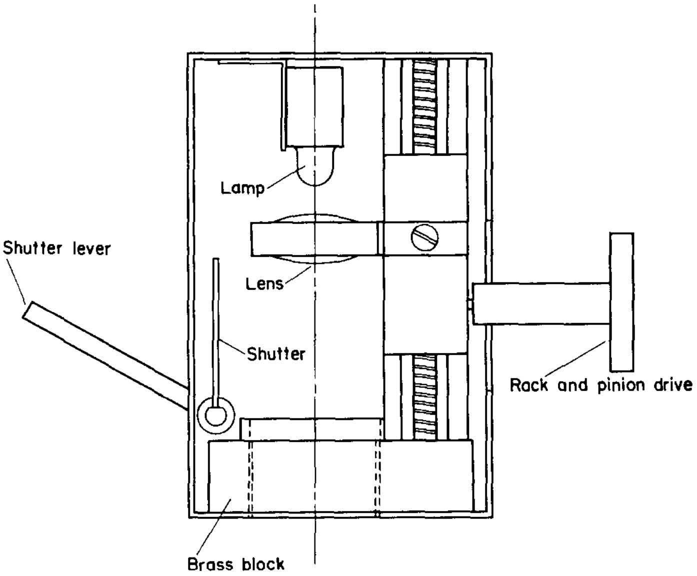

Fig. 3.—Interior detail of the lamp housing.

If it is desired to use individual interference filters, the wedge is removed from its holder and the filter of interest is placed in the filter holder. When the wedge is to be used, an auxiliary cut-off filter is necessary (see below) and this filter is placed in the filter holder. If the wedge is expected to be the only monochromator, the shutter on the filter is unnecessary and can be omitted from the construction of the instrument.

A stripped down microscope stage (Catalogue #F-362L, Lafayette Electronics, Syosset, N.Y.) is screwed to the inside bottom of the box. A brass heat sink, to receive the 1N2175 photoreceptor, is attached to the stage. By turning the two knobs on the stage, it is readily possible to bring the photoreceptor under the focus of the light beam.

The exciter lamp circuit is shown in Fig. 4. The rheostat allows a coarse adjustment of the light intensity when setting 100% T. The rheostat and fixed resistor are located in a small housing on the outside of the body of the instrument so that the heat dissipated by these resistors will not affect the photodetector. An aluminium comb, mounted on a threaded drive mechanism (see Fig. 1) is used for fine adjustment of the light intensity.

The 1N2175 silicon diffused photoduodiode (Texas Instruments Co.) is particularly qualified for the present application by its extremely small size. The device is only 12 mm in length by 2 mm in diameter; the light sensitive area is less than 1 mm^2. The 1N2175 is adequately sensitive (about

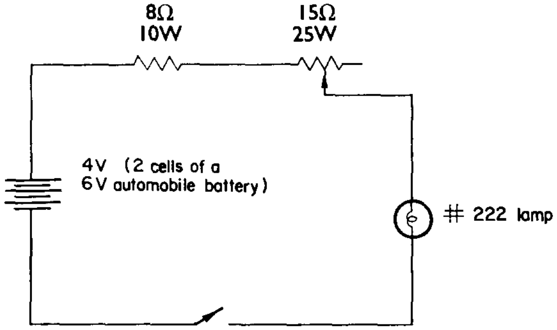

Fig. 4.—Exciter lamp circuit.

22 μA/mW/cm^2) throughout the visible region. The maximum sensitivity falls at about one micron; interference filters for use in the visible region often pass near infrared radiation so that additional filtering is necessary with this photoreceptor. The Texas Instruments LS-400 silicon photodiode is physically similar to the 1N2175 but is more sensitive (about ten times) and less affected by temperature changes. The unit tested in this laboratory was quite noisy, however, so the 1N2175 was used for the present application.

The 1N2175 photoduodiode requires a low impedance load (10 KΩ or less) if the current output is to be linear. A Rubicon galvanometer (Catalogue #3434, Minneapolis-Honeywell Co., Philadelphia, Pa.) was found to be a suitable readout device. This galvanometer has an internal resistance of about 4·5 KΩ, a sensitivity of about 0·0006 μA/mm and a critical damping resistance of about 80 KΩ.

The circuit shown in Fig. 5 was designed for use with the 1N2175 and this galvanometer. Appropriate changes in the circuit would be necessary if a galvanometer with different characteristics was to be used.

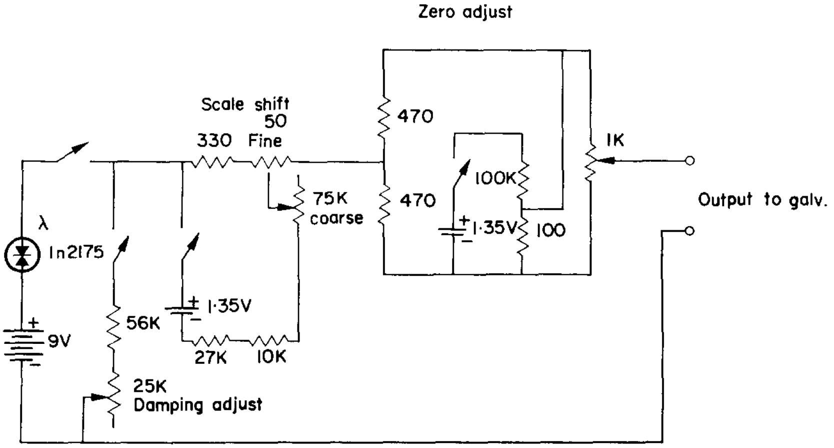

FIG. 5.—Photoreceptor circuit.

The battery is a 9-V transistor radio battery (Eveready #226). At the low currents required (less than 0·1 μA), this carbon-zinc battery is sufficiently stable and may be used instead of a mercury battery. Using a higher voltage battery will result in higher sensitivity (the 1N2175 is rated at 50 V, maximum); more sensitivity than is provided by the 9-V battery is required only when titrating highly absorbing samples at wavelengths below about 450 nm.

The zero adjust portion of the circuit allows compensation for dark current and provides a simple, electrical means of adjusting the zero point at the galvanometer. The total resistance of this portion of the circuit varies from about 370 Ω to about 500 Ω as the control is rotated. This small change in resistance has a negligible effect on the damping and sensitivity of the galvanometer.

The scale shift portion of the circuit provides a means to shift the scale zero when high precision methods are to be used.[13,14] With this circuit and the above galvanometer, somewhat above 400 scale divisions of zero suppression are available where the full galvanometer scale is 100 scale divisions (depending slightly on the setting of the damping resistor). It is unlikely that more suppression will be required; if it should be, it can be obtained by shorting the 10 KΩ or 27 KΩ resistor. Small mercury batteries are used in both the zero adjust and scale shift circuits although 1·5 V carbon-zinc cells would probably serve as well. The current drain in both circuits is low and battery life should be several years.

All controls and switches are mounted on the front panel of the instrument case. The controls are arranged so that all leads are as short as practical; this is done in order to minimise noise pickup. The batteries are mounted inside the case and near the control panel. A shielded phone jack is located at the back of the instrument case for connection of the shielded galvanometer leads. The most noise-free operation was obtained with the galvanometer lead shielding connected to the instrument case, the case grounded and the photoreceptor circuit floating.

PERFORMANCE TESTS

The instrument was tested to determine its sensitivity to external light, stability and linearity of response.

Ambient light. The effectiveness of exclusion of ambient light was tested by covering and uncovering the laboratory windows and turning the room lights on and off; no effect was noted. The apparatus was further subjected to the light of a 75-W lamp, held above and about the light housing. The greatest effect observed was about 0·3 scale divisions, indicating that the light housing is sufficiently large to prevent most ambient light from entering within the critical angle.

Stability. Over-all stability requires stability of the photoreceptor dark and light currents, the electrical circuitry, and the light source.

The dark current arises from a small conductance of the photodetector at zero illumination and is compensated by the zero adjust circuit. The stability of the zero reading is thus determined by the constancy of the dark current and of the current provided by the zero adjust circuit. In several experiments, the 0% T point was found to suffer no short term fluctuations; the maximum observed long term drift was about 0·2 scale divisions (on the 100 division scale)/hr. The scale shift circuit was tested by using the coarse (mechanical) adjustment on the galvanometer to set the pointer to about 100 scale divisions and returning the pointer to zero with the scale shift control. Again, no fluctuations were noted and the long term drift was less than 0·2 scale divisions/hr.

With the stability of the zero point assured, the stability of the light source and photoreceptor light current were investigated. Stability of the light source was achieved by operating the exciter lamp at low power levels (less than 3 W) from a high capacity, well charged lead accumulator. At lower light intensities, the galvanometer drift from a preset transmittance value was negligible, indicating stability of both photoreceptor and light source. At the highest light intensities, a warmup period of several minutes was necessary; after that period, the drift was found to be about 0·5–1·0 scale divisions/hr and no short term fluctuations were noted. Because most photometric titrations are performed in a matter of 5–10 min, this is adequate stability. If required, better stability can be obtained by using two batteries in parallel to power the exciter lamp.

Linearity of response. With stability and insensitivity to ambient light established, the instrument was tested for linearity of response. From earlier work the galvanometer was known to be stable and linear so that it was necessary only to investigate the photodetector and associated circuitry, using the galvanometer for readout. For the absorbance measured to be a linear function of concentration, it is necessary that, among other things, the indicated photocurrent (corrected for dark current) be directed proportional to the radiant power incident on the photocell. The testing of this linearity requires a means of increasing or decreasing the radiant power by known amounts. During this test, it is necessary that the relative intensities of all wavelengths of light reaching the photodetector be constant.

It was decided to perform the linearity test by decreasing the radiant power with screens. If the effect of diffraction at the wire edges can be neglected, screens are perfectly grey in the spectral region of interest, *i.e.*, they attenuate light equally at all wavelengths. The six screens available were calibrated by measuring their absorbances with a Cary Model 14 spectrophotometer, then the transmittance (and thus the absorbance) of each screen was measured in the phototitrator. For each screen, the absorbance measured in the phototitrator was found to be higher than that measured in the Cary. However, if the absorbance of each screen as determined in the Cary was plotted *vs.* the absorbance found with the phototitrator, a straight line with a slope less than one was obtained; a plot of this type is presented in Fig. 6. An analogous plot of absorbance determined in the Cary *vs.* absorbance determined in a Bausch and Lomb Spectronic 505 gave another straight line having a slope somewhat greater than one. Changing the wavelength at which the absorbance measurements were performed had no effect on the results.

For an explanation of the different slopes, consider a single wire of a screen, located between a light source and an aperture. Consider further the fraction of the aperture which is shadowed by the wire. When illuminated by parallel light, the wire and its shadow will have the same area/unit length. However, if the light is diverging, the fraction of the aperture shadowed by the wire will be increased, *i.e.*, the absorbance of the wire will be increased. Likewise, if the light is converging, the absorbance will be decreased. As long as the whole aperture is illuminated and the screen wires are much smaller than the aperture, the measured screen absorbance will depend on the degree of convergence or divergence of the light beam; for a given focussing, however, the plot described should be linear, if the instrument is linear. In order to test this explanation, advantage was taken of the ability to change the focussing of the phototitrator. The absorbances of the screens were determined under two conditions—first with the filament image focussed on the screen and second with the focussing lens moved away from the exciter lamp in order to obtain a strongly divergent beam. The results, presented in Fig. 6, support the hypothesis. In both cases, linear calibrations were obtained. This was taken as a strong indication that the photodetector-galvanometer combination responds linearly.

With the stability of the instrument assured and the linearity of the response strongly implied, it was possible to examine the effects of non-monochromacy.

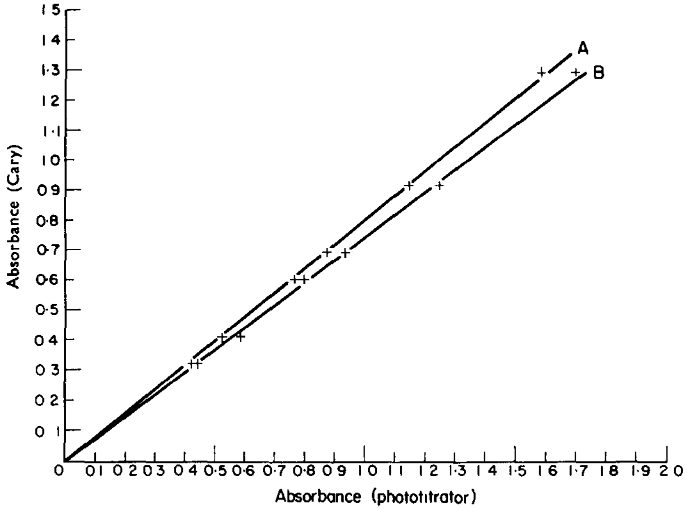

FIG. 6.—Effect of increased divergence of light on measured screen absorbance:–
A. Filament image focussed on the screen.
B. Light beam defocussed (diverging).

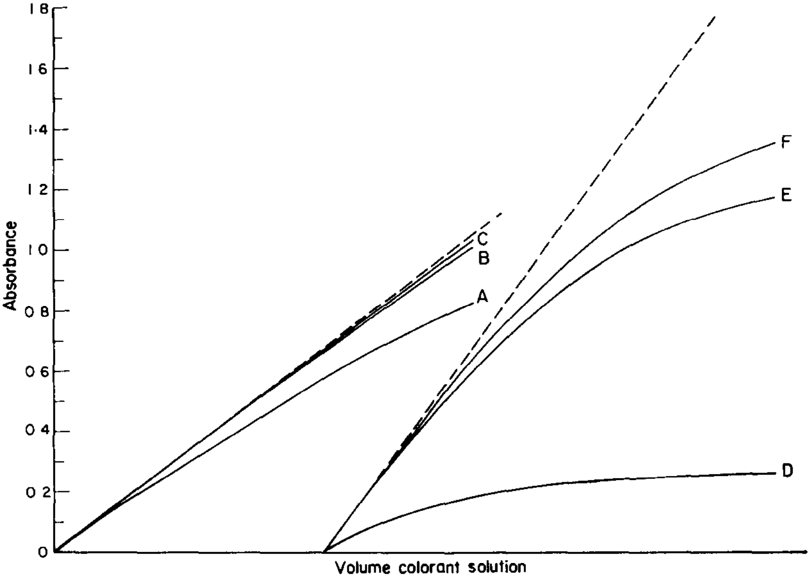

FIG. 7.—Monochromacy Tests:–
A, B and C: $CuSO_4$ solution added to ammonia buffer (pH 10); interference wedge set at 630 nm
A: wedge alone.
B: wedge + yellow filter (Corning #3486).
C: wedge + yellow filter + IR filter (Corning #4600).
D, E and F: Methyl Orange solution added to ammonium acetate solution (pH 7); interference wedge set at 466 nm.
D: Wedge alone (the curve obtained with the wedge + the blue filter was essentially identical to D).
E: Wedge + IR filter (Corning #4600).
F: Wedge + IR filter + blue filter (Corning #5031).

The Bausch and Lomb interference wedge employs the second order of interference. Thus, when set for 600 nm, the wedge also passes radiation of wavelengths 1200 nm and 400 nm, 300 nm, 240 nm, *etc.* Considerable nonmonochromacy errors were, therefore, expected, especially because of the passage of light at the first order wavelengths (*i.e.*, in the near infrared) where detector sensitivity is at a maximum and where maximum radiant power is emitted by an incandescent lamp.

Experiments were performed in which successive increments of a colorant solution were added to a solution in the titration vessel and absorbance at the wavelength of maximum absorptivity of the colorant was followed. The colorants and solutions were selected so that equilibrium effects would not produce curvature in the plots of absorbance *vs.* volume of colorant added. An infrared filter and several band pass filters were employed to attenuate, respectively, the first order infrared radiation and the third and higher order blue and near ultraviolet radiation. The curves obtained with and without these filters in the light beam, are shown in Fig. 7. All absorbance readings were corrected for dilution. From these curves, it is clear that the interference wedge monochromator, in conjunction with auxiliary filters, provides sufficiently monochromatic radiation for photometric titration purposes so long as the absorbance of the sample is below about 1·0. The #4600 Corning infrared blocking filter used does not cut off completely below about one micron; the use of an infrared filter which is opaque down to nearly 700 nm would probably allow an extension of the linear range, especially for work at lower wavelengths. Because an infrared filter is needed in most work, it is convenient to glue one to the inside of the light entrance hole of the instrument case. This placement of the filter also aids in preventing the entrance of dust.

Titrations can often be performed in the non-linear absorbance range if the absorbance change during the course of a titration is small. This is because of the fact that, within a short portion of a curve, linearity is closely approximated. Titrations with step indication can often be performed in the non-linear range because only a small portion at the beginning or end of the step is utilised to detect the end-point and, again, linearity is sufficiently approximated.

CALIBRATION AND ALIGNMENT

The interference wedge must be calibrated before being put into use. For the wedge in the present instrument, this was done with the aid of the strong mercury emission lines of a fluorescent lamp at 435, 546 and 578 nm. The lamp, when viewed through the wedge, produces three bright lines, corresponding to those wavelengths. Each line was centred, successively, in the 1-mm slit and the corresponding reading was noted from a scale attached to the wedge holder. Because the wedge is linear,[11] the data were then fitted to a straight line to obtain the calibration:

$$\text{Scale reading (cm)} = \frac{758 - \text{wavelength (cm)}}{53{\cdot}3\ \text{(nm/cm)}}.$$

The alignment of the optical system is accomplished as follows: with the path length set at several centimetres, the exciter lamp is turned on and the focussing lens is moved *via* the rack and pinion drive until a filament image is focussed at the top of the instrument case. The light housing is rotated until the image is centred in the entrance hole on top of the case (the image is made visible by placing a piece of tissue paper over the hole) and the housing is then fixed in place by means of the appropriate thumbscrew. The wedge monochromator is rotated until the light beam is centred in the slit and is also fixed in place. Next, by raising or lowering the filter holder, the condensing lens attached to it is brought into the position such that the smallest spot of light is obtained in a plane level with the top of the photo-cell; the filter holder is then fixed firmly in place with its set screw. The position of the condensing lens and wedge holder may be left unchanged thereafter. With the lamp and photoreceptor on, the focussing lens and microscope stage are successively adjusted until maximum galvanometer deflection is obtained. The optical alignment is then complete.

When the light path length has been changed for realignment of the system, it is usually only necessary to rotate the light housing until maximum galvanometer deflection is again obtained. If the path length change is large or if a new titration vessel is inserted, it may be necessary to touch up the adjustments of the focussing lens (rack and pinion) and photocell (microscope stage).

OPERATION

Zero % T is set by closing the shutter in the light housing, turning on the zero adjust circuit and turning the zero adjust control until the galvanometer pointer is at zero scale divisions. To set 100% T, the reference solution is placed in the titration vessel, the shutter is opened and the light control rheostat is adjusted until a reading near 100 scale divisions is obtained. The fine adjustment is then performed with the comb. If a suppressed zero is required, zero and 100% T are set exactly, the zero suppress circuit is turned on, and its controls are adjusted to return the pointer to zero. Zero % T is then at −100 scale divisions. Next, the rheostat and comb are used to reset 100%. More zero suppression can be obtained by repeating the process.

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Résumé—On discute des principales différences entre les exigences d'un photomètre et celles d'un appareil de phototitrage et l'on montre qu'un instrument spécifiquement conçu pour les titrages photométriques présente plus de possibilités qu'un photomètre modifié. Les principales exigences d'un appareil de phototitrage sont l'opération dans un récipient placé en lumière ambiante, la liberté de ne pas utiliser de cuves spéciales et la possibilité de régler la longueur utile du faisceau lumineux par des moyens autres qu'un changement de récipients. On décrit un appareil de phototitrage polyvalent, bien que simple, qui remplit ces conditions.

Zusammenfassung—Die prinzipiellen Unterschiede in den Anforderungen an ein Photometer und ein photometrisches Titrationsgerät werden diskutiert, und es wird gezeigt, daß ein speziell zur photometrischen Titration bestimmtes Gerät vielseitiger ist als ein umgebautes Photometer. Die primären Anforderungen an ein Phototitrationsgerät bestehen in folgendem: man muß mit dem Titrationsgefäß am Außenlicht arbeiten können; es sollten keine besonderen Küvetten notwendig sein; die Schichtdicke sollte sich auch anders als durch Gefäßwechsel ändern lassen können. Es wird ein einfaches und doch vielseitiges Phototitrationsgerät beschrieben, das diese Anforderungen erfüllt.

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TALANTA REVIEW*

PRESENT STATE OF COMPLEXOMETRY—I

DETERMINATION OF QUADRIVALENT AND TERVALENT METALS

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Summary—A review of the visual complexometric determination of quadrivalent and tervalent metals, whether achieved by using new indicators, new titrants, masking agents or new separatory methods, is presented. Attention is paid to the complexometric behaviour of such metals and to the problems of interferences in particular determinations. Older methods, except those which are irreplaceable, are not mentioned.

EDTA COMPLEXES of particular metals differ from each other in their stability, as measured by their thermodynamic stability constants and their "conditional" or "effective" constants. Because this review does not deal with the theory of complexometric titrations the reader is referred to the appropriate literature.[1,2] Here, only a survey of recently published and more important determinations of single quadrivalent and tervalent metals will be given. Determinations of anions have not been included because they have recently been thoroughly reviewed.[3] Interferences will be mentioned and examples of masking, separation and practical applications will be given. The elements are arranged in order of decreasing stability constants of the EDTA complexes. The reason is obvious: elements with complexes of high stability can be reliably determined at low pH without interference from elements forming weak complexes.

ZIRCONIUM

$(\log K_{ZrY} = 19{\cdot}4, 21{\cdot}9 - 29{\cdot}5)^{4-6}$

The chemistry of aqueous solutions of zirconium salts presents some problems from the complexometric point of view. First, the reported values of the stability constant of the ZrY° complex are somewhat confusing. The lowest values have been found by Morgan and Justus[4] ($\log K = 19{\cdot}4$) and by Iwase[5] ($\log K = 21{\cdot}9$). Kyrš and Caletka[6] gave the following values for $\log K_{ZrY}$: $28{\cdot}5 \pm 0{\cdot}3$ (in $1M\ HNO_3$), $30{\cdot}6$ (in $5M\ HNO_3$) and $29{\cdot}5 \pm 0{\cdot}5$ ($\mu = 0{\cdot}1$).

It is still uncertain under which conditions zirconium(IV) or oxozirconium(IV) ions predominate in solution. The same uncertainty applies to the process of hydrolysis of zirconium salts, which is always complicated because of polymerisation and complex formation with anions present in the solution. From recent experiments[7,8] it appears that in a solution of zirconium salts equilibria are formed between simple

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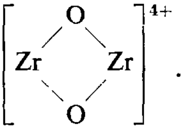
[*] For reprints of this Review see Publisher's Announcement at the end of this issue.

hydrated cations and probably polycations of the type



It follows from these considerations that the following results are typical. A solution has been prepared by dissolving zirconium hydroxide (precipitated with sodium hydroxide in the presence of triethanolamine, for masking traces of iron always present in common zirconium compounds) in hot dilute nitric, hydrochloric, sulphuric or perchloric acid and diluting the solution to a final acidity of 0·3–0·5N. The solution has been heated almost to boiling and titrated with 0·05M EDTA with Xylenol Orange as indicator. The results of all these titrations in "fresh solutions" were always low. The amount of "available" zirconium increases with the aging of the solution and usually reached the theoretical value in a few hours or days (in nitric acid: 15 hr; in perchloric acid: 8 days). On the other hand, longer heating before titration results in the amount of available zirconium again decreasing, the rate depending upon the nature of the acid used. In a solution of zirconium sulphate boiled for 20 min, the amount of available zirconium drops to half the total present, then remains essentially constant. However, if the sulphate solution is evaporated to white fumes, then diluted to the same acidity, correct results are obtained. Individual results are, of course, also dependent upon the concentration of zirconium. None of the above-mentioned phenomena (depolymerisation and polymerisation) has been observed with the indirect determination of zirconium, *e.g.*, by back-titration with bismuth nitrate at pH 1 after boiling the zirconium solution with an excess of EDTA.

Direct determination. For the direct determination of zirconium only a few indicators have been proposed, of which the best is Xylenol Orange and Methylthymol Blue,[9,10] which can be used even at high acidities.[11]

Indirect determination. In the past, some authors have proposed back-titration of an added excess of EDTA, *e.g.*, with bismuth nitrate or iron(III) chloride using different indicators. Here, also, one of the best procedures is the back-titration with bismuth nitrate and Xylenol Orange at pH 1–2.[12]

Interferences. The direct determination of zirconium can be carried out in the presence of a great number of elements, including thorium, scandium, titanium and lanthanides. Only iron and bismuth interfere. The influence of common anions has already been mentioned. Fluoride and phosphate also interfere. Large amounts of sulphate interfere because they accelerate hydrolysis or polymerisation in hot solutions. Sulphate, however, does not interfere, even in high concentration, in the indirect determination of zirconium.

Separation. There are many ways, some lengthy, to eliminate the interference of zirconium in the determination of other elements. For the separation of zirconium two exchange methods were proposed by Korkisch and Farag.[13] The precipitation of zirconium as barium hexafluorozirconium(IV)[14] or as mandelate[15] has also been used. Endo and Takagi[16] precipitated zirconium, together with magnesium hydroxide, from a solution containing hydrogen peroxide and EDTA (for masking titanium and heavy metals). Recently, it was found[9,10] that zirconium may be easily separated, together with titanium, thorium and uranium, by simple precipitation with sodium hydroxide in the presence of triethanolamine and EDTA (for masking iron and a number of other metals). After dissolution of the hydroxides the mixture can be analysed by successive titration with EDTA.[10]

There are also methods for separating or masking elements interfering in the determination of zirconium. Iron, titanium, copper and tin can be separated from zirconium, according to Wakamatsu,[17] by precipitation with cupferron in the presence of EDTA and by subsequent extraction with ether. In the aqueous phase zirconium is determined by back-titration of EDTA with copper sulphate, using 1-(pyridylazo)-2-naphthol (PAN) as indicator. However, some interfering metals can be masked in a more simple way, *e.g.*, thorium with ammonium or sodium sulphate,[18,19] copper with thiourea and iron by reduction to the bivalent state.

Masking. No method of masking zirconium has yet been described, but it could probably be effected by boiling the solution with hydrogen peroxide.[10]

Practical applications. The complexometric determination of zirconium has found considerable application in the analysis of zirconium alloys with uranium,[15] cerium,[20] iron[17] and with tantalum and niobium,[21] and for the determination of zirconium in metallic tungsten and its alloys,[22] ores,[23] zirconium nitrides and borides,[24] in glasses[25] and siccatives.[26]

THORIUM

($\log K_{ThY} = 23{\cdot}2$)

Direct determination. A number of indicators have been proposed for the direct determination of thorium. Among the first proposed Pyrocatechol Violet[27] was the best and it found considerable practical application. It has, however, been surpassed by Xylenol Orange[28] and Methylthymol Blue.[29] The first of these is now the most widely used indicator for thorium. Titration is always carried out at pH 2–3, usually in the cold.

Indirect determinations. Back-titration of an added excess of EDTA, *e.g.*, with iron(III) chloride or bismuth nitrate, is used only in the presence of other elements such as titanium and zirconium.

Interferences. Moderate amounts of bivalent cations interfere slightly or not at all. Also, some lanthanides do not interfere. On the other hand, scandium, iron, zirconium, bismuth and thallium interfere or are quantitatively cotitrated. Fluoride, phosphate and, below pH 2, sulphate interfere. There are different ways for eliminating the interference of the above metals, without previous separations. For instance, iron and mercury can be reduced with ascorbic acid and thorium titrated directly with EDTA at pH 3 using Pyrocatechol Violet.[30] Probably, thioglycolic acid could be used as well. Other important examples follow.

Determination of thorium and zirconium. Their sum is determined by back-titration with bismuth nitrate and Xylenol Orange at pH 2·5. The solution is then acidified to pH 1, thorium masked with excess of ammonium sulphate and the liberated EDTA titrated with bismuth nitrate.[18,19] The successive determination of zirconium in nearly boiling nitric acid solution (0·4–0·6*M*) with subsequent titration of thorium at pH 2·5–3·5 gives, in my experience, very accurate results.[8] Xylenol Orange is used as the indicator for both titrations.

Determination of thorium and lanthanides. All lanthanides whose log K value lies between 16 and 18 do not interfere. On the contrary, it is possible to titrate successively thorium at pH 2·5 and the other lanthanides at pH 5–5·5 in urotropine buffered solutions. Unfortunately, EDTA is not a suitable titrant because at a pH above 4 the primary thorium-EDTA complex reacts with indicators (Pyrocatechol Violet, Xylenol Orange, Methylthymol Blue, *etc.*) giving intense colourations, which make further determination impossible. This can be overcome by using other titrants, such as triethylenetetraminehexa-acetic acid (TTHA) or diethylenetriaminepenta-acetic acid (DTPA), because their thorium complexes are inactive to these indicators, even in neutral solutions.[31]

Determination of thorium and scandium. These elements form EDTA complexes of the same stability and no specific masking agent is known for either of them. Nevertheless, it is possible to determine both in the presence of each other, because of their different behaviour with TTHA. Their sum can be determined by direct titration with EDTA at pH 2–3 using Xylenol Orange. If one then adds to the solution the same amount of the disodium salt of TTHA, only thorium reacts according to the following equation:

$$\text{Th-EDTA} + \text{TTHA} \rightarrow \text{Th-TTHA} + \text{EDTA} \qquad (1)$$

This reaction is quantitative in hot solutions buffered with urotropine. The excess of TTHA and the liberated EDTA are titrated with lead nitrate using Xylenol Orange.[32] Calculation of the concentration of thorium and scandium is simple, because lead forms with EDTA a 1:1 complex and with TTHA a 2:1 complex:

$$\text{TTHA} + \text{EDTA} + 3\,\text{Pb} \rightarrow \text{Pb}_2\text{-TTHA} + \text{Pb-EDTA}. \qquad (2)$$

Separation. Several aromatic acids and potassium iodate have been proposed for the separation of thorium.[33] Extraction methods can also be applied. Banks and Edwards[34] improved the older method of Levine and Grimaldi[35] based on extraction of thorium with mesityl oxide from nitric acid. Milner and Nunn[36] and Milner and Edwards[37] separated bismuth from thorium by ion-exchange methods and determined thorium in the eluate either complexometrically or colorimetrically.

Masking. Only sodium or ammonium sulphate has been used (see above). This is very suitable for the determination of titanium in the presence of large amounts of thorium.[38]

Practical applications. Amongst the widely used complexometric methods the analysis of thorium containing uranium,[37] or uranium and bismuth,[36] tungsten[39] or magnesium[40] is worth mentioning as well as the highly successful determination of thorium in monazite sands, thorium ores and concentrates.[41–43]

BISMUTH

(log $K_{\text{BiY}} = 27{\cdot}94$)

Bismuth forms with EDTA a very stable complex, whose stability constant has been determined polarographically by Miklós and Szegedi[44] to be $10^{27\cdot94}$. This value is a little higher than that found for the Bi-DCTA complex (log K = 23·9–24·5) recently by Selmer-Olsen.[45] However, it has been generally found that complexes with DCTA (1,2-diaminocyclohexanetetra-acetic acid) are always more stable than the analogous EDTA complexes, by a factor of 100, on the average.

Direct determinations. Only direct complexometric methods at pH 1–3 need be considered. Pyrocatechol Violet, Xylenol Orange and Methylthymol Blue are the most suitable indicators. Titrations occur smoothly at normal temperature. Gattow and Schott[46] have tested the accuracy of titrations by using about ten different indicators. According to their results Xylenol Orange gives slightly higher results than Pyrocatechol Violet or Methylthymol Blue. This conclusion seems to me, however, a little arbitrary because all the determinations were compared with that using Pyrocatechol Violet, which is a less sensitive indicator for bismuth than, for example, Xylenol Orange. In insufficiently acid solutions or at high concentrations of bismuth a turbidity, which reacts slowly with EDTA, arises during the titration. At the end of the titration the indicator "returns" and, therefore, it is necessary to titrate very slowly. Reliable adjustment of pH of the acid bismuth solutions has been recently studied by Gattow and Schott.[47] They consider neutralisation with hydroxides or ammonia to be unsuitable. Negative errors are caused by the formation of "polycations". No errors arise, however, by neutralising with $1M$ sodium bicarbonate or $1M$ sodium acetate.

Interferences. The titration of bismuth at pH 1–2 is not affected by lead, zinc, cadmium, *etc.* The successive determination of bismuth and lead has been investigated in detail by Kotrlý and Vřešťál.[48] The other tervalent and quadrivalent elements are cotitrated.

Separation. Recently, Gattow and Gotthardt[49] described a method of almost universal applicability. It is based on precipitation of bismuth with sodium diethyldithiocarbamate (Cupral) in the presence of EDTA and potassium cyanide. After extraction of the bi-Cupral complex with chloroform and destroying it with concentrated nitric acid, bismuth is determined at pH 1·1 using Methylthymol Blue as indicator.

Masking. A few methods have been proposed to eliminate interferences. For example, iron or mercury can be reduced with ascorbic acid.[30] Triethanolamine has been proposed for masking bismuth during the determination of calcium with Murexide or calcium and magnesium with Methylthymol Blue.[50] In special cases thioglycollic acid may be used for masking bismuth.[51]

Practical applications. The complexometric titration of bismuth has been applied to the analysis of different alloys with lead[52] and uranium,[53] low melting alloys[57] containing also indium,[54] *etc.*[55] The determination of bismuth in ores has been described by Wollmann.[56] Considerable attention has been paid to the analysis of pharmaceuticals; many papers have appeared and the complexometric titration of bismuth has been introduced into some European Pharmacopaeia.

INDIUM

$(\log K_{\mathrm{InY}} = 24{\cdot}9)$

Direct determinations. Because of the high stability of the indium-EDTA complex I prefer to use an acidic medium. For such titrations Xylenol Orange,[58] Pyrocatechol Violet[59] and PAN[60] have been used. The whole group of azo dyes has also been studied.[61]

Interferences. Only those few metals having greater stability constants with EDTA interfere, *e.g.*, iron, thorium, scandium, zirconium, bismuth and gallium.

Practical applications. Because indium only appears in natural materials in minute amounts, the application of complexometry is rather limited. Indium has been determined in concentrates,[62] in alloys with lead and silver,[63] and in special alloys with bismuth, lead, cadmium and tin.[54]

GALLIUM

(log K_{GaY} = 20·3)

Direct determinations. Busev[64] and his coworkers proposed 7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid for the direct determination of gallium at pH 2·3, as well as indicators PAN and 4-(2-pyridylazo)-resorcinol (PAR).[65] A great number of dihydroxyazo dyes were studied for these purposes by other Russian chemists.[66] Gallocyanine,[67] 8-hydroxyquinoline[68] and Morin[69] have also been proposed.

Indirect determinations. Gallium can be determined satisfactorily by back-titration with thorium nitrate using Xylenol Orange as indicator.

Separation. Small amounts of gallium can be separated from a strongly acidic medium (5·6-6*M* HCl) by precipitation with diantipyrylpropylmethane[70] or by extraction with butyl acetate. The latter allows separation from aluminium.[71]

Practical applications. The complexometry of gallium has not been much exploited. The determination of gallium in gallium-uranium alloys[72] and in alloys containing gallium, aluminium and antimony[73] has been reported.

The determination of gallium and indium in the presence of each other is of importance in the analysis of materials such as their mixed arsenides or phosphides. One method is based on the different behaviour of gallium and indium towards TTHA according to the equations:

$$2\,\mathrm{Ga} + \mathrm{TTHA} \rightarrow \mathrm{Ga_2TTHA} \qquad \mathrm{In} + \mathrm{TTHA} \rightarrow \mathrm{InTTHA} \qquad (3)$$

With EDTA, of course, in both cases only 1:1 complexes are formed. The procedure is very simple. In one aliquot the excess of EDTA is determined by back-titration with zinc using Xylenol Orange in a urotropine medium. In the second aliquot the excess of TTHA is determined by an analogous titration. Simple simultaneous equations based on (3) and the volumes of titrants consumed allow both gallium and indium to be determined.[74]

THALLIUM(III)

(log K_{TlY} = 22·5)

The stability constant of thallium(III) with EDTA has been reported recently by Busev and coworkers[75] to be $10^{22\cdot5}$. Thallium(I) forms a very weak complex with EDTA (log K = 5·8) so the complexometric determination is best carried out with thallium(III) in an acidic medium using Xylenol Orange,[58] PAN or PAR as indicators.[76,77]

Interferences. At pH 3–3·2 thallium(III) may be determined in the presence of a high concentration of thallium(I).[78] Elements with a low stability constant do not interfere. The determination of some elements in the presence of thallium (and in this way indirectly also of thallium) can be carried out by reduction of thallium with sodium erythrobate.[79] Determination of thallium in the presence of iron and bismuth has been described by Busev and Tiptsova.[80]

Practical applications. The complexometric determination of thallium has not so far been used on a large scale with the exception of the determination of thallium(I) iodide in monocrystals of sodium chloride[81] and the analysis of thallium-lead alloys.[79]

IRON(III)

($\log K_{Fe} = 25{\cdot}1$)

Direct determinations. Direct complexometric titrations of iron have poor end-points. Indicators are generally well known reagents for iron, such as thiocyanate, salicylic and sulphosalicylic acid, Tiron, *etc.* The sharpness of the colour change is obscured by the yellow colouration of the iron-EDTA complex formed. In addition, at normal temperature the formation of the iron-EDTA complex occurs slowly and, therefore, a higher temperature (up to 60°) is advisable, but this increases the risk of hydrolysis in insufficiently acid solutions (the pH should be about 1). Thus, indirect determinations of iron are preferable, because they can be carried out over a wide range of pH. For the direct titration of iron, Xylenol Orange[82] can be used if there is a sufficient amount of iron(II) in the solution. The titration has to be carried out, of course, in an inert atmosphere.

Indirect determinations. Iron(III) can be determined very reliably by back-titration with bismuth nitrate at pH 1–2, with thorium nitrate at pH 2·5–3·5 or with lead nitrate at pH 5–5·5, using Xylenol Orange as indicator. Colour changes are very sharp and they can hardly be compared with the indistinct end-points obtained with indicators recommended for direct titrations.

Interferences. The determination of iron at pH 1 is very selective and a number of bivalent metals do not interfere. Interferences include zirconium, thorium, copper, nickel, large amounts of aluminium, *etc.* Aluminium can be masked with ammonium fluoride or salicylic acid[83] and copper with thiourea.[84]

Separation. Because iron interferes with the determination of other metals and blocks the indicators, it has to be separated from the solution. Different methods may be used. The precipitation, together with aluminium, *etc.*, with urotropine or ammonia is widely employed. A number of extraction methods have been proposed as well as an anion-exchange procedure using the chloro- or EDTA complex.

Masking. Triethanolamine, which also masks aluminium and a small amount of manganese, is generally used in an alkaline medium.[85,86] The introduction of triethanolamine enables all analyses of calcerous material to be carried out more rapidly. Recently, the masking of iron in a slightly acidic medium with a mixture of ammonium fluoride and potassium salt has been reported. After a while fine crystalline potassium hexafluoroferrate(III) precipitates from the solution. It does not react with EDTA or DCTA, even after many hours. This method permits the determination of lead, zinc, nickel and cobalt in the presence of iron, aluminium and titanium, which are simultaneously also masked with fluoride.[87]

Practical applications. Determination of iron is of importance, especially if it is connected with the complexometric determination of aluminium, titanium, chromium, *etc.* A number of procedures for complete analyses of mineral raw materials, ores, slags, alloys, ferrites, pharmaceuticals, *etc.*, have been published during recent years.

TITANIUM

($\log K_{TiY^{0}} = 17{\cdot}7$, $\log K_{TiOY} = 17{\cdot}3$, $\log K_{Ti(H_2O_2)Y} = 20{\cdot}43$)[88]

Indirect determinations. The strongly hydrated and easily hydrolysed cation Ti^{4+} is quite unsuitable for direct complexometric determination. Also, the older methods based on the back-titration of added excess EDTA are not accurate enough and will not be mentioned here. The reason for the inaccuracy is that some titanium-hydroxy complexes are formed during the back-titration. Only the yellow EDTA-peroxy complex is stable enough to prevent this, and all methods for titanium discussed here are based on its formation. The best method is that proposed by Bieber and Večeřa.[89] It is based on back-titration with bismuth nitrate at pH 1–2 with Xylenol Orange as indicator in the presence of hydrogen peroxide. Titrations are carried out at a temperature below 20°, and they are limited to 40 mg of titanium because of the yellow colouration of the titanium-EDTA-peroxy complex. Similar methods employing other titrants and indicators at considerably higher pH (*e.g.*, 4–6) loose their selectivity, because other bivalent and tervalent cations interfere.

Interferences. Metals forming stable complexes with EDTA at pH 1–2, such as zirconium, thorium, iron and scandium, interfere in Bieber and Večeřa's method as does fluoride and phosphate. Aluminium can be masked with salicylic acid,[90] and thorium (up to 200 mg) can be masked with ammonium or sodium sulphate.[91] Zirconium can be determined in 0·3–0·6*M* nitric acid before the determination of titanium.[91]

Separation. Titanium could be easily separated from aluminium, iron and bivalent metals by precipitation with sodium hydroxide in the presence of triethanolamine and EDTA.[9,10]

Practical applications. The complexometric determination of titanium has been of use in the analysis of minerals, slags, ferrotitanium[92] and titanium-aluminium alloys.[93]

CHROMIUM(III)

$(\log K_{CrY} = 23, \log K_{Cr(OH)Y} = 7{\cdot}6, \log K_{Cr(OH)_2Y} = 10{\cdot}0)$

The strongly hydrated chromium(III) ion reacts, in a slightly acidic medium, with EDTA very slowly at normal temperature. By heating, however, an intense violet complex CrY^-, or $Cr(H_2O)Y^-$, is formed. Many authors have studied in detail not only the kinetics of the formation of chromium-EDTA complexes, the equilibria between single complexes, but also their structure. Depending on the acidity of the solution the complex CrHY may be formed. Because the complexes differ in colour [$Cr(OH)_2Y$ is, for instance, blue] spectrophotometry has been most useful in these studies, *e.g.*, by Furlani and coworkers.[94]

Indirect determinations. The slow formation of chromium(III)-EDTA complexes allows only the indirect determination of chromium in an acidic as well as in an alkaline medium. The chromium(III)-EDTA (or DCTA) complex formed by boiling in an acidic medium is stable enough, but its intense colouration restricts the titratable amount to a few milligrams. In an alkaline medium, however, only blue complexes, $Cr(OH)Y^{2-}$, $Cr(OH)_2Y^{3-}$, exist and these interfere to a considerably less extent than the violet CrY^- complex.

For the indirect determination of chromium in an alkaline medium a number of methods have been proposed, such as back-titration with manganese,[95] zinc,[96] nickel[97] and calcium[98,99] using Eriochrome Black T, Murexide, Calcein, Fluorexon and Thymolphthalexon, respectively. Potentiometric indication, which is independent of the colour of the solution, has been used for the back-titration, in an acidic medium, with iron(III) chloride by Patzak and Doppler.[100,101] In an acidic medium, visual titrations can be carried out with thorium or bismuth nitrate as titrant using Xylenol Orange as indicator,[58] or copper as titrant and Calcein as indicator.[102,103]

Interferences. Determination of chromium at pH 1–2 (back-titration with bismuth nitrate) is fairly selective, being affected only by elements with a very high stability constant. All these metals, however, react with EDTA in the cold, so that they can be determined separately before the solution is boiled with a new excess of EDTA. In an alkaline medium the interferences of some metals can be eliminated with common masking agents, such as potassium cyanide or triethanolamine. A very important problem is the determination of chromium(III) in the presence of chromate. Statements in the literature are rather confusing. Because the formation of the chromium-EDTA complex requires boiling with an excess of EDTA, a partial reduction of chromate is also to be expected. Weiner and Ney[104,105] did not observe a reduction of chromate with EDTA. My experiences and those of Verma and Agarwal[106] are to the contrary. They recommend, for the complexometric determination of chromium in the presence of chromate, a specially purified DCTA, which is not oxidised by boiling with chromate at pH 3–5.

Masking. For the masking of chromium triethanolamine has been used.[99] Ascorbic acid is also very suitable, allowing the determination of calcium, nickel or manganese in the presence of large amounts of chromium.[99]

Practical applications. Chromium has been determined complexometrically in some iron-nickel-chromium alloys.[98]

COBALT(III)

$(\log K_{\mathrm{CoY}} = 40{\cdot}7)$

Cobalt(III) forms with EDTA an intense ruby red complex, $\mathrm{CoY^-}$. It is formed very easily in slightly acid solutions of cobalt(II) in the presence of EDTA and various oxidising agents, *e.g.*, hydrogen peroxide, cerium(IV) sulphate, permanganate, *etc.* In an alkaline medium, after addition of hydrogen peroxide, a blue peroxy complex is formed, which is also very stable and does not react with potassium cyanide in ammoniacal buffer.[107] Cobalt(III) differs substantially from cobalt(II), which forms with EDTA a much weaker complex ($\log K = 16{\cdot}3$).

Indirect determinations. In view of the chemical behaviour of cobalt(III), only indirect determinations are possible. The very intense colouration of the $\mathrm{CoY^-}$ complex lowers the maximum limit of cobalt concentration that can be titrated. In acidic solutions, thorium nitrate can be used as back-titrant. In an alkaline medium the back-titration is carried out with magnesium chloride and Eriochrome Black T[107] or with calcium chloride and Calcein.[108] Nickel, zinc, copper and cadmium can be masked in ammoniacal buffer solutions.[107]

Masking. Recently, it has been found that cobalt is easily oxidised with hydrogen peroxide in the presence of triethanolamine to a red complex. In strongly ammoniacal solution nickel can be determined directly with EDTA and Murexide in the presence of 20 mg of cobalt/500 ml.[109] The complex $\mathrm{Co(CN)_6{}^{3-}}$ which is formed in an ammoniacal solution in the presence of hydrogen peroxide and potassium cyanide has little colour. Nickel can be displaced from its cyanide complex by silver nitrate and determined directly with EDTA.[110]

Practical applications. Cobalt has been determined complexometrically in iron-nickel-cobalt alloys.[111]

VANADIUM

[VY^{2-} log K = 12·7; VY^{-} log K = 25·9; $V(OH)Y^{2-}$ log K = 9·6; $(VO)Y^{2-}$ log K = 18·8; $(VO_2)Y^{3-}$ log K = 18·1]

Vanadium in its different valency states forms a number of complexes with EDTA as shown above. At present only the blue complex of vanadium(IV), VOY^{2-}, is of importance for complexometry. It arises very easily by the reduction of vanadates with ascorbic acid in the presence of excess EDTA, which is back-titrated with thorium nitrate at pH 2–3 using Xylenol Orange as indicator.[112] For vanadium only two "direct" titrations with EDTA are known. Both are based on the displacement reaction between vanadium and the manganese-EDTA complex[95] or copper-EDTA complex, respectively[113]. The displaced manganese is determined with Eriochrome Black T as indicator at pH 10; the displaced copper is determined at pH 4·5–5 with PAN as the indicator.

Practical applications. The latter method has been used by Lassner and Scharf[114] for the determination of vanadium in tungsten alloys after masking tungsten with tartaric acid. This is the only practical example yet published.

TIN(IV)

(log K unknown)

Both valency states of tin form, in an acidic medium, sufficiently stable complexes with EDTA, and the tin(II)-EDTA complex is also stable towards ammonia.

Indirect determination of tin(IV). Kinnunen and Wennestrand[112] have proposed a back-titration with thorium nitrate at pH 2 using Xylenol Orange as indicator, and Jankovský[115] a back-titration with zinc acetate and Pyrocatechol Violet. At the end-point traces of tin are displaced from the EDTA complex and give a blue colouration with the indicator. Sajó[116] also recommends back-titration with zinc acetate using the 3,3′-dimethylnaphthidine-hexacyanoferrate(III)/hexacyanoferrate(II) redox system as indicator.

Masking and separations. The masking of tin in an alkaline medium with triethanolamine has been proposed for the determination of lead, zinc, *etc.*[117] Separation of tin, especially in the analysis of alloys, presents no difficulty. Already during the evaporation with nitric acid, stannic acid is isolated as an insoluble residue. It can be washed with a slightly ammoniacal EDTA solution to remove adsorbed cations and weighed directly as stannic oxide.[118]

Practical applications. Tin has been determined in white metals[119] by complexometric titration.

ALUMINIUM

(log K_{AlY} = 16·3)

Aluminium forms a medium to strong complex with EDTA. The formation takes place slowly in a slightly acidic medium. Ringbom[120] explains this by the formation of polynuclear complexes during the hydrolysis of aluminium salts. Their formation is optimum over the rather narrow range of pH 3·5–4. The author thus explains the instantaneous formation of the EDTA complex at just pH 3·5. At a pH lower than 3·5 the equilibrium of the reaction is unfavourable, whereas at a pH higher than 4 heating is necessary to complete the reaction. This also explains why the proposed direct titrations of aluminium with different indicators are not very satisfactory. Therefore, indirect determinations are commonly used.

Indirect determinations. A number of methods have been proposed for the indirect determination of aluminium. All are based on back-titration of an added excess of EDTA with different metal solutions, using various indicators. Some years ago Sajó[121] described a very popular method based on the back-titration of EDTA with zinc acetate solution using the hexacyanoferrate(III)/hexacyanoferrate(II)/benzidine system as a redox indicator. From the metallochromic indicators and numerous back-titrants only dithizone and zinc sulphate[122] and Xylenol Orange and thorium, zinc or lead nitrate[123] need to be mentioned here. Both systems have attracted considerable attention. The dithizone method of Wänninen and Ringbom has been critically evaluated, *e.g.*, by Nydahl[124] and slightly modified by Gottschalk.[125] The back-titration of an added excess of EDTA with lead or zinc (in the presence of phosphate or fluoride) using Xylenol Orange as indicator is now currently used in a series of practical applications (see below) and considered to be more attractive[126] than the dithizone method.[122]

This enumeration is rather small in comparison with the number of published papers, the majority of which, however, offer practically no improvements.

Interferences. Because of the comparatively low stability constant of the aluminium-EDTA complex and because of the necessity to carry out the determination indirectly at pH 4–5·5, all elements interfere with the exception of alkaline earths. Nevertheless, some methods for the determination of aluminium in the presence of other metals have been described. Attention has been concentrated mainly on the systems iron-aluminium, iron-aluminium-titanium, aluminium-iron-manganese, aluminium-chromium, *etc.* Some of these proposals are not without interest, even though they can be criticised. Thus, the low reactivity of aluminium with EDTA at pH 1–2 has been used for the step-wise determination of iron and aluminium. Iron is titrated directly with EDTA using salicylic acid as indicator at pH 2, then aluminium is titrated at pH 3 with copper-PAN indicator.[127] The slight difference in the pH of these titrations gives rise to doubts about the reliability of the method. Similar step-wise titrations of iron and aluminium have been described by a number of authors. Various ways have been proposed for the determination of aluminium and chromium. Liteanu and coworkers[128] recommend an indirect determination of aluminium at pH 5–6 by back-titration with iron(III) chloride and Tiron as indicator. The solution has to be heated to 50–60° before the titration takes place. Determination of chromium is carried out in the same way after addition of a further excess of EDTA and after boiling for 5 min. Surprisingly, it has been found that aluminium forms, almost instantaneously, a complex with DCTA, even at room temperature and in the presence of a large excess of neutral salts.[129] This fact has been used for the determination of aluminium in the presence of chromium(III) and chromate.[130] Chromium is then determined indirectly after boiling with a new excess of DCTA. In both titrations lead nitrate has been used as titrant and Xylenol Orange as indicator. Burke and Davis[131] and Pritchard[132] successfully applied this new principle for the determination of aluminium in various alloys.

Of other titrants, hydroxyethylenediaminetriacetic acid (HEDTA) has to be mentioned. According to Wilkins,[133] HEDTA can be used for the determination of aluminium (and nickel) in the presence of manganese, which forms with HEDTA a very weak complex in an acidic medium. Aluminium is determined indirectly by back-titration with copper at pH 5 using Methyl Calcein or Methyl Calcein Blue as fluorescent indicator.

Masking. Only a few masking agents for aluminium are known. For an alkaline medium triethanolamine (TEA)[134] is well known and ammonium fluoride for both an alkaline and acidic medium.[129,135,136] Other masking agents for aluminium are salicylic or aminosalicylic acid (PAS);[137] the latter has been successfully used in the determination of iron or titanium in the presence of aluminium.[138] Some interfering metals can be masked in various ways according to the nature of the element present. Well known is the masking of copper with thiourea and of zinc, cadmium, *etc.*, with *o*-phenanthroline in a slightly acidic medium.[139]

Separation. Many methods have been proposed for the separation of aluminium, including classical and ion-exchange methods. Milner and Woodhead[140] precipitated aluminium with ammonium benzoate, while Hallász and coworkers[141] separated aluminium as sodium aluminium silicate and determined magnesium in the filtrate complexometrically.

Practical applications. Next to calcium and magnesium, aluminium has attracted most attention in complexometry. Older methods used less suitable principles, *e.g.*, determination of aluminium in an alkaline medium. Taking into account the present state of knowledge, however, new methods based on back-titration with zinc solution using dithizone[122] or Xylenol Orange[123] should be considered. The dithizone method cannot be used, for example, after the melting of the sample in a silver crucible.[142] To a smaller extent similar interference arises with the method using copper-PAN indicator.[143] It is to be expected that the use of DCTA[129–132] will find greater application because of the above-mentioned advantages.

A large number of papers deal with the determination of aluminium in different kinds of natural[144,145] and artificial silicates, such as cements,[146] refractories,[147] ceramics,[148] *etc.* Some papers in this field describe a whole scheme for the complexometric analyses of silicates and similar materials.[149] Others propose even semimicromethods.[150] Complexometry competes considerably even with colorimetric methods, *e.g.*, in the determination of aluminium in steels,[151–153] in high temperature alloys,[154] in ferrosilicon,[155] ferrotitanium,[156] *etc.* It has also been successfully used for the analysis of different alloys, such as those with magnesium,[157] zinc[158] and nickel,[159] bronze and brass,[160] and even alloys with plutonium.[161]

The number of papers dealing with the complexometry of aluminium is steadily increasing. Most of them are, however, collating the proposed methods or using them with only small alterations.

Zusammenfässung—Es wird eine Übersicht über die Bestimmung vier- und dreiwertiger Metalle durch visuelle komplexometrische Titration gegeben. Dabei werden neue Indikatoren, Titranten, Maskiermittel oder Abtrennmethoden berücksichtigt. Es wird auf das komplexometrische Verhalten der Metalle sowie auf Störungsmöglichkeiten bei besonderen Bestimmungen aufmerksam gemacht. Ältere Methoden werden nicht erwähnt, wenn sie nicht unersetzlich sind.

Résumé—On présente une revue sur le dosage complexométrique visuel de métaux tétravalents et trivalents, effectué avec emploi de nouveaux indicateurs, de nouveaux agents titrants, d'agents dissimulants ou de nouvelles méthodes de séparation. On attire l'attention sur leur comportement complexométrique et sur les problèmes d'interférence dans des dosages particuliers. On ne mentionne pas de méthodes plus anciennes, à l'exception de celles qu'on ne peut remplacer.

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RADIO-FREQUENCY METHODS IN ANALYTICAL CHEMISTRY*

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Summary—An earlier review on the theory and applications of radio-frequency measurements in analytical chemistry is extended to cover the literature from 1960 to early 1965.

THEORY

A SERIES of papers by Ermakov *et al.* have considered further the theory of radio-frequency conductance measurements. Design criteria for the measuring cell have been discussed. The *capacitative* type of cell was represented by the usual equivalent circuit, as shown in Fig. 1. Independent determinations of radio-frequency conductivity and permittivity of solutions were made using circuits which enabled the cell parameters to be determined under resonance conditions.[2] However, the precision with which these parameters must be measured is very high. In the following example, R_p and C_p represent the equivalent parallel resistance and capacitance, respectively, at frequency f; R_1, C_1 and C_2 are the parameters in the circuit of Fig. 1.

R_p, *kohm*	C_p, *pF*	*f, Mc/s*	R_1, *kohm*	C_1, *pF*	C_2, *pF*
36·4	12·073	2	9·999	22·002	20·095
35·6	11·797	4			
36·4	12·000	2	11·468	20·594	21·116
35·6	11·800	4			

Thus, a change of 0·6% in C_p changes R_1 by 14·7% and C_1 by 6·5%.† It was concluded[2] that for the measurement of permittivity, the electrodes should be of large surface area; for conductance measurements, a small cell constant is desirable.

The *inductive* type of cell was discussed in terms of the circuit shown in Fig. 2, and its equivalent form, Fig. 3. Using this type of cell, the ratio L_2/R_2 is obtained rather than the individual values; L_i and R_i are the *insertion* effects of the cell upon the primary circuit. The Q-factor of the cell was enhanced by increasing the cross-sectional area of the cell and by operating at higher frequencies.

Lee and Saadi[3] showed that the Q-factor of the complete circuit was dependent mainly upon the conductance of the solution in the cell. An aqueous solution containing hydroxyl ions, and a solution of ethoxide ions in ethanol, both of the same low-frequency resistivity R, produced very similar Q-factors (Fig. 4). They confirmed the results of Zagorets *et al.*[4] which showed that at low conductances the cell coupled with the *electrostatic* component of the oscillatory field. Thus, the Q-factor was not

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* For a review of the literature to 1960 see reference 1.

† Authors' calculations.

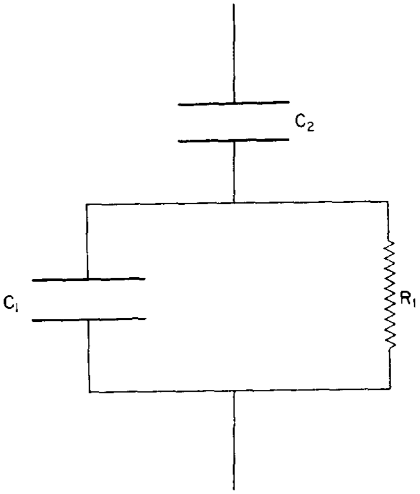

FIG. 1.—Equivalent circuit of capacitative cell.

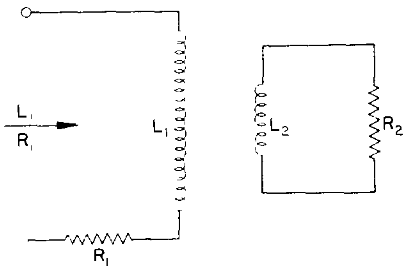

FIG. 2.—Equivalent circuit of inductive cell.

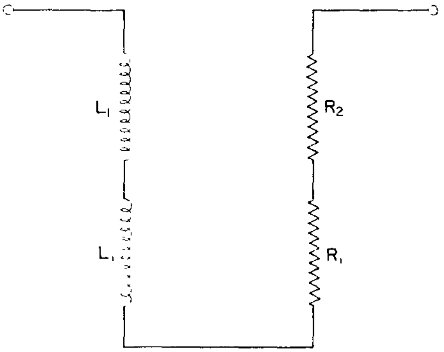

FIG. 3.—Reduced form of equivalent circuit of inductive cell.

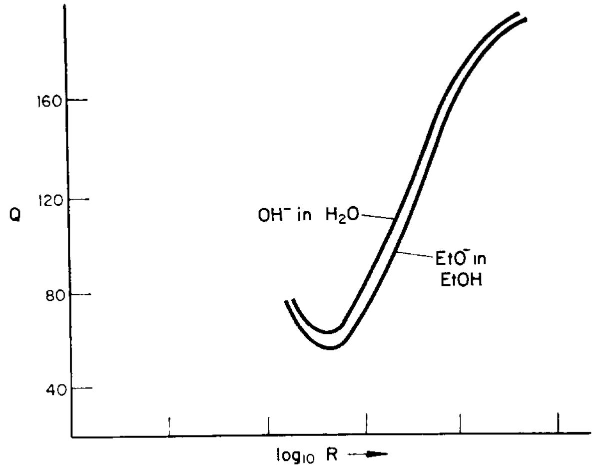

FIG. 4.—Variation of Q-factor with conductance of solution, for an inductive cell.

altered, with a given solution in the cell, by replacing water in the outer jacket by a concentrated solution of iron(III) acetylacetonate which is highly paramagnetic.

The effect of an electrostatic screen between the secondary coil and the solution in an inductive-type cell was investigated.[4] For the capacitative-type cell it was shown that the concentration $c_{\max}$ at which maximum high-frequency conductance occurred depended upon the low-frequency conductance and permittivity of the solution and upon the frequency of the applied field.[5] For uni-univalent electrolytes and a frequency not greater than 35 Mc/s, $c_{\max}$ was given by the equation:

$$c_{\max} = (7{\cdot}8\ \varepsilon f/\Lambda_0)\,.\,10^{-4} \qquad (1)$$

where f is the frequency in Mc/s, ε is the permittivity of the solution and Λ_0 is the equivalent conductance at infinite dilution. Equation (1) gives $c_{\max}$ in mole/litre.

Inclusion of the relaxation time θ of the ionic atmosphere, as given by the Debye-Falkenhagen dispersion theory,[6] led to a modification of equation (1). Equating θ to $1/(2\pi f)$ gives

$$c_{\max} = \frac{(5{\cdot}52\ \varepsilon f \sum_i z_i)\,.\,10^{-4}}{\Lambda_0 \sum_i \nu_i z_i^2} \qquad (2)$$

where ν_i is the number of ions of the ith type/formula weight of the electrolyte. The following example was quoted to show the application of these equations:

	$10^4 . c_{\max}$, *mole/litre*			*f, Mc/s*
	Eq. (1)	Eq. (2)	Expt.	
HCl	9·18	6·62	5·5	5·8
	19·0	14·2	18·2	12·4
	58·2	42·0	44·5	36·8
KCl	26·6	19·2	23·4	5·8
	57·0	42·0	54·0	12·4
	169·0	122·0	190·0	36·8
$MgCl_2$	—	11·3	9·1	5·8
	—	27·0	20·0	12·4
	—	80·0	63·0	36·8

Deviations from the theoretical values of c_{max} occurred when the size of the solvated ions became compatable to the diminished thickness of the ionic atmosphere at the higher concentrations.

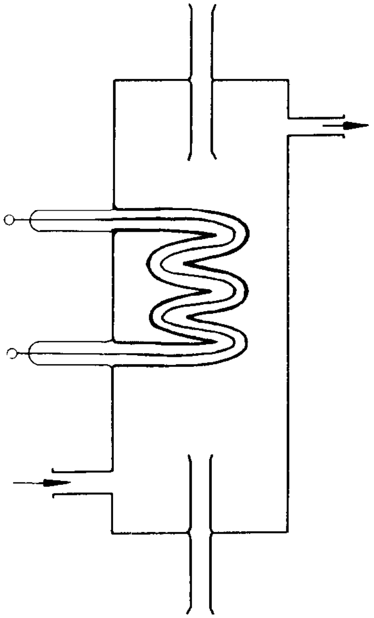

Fig. 5.—Inductive cell (after Zagorets[7]).

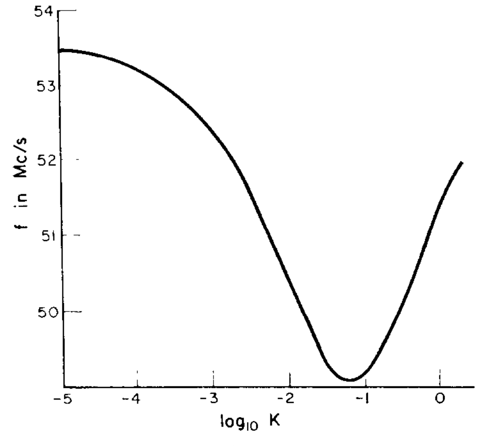

Fig. 6.—Variation of frequency with conductance for the cell of Fig. 5.

The changes in frequency of the oscillator when loaded with a conducting solution have been measured using an *internal inductance* cell (Fig. 5). The coil is insulated from the solution by a glass spiral. In Fig. 6, the oscillator frequency is shown as a function of the low-frequency specific conductance for a series of potassium chloride solutions.[7] This large change in frequency is not observed with the more usual type of inductive cell in which the vessel is placed inside the inductor. The frequency changes shown in Fig. 6 were related to changes in the effective dielectric constant of the solution with changes in electrolyte concentration. Using potassium chloride as a reference electrolyte, the relative changes in dielectric constant of several electrolyte solutions were calculated, with the results illustrated in Fig. 7. It was considered that these results showed that the firmness of attachment of water molecules to the ions increased along the series:

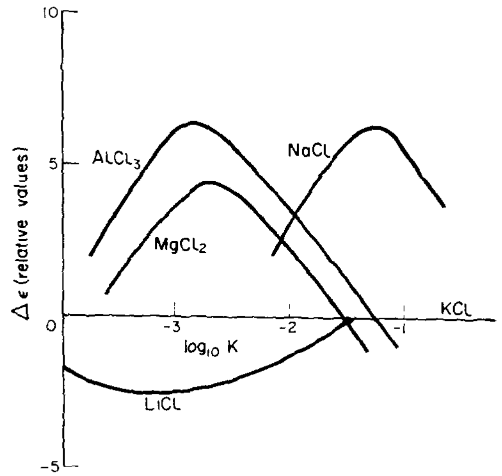

FIG. 7.—Variation of dielectric constant with conductance, for several electrolytes, for the cell of Fig. 5 (relative scale).

$$Cl^- < K^+ < Na^+ < Mg^{2+} < Al^{3+} < Li^+.$$

Further studies of the variation of c_{max} with electrolyte concentration have been carried out at frequencies up to 200 Mc/s.[8] Stepwise curves were obtained, indicating the changes in structure of hydrate complexes, each with its characteristic lifetime.[9]

A comparison of low-frequency conductance and high-frequency titration curves has been given by Guriev and Zarinskii.[10] They used a capacitative-type cell together with the 5 Mc/s apparatus described by Zarinskii and Mandel'berg.[11] The titrations

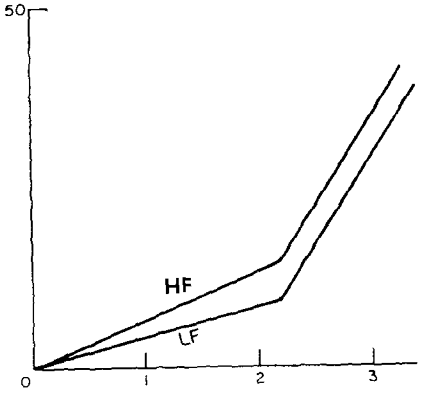

FIG. 8.—Comparison of radio-frequency and low frequency conductances.

of bases, amino acids and salts of weak acids in glacial acetic acid with 0·1*M* perchloric acid showed very similar curves at low and at high frequencies (Fig. 8). The change in capacitance during these titrations is negligible, in agreement with previous investigations in the solvents dioxan, ethanol and ethylene glycol monoethyl ether.[12]

APPARATUS

Two new commercial instruments have been produced. The P.C.L.* instrument operates at frequencies of 10, 20 and 30 Mc/s and uses a plug-in external band cell. Changes in anode current are measured across a bridge circuit.[13] Pungor's apparatus† operates at a fixed frequency between 100 and 120 Mc/s. A band-type cell is used and changes in grid current are measured.[14]

Several radio-frequency titrimeters have been produced by independent investigators; they incorporate the principles which have been described previously.[1] The highest frequency used is 190 Mc/s, a parallel transmission line constituting the tuned circuit of the oscillator; the grid current is passed through a 1 kΩ "Helipot" and the voltage drop measured on a 50-mV potentiometer recorder. The glass cell is inserted between the anode and grid lines and holds about 30 ml of solution.

An inductive-type cell is connected in parallel with an inductance in the unknown arm of a radio-frequency bridge fed by a variable-frequency oscillator; the bridge is balanced by adjusting the C_p and G_p controls for zero output.[16] Modulation of the signal fed to a Twin-T type bridge obviates the need for a beat-frequency oscillator in the receiver circuit.[17] Two crystal-maintained circuits, operating at 4·6 Mc/s[18] and 7 Mc/s,[19] have been described; simple applications of these instruments to titrimetry have been given. *Q*-meter measurements on a capacitative-type cell have been reported.[20] The change of frequency of an oscillator operating in the range 5 to 30 Mc/s was used to follow conductance changes. As we have pointed out, these changes are usually very small, and it was necesssary to measure the frequency with a precision

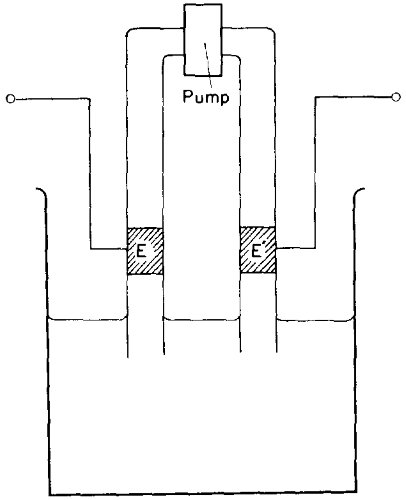

FIG. 9.—Capacitative flow-cell (after Collins[22]).

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* Polymer Consultants Ltd., Ardleigh, Colchester, Essex, England.

† Shandon Scientific Instruments Co., Pound Lane, Willesden, London N.W. 10, England.

of ±0·03 c/s. Measurement of the frequency to ±0·25 c/s was claimed to be equivalent to a change in conductivity corresponding to $\pm 5 \times 10^{-6}$ mole/litre of hydrochloric acid.[21]

The design of radio-frequency conductance cells to cover a wide range of concentrations at a frequency of 1 Mc/s has been considered.[22] In the equivalent circuit (Fig. 1), C_2 should be large for adequate sensistivity. This, together with efficient mixing of the solution, was achieved by the arrangement shown in Fig. 9. The electrodes EE′ consisted of copper tubing coated internally with an insulating layer of Araldite 985E.

PRACTICAL APPLICATIONS

The radio-frequency technique has been applied to acid-base titrations, precipitations, redox processes and to the measurement of dielectric constants and dielectric loss factors.

The titration of $1{\cdot}5 \times 10^{-3}M$ hydrochloric acid by $0{\cdot}1M$ sodium hydroxide has been studied in the presence of varying concentrations of sodium chloride up to $1{\cdot}5 \times 10^{-2}M$; the Sargent Oscillometer Model V was used. The V-shaped titration curves became almost horizontal above this concentration of sodium chloride; the end-point is satisfactory up to $6 \times 10^{-3}M$ sodium chloride. The precipitation of $10^{-3}M$ solutions of lead nitrate with $0{\cdot}1M$ potassium chromate was satisfactory in the presence of potassium nitrate to a concentration of $6 \times 10^{-3}M$, and the precipitation of $10^{-3}M$ silver nitrate with $0{\cdot}1M$ potassium chloride in the presence of nitric acid produced a sharp end-point in acid concentrations up to $10^{-3}M$.[23] Acid-base titrations have been followed by *Q*-meter measurements.[24,25]

The absorption of carbon dioxide in baryta has been followed by means of radio-frequency conductance measurements; it is pointed out that the use of internal electrodes for this purpose involves their frequent cleaning and replatinisation. The gas was absorbed in 500 ml of 1% baryta solution and a calibration curve relating the current to the weight of carbon dioxide absorbed was produced.[26]

Solutions of aluminium chloride, bromide and sulphate have been titrated with sodium hydroxide, baryta and triethylamine, using the apparatus of Pungor.[14] The titration curves showed the formation of $Al(OH)_3$ and its dissolution as the $Al(OH)_4^-$ ion.[27] The shapes of these curves have been examined further; breaks occur after the titration of the acid initially present, after the precipitation of the hydroxide and also following its complete conversion to aluminate.[28] The complexometric titrations of Hara[29] have been re-examined[30] and also the kinetics of complex formation between aluminium(III) and Complexone III and Complexone IV; $0{\cdot}1M$ solutions of aluminium bromide and $0{\cdot}1M$ solutions of Complexones III and IV were used and the change of conductance with time followed with the Pungor titrimeter.[31] The energies of activation are 23·5 kcal/mole and 23·2 kcal/mole for reactions with Complexone III and Complexone IV, respectively. The kinetics of several radio-frequency titrations have been studied using a capacitative-type cell and a heterodyne beat technique.[32]

Aluminium, cadium, zinc, manganese and magnesium have been determined in aqueous solution and in aqueous ethanol by titration with $0{\cdot}1M$ diammonium hydrogen phosphate solution, using the HFT3OC apparatus[1] operating at 30 Mc/s. Satisfactory results were obtained with zinc and manganese in $0{\cdot}1M$ concentration.[33]

Thorium has been determined by titration with diammonium hydrogen phosphate solution; the curves show two breaks, at Th:P ratios of 1:1 and 1:2. The following reactions, which account for these breaks, were confirmed by analyses of the compounds formed:[34]

$$ThOH^{3+} + HPO_4^{2-} \rightarrow Th(OH)PO_4 + H^+$$
$$Th(OH)PO_4 + 2H^+ + HPO_4^{2-} \rightarrow Th(HPO_4)_2 + H_2O.$$

A similar titration curve was obtained with zirconium, the second break corresponding to the formation of $Zr(HPO_4)_2$. The addition of 60% ethanol or methanol was desirable in this titration. The titration of barium, lead, silver and thallium(I) with potassium chromate solution was also studied, and again the addition of alcohol improved the accuracy of the titration.[35]

Radio-frequency titrations involving the precipitation of CaC_2O_4, $MgNH_4PO_4$ and $[Co(NH_3)_6][Cr(C_2O_4)_3]$ have been investigated with the Pungor titrimeter. The effects of changes in titrant concentration, pH, cell dimensions and frequency were studied.[36]

Precipitation reactions between each of silver and thallium(I) with sodium tetraphenylboron have been followed by means of the Sargent Oscillometer. 100 ml of solution of either metal were used, at concentrations between $10^{-4}M$ and $10^{-3}M$ and with a similar concentration of sodium tetraphenylboron; errors were reported as about 1%.[37]

Titrations in electrolyte solutions of concentrations to $1M$ have been reported, using the 190 Mc/s transmission-line apparatus already described.[15] The titration of $7 \times 10^{-3}M$ hydrochloric acid by $0{\cdot}1M$ sodium hydroxide was not impaired by addition of chloride ions to a concentration of $0{\cdot}1M$, but the titration curve was considerably flattened on further raising the chloride ion concentration to $1M$. The apparatus has been employed mainly in the study of radioactive materials. The titrations of $6 \times 10^{-3}M$ solutions of strong acids by $0{\cdot}1M$ sodium hydroxide in the presence of uranyl salts at concentrations up to 11·66 g of uranium/litre show two breaks, at the free acid and the uranium end-points; the second of these end-points is masked by the addition of fluoride ions. Sulphate determinations with $0{\cdot}25M$ barium chloride were carried out up to a sulphate concentration of $0{\cdot}028M$; uranyl sulphate could be titrated similarly after the addition of sodium citrate or sodium fluoride. In the titration of 2·45 g of thorium(IV)/litre with $0{\cdot}22M$ oxalic acid in unbuffered solutions, two breaks were obtained, corresponding to:

$$Th^{4+} + H_2C_2O_4 \rightarrow [ThC_2O_4]^{2+} + 2H^+$$
$$[ThC_2O_4]^{2+} + H_2C_2O_4 \rightarrow Th(C_2O_4)_2 + 2H^+.$$

Only the second break was reproducible. A similar titration using $0{\cdot}14M$ EDTA was investigated up to a thorium(IV) concentration of 1·93 g/litre.

The radio-frequency technique has been used to determine the percentage of fluorine in fluoropolymers. After suitable treatment the fluoride ion was titrated with $0{\cdot}05N$ calcium acetate solution; the error was about 1%.[38]

Titrations of acids in dioxan-water mixtures have been reported.[39] The technique of back-titration with $0{\cdot}1M$ hydrochloric acid was adopted in order to determine a number of carboxylic and phenolic acids of pK_a (in water) between 2 and 13. In the titration of weak acids in organic solvents the use of a base which produces an insoluble salt of the acid improves the sensitivity.[40]

A series of organic bases has been titrated separately and in mixtures, using the Sargent Model V Oscillometer; the solvent was glacial acetic acid and the titrant 0·1M perchloric acid in glacial acetic acid. The following bases were studied: triethylamine, mono-, di- and tri-ethanolamines, acridine, quinaldine, 2-picoline, quinoline, iso-quinoline, pyridine, 7,8-benzoquinoline, *o*- and *m*-chloranilines, *m*- and *p*-nitranilines and anthranilic acid.[41]

Alkalimetric and precipitation titrations of aniline hydrochloride and *m*- and *p*-phenylenediamine hydrochlorides with 0·01M sodium hydroxide and with 0·1M silver nitrate have been carried out.[42] Several alkaloids were estimated as their hydrochlorides in this way. The Lewis acids aluminium trichloride and tin(IV) chloride have been used to titrate nitrogen bases in the solvent acetonitrile;[43] 1:1 complexes were reported between aluminium and tin and the bases pyridine and piperidine. Errors of about 0·5% were quoted. Tin(IV) chloride formed 1:2 complexes with the alcohols R—OH, where R = methyl, ethyl, propyl and butyl.

The titration of 0·1 g of melamine in aqueous solution with cyanuric acid of concentration 0·1 g/litre has been carried out[44] using the apparatus of Zarinskii and Mandel'berg.[11] The titration of sodium dodecylamine sulphate or of the corresponding hydrochloride has been reported;[45] these titrations were insensitive to the presence of sodium salts.

Solutions of acids in dimethylformamide have been titrated with a solution of an alkali-metal methoxide, CH_3OM, where M = Li, Na, K, Rb and Cs, in 9:1 benzene-methanol mixture. The Sargent Model V Oscillometer was used. It was found that, with the exception of lithium, the methoxides behaved as strong bases at the concentrations used (10^{-4} to $10^{-3}M$). The acids studied were ammonium iodide, β-naphthylamine hydrochloride, dichloracetic acid, benzoic acid, *o*-nitrobenzoic acid and salicylic acid.[46]

MISCELLANEOUS APPLICATIONS

Radio-frequency titrations in liquid ammonia have been studied.[47] The sulphur dioxide content of paper cooking liquors has been determined by the oxidation of a diluted sample with hydrogen peroxide and subsequent titration using standard baryta.[48]

The determination of lead in petroleum fuels has been carried out by titration with standard chromate solution, after suitable treatment; the apparatus used has been described above.[18]

The radio-frequency technique has been used to follow polymorphic changes in solids at high pressures; the *Q*-factor of a coil wound around the outside of the specimen tube indicated the changes. Pressures up to 65 kbar were applied, and volume changes as small as 0·1% were observed. Using a Bi-Tl-Ba (80–10–10) alloy, transition-points were found as follows:[49]

Bi(I) to Bi(II)	25 kbar
Bi(II) to Bi(III)	28 kbar.

Further transitions were observed at 36 kbar and 58 kbar.

A dielectric constant meter operating at 3 Mc/s has been used to measure dielectric constants up to 100 and dielectric loss to tan $\delta = 0{\cdot}25$. It was used as a null instrument, balancing the test cell with a variable standard capacitor; alternatively, the out-of-balance current was calibrated in terms of dielectric constant.[50] Applications of this instrument to radio-frequency titrations and to system monitoring have been reported.[51]

A very sensitive dielectric constant meter has been described, in which a micrometer capacitor is adjusted to obtain the required Lissajou pattern on a cathode-ray tube screen.[52] This instrument is sufficiently sensitive for the determination of the dipole moments of polar molecules in non-polar solvents.

The course of the polymerisation of formaldehyde to form the sugar formose has been followed by the change in high-frequency conductance of the solution. Breaks in the current-time curve indicate stages in the polymerisation.[53]

Résumé—On a étendu une revue antérieure sur la théorie et les applications en chimie analytique des mesures de radio-fréquences, de façon à couvrir la littérature de 1960 au début de 1965.

Zusammenfassung—Eine früher gegebene Übersicht[1] über Theorie und Anwendungen von Radiofrequenzmessungen in der analytischen Chemie wird auf die Literatur von 1960 bis Anfang 1965 ausgedehnt.

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A NEW OXIDIMETRIC REAGENT: POTASSIUM DICHROMATE IN A STRONG PHOSPHORIC ACID MEDIUM—V*

POTENTIOMETRIC DETERMINATION OF URANIUM(VI)

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Summary—A critical review of the more important methods for the determination of uranium(VI) through reduction to uranium(IV) and subsequent titration with an oxidimetric reagent is given. A new method is described involving reduction to uranium(IV) by an excess of iron(II) in a strong phosphoric acid medium followed by potentiometric titration with a standard solution of potassium dichromate. This method has the advantages that the uranium(VI) is reduced quantitatively only to the uranium(IV) stage and that the potentiometric titration can be carried out at room temperature without the need for an inert atmosphere. It is also subject to less interferences than the other methods.

THE most widely adopted titrimetric method for uranium(VI) consists in the reduction of uranium(VI) to uranium(IV) and titration of the reduced form with a suitable oxidising agent. Among the reducing agents employed are metallic zinc, silver, lead or mercury. Zinc is used in the form of a solid amalgam as in the Jones Reductor or as a liquid amalgam according to Nakazono.[1] In both procedures uranium(VI) is reduced in a 2–5% *v*/*v* sulphuric acid medium to a mixture of uranium(IV) and uranium(III). The uranium(III) can be oxidised to uranium(IV) by passing a rapid stream of air through the solution for about 10 min as was shown by Lundell and Knowles.[2] Rodden[3] states that according to Miller, Morgan, Givens and Duane,[4] the oxidation is slow if the solution is not agitated either by a rapid stream of bubbles or by stirring. Moreover, in solutions containing 0·4 g of uranium and 0·25–90 mg of molybdenum/100 ml, the oxidation of molybdenum(III) to molybdenum(IV) causes the oxidation of uranium(III) to go beyond the quadrivalent state during aeration. If the concentration of molybdenum is over 90 mg/100 ml, complete oxidation of the molybdenum from the tervalent to the quadrivalent state by aeration is difficult and high results may be obtained for uranium. Although copper is precipitated in the Jones reductor, some is washed through with the reduced solution. It rapidly redissolves and markedly accelerates the oxidation of uranium(IV) by air to uranium(VI).

Recently, Sill and Peterson[5] made a thorough investigation on the use of the Jones reductor for determination of milligram quantities of uranium(VI). They stated that the solution to be titrated for uranium should have a volume of about 75 ml and

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* Part IV: see reference 25.

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‡ Those parts of the paper dealing with elimination of the interference of manganese(II) and cerium(III) and the analysis of Samarskite were received on 14 October 1964.

contain 6 ml of concentrated sulphuric acid. After being cooled to 15–20°, the solution is reduced by passing it through an air-free Jones reductor having a bore of 12 mm and a 30-cm column of 20- to 30-mesh amalgamated zinc (1% mercury). The flask and reductor are then washed with 50 ml of cold $1M$ sulphuric acid followed by 50 ml of cold water, added in small portions to obtain maximum washing efficiency. Each solution should be poured down the side of the reductor tube to prevent the formation of air bubbles that might be drawn into the zinc column. It is extremely important to keep the column free from air in order to prevent formation of significant amounts of hydrogen peroxide. The solution is then aerated by passing a fairly rapid stream of clean air through it for 5 min.

In as much as vanadium is reduced to the bivalent state by a Jones reductor and is not fully oxidised by air, its presence should lead to high results for uranium. When the quantity of uranium involved is small, this is the case, but with relatively large quantities of uranium, the results are surprisingly low. When a solution containing uranium equivalent to 25·0 ml of $0{\cdot}00997M$ sulphatoceric acid was titrated in the presence of 0·90 mg of vanadium, a titre of only 23·7 ml was obtained. From this it can be concluded that air oxidation of bivalent and tervalent vanadium apparently induces the air oxidation of quadrivalent uranium. Thus, the results can be either high or low, depending on the relative amounts of uranium and vanadium. With ions that can exist in several valency states, such as vanadium, molybdenum and tungsten, either high or low results can be obtained, depending on the metal:uranium ratio. Generally, the small quantity of metals not removed in the usual macro separations will cause high results for small quantities of uranium and low results for larger quantities. In the case of titanium, all results will be low because of induced oxidation of uranium and because the titanium(III) is more or less completely oxidised by air, leaving nothing capable of consuming the oxidant. This is also the predominant effect with copper, niobium and chromium. Silver and mercury cause high results. The error caused by iron is always positive, but, unlike any of the others, is an exact stoichiometric function of the quantity present. The interference of nickel in procedures involving the Jones reductor has been pointed out by Furman and Huberling.[6] Cobalt also interferes in this method. Large quantities of calcium interfere by occlusion of uranium in the calcium sulphate formed in the sulphuric acid solution.

From the foregoing it is evident that, when a Jones reductor is used, great care should be exercised to see that the column is air-free, otherwise hydrogen peroxide formation seriously interferes in the determination of uranium. Moreover, this procedure is subject to interference by nitrate, vanadium, molybdenum, tungsten, titanium, copper, nickel, cobalt, chromium, silver, mercury, iron, *etc.* Kennedy[7] worked out conditions for the quantitative reduction of uranium(VI) to uranium(III) in a nitrogen atmosphere with amalgamated zinc and $1M$ hydrochloric acid or perchloric acid. The equivalent amount of iron(II) produced in an iron(III) alum collecting solution was determined by dichromate titration. However, sulphate seriously interferes with the complete reduction of uranium(VI) to the tervalent state. Combination of this procedure with an air oxidation procedure was suggested as a means of analysing mixtures of titanium or iron and uranium.

Metallic silver has been used (as in the silver reductor by Birnbaum and Edmonds[8]) for the reduction of uranium(VI) to the quadrivalent state. This procedure necessitated a high temperature (60–90°) and controlled acidity of $4M$ hydrochloric acid.

In $1M$ hydrochloric acid, uranium(VI) is not reduced in the silver reductor, and even at a temperature of 60–90° there is only a slight reduction. Nitric acid, iron, molybdenum, vanadium and copper must be absent because they are reduced in the silver reductor. The formation of small amounts of hydrogen peroxide during reactions of dilute acids on silver reductors[9] and liquid metal amalgams[10] in the presence of air has been observed many times.

Koblic[11] reduced uranium quantitatively to the quadrivalent state with lead. However, his procedure is inconvenient because the solutions have to be boiled in an inert atmosphere of carbon dioxide in the presence of hydrochloric acid for at least 30 min. Cooke, Hazel and McNabb[12] and also Sill and Peterson[5] used a lead reductor to reduce uranium(VI) in hydrochloric acid solution quantitatively to uranium(IV) at room temperature. The use of a lead reductor has probably been limited because of the difficulty of applying it to sulphuric acid solutions. When sulphuric acid solutions are reduced with lead, an adherent film of lead sulphate is formed which soon decreases the efficiency of the reducing agent. Cooke, Hazel and McNabb[12] have shown that the formation of a lead sulphate film may be prevented if the concentration of hydrochloric acid is greater than $2{\cdot}5M$. In their method nitrate and iron(III) must be absent because they are also reduced. Conflicting statements are made in the literature concerning the formation of hydrogen peroxide in the lead reductor. Cooke, Hazel and McNabb[12] state that the reductor need not be freed from air, because its presence does not introduce errors. Sill and Peterson[5] state that hydrogen peroxide is formed in the lead reductor. They emphasise that air bubbles must be removed to prevent its formation. Sill and Peterson[5] found that chromium and titanium interfere in the determination of uranium when a lead reductor is used to reduce uranium(VI) to uranium(IV).

Caley and Rogers[13] used metallic mercury for the determination of uranium(VI). They state that the reduction of uranium(VI) solutions with mercury is never entirely complete even when using hydrochloric acid in very high concentration (7–$9M$). The degree of incompleteness of reduction varies from 4 to 7 parts per thousand, depending upon the exact conditions of experiment and manipulation. In spite of the incompleteness of the reduction, they used a mercury reductor for the determination of uranium by applying a positive correction factor of $0{\cdot}5\%$. The uranium(IV) formed is filtered into an excess of standard potassium dichromate and the excess back-titrated with a standard solution of iron(II) sulphate. Antimony, iron, molybdenum and vanadium interfere. Obviously, procedures requiring the use of the various reductors discussed above for the determination of uranium(VI) are tedious, because the reductors must be washed completely free from any uranium(IV); moreover, the procedures are subject to many interferences.

From the foregoing it is evident that the use of a Jones reductor, silver reductor, mercury reductor and even a less powerful reductor like metallic lead, are not fully satisfactory for the reduction of uranium(VI) to uranium(IV) before its titration with an oxidising agent.

Korach and coworkers[14,15] used chromium(II) solution for the reduction of uranium in 5% sulphuric acid. The resulting quadrivalent uranium is titrated to a potentiometric end-point with iron(III) sulphate, at a temperature of 95° and in an atmosphere of carbon dioxide. Recently, Jones[16] modified this procedure as follows: uranium(VI) is reduced with excess of chromium(II) in sulphuric acid, excess of chromium(II) is oxidised by passage of air through the solution, then the mixture is treated with an excess of iron(III). The resulting iron(II) is titrated with cerium(IV) sulphate solution using a potentiometric end-point with an automatic titrator. At the 50-mg level of uranium, a precision better than ±0·5% is reported. Tin(IV), iron(III), copper(II), silver(I), lead(II), tin(II), bismuth(III), mercury(II), antimony(III) and tungsten(VI) are reduced by chromium(II) ions and hence interfere. Moreover, chromium(II) solutions require special storage conditions because they are highly sensitive to atmospheric oxidation.

Main[17] reduced uranium(VI) with tin(II) chloride. The uranium(VI) solution is made $6M$ with respect to hydrochloric acid and $0{\cdot}75M$ with respect to phosphoric acid. Two ml of $0{\cdot}02M$ iron(III) chloride/40 ml are used as a catalyst. The reduction is carried out (inert atmosphere) at a temperature of 96–99° with excess of tin(II) chloride for 10–15 min. After cooling, the excess of tin(II) chloride is eliminated with mercury(II) chloride and the solution treated with excess of iron(III) chloride; the iron(II) formed is titrated with a standard solution of potassium dichromate using diphenylamine sulphonic acid as indicator. The titration is reported to be accurate to 0·5%. Arsenic, perchlorate, tungstate, permanganate, ammonium ions, pyridine, bismuthate, cobalt(II), sulphate, chloride and less than 5 mg of nitrate are reported not to interfere. Molybdenum(VI), copper(II), titanium(IV) and vanadium(V) interfere. From the procedure it is obvious that the method is tedious because (1) it involves a long heating at a high temperature, (2) the method is indirect, and (3) a correction has to be applied for the amount of iron(III) used as catalyst.

According to Newton and Hughes,[18] uranium(VI) can be reduced with an excess of titanium(III), the unreacted titanium(III) then being oxidised with excess bismuth trioxide, which is reduced to the metal. The bismuth metal and excess oxide are removed by filtration and the filtrate titrated in the ordinary manner to determine uranium(IV). Recently, Helbig[19] described the determination of uranium(VI) by reaction with excess titanium(III) followed by potentiometric titration with cerium(IV) in sulphuric acid. With a platinum indicating electrode, two potential breaks were observed, the first corresponding to excess titanium(III) and the second to uranium(IV) Even more recently, Corpel and Regnaud[20] described a method for the titrimetric determination of iron(III), uranium(VI) or plutonium(VI) and plutonium(IV) in a mixed sulphuric-nitric acid medium ($0{\cdot}5M$, $1M$). They are reduced with titanium(III) chloride solution in the presence of sulphuric acid to iron(II), uranium(IV) and plutonium(III), respectively, then titrated with $0{\cdot}01M$ cerium(IV) sulphate solution using ferroïn as indicator. Precautions normally taken for nitric acid media are unnecessary.

Because the use of various reductor columns and reducing agents like chromium(II) chloride, tin(II) chloride, *etc*., for the reduction of uranium(VI) to uranium(IV) before titration with an oxidising agent is attendent with so many difficulties and interferences, we have investigated the use of a reducing agent which is free from these defects.

Investigations have now been carried out to ascertain if the observation of Gopala Rao and Sagi[21] that uranium(VI) is quantitatively reduced by iron(II) in a strong phosphoric acid medium at room temperature can be used for developing a redox procedure for the determination of uranium(VI). Thus, when an excess of iron (II) is added to uranium(VI) in a strong phosphoric acid medium, the mixture will contain unreacted iron(II), uranium(IV) and iron(III). Attempts to oxidise the unreacted iron(II) completely by passing a stream of air were unsuccessful. Even after passing air for over 1 hr some iron(II) still remained. This is in accordance with the observations of Duckitt and Goode,[22] who found that in a mixture of uranium(IV) and iron(II) only up to 0·1% of iron(II) can be oxidised by aeration for 15 min. Higher percentages of iron(II) give errors. We have, however, observed that when a mixture of iron(II) and uranium(IV) is titrated potentiometrically at room temperature with potassium dichromate solution, two different breaks are obtained in the potential *vs.* volume curve: the first corresponds to the oxidation of iron(II) to iron(III) and the second (*i.e.*, the dichromate consumed between the two potential breaks) to the oxidation of uranium(IV) to uranium(VI). Before the equivalence point for iron(II) the potentials are stabilised in about 1 min, but at the equivalence point about 10 min are required for potential stabilisation. The break in potential is about 190 mV/0·04 ml of 0·2N dichromate solution. During the part of the titration corresponding to the oxidation of uranium(IV), the potentials are stabilised in about 1 min in the early stages and in about 3 min near the equivalence point. The second break in potential is about 260 mV/0·04 ml of 0·2N potassium dichromate solution when the volume of titration solution is about 50 ml.

This method is suitable for the determination of uranium(VI) in mixtures with tungsten(VI), copper(II), iron(III), titanium(IV), chromium(III), chromium(VI), cobalt(II), nickel(II) and tin(IV) because these do not interfere. Manganese(II), manganese(VII), cerium(III), cerium(IV), vanadium(IV), vanadium(V), molybdenum(V) and molybdenum(VI) interfere. The new method is quite convenient because it can be carried out at room temperature without the need for an inert atmosphere. The direct titration of uranium(VI) with iron(II) in a strong phosphoric acid medium previously proposed by Gopala Rao and Sagi[21] also has these advantages, but is subject to the inconvenience of a low potential break at the equivalence point (100–150 mV) and to the disadvantage of a sluggish attainment of equilibrium potentials. These are eliminated in the procedure now described. Moreover, the latter has the advantage that the determination of uranium(VI) is made through potassium dichromate, which is a primary standard.

EXPERIMENTAL

Reagents

0·05M *Uranium*(VI) *solution.* Prepared from analytical reagent grade uranyl acetate of British Drug Houses Ltd. (England) so as to be 0·5M in sulphuric acid. This solution is standardised by reduction in a Jones reductor, followed by titration with a standard solution of potassium dichromate according to the procedure of Kolthoff and Lingane.[23]

0·2N *Potassium dichromate solution.* Prepared from "Pro Analysi" grade potassium dichromate of E. Merck (Germany).

0·5M *Iron*(II) *solution.* Prepared from analytical reagent grade Mohr's salt supplied by British Drug Houses Ltd. (England) so as to be 0·5M in sulphuric acid.

Phosphoric acid. "Pro Analysi" grade phosphoric acid of E. Merck (Germany) is used in this investigation.

All other chemicals employed in this investigation are analytical reagent grade.

Apparatus

The potentiometric assembly used is as described in Part I of this series.[14]

Procedure

From 2 to 8 ml of 0·05M uranium(VI) solution are taken in a 150-ml Pyrex beaker and treated with 40–50 ml of phosphoric acid. The mixture is connected to the saturated calomel electrode through a saturated sodium perchlorate bridge and a saturated sodium nitrate bridge. A bright platinum rod is used as indicator electrode. The mixture is stirred electromagnetically. 0·5M Iron(II)

TABLE II.—POTENTIOMETRIC TITRATION OF URANIUM(VI) WITH POTASSIUM DICHROMATE IN A 12*M* PHOSPHORIC ACID MEDIUM AFTER REDUCTION WITH IRON(II)

Uranium(VI), *mg*	
Taken	Found
21·18	21·18
42·71	42·72
52·50	52·50
59·59	59·77
60·91	60·96
80·85	80·61

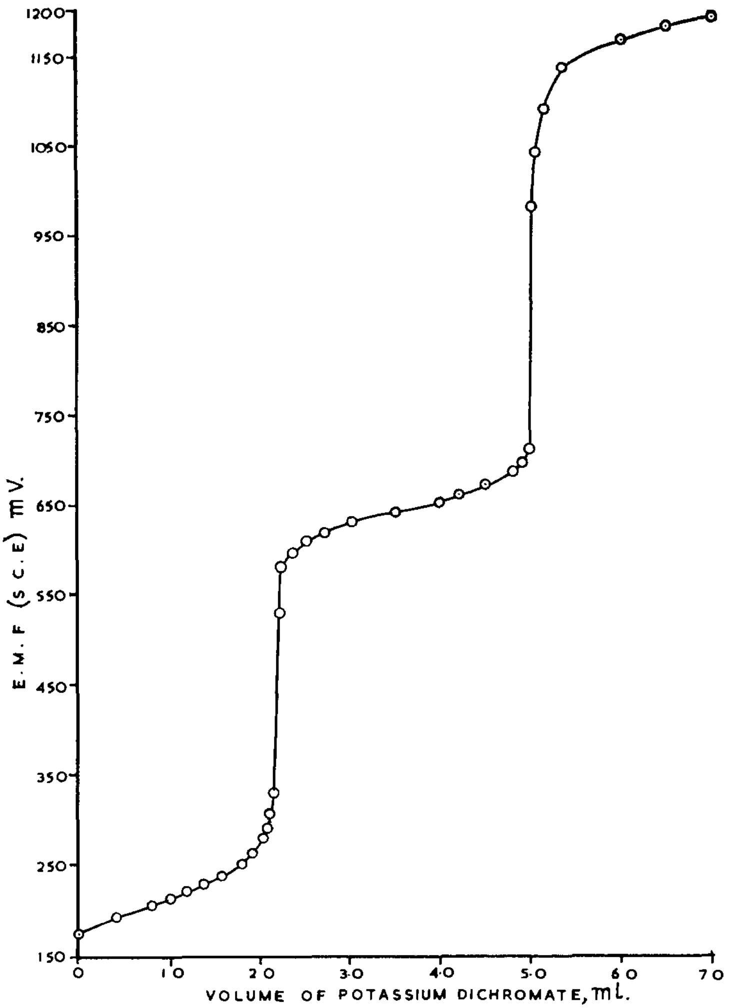

FIG. 1.—Potentiometric titration of uranium(VI) (67·12 mg) with 0·2*N* potassium chromate in a 12*M* phosphoric acid medium after reduction with excess iron(II).

solution (0·5–2 ml) is slowly added to the mixture from a graduated pipette until the cell potential becomes less than about 0·180 V. This indicates that the iron(II) added is in excess of that required for the complete reduction of uranium(VI). The mixture is then titrated with 0·2*N* potassium dichromate solution, noting the potentials 1 min after the addition of each portion of dichromate until near the first equivalence point and after 10 min at the equivalence point, which indicates complete oxidation of the excess iron(II). Thereafter, the potentials are noted about 2–3 min after the addition of each portion of potassium dichromate solution. The volume of potassium dichromate solution lying between the first and second breaks corresponds to that required for uranium(IV). A representative potentiometric titration curve is shown in Fig. 1. Typical results of assays of uranium(VI) made in this manner are given in Table I. They show that the error of determination does not exceed 0·3% (relative).

INTERFERENCES

Oxygen of the air does not interfere. In the presence of chloride no break is observed at the second equivalence point, although the first break is obtained. Nitrate interferes in the titration. Large quantities of iron(III) or iron(II) do not interfere, which is a decided advantage over the previous procedures. Tungsten(VI) does not interfere because it is not reduced by iron(II) in a strong phosphoric acid medium. Chromium(VI) and chromium(III) do not interfere because chromium(VI) is reduced to chromium(III) along with uranium(VI) by iron(II) and the chromium(III) is not re-oxidised by dichromate. Cobalt(II), nickel(II), copper(II), tin(IV) and titanium(IV) do not interfere.

In this titration manganese(VII) [or manganese(II)] and cerium(IV) [or cerium(III)] interfere, because the manganese(II) or cerium(III) formed by reduction react simultaneously with the potassium dichromate after about 50% of the uranium(IV) is reoxidised. Molybdenum(VI) interferes because it is reduced to molybdenum(V). Molybdenum(V) and uranium(IV) are simultaneously oxidised by the potassium dichromate to molybdenum(VI) and uranium(VI), respectively, after the first break in potential is obtained.

The interference of manganese(II) [or manganese(VII)] and cerium(III) [or cerium(IV)] can be eliminated as follows. After the iron(II) equivalence point, the titration mixture is diluted with distilled water such that the concentration of phosphoric acid lies between 6 and 9*M* at the second equivalence point. When the titration is completed under these conditions, only the uranium(IV) reacts with potassium dichromate.

Vanadium(IV) and vanadium(V) also interfere in the determination of uranium(VI) and this is under further investigation.

APPLICATION TO DETERMINATION OF URANIUM IN SAMARSKITE

Procedure I

One g of powdered and dried Samarskite is taken in a 250-ml platinum dish and treated with a mixture of 10 ml of 40% hydrofluoric acid and 10 ml of nitric acid (1:1), then carefully heated almost to dryness. The residue is again treated with 10 ml of hydrofluoric acid and heated almost to dryness to remove completely any silica left after the first treatment. Finally, the residue is heated with 10 ml of sulphuric acid (1:1) to fumes of sulphuric acid. At this stage care should be taken to see that there is no mechanical loss.

The residue is extracted with hot 1*M* sulphuric acid, cooled and filtered through a Whatman 42 filter paper into a 150-ml Pyrex beaker. The white mass (oxides of niobium and tantalum) left on the filter paper is washed several times with 1*M* sulphuric acid. The filtrate plus washings are carefully evaporated on a hot-plate until the volume is reduced to about 10 ml. During this process some white material is precipitated. After cooling, the residue is treated with 40 ml of syrupy phosphoric acid. The solution becomes clear after standing for about 0·5 hr. It is then treated with an excess of iron(II) and titrated potentiometrically with standard 0·2*N* potassium dichromate according to the procedure already described.

To check the uranium content in the ore by a standard method, 2 g of the ore is treated as described above. The solution is passed through a Jones reductor and shaken in air for about 10 min to oxidise any uranium(III) that is formed. Because of the presence of iron in the ore the method of Kolthoff and Lingane[23] could not be applied for the determination of uranium. Therefore, we have carried out a potentiometric titration of the mixture (10 ml) in a 12M phosphoric acid medium with standard 0·05N potassium dichromate solution according to the procedure described in a previous paper.[25] Two breaks are obtained, the first corresponding to the oxidation of iron(II) and the second to that of uranium(IV). The volume of dichromate between the first and second breaks corresponds to that required for the uranium.

Procedure II

To avoid filtrations the following procedure is adopted. About 1 g of the well powdered and dried sample is taken in a 250-ml platinum dish and treated with a mixture of nitric acid and hydrofluoric acid and finally with sulphuric acid (1:1) as described in *Procedure I.*

After cooling, 20 ml of water and 10 ml of syrupy phosphoric acid are added and the contents of the platinum dish transferred to a 150-ml Pyrex beaker. The dish is washed with 10-ml portions of syrupy phosphoric acid and the washings also transferred to the beaker. Altogether 50 ml of phosphoric acid are added. This solution becomes almost clear. After cooling, the solution is treated with an excess of iron(II) and titrated potentiometrically with standard 0·2N potassium dichromate as described in *Procedure I.* The slight turbidity does not interfere in the titration.

Some typical results from the analysis of a sample of Samarskite of the Nellore District, Andhra State, India, are given in Table II.

TABLE II

Uranium found by present method, %	Uranium found by method of Gopala Rao and Kanta Rao,[25] %
Procedure I	
7·247, 7·265	7·289,
Procedure II	
7·259, 7·283	7·289

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Zusammenfassung—Eine kritische Übersicht über die wichtigeren Methoden zur Bestimmung von Uran(VI) durch Reduktion zu Uran (IV) und anschließende oxydimetrische Titration wird gegeben. Eine neue Methode wird beschrieben; dabei wird mit überschüssigem Eisen(II) in starker Phosphorsäure zu Uran(IV) reduziert, dann potentiometrisch mit eingestellter Kaliumdichromatlösung titriert. Der Vorteil dabei ist, daß Uran(VI) quantitativ nur zu Uran(IV) reduziert wird und die potentiometrische Titration bei Zimmertemperatur ohne Inertgas ausgeführt werden kann. Sie ist auch weniger störungsanfällig als die anderen Methoden.

Résumé—On présente une revue critique des méthodes les plus importantes de dosage de l'uranium(VI) par réduction en uranium(IV), suivie d'un titrage au moyen d'un réactif oxydimétrique. On décrit une nouvelle méthode basée sur la réduction en uranium(IV) au moyen d'un excès de fer(II) en milieu fortement concentré en acide phosphorique, suivie d'un dosage potentiométrique par une solution étalon de bichromate de potassium. Les avantages de cette méthode sont la réduction quantitative de l'uranium(VI) en uranium(IV) exclusivement, et la possibilité de mener le dosage potentiométrique à température ambiante sans qu'il soit nécessaire d'opérer en atmosphère inerte. Elle est aussi moins sujette aux interférences que les autres méthodes.

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SHORT COMMUNICATION

Transition potentials of some triphenylmethane dyestuff redox indicators

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THE formal potential of the cerium(IV)/cerium(III) system is considerably higher in a perchloric acid medium than in sulphuric acid solution. Tris(1,10-phenanthroline)iron(II) sulphate, commonly called ferroïn (1·06 V), is unsuitable as an indicator in titrations with hexaperchloratocerate(IV) because its potential is too low. Indicators which have been recommended are nitroferroïn (1·25 V)[2] and tris(2,2′-dipyridyl)ruthenium(II) chloride (1·25 V).[12] Rao and Rao[1] have more recently recommended the three triphenylmethane dyestuffs Eriogreen B (EGB): C.I. 44025, Erioglaucine A (EGA): C.I. 42090 and Xylene Cyanol FF (XCFF): C.I. 42135 as indicators with hexaperchloratocerate(IV), because they have the advantage of cheapness. The reported potentials of all three dyestuffs are about 1·0 V; their behaviour, therefore, seems anomalous because ferroïn, with a higher potential, is unsuitable. This problem was discussed in a previous communication.[3]

TABLE I

Indicator	Previous values for E°′, *V*	Transition ranges, *V* $1F\ H_2SO_4$	$1F\ HClO_4$
EGA	1·01	1·10–1·16	1·12–1·19
EGB	1·01	1·12–1·16	1·14–1·20
XCFF	0·98–1·01	1·09–1·15	1·13–1·20

Two possible explanations for this apparent anomaly are that either the reported potentials are incorrect (the available figures are, in general, more than 30 years old) or the potentials may be higher in a perchloric acid medium. Our findings indicate that both are true.

Knop[4–6] determined the potentials (probably transition potentials) only in the iron(II)-permanganate titration (sulphuric acid medium). The only further determinations seem to be those of Adams and Hammaker,[7] who determined the transition potentials of Alphazurine G (Disulphine Blue V, Patent Blue V, C.I. 42051) in both sulphuric and perchloric acid media, and Tomlinson, Aelpi and Ebert[8] who determined the transition potential of Xylene Cyanol FF in a sulphuric acid medium. The latter investigators recommend Xylene Cyanol FF as an indicator in cerium(IV) titrations and seem to be unaware that it was used as such before the advent of ferroïn. They do not quote the index number; hence it is not possible to judge what their compound was, because the material available nowadays (C.I. 42135)[9] is different from that used in the early days of cerium(IV) titrimetry (C.I. 43535).

Adams and Hammaker[7] found the following transition potentials for Alphazurine G, 1·03 V (1·0F H_2SO_4) and 1·07 V (1·0F $HClO_4$). Tomlinson *et al.* found for Xylene Cyanol FF, 0·98 V (1·0F H_2SO_4) and a further figure of 1·1 V for what they term the irreversible potential, *i.e.*, the point at which the indicator is destroyed. Although Adams and Hammaker were dealing with a different indicator, they found a significant increase in the transition potential when determined in a perchloric acid medium.

We have found it impossible to measure the formal redox potentials, because these dyestuffs are too readily oxidised irreversibly; accordingly, transition potentials were measured.

The potentials were determined in sulphuric acid and in perchloric acid media (Table I). It will be seen that the newly determined potentials in a sulphuric acid medium are higher than the original values, and in perchloric acid the values are increased still further; the latter figures presumably account for the behaviour of the indicators under the conditions of Rao and Rao.

The order of increase of potential in perchloric acid is similar to that found by Adams and Hammaker. Although their results were obtained on a different indicator, it is rather surprising that there is such an appreciable difference between their values and ours in a sulphuric acid medium. It is difficult to compare our result for Xylene Cyanol FF with that of Tomlinson *et al.*,[8] for the reason given earlier, but even if their compound were different, one would not expect such a marked variance in the sulphuric acid medium.

There is some further evidence, however, that the previously reported values in a sulphuric acid medium may be too low. It is well-known that none of the triphenylmethane dyestuffs functions in the dichromate-iron(II) titration. The formal potential of 5,6-dimethylferroïn is 0·97 V (1*F* H_2SO_4) and its transition potential is 1·03 V.[9] This indicator functions well in the dichromate-iron(II) system. Accordingly, if the triphenylmethane dyestuffs had, in fact, transition potentials of 1·03 V or lower, they should function in the same system, which they do not. Tris(2,2′-dipyridyl)iron(II) sulphate (transition potential 1·08 V)[9] does not function; unfortunately, there are no known ferroïn or dipyridyl derivatives which have potentials in between 1·03 and 1·08 V which would allow us to narrow the gap and to say exactly at which potential an indicator does not function satisfactorily in the dichromate-iron(II) system. Probably this potential is about 1·05–1·06 V, but one would expect a grading of properties around this figure. If it can be assumed that indicator behaviour in the dichromate-iron(II) system is a fair comparison, then indicators which do not function would be expected to have transition potentials higher than 1·05–1·06 V.

It is known that 5-methylferroïn (transition potential 1·08 V)[10] functions in the dichromate-iron(II) titration, *provided that* the acidity is 4*F* in sulphuric acid; with increase in acidity the equivalence potential of the dichromate-iron(II) system is enhanced and the potential of the indicator is lowered. Some tests were done with Erioglaucine A at acidities of 1*F*, 2*F* and 4*F* in sulphuric acid. At 4*F* a reversible end-point was obtained almost immediately when a slight excess of dichromate was present. In 1*F* and 2*F* media the oxidised form of the indicator was only obtained after several minutes. These results seem to indicate that the lower limit of the transition range of Erioglaucine A is similar to that of 5-methylferroïn and should be at least 1·08 V.

It is not possible from our present knowledge to suggest why the indicator potentials should increase in a perchloric acid medium, especially when the mechanism of oxidation remains unknown despite various attempts at elucidation.[4,9] It is almost certain that ferroïn or its derivatives are not affected in the same way. Although it is not possible to measure their potentials directly in a perchloric acid medium because of the insolubility of the 1,10-phenanthroline perchlorates, there are two indirect pieces of evidence: (i) the behaviour of ferroïn and of nitroferroïn in this system is in accordance with their potentials as determined in a sulphuric acid medium; (ii) sulphonated derivatives of ferroïn, which are soluble in a perchloric acid medium, exhibit virtually the same potentials in either sulphuric or perchloric acid media.[11]

EXPERIMENTAL

The transition potentials were measured under titration conditions in 1*F* sulphuric and perchloric acids using a 'Vibron' pH meter and a platinum-saturated calomel electrode pair to measure the potentials.

A mixture of a small quantity of iron(II) solution in the appropriate acid (1*F*) with 0·5 ml of aqueous indicator (0·1 %) and 0·5 ml of 2*F* acid was titrated drop-wise with 0·001*N* sulphatocerate(IV) or perchloratocerate(IV) solution in 1*F* acid. The potential at which the colour transition occurred was noted. 0·001*N* Iron(II) solution in 1*F* acid was then added to reverse the change, and the transition potential again noted. The end-point was traversed several times.

With each indicator, the colour change in both directions occurred over a range of about 50 mV.

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Summary—The transition ranges of three triphenylmethane dyestuff redox indicators have been redetermined. The figures found in 1*F* sulphuric acid are appreciably higher than earlier values; the new figures are more in accord with the behaviour of these indicators when compared with 2,2′-dipyridyl and substituted ferroïns. At high acidities the indicators function in the dichromate-iron(II) system. In a perchloric acid medium the figures are significantly higher and fall into a range which accounts for the fact that all three dyestuffs function as indicators with hexaperchloratocerate(IV) titrant. The potentials of ferroïn and its derivatives are apparently unaffected by change of medium.

Zusammenfassung—Die Übergangsstufen von drei Redox-Indikatoren aus der Klasse der Triphenylmethanfarbstoffe wurden neu bestimmt. Die in 1*F* Schwefelsäure ermittelten Werte sind merklich höher als die früheren Werte; die neuen Werte stimmen besser mit dem Verhalten dieser Indikatoren überein, im Vergleich zu 2,2′-Dipyridyl und substituierten Ferroinen. Bei hohen Säurestufen können die Indikatoren im System Bichromat-Eisen (II) angewendet werden. In einem perchlorsauren Medium werden bedeutend höhere Werte erhalten: sie fallen in einen Bereich, in Übereinstimmung mit der Tatsache, dass sich alle drei Farbstoffe mit Hexaperchloratocerat (IV) lösung als Indikatoren verhalten. Die Potentiale des Ferroins und seiner Derivate werden durch Veränderungen des Mediums scheinbar nicht beeinflusst.

Résumé—On a déterminé à nouveau les domaines de transition de trois indicateurs redox, colorants du groupe triphénylméthane. Les chiffres trouvés en acide sulfurique 1*F* sont assez fortement supérieurs aux valeurs antérieures; les nouveaux chiffres sont en meilleur accord avec le comportement de ces indicateurs, comparé à ceux du 2,2′-dipyridyle et des ferroïnes substituées. Aux fortes acidités, les indicateurs fonctionnent dans le système bichromate-fer (II). En milieu acide perchlorique, les chiffres sont notablement plus élevés et tombent dans un domaine qui rend compte du fait que les trois colorants fonctionnent comme indicateurs lorsque l'agent de titrage est l'hexaperchloratocérate (IV). Les potentiels de la ferroïne et de ses dérivés ne sont apparemment pas affectés par le changement de milieu.

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PRELIMINARY COMMUNICATION

Continuous substoichiometric analysis

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In continuous analysis test samples in the form of a flowing stream are processed in such a way as to measure the content of the required constituent. This type of analysis is much more suitable for automatisation than normal repetitive analysis in which each sample is processed virtually individually. Considerable progress has been achieved in recent years in automatisation of continuous analysis[1-3] and a variety of methods have been developed, based on spectrophotometry, flame photometry and fluorimetry, using flow cells and automatic recording of the measurements. The flow diagram of one of the most successful instruments for this purpose, the Technicon AutoAnalyzer (Technicon Instruments Company Ltd., Hanworth Lane, Chertsey, Surrey, England), is seen in Fig. 1. The success of these continuous methods of analysis stimulated the suggestion to develop flow cells suitable for measurement of other properties, such as conductivity, dielectric constant, electrochemical potential, *etc.*[4] Although flow cells for the sensitive and precise measurement of both beta and gamma radiation are commercially available, radioisotopes have not been widely applied for continuous analysis of non-active materials in solutions. This is because a chemical method must be developed which guarantees that a measured change of radioactivity is proportional to the amount of determined non-active species present in a test sample. In our opinion this can probably be achieved using the principle of substoichiometry, which has previously been applied successfully to the determination of a number of elements by neutron activation and isotope dilution analysis.[5]

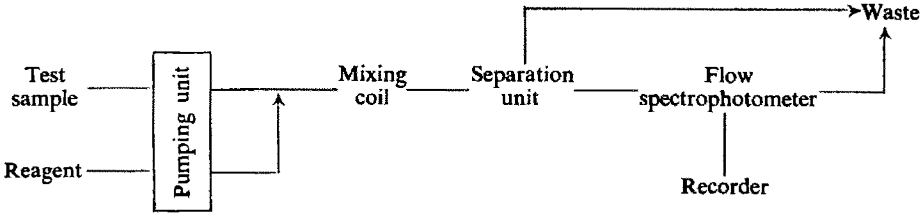

FIG. 1—Flow diagram of the AutoAnalyzer system for continuous spectrophotometric analysis.
Reagent and test sample are mixed in the mixing coil, where they react to form a coloured species. Undesirable species are separated (by dialysis) in the separation unit, then the absorbancy of the solution is measured, recorded and evaluated.

Although automatisation of *activation analysis* in conjunction with the AutoAnalyzer cannot be excluded, only substoichiometric determination by *isotope dilution* is considered in this communication. The reason is that very low activities are employed in the latter method and this enables it to be used in ordinary laboratories and for industrial purposes.

In the determination of a non-active element by isotope dilution one mixes the test sample with a known amount (y_s) of the standard radioisotope of original activity s_s. From the decrease of this specific activity to a value s, the amount of the non-active element (y) can be calculated

$$y = y_s\left(\frac{s_s}{s} - 1\right) \qquad (1)$$

Because the specific activity is an activity related to the unit of mass ($s = a/m$), not only the activity (a) but also the mass (m) of the isolated element (or its compound) must be determined after isotope dilution to complete the analysis. However, if one separates from both a standard radioisotope solution and from the solution formed by isotope dilution *exactly equal amounts in weight* of the element to be determined ($m = m_s$), the amount of element in the test sample can be calculated directly from the isolated activities

$$y = y_s\left(\frac{a_s}{a} - 1\right) \tag{2}$$

Such an isolation can be carried out substoichiometrically, which means that to both the above-mentioned solutions must be added an exactly equal amount of reagent; this amount must be smaller than that corresponding stoichiometrically to the quantity of element present in the standard radioisotope solution (y_s). The reagent used must be consumed completely in the reaction with the element to be determined and the compound formed must be easily separable from the excess of unreacted element.[5,6]

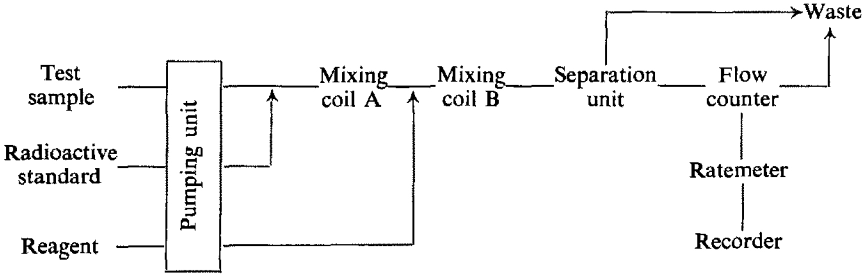

Fig. 2—Proposed flow diagram for continous substoichiometric analysis with the AutoAnalyser system:

separation unit = electrolyte trap for solvent extraction, column for ion exchange; flow counter = scintillation counter with NaI(Tl) crystal for gamma emmiters, Geiger-Müller counter for beta emmiters.

In Fig. 2 is presented a proposed flow diagram for continuous substoichiometric analysis with the AutoAnalyzer. To obtain the value a_s the test sample is replaced by pure diluent (water) and the concentration of the standard radioisotope solution is adjusted to a level which corresponds (by an order of magnitude) to the expected amount of test element in the sample under analysis. The concentration of reagent is adjusted to be substoichiometric (about 50–75% stoichiometry) to the standard radioisotope solution. The pump tubes are chosen in such a way that the same, constant delivery of both solutions is guaranteed. After mixing and reacting (coil B), the compound formed is continuously separated in a separation unit (see below) and the activity continuously measured by a scintillation or Geiger-Müller flow counter. When a test sample is introduced into the system, isotopic exchange takes place during mixing (coil A) and the resulting mixture, isotopically diluted, is reacted (coil B) with the reagent. As a result of this (and the substoichiometric separation) the activity measured by the flow cell decreases to the value a. The amount of non-active element present in the test sample is calculated according to equation (2). By means of several non-active standard solutions the instrument could be calibrated for direct reading of values of y. This calibration must, of course, be repeated if the standard radioisotope solution or reagent is changed.

It is anticipated that the following techniques could be used in continuous substoichiometric analysis:

(a) *Complexation followed by ion exchange.* The determination of iron will be used as an example. Iron reacts with a substoichiometric amount of EDTA according to the equation

$$2Fe^{3+} + Y^{4-} \rightleftharpoons FeY^{-} + Fe^{3+}$$

forming a negatively charged chelate, which can be easily separated from the unreacted iron on a cation exchanger. In this case the separation unit (Fig. 2) is a column of cation exchanger (sodium form) of suitable mesh (or possibly an AutoAnalyzer dialyser unit in which the cellophane membrane is replaced by a cation-exchange membrane and the dialyser coils connected in series). The optimum conditions (pH, masking agents) for the above chemical reaction can be chosen according to the theory of substoichiometry[5] and necessary solutions (buffer, *etc.*) added to the flow stream in the normal way for the AutoAnalyzer system. This method should be capable of wide application to the determination of metals, many of which form negatively charged chelates with complexing agents such as EDTA.

(b) *Solvent extraction.* In this method an organic reagent, forming an extractable chelate with the test element, is added in a substoichiometric amount. This reagent (dithizone, diethyldithiocarbamate, 8-hydroxyquinoline, *etc.*) dissolved in an organic solvent (chloroform, carbon tetrachloride, *etc.*) is equilibrated with the test solution in an extraction coil (B) and the resulting organic extract, the activity of which is to be measured, is continuously separated in a special separation unit (electrolyte trap). Solvent extraction offers a number of possibilities for the determination of various metals and the theory of substoichiometric separation by solvent extraction[6] has been developed and verified in recent years.

(c) *Precipitation reactions.* Although applicable in principle such reactions are not very suitable in practice for technical reasons. Continuous separation of precipitates from a flow stream is still not perfected; moreover, continuous measurement of the activity of the resulting precipitate is much more difficult than measurement of the activity of a stream of liquid.

The advantage of continuous substoichiometry compared with the widely used continuous spectrophotometric analysis is that the sensitivity of detection of radioactivity is very high. Furthermore, reagents the reaction products of which are colourless (EDTA, HEDTA, *etc.*) or only slightly coloured (cupferron, diethyldithiocarbamate, *etc.*) can be used, providing they fulfil the requirements of substoichiometry. Substoichiometric separation is also generally more selective[5] than methods which employ an excess of reagent for separation, complexation or colour development. The use of a substoichiometric amount of reagent has a disadvantage because the time necessary for reaching (extraction or complexation) equilibrium is longer than when a great excess of reagent is employed; in the substoichiometric determinations so far developed it is mostly about 1 min and not longer than 3–5 min. Although solvent extraction by shaking is more effective than extraction in coils, continuous analysis with the AutoAnalyzer allows the use of chemical reactions which are not brought to completion. (Recently, methods[7,8] based on incomplete reaction using a substoichiometric amount of reagent have been proposed. Their use for repetitive (batch) analysis is, in our opinion, not to be recommended, but such methods offer some possibilities in the case of continuous substoichiometric analysis.) Reaching reaction equilibrium is, of course, more desirable because it avoids the necessity of a calibration curve.

Finally, it can be mentioned that most of the substoichiometric determinations proposed until now (some 20 elements) can probably be automatised as outlined above. The disadvantage of using radioactive isotopes is offset by the fact that the activities involved will be very low and the handling of active solutions is minimised with the AutoAnalyzer system, from which even waste is discharged automatically. It is expected that it will be possible to determine amounts of various elements of the order of 10^{-3} to 10^{-9} g/ml of test solution.

All the above possibilities are currently being verified in this laboratory. The results will be reported as they become available.

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Summary—A method for carrying out continuous substoichiometric analysis by isotope dilution is proposed. Separations based on the use of solvent extraction, ion exchange and precipitation reactions are discussed. It should be possible to determine amounts of elements of the order of 10^{-3} to 10^{-9} g/ml of test solution.

Zusammenfassung—Eine Methode zur kontinuierlichen unterstöchiometrischen Analyse durch Isotopenverdünnung wird vorgeschlagen. Abtrennungen mittels flüssig-flüssig-Extraktion, Ionenaustausch und Fällung werden diskutiert. Man sollte Mengen in den Größenordnungen von 10^{-3} bis 10^{-9} Gramm pro ml Probelösung bestimmen können.

Résumé—On propose une méthode d'analyse substoechiométrique continue par dilution isotopique. On discute de séparations basées sur l'emploi d'extraction par solvant, d'échange d'ions et de réactions de précipitation. Il serait possible de doser des quantités d'éléments de l'ordre de 10^{-3} à 10^{-9} g/ml de solution d'essai.

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EDITORIAL NOTE

Authors are asked to note that, starting in 1966, the journal-name abbreviations in *Talanta* will be those in *Chemical Abstracts*. These abbreviations were adopted as an international standard for chemistry by the International Union of Pure and Applied Chemistry.

One of the major tasks in editing a paper for publication in *Talanta* has proved to be the transformation of references to the form used by the journal. Starting in 1966, the form will be as follows:

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, Oxford, 1956.
3. A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
4. W. Jones, *Brit. Pat.* 654321, 1959.

References should be indicated in the text by consecutive superior numbers, and the full references should be given in a list at the end of the paper.

Authors are particularly requested to observe the above conventions. Also, authors should check the correctness of their references against the original papers wherever possible; second-hand references are a frequent source of error.

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SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM WITH 4-(2-THIAZOLYLAZO)RESORCINOL

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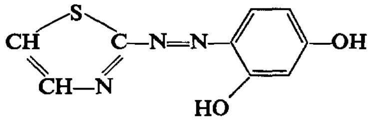
Summary—4-(2-Thiazolylazo)resorcinol forms a carmine red complex with niobium in an acetate-tartrate medium over the pH range 5–6. In the presence of ethylenediaminetetra-acetic acid (EDTA) or diaminocyclohexanetetra-acetic acid (DCTA) the reaction is almost specific for niobium: only vanadium and more than a 7–10 times excess of molybdenum, titanium, uranium and thorium interfere.

ONLY a few colorimetric methods are available for the determination of niobium. These methods include the use of catechol and EDTA,[1] Xylenol Orange[2] and some azo dyes.[3–5] A rhodanide method is sensitive but its reproducibility is poor.[6,7] It seems that the best colorimetric method at this time with respect to sensitivity, reproducibility and minimum influence of foreign ions is that using 4-(2-pyridylazo)resorcinol.[8,9] A similar reaction is found with 4-(2-thiazolylazo)resorcinol, which has been described as a metallochromic indicator.[10] The properties of thiazolylazoresorcinol (TAR) and pyridylazoresorcinol (PAR) are very similar, but TAR can be easily prepared by a simple diazotisation from aminothiazole, while to prepare PAR diazotisation of aminopyridine with amyl nitrite is necessary. The structural formula of TAR is:



OPTIMAL CONDITIONS FOR REACTION OF TAR WITH NIOBIUM

The basic variables affecting the reaction were studied to discover the optimal conditions. Measurements were generally made in a 50-ml volume, with 2·5 ml of 0·1% TAR solution in the pH range 5·0–6·0 (optimum) and with 1-cm cells. One ml of 10% tartaric acid was added. The absorption maximum is at 540 mμ (Fig. 1).

Influence of pH

Table I summarises the effect of pH on the absorbance. It is evident that the optimal pH range is 5–6.

TABLE I.—INFLUENCE OF pH

pH	4	4·5	5	5·5	6	6·5	7
Absorbance	0·55	0·88	0·90	0·91	0·90	0·87	0·62

0·3 mg of Nb_2O_5 taken; absorbance measured at 540 mμ relative to a reagent blank.

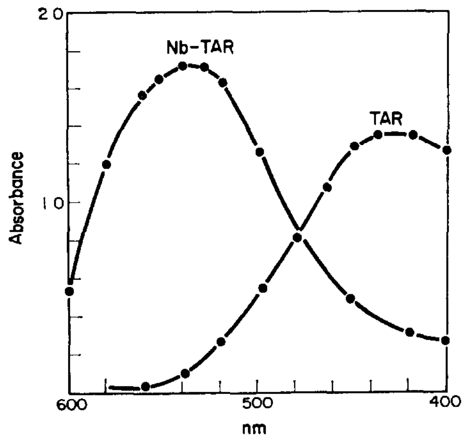


FIG. 1.—Absorption spectra of Nb-TAR complex and TAR (1 mg of Nb_2O_5, 2 ml of 0·1% TAR at pH 5·4).

Influence of temperature and time on development of colour

It was found that the absorbance is constant with a 20–30 min colour development at room temperature. Slight warming or boiling is without positive effect (Table II).

TABLE II.—EFFECT OF TEMPERATURE AND TIME

Temp. \ Time, *min*	5	10	15	20	30	45	60
Cold solution	0·64	0·85	0·88	0·89	0·90	0·90	0·90
60°	—	0·74	0·77	0·79	0·80	0·81	0·82
100°	—	0·83	0·84	0·85	0·85	0·85	0·85

0·3 mg of Nb_2O_3 taken.

Interferences

Effect of anions. The absorbance of the niobium complex is affected by tartaric, citric and oxalic acids, EDTA, phosphates, fluorides and hydrogen peroxide. Ascorbic and tartaric acids interfere least. It is interesting that EDTA or DCTA alone lowered the absorbance much more than the same amount mixed with tartaric acid, probably because of hydrolysis.

Effect of cations. The influence of some foreign cations is shown in Table III. Nb_2O_5 (0·1 mg) can be determined with an error of ±7% even in the presence of 10 mg of Ta_2O_5, 6 mg of TiO_2, 6 mg of ZrO_2, 6 mg of SnO_2, 6 mg of W or 3 mg of Sc. Traces of ferric ion must be screened by EDTA or DCTA; ascorbic acid is not sufficient. The same reagents also complex Al, Zn, Mg, Mn, *etc.* Only vanadium, uranium and thorium interfere. The influence of vanadium can be diminished by reduction to VO^{2+} by hydroxylamine chloride or by a saturated solution of ammonium oxalate. Because niobium is normally separated in the first step of the analytical procedure with silica, tantalum, tungsten and coprecipitated zirconium, titanium and

TABLE III.—DETERMINATION OF NIOBIUM IN THE PRESENCE OF FOREIGN IONS*

Nb_2O_5, *mg* Taken	Nb_2O_5, *mg* Found	Difference, *μg*	Error, %	Also added, *mg*
0·1	0·10	0·0	0·0	1 Ta_2O_5
	0·11	10	10·0	10 Ta_2O_5
0·2	0·20	0·0	0·0	10 Ta_2O_5
0·1	0·10	0·0	0·0	0·2 TiO_2
	0·105	5·0	5·0	2·0 TiO_2
	0·11	'010	10·0	6·0 TiO_2
	0·0	0·0	0·0	1·1 Sn
	0·103	3·0	3·0	4·4 Sn
	0·105	5·0	5·0	1·0 Zr
	0·11	10·0	10·0	1·0 Mo
	0·11	10·0	10·0	1·1 U†
	0·12	20·0	20·0	1·0 V^{4+} †
0·2	0·19	10·0	5·0	4·5 Zr
	0·228	28·0	14·0	3·0 Th
	0·185	15·0	7·5	2·8 Sc
	0·215	15·0	7·5	9·1 W
	0·204	4·0	2·0	3·6 W
	0·215	15·0	7·5	5·5 Fe^{3+}
	0·204	4·0	2·0	2·7 Fe^{3+}

* 1 ml of 10% tartaric acid and 1 ml of 0·1*M* EDTA in 50 ml of solution
† 1 drop of 4% ammonium oxalate

iron, the determination of niobium is practically specific. The best methods of separation for niobium and tantalum are using 7,8-dihydroxy-4-methylcoumarine,[11] phenylarsonic acid[12,13] or by paper chromatography.[14]

Composition of Nb-TAR complex

The nature of the complex formation between TAR and niobium was studied by a continuous variations method (Fig. 2). Niobium and TAR react in the molar ratio of 1:1.

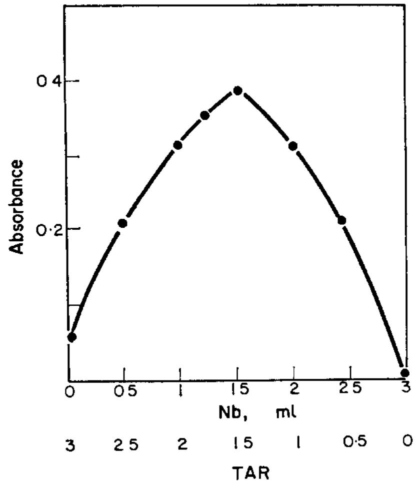


FIG. 2.—Continuous variation plot of Nb-TAR system.

EXPERIMENTAL

Apparatus

Spectrophotometers. The absorption curves were obtained with a Hilger Uvispek spectrophotometer. Spectrophotometric measurements were carried out with a Hilger Spekker spectrophotometer.

pH meter. Model "K", Laboratorní potřeby.

Reagents

Niobium solution. Fuse 0·100 g of Nb_2O_5 with about 5 g of $KHSO_4$ in a platinum crucible. Cool and extract the melt with 10 ml of 20% tartaric acid solution by boiling. Cool and dilute with water to 100 ml. Dilute 10 ml of this solution again to 100 ml. One ml of this solution (freshly prepared) contains 0·1 mg of Nb_2O_5 and 2 mg of tartaric acid.

4-(2-Thiazolylazo)-resorcinol (TAR). Obtained from Lachema n.p. Brno. Prepare a 0·1% solution in methanol; this is stable for several weeks.

Buffer solution (pH 5·4). Dissolve 80 g of ammonium acetate in water, add 7 ml of glacial acetic acid and dilute to 1 litre.

0·1*M* EDTA *and* DCTA *solutions*

10% *Tartaric acid solution*

Procedures

Calibration curve. Transfer the standard solution containing 0·05–0·5 mg of Nb_2O_5 to a 50-ml volumetric flask, add 1 ml of 10% tartaric acid, 1·0 ml of EDTA or DCTA for masking traces of iron, *etc.*, dilute with water, then add aqueous ammonia to adjust the pH to approximately 5–5·5. Add 5 ml of buffer solution, 2·5 ml of 0·1% TAR solution and dilute to 50 ml with water. Mix and let stand for 20–30 min. Measure the absorbance at 540 mμ (or yellow-green filter) against a blank solution containing the same amount of reagent. Beer's law is obeyed, and the molar absorbtivities for various conditions are given in Table V. Because tartaric acid and EDTA influence the absorbance, it is necessary to keep their concentrations constant.

Analysis of metals and alloys. Dissolve 0·1–1 g of sample in HCl–HNO_3 or HNO_3–HF mixture and evaporate to dryness. In the presence of HF add 1 ml of concentrated H_2SO_4. Extract the residue with 25 ml of 2–4*M* HCl, add 1–2 ml of a saturated solution of phenylarsonic acid and filter after 1 hr. Wash with 5% HCl and a small amount of phenylarsonic acid, dry and ignite. If the residue contains silica, evaporate with 3–6 ml of 40% HF and 0·5 ml of H_2SO_4 (1+1) till white fumes appear. Melt this residue with $KHSO_4$, cool and extract by boiling with 10 ml of 10% tartaric acid. Dilute to 50 or 100 ml in a volumetric flask. Take an aliquot containing less than 0·3 mg of Nb_2O_5 (10-mm cuvettes) or 0·1 mg of Nb_2O_5 (40-mm cuvettes), add 1 ml of 0·1*M* EDTA or DCTA and sufficient tartaric acid to bring the total in the aliquot to the equivalent of 1 ml of 10% solution.

TABLE IV.—DETERMINATION OF NIOBIUM IN ORES

Sample	Nb_2O_5 found, %		Separation method for Nb
	TAR method	Control method	
Syenite I (containing pyrochlore)	0·026 0·026	0·028 X-ray	silica + PA
Syenite II	0·093 0·094 0·094	0·094 X-ray 0·092 PAR 0·093 PAR	silica + PA silica silica DHC
Syenite III	0·014 0·014	0·014 X-ray 0·013 PAR	 silica + PA
Syenite IV	0·086	0·078 X-ray	silica + PA
Wolframite (containing columbite)	0·61	0·61 PAR 0·62 EDTA + catechol	silica + PA

PA = phenylarsonic acid, DHC = dihydroxymethylcoumarine.

TABLE V.—COMPARISON OF TAR AND PAR METHODS

	PAR	TAR
Absorption maximum	535 mμ	540 mμ
Optimum pH range	5·8–6·4	5·0–6·0
Molecular extinction coefficient:		
0·02% tartaric acid	39,000	31,500
0·2% tartaric acid	38,700	29,600
2·0% tartaric acid	30,000	15,000
0·2% tartaric acid + 0·002*M* EDTA	37,500	28,500
0·08% ammonium oxalate	28,000	17,200
Interfering cations	(V,U)	V, U(Th)
pH changes	deep yellow 4·0 lemon yellow 4–11·5	orange 2·0 lemon yellow 2·0–6·0 orange 6·0 red 8·0

Neutralise if necessary and add buffer solution and 2·5 ml of TAR solution. Dilute to 50 ml, mix, let stand 20–30 min and measure the absorbance against a TAR blank at 540 mμ.

Ores and silicates

The analytical procedure is the same as above, but the sample must be decomposed by melting with either sodium carbonate or a mixture of sodium hydroxide and peroxide or peroxide alone. The melt is decomposed by water and hydrochloric acid and evaporated to dryness in the usual way for the determination of silica. The procedure then follows that above with phenylarsonic and hydrochloric acids.

Note. If the residue with silica contains much tungsten or titanium, separation is necessary. Niobium and tantalum are separated from tungsten and tin and most of the titanium by 7,8-dihydroxy-4-methylcoumarine in the presence of EDTA, tartaric acid and catechol[11] at pH 5·8–6·5 or by phenylarsonic acid from EDTA-tartaric acid solution at pH 1–2 (titanium partly coprecipitated), or by the same reagents from 4–6*M* HCl (tungsten partly coprecipitated).[12,13]

The best mixture for paper chromatographic separation is: 50 ml of acetone, 10 ml of 10% oxalic acid, 10 ml of 2*M* HCl and 30 ml of water. The R_f values are: Fe(III) 1·00, Mo 0·95, Sn(IV) 0·90, Nb,W 0·85, Ta 0·65, Ti 0·45. Run for 3–5 hr, dry and spray with a 2% solution of tannin or dihydroxymethylcoumarine and aqueous ammonia.[14,15]

Some results of the analysis of syenites and wolframite are shown in Table IV.

Comparison of TAR and PAR methods

From Table V it is evident that the properties of TAR and PAR are nearly equal with respect to sensitivity, influence of foreign ions and physical properties.

Acknowledgement—The author wishes to thank Ing. Novotný for carrying out the X-ray analyses.

Zusammenfassung—4-(2-Thiazolylazo)-resorcin bildet mit Niob in einem Acetat-Tartrat-Medium bei pH 5–6 einen karminroten Komplex. In Gegenwart von Äthylendiamintetraessigsäure (EDTA) oder Diaminocyclohexantetraessigsäure (DCTA) ist die Reaktion fast spezifisch für Niob: nur Vanadin und größere als 7-10-fache Überschüsse von Molybdän, Titan, Uran und Thorium stören.

Résumé—Le 4-(2-thiazolylazo)résorcinol forme, avec le niobium, un complexe rouge carmin en milieu acétate-tartrate, entre pH 5 et 6. En présence d'acide éthylènediamine tétracétique (EDTA) ou d'acide diaminocyclohexane tétracétique (DCTA), la réaction est presque spécifique du niobium: seuls interfèrent le vanadium et, à une concentration 7 à 10 fois plus élevée, le molybdène, le titane, l'uranium et le thorium.

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APPLICATION OF ACTIVATION ANALYSIS TO THE DETERMINATION OF SOME IMPURITIES IN NUCLEAR-GRADE URANIUM

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Summary—Activation analysis is applied to the determination of nine trace elements in some uranium compounds including three samples of "nuclear pure" uranium oxides. The method of analysis is based on the pre-separation of uranium by ion exchange, using three different systems according to the impurities involved. The elements considered are, thorium, lanthanum, chromium, copper, cobalt, manganese, sodium, tungsten and molybdenum. No chemical yield corrections are necessary because the method provides quantitative recoveries. Technique and results are discussed and it is shown that reagent blanks do not represent a serious problem. The impurities studied can be determined in relatively small sample aliquots with a precision (2σ) of $\pm 20\%$ in concentration ranges down to a few ppb.

INTRODUCTION

The nuclear characteristics of uranium are such that they make the determination of impurities in it by activation analysis extremely tedious, although there has been some recent work on the determination of cobalt, manganese, copper and chromium.[1] Fission products and neptunium formed during irradiation complicate the system and subsequent analysis for concentrations of impurities representative of nuclear pure uranium is almost impossible, even when applying γ-ray spectrometry combined with chemical separations. Activation analysis, however, offers considerable advantages, because of its sensitivity for many elements (particularly those whose limits of detection by emission spectroscopy are poor), if the problem of the presence of fission products and neptunium can be solved.

The chemical behaviour of uranium differs in many respects from that of other elements and it can be separated without affecting the composition of the sample as far as many impurities are concerned. Pre-separation followed by irradiation of the separated impurities results, in principle, in the loss of a principal advantage of activation analysis, *i.e.*, freedom from reagent-blank correction. This draw-back, however, does not exist for a number of important impurities (thorium, lanthanum, molybdenum and cobalt) because they are most unlikely to be present in significant amount in any of the reagents used either for dissolution of the sample or for the separation of uranium. Even in the case of elements which may be present in the reagents (*e.g.*, sodium, manganese, copper, chlorine) the difficulties are not serious because of the simplicity and efficiency of some separation techniques for uranium. Advantage can then be taken of the unique sensitivity of activation analysis when dealing with a limited amount of sample or with impurities for which the sensitivities of other techniques are inadequate.

Removal of uranium followed by the determination of impurities in the residue has been used in several cases. Extraction of uranium with tributyl phosphate (TBP)

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before spectrographic analysis of the residue by the copper or graphite spark method is widely used. It has been recently applied[2] also to the determination by activation analysis, of manganese, copper and cobalt, in an intercomparison solution, distributed by the International Atomic Energy Agency to a number of laboratories in order to collect information about the accuracy and precision of available methods for impurities in uranium. The concentration of the three elements in this solution was relatively high (100 — 200 ppm with respect to uranium) and did not, therefore, represent a typical nuclear-grade material. When the concentrations of impurities are very low as in nuclear-grade uranium oxides, however, TBP extraction no longer provides a satisfactory separation. Microgram amounts of uranium remain in solution and on irradiation appreciable amounts of fission products and neptunium are formed. Similarly, preseparation of uranium from impurities by paper chromatography has been used and preliminary qualitative results showed that separation is incomplete and this limits the application of this technique to higher levels of impurity.[3]

Adsorption of uranium on ion exchangers, which has also been used as a means of removing uranium before the determination of some impurities by spectrography or polarography, offers better possibilities. The removal of uranium can be made complete by adsorbing it on anion exchangers as chloride, sulphate or carbonate complexes or on cation exchangers as uranyl- or uranium(IV) cations. Blank values for impurities in the stage preceding irradiation can be avoided for some impurities or kept negligible for others because pre-separation involves only a few simple operations (dissolution, adsorption and evaporation) and is based on the use of reagents, in limited quantity, which are available in the greatest purity or which can easily be purified (acid, water, hydrogen peroxide, ion exchanger).

The following common impurities in uranium were considered: thorium, lanthanum, cobalt, chromium, copper, manganese, sodium, molybdenum and tungsten. Nuclear-grade uranium oxides normally contain these elements in concentration ranges between 100 ppm to a few ppb. Even at the lower level they can be determined with a precision of 10–30% at the 95% confidence limit, using 1-g samples. Such a possibility is especially important for elements such as thorium and lanthanum for which other techniques either involve tedious procedures or very elaborate and expensive equipment.

Outline of the method

With the ion-exchange separation technique, impurities can be grouped according to their behaviour in various media. From an $8M$ hydrochloric acid solution uranium is quantitatively adsorbed on a strongly basic anion exchanger in chloride form.[4,5] The effluent contains a group of impurities among which are found thorium, lanthanum, chromium, manganese and sodium. If the anion exchanger is in sulphate form[6] and the solution is made $0{\cdot}01$–$0{\cdot}1N$ with respect to sulphuric acid, cobalt, copper, manganese, sodium and chromium will be found in the effluent. Because in the first case the concentration of hydrochloric acid is relatively high and the quantity is appreciable compared with the amount of sulphuric acid required in the second case, manganese and sodium are better determined after a sulphate separation of uranium, in order to minimise the reagent blank for these two elements. No blank correction was found necessary with any reagents used at the impurity concentrations reported here.

Anion-exchange separation cannot be applied to certain impurities even though they have high cross-sections and other convenient nuclear characteristics because they are partially or completely adsorbed with uranium from a chloride or sulphate system, either as typical anions (halides) or as anionic complexes (tungsten, arsenic and molybdenum). Experiments with a cation exchanger, using tracers, have shown on the other hand that these are recovered with a yield of 98% or better if uranium is adsorbed as a cation from dilute nitric acid solution. Because, with the exception of molybdenum, the sensitivity of spectrography for these elements is very poor, activation analysis represents a simple and advantageous approach.

In all cases, the effluent, after removal of uranium, is evaporated to small volume and irradiated. Simple chemical separations and gamma spectrometry are then applied and the impurities are determined from the γ-activity of the solution. If separation procedures, which give quantitative recoveries, are used there is no need to determine the yield; this simplifies the analysis, improves the precision and considerably reduces the time required.

So far, the general procedure described above has been applied to the analysis of uranium dioxide, triuranium octoxide, uranyl nitrate and uranyl acetate but it could be extended to uranium metal as well as to other salts without essentially modifying the procedures (Table I).

EXPERIMENTAL

Dissolution of sample

Uranium dioxide and triuranium octoxide dissolve very readily in hydrochloric acid or sulphuric acid if hydrogen peroxide is added to the warm mixture. As little as 4 ml of $4N$ HCl or $4N$ H_2SO_4 and 0·3 ml of H_2O_2 (30%) were sufficient to dissolve 1 g of the oxide. Silica Kjeldahl-flasks of 25-ml capacity were used for the dissolution. Hydrogen peroxide was added dropwise with continual agitation until a clear solution was obtained. This was then evaporated almost to dryness on an open flame and the residue taken up in $8N$ HCl (for Th, La and Cr) or in $0{\cdot}01N$ H_2SO_4 (for Mn, Cu, Co and Na). Nitric acid ($0{\cdot}05 - 0{\cdot}1N$) was used for cation-exchange separations. Solid uranyl nitrate or acetate can be dissolved in a minimum amount of hydrochloric or sulphuric acid of appropriate concentration as given later. Solutions containing high concentrations of free acid must be evaporated to dryness and the residue taken up in appropriate acid as above. Those of low acidity with up to 200 mg/ml of uranium, for example, were applied directly to the ion-exchange column in sulphate form. In the case of nitrate the high local concentration of nitric acid set free during the adsorption causes the uranium band to move a few centimeters down the column before it is fixed. However, for the chloride separation, the solution must be made $8N$ by the addition of concentrated hydrochloric acid before transferring it to the ion exchanger in chloride form.

Preparation of ion-exchange columns

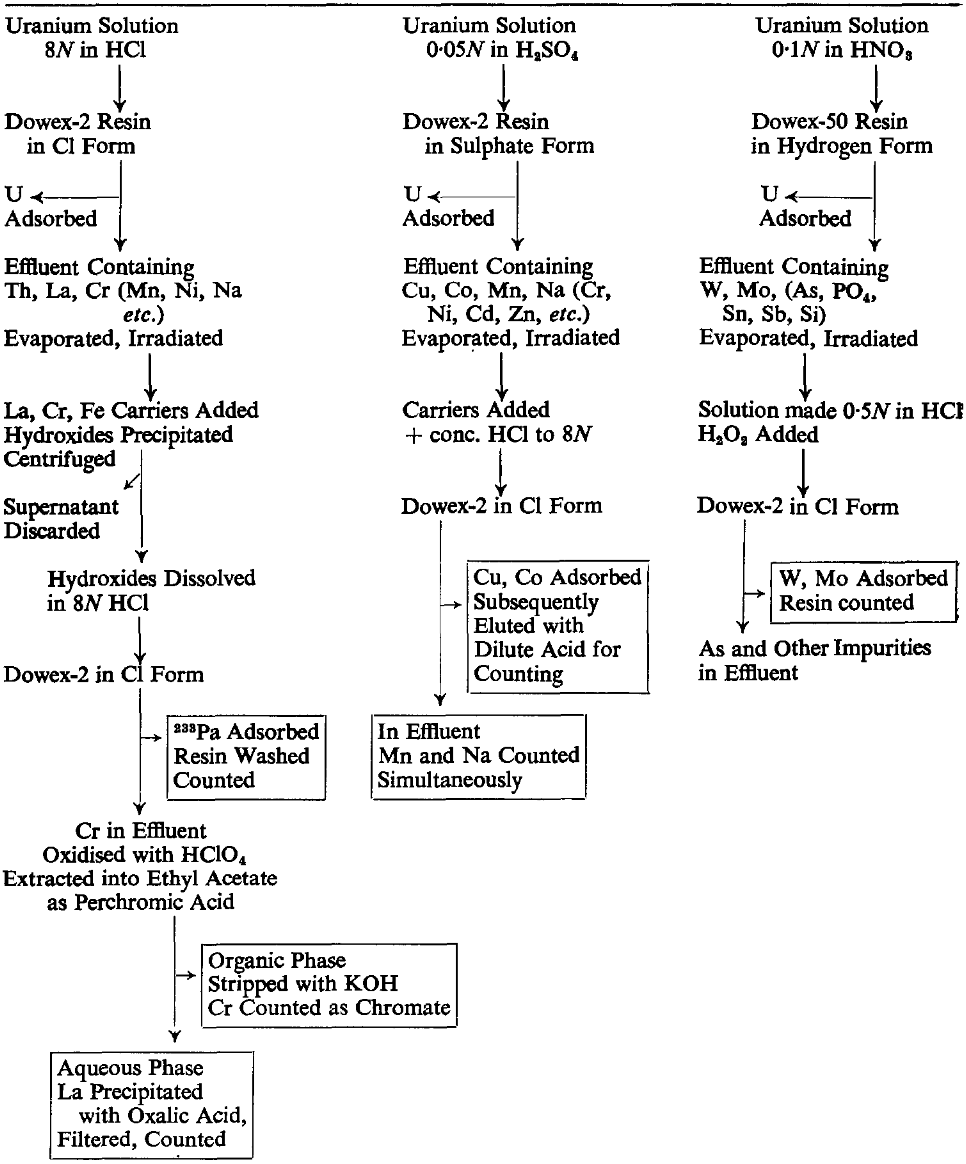
The anion-exchange resin used was Dowex 2 × 8, 100–200 mesh, AnalaR grade. For the purification of the resin, batches of about 200 g were washed in a column with 20 column-volumes of $2N$ H_2SO_4, 10 column-volumes of $0{\cdot}05N$ H_2SO_4 and finally with water, while for chloride separations the exchanger was treated similarly with $2N$ HCl and with water. Cation-exchange resin was purified with $2N$ nitric acid followed by $0{\cdot}1N$ acid and water.

Two sizes of glass columns were used for the separation of uranium and impurities. The larger (20-mm diameter 40-ml capacity with a 50-ml reservoir at the top) was used for quantities of uranium of the order of 1 g. Smaller columns (10-mm diameter, 8-ml capacity with a 15-ml reservoir) were used for the separation of impurities after irradiation. Resin columns were preconditioned according to the separation involved.

Purification of reagents

The water used was doubly distilled from a quartz still and stored in polyethylene bottles. Another efficient method was to pass the water through a bed of AnalaR grade cation exchanger which removes

TABLE I.—SEPARATION SCHEMES FOR IMPURITIES IN URANIUM



copper and manganese to such an extent that their presence could not be detected by activation analysis. Acids were analytical-reagent grade and were used without further purification.

Irradiation and radiation measurement

Solutions were irradiated in polyethylene ampoules (Tubes hémo-etran available from Medi Sciences, Paris), with a capacity of 8 ml, but the actual volume of solution was kept between 1 and 3 ml. Solutions were irradiated under reduced pressure (by pressing the walls of the ampoule while sealing) in order to compensate for any increase in pressure due to the formation of radiolytic gases. The sealed samples and appropriate standards were placed in a cylindrical aluminium holder capable of holding 10 samples. It was rotated during the irradiation in the Astra reactor of the "Oesterreichische Studiengesellschaft für Atomenergie" along the vertical axis at a speed of 6 revolutions/min in order to ensure equal neutron flux for samples and standards. Normally the irradiation time was 5 hr at a neutron flux of 10^{13} n.cm^{-2}.sec^{-1}. This was sufficient to allow detection of submicrogram amounts of elements forming long-lived radioisotopes (*e.g.*, Cr, Co) and at the same time caused a negligible formation of radiolytic gases. Times were shortened accordingly when concentrations of impurities were relatively high or when only manganese, copper and sodium were to be determined.

Standard solutions of the elements considered were prepared and kept in small polythene flat-bottomed hexagonal ampoules of approximately 10-ml capacity. They contained 1-10 μg/g of solution and were slightly acid except for the molybdenum and tungsten solutions, which were slightly ammoniacal. The neck was drawn into a fine capillary at the top and the whole was used as a storage bottle and at the same time as a weight burette. This avoids the calibration and the use of micropipettes, increases the accuracy and at the same time eliminates the risk of contamination by frequent transfer of solutions.

The activity of the solution of the radionuclide, after chemical separation, was normally determined in polyethylene specimen tubes, 20 mm in diameter, and the volume and density kept constant within one set of measurements. Measuring equipment consisted of a 3″ × 3″ NaI (Tl) crystal photomultiplier assembly connected to a RIDL 400 channel pulse-height analyser, Counting times ranged between 1 min and 1 hr and the background was deducted when counting rates were low. The areas of the γ-peaks were evaluated by the usual method.[7]

Discussion of Method

Elements separated from hydrochloric acid medium

Pipette an aliquot of solution equivalent to 1 g of uranium (in the case of nuclear-grade material) on to a Dowex 2 resin column (80-mm length, preconditioned with 30 ml of 8*N* HCl) and leave to drain through the resin, then wash with 60 ml of 8*N* HCl. Collect the effluent in a 100-ml silica dish and evaporate to dryness (infrared lamp) at low temperature. Moisten the residue with 3–5 drops of HNO_3, evaporate to dryness again and then dissolve in 1 ml of boiling 1*N* HNO_3. Transfer the solution into the irradiation ampoule followed by two 1-ml washings with warm water (using a fine polyethylene transfer pipette). Seal the ampoule and irradiate together with appropriate standards. When impurity levels are known to be high, a smaller aliquot of the uranium solution and a smaller column are used for each determination.

The effluent from the separation is analysed for thorium, lanthanum and chromium but may contain also elements such as manganese, sodium and nickel, *etc.*

Thorium. The concentration of thorium in uranium depends on the type of the ore, and, in the final product, on the mode production and purification of the uranium. Its concentration can vary within wide limits. In two samples analysed in this laboratory, thorium represented the main impurity (Table II) although its presence was not indicated in the specifications. As a source of the fissionable isotope of uranium ^{233}U, thorium could to some extent shift the isotopic composition of the fuel when present in higher concentration, a fact which makes the thorium determination interesting. Activation analysis offers a unique possibility for its control because of the simplicity, accuracy and precision.

The determination of Th is based on the formation of ^{233}Pa (27 days), by the ^{232}Th (n,γ) ^{233}Th $\beta \xrightarrow[\text{min}]{}$ ^{233}Pa reaction, and its subsequent measurement. Strictly speaking this reaction will measure only the ^{232}Th content and if ionium, ^{230}Th, is present in appreciable quantities, this will not be determined as ^{231}Th and its decay products would not be detected by our procedure. However, the ionium content of thorium from most natural ores is negligible (although in very low thorium-containing uranium ores, ionium contents of 30% of the ^{232}Th are known).

Protactinium is similar to uranium in its ion-exchange behaviour and can, therefore, be isolated under the conditions applying for uranium. This improves the selectivity of the separation because all other impurities which might behave similarly have been adsorbed with uranium in the pre-separation stage. The only observed interference was due to bromide present as an impurity in hydrochloric acid. It accumulates during purification and pre-conditioning of the ion exchanger. Part of the bromide is displaced by the adsorbing uranium and contaminates the effluent. If a hydroxide precipitation of protactinium, using lanthanum as carrier, is included bromide can easily be removed; protactinium can then be subsequently adsorbed after dissolution of the precipitate in hydrochloric acid.

Procedure for determination of thorium. After irradiation and a "cooling" period of about 2 hr open the ampoules and transfer the contents with washings into a 50-ml centrifuge tube. Dilute the solution to 30 ml, add carriers (10 mg of lanthanum and 1 mg of chromium as chlorides) and precipitate the hydroxides from the warm solution with caustic soda. Centrifuge the precipitate, dissolve in 3 ml of 10*N* HCl and adsorb protactinium on a small Dowex 2 column, preconditioned with 8*N* HCl. Wash the column with three 2-ml portions of 8*N* HCl (collect the effluent and washings in a 25-ml Kjeldahl-flask for the determination of chromium). Transfer the resin with the adsorbed ^{233}Pa to a counting vial and allow for the decay of shorter activities before evaluation. Transfer the thorium standards directly into the counting tubes using the same quantity and concentration of the acid mixture. Use the γ-ray peak at 0·3 MeV for quantitative evaluation. On many occasions, a significant adsorption of ^{233}Pa on the walls of the irradiation capsule was noticed, but in the case of standards only. The sample solution has a much more complex character and also contains a small amount of resin dissolved colloidally, which probably takes the role of a mechanical carrier for ^{233}Pa and reduces its adsorption on the walls of the container. Any adsorbed material, however, is readily soluble in dilute HF and this solution is added to the counting tube.

Chromium. Extraction of perchromic acid with ethyl acetate was used in order to prevent any possible interference from thorium because the gamma-ray peaks of ^{51}Cr and ^{233}Pa overlap in the 0·3 MeV energy range. In some samples the activity of ^{233}Pa was about 100 times higher than that of ^{51}Cr and thus a specific separation of chromium was required. For samples of low thorium content (less than 5 ppm), chromium could be separated by a simpler method.

Procedure for determination of chromium. Evaporate the effluent from the adsorption column for Pa and washings to small volume on a direct flame, add 1 ml of perchloric acid and boil the solution until it turns to the orange of oxidised chromium. Wash the contents into a 100-ml separatory funnel with a minimum amount of water (10 ml), adjust the pH to 1·7 with aqueous ammonia and cool the solution to 10° or less.

Shake the solution with 20 ml of ethyl acetate after addition of 5 drops of 3% H_2O_2.[8] Save the aqueous phase for isolation of lanthanum. Wash the blue organic phase with 5 ml of a cold solution of perchloric acid, of pH 1·7, and separate. Strip chromium from the organic layer by 2 ml of 10% KOH followed by two more 2-ml portions of water. Collect the aqueous phases in a tube for activity measurements. Carry out the same procedure, with standards and compare their activity with that of the sample. Because the solvent extraction of perchromic acid is not quantitative (normally 85–95%), a determination of the chemical yield may be necessary. Because the chromium is present as chromate in the final solution used to determine ^{51}Cr activity, the yield may be directly measured spectrophotometrically.

Lanthanum. Lanthanum is determined in the aqueous phase after solvent extraction of the chromium. Because of the selective reaction of lanthanum with oxalic acid and the characteristic γ-spectrum of ^{140}La there is no need for tedious separation procedures. A single precipitation from dilute perchloric acid using lanthanum carrier usually gives a sufficiently pure spectrum to allow measurement without further purification. A very high activity of low-energy compared with lanthanum standards indicates the presence of other radioisotopes of the rare earths, many of which emit γ-rays in the range up to 100 KeV. No attempt was made in this work to identify any one of them and the concentration of lanthanum was taken as indicative of the total rare-earth concentration.

Procedure for determination of lanthanum. Dilute the aqueous solution left after the extraction of chromium to 50 ml, heat to boiling and add 15 ml of a saturated solution of oxalic acid in order to precipitate the lanthanum. Keep the mixture warm for 2 hr and then filter, using a demountable filtration apparatus and a flat circular filter paper disc, 20-mm in diameter. Wash the precipitate thoroughly with a 2% solution of oxalic acid in 0·5N HCl and dry. Evaluate the amount of lanthanum by comparing the activity of ^{140}La at the 0·33 or 0·48 MeV peak with standards irradiated and precipitated under identical conditions.

Elements separated from sulphuric acid medium

For reasons already mentioned, the separation and determination of manganese and sodium is considered in this group of impurities which also includes cobalt and copper. These elements, with the exception of cobalt, represent a more serious problem with regard to blank values and contamination of the sample before irradiation. The weakly acid solution of uranium is passed through the ion exchanger in sulphate form and uranium is quantitatively adsorbed. However, the amount of sulphuric acid required for dissolution of the sample and washing of the column is small and does not contribute appreciably to blank values.

A radiochemical separation scheme was developed for the determination of the four elements in sequence. Uranium is removed first as the sulphate complex and the effluent from the column is evaporated to small volume and irradiated. It is then made 8N in hydrochloric acid, carriers are added and the solution is passed over the small chloride column. Copper and cobalt are quantitatively adsorbed and their bands, blue and green respectively, can be observed as they slowly separate with the increasing volume of hydrochloric acid used for washing. Later they are eluted with dilute ammonia or hydrochloric acid and the activity of the solution determined. Manganese and sodium are determined by direct measurement in the effluent after chloride separation.

Procedures for manganese, sodium, copper and cobalt. Adsorb uranium from a 0·05N H_2SO_4 solution on approximately the same amount of resin as was used in the case of the chloride group but in the sulphate form. Wash the column with 10 ml of 0·05N H_2SO_4 followed by five 10-ml portions of 0·01N acid. Collect the effluents in a 100-ml silica dish, evaporate the solution just to fuming and transfer into the irradiation ampoule, using an amount of water as small as possible for dilution and washing.

After irradiation transfer the solution and ampoule washings into an evaporating dish. Add 1 mg each of Co, Cu, Mn, Cr and Na carriers and evaporate the solution almost to dryness. Take up the residue in 2 ml of 8N HCl from which cobalt and copper are adsorbed on the small column of Dowex 2 in chloride form. Wash the column with 10 ml of 8N HCl to remove ^{32}P formed from the sulphate by the ^{32}S(n,p)^{32}P reaction. Collect the effluent in a polythene tube and determine manganese and sodium from the activities at the 0·82 MeV and 2·75 MeV peak areas, respectively, by comparison with mixed standards of known manganese and sodium content measured under the same geometrical conditions. In the case of a very low manganese and high sodium content, precipitate manganic acid, using ferric hydroxide as collector. Centrifuge, dissolve the precipitate in nitric acid and 1 drop of H_2O_2, and measure the activity of the two nuclides separately, sodium in the supernatant solution after centrifugation and manganese in the dissolved precipitate.

Copper and cobalt can be eluted directly into the polythene tube with 5 ml of 0·5N HCl. In the case of high thorium and/or iron content, however, 5 ml of 2N aqueous ammonia are preferable. In the effluents the annihilation radiation of ^{64}Cu at 0·51 MeV shows clearly, even when the concentration of copper is much below that normally tolerated for this element in uranium compounds of nuclear purity.

Cobalt requires considerably longer counting times because of its lower sensitivity. This usually makes its simultaneous determination with copper impracticable. Overlapping of ^{60}Co γ-ray peaks (1·17 and 1·33 MeV) with those of ^{59}Fe and ^{24}Na presents some difficulty. All iron and some traces of sodium are usually left on the chloride column even after prolonged washing with 8N HCl but contaminate the Co/Cu fraction when these are eluted with 0·5N HCl. If ammonia is used for elution, iron is eliminated but sodium still persists and the simplest way to increase accuracy and precision is to allow 2–3 days for the decay of ^{24}Na. Alternatively, a selective radiochemical separation such as the precipitation of potassium hexanitritocobalt (III) can be used.

This scheme is readily adaptable to special situations and can be shortened or simplified if there is no need for the determination of the entire group. After irradiation, copper, for example, can be isolated selectively by reducing it with $TiCl_3$ to the monovalent state and adsorbing it on a chloride column from dilute hydrochloric acid (up to 1N).

Note. At an earlier stage of this investigation, chromium was also determined in this group. However, its recovery in the preseparation was always incomplete because up to 15% remained on the sulphate column. On the other hand, quantitative yields were obtained with a chloride system, and provided the hydrochloric acid does not contain any chromium, the chloride separation is preferable. This has the added advantage that solutions are free from ^{32}P (because no sulphate ion is present in the irradiated solution) and eliminates the high bremsstrahlung effect from ^{32}P β-rays during the measurement of ^{51}Cr.

Elements separated through cation exchange: tungsten, arsenic and molybdenum

Similarity in the chemical behaviour of molybdenum and tungsten makes their determination by chemical methods tedious and difficult in the presence of each other. For molybdenum as trace element in uranium, emission spectroscopy seems to be the simplest approach, giving high sensitivity and reasonable precision. For tungsten, activation analysis appears to be a most promising and simple technique because advantage can be taken of the high neutron absorption cross section and the very typical γ-ray spectrum of ^{187}W. The γ-ray peaks of 0·49 and 0·69 MeV can be easily evaluated even when the amount of Mo present exceeds that of tungsten by a factor of 100 or more. Molybdenum alone can be determined by measuring the activity of the 0·14 MeV γ-ray of its decay product ^{99}Tc but in the presence of tungsten this is almost coincident with a γ-ray of ^{187}W. It is, therefore, necessary either to separate Mo from W, or W and Mo from Tc in order to determine both elements. Considering that the sensitivity of activation analysis for molybdenum is moderate and that considerable time is involved, because of the relatively slow build-up of ^{99}Tc activity ($T_{1/2} = 6$ hr) in the irradiated molybdenum, this technique was only applied in the case of the intercomparison solution which contained molybdenum in a concentration of 200 ppm with regard to uranium and no detectable concentration of tungsten.

Both molybdenum and tungsten are very strongly and irreversibly adsorbed by anion exchange resin in chloride form from all mineral acid solutions[9] up to a concentration of at least 2M if H_2O_2 is present. This provides a simple and very selective separation of these two elements together after irradiation and makes an immediate determination of tungsten possible by measuring the activity of the resin column on the multichannel analyser. The same procedure was used for the determination of molybdenum in the intercomparison solution with the only difference that measurement was delayed in order to allow ^{99}Tc to grow in the sample.

Procedure. Prepare a column of approximately 50-mm length (for 1 g of uranium) from an appropriate amount of Dowex 50W × 8 cation exchange resin, 100 — 200 mesh, which has been thoroughly washed with $2N$ HNO_3 followed by water. Adsorb uranium from dilute nitric acid solution and wash the column with three times its volume (50 ml) of $0{\cdot}01N$ HNO_3.

Evaporate the effluent to small volume, transfer into the irradiation capsule, seal and irradiate with a set of standards for 3–5 hr at 10^{13} n.cm^{-2}.sec^{-1}. After irradiation make the solution $0{\cdot}5N$ with respect to HCl and $0{\cdot}1M$ with respect to H_2O_2 and pass through a small column of Dowex 2 × 8, 100–200 mesh.

Thoroughly wash the resin, transfer into the polyethylene vial and determine the tungsten by means of its 0·45 MeV γ-ray or molybdenum by the 0·14 MeV γ-ray after ^{99}Tc has grown in (in the absence of W only).

This simple procedure proved satisfactory for the analysis of samples included in Table I but might need modification if the relative abundances of impurities separated within the group were unfavourable.

To avoid the contamination by the fission product molybdenum, it is extremely important that here are no traces of uranium present in solutions to be analysed for molybdenum. The contribution of molybdenum formed by fission can be quite significant, even at very low uranium levels, because 1 μg of uranium gives a yield of fission product ^{99}Mo equal to that produced from the same amount of molybdenum.

The effluent from the uranium separation stage will, in addition to molybdenum and tungsten, also contain other impurities which appear either as undissociated acids or as colloids such as silicon, boron, phosphorus, arsenic, antimony and tin; they are not considered here because they were not present in sufficient quantity in any of the analysed samples to interfere in activation analysis. We have, however, some evidence from tracer experiments to justify mentioning the possibilities offered by this system.

The recovery of arsenic, for example, is quantitative, and it can easily be determined in the effluent after removal of molybdenum and tungsten. The determination of halides should not present any difficulties in the analysis of soluble salts such as nitrate or acetate. According to tracer experiments, quantitative recoveries are obtained by simply passing an aqueous solution through the cation column to remove uranium and irradiating an appropriate aliquot of the effluent. Carriers are then added, silver halides precipitated and the activity of the precipitate measured. A radiochemical separation, would be necessary for iodide in the presence of large quantities of bromide and/or chloride. Except for tracer experiments, their determination was not considered in the present investigation.

CONCLUSION

The results obtained when applying the procedures described above are summarised in Table II and compared with the figures given in the specifications. They show clearly that the values reported as upper limits for some elements (left column) differ from the real values by one or several orders of magnitude. On the other hand, some other impurities are not covered by the specification, although they might be present in appreciable concentration.

Ion-exchange separation of uranium offers the possibility of recovering almost all impurities free from the matrix. In this way, their determination by any technique is simplified and in particular activation analysis can be applied to these elements. Blank values can easily be kept under control in view of the simplicity of the separation procedure.

According to the type of resin and system used, impurities are grouped and can be analysed in sequence within a group, using one irradiation. Radiochemical separations are essentially based on ion exchange in order to simplify and reduce the work involved by keeping the selection of reagents and equipment limited.

As compared to spectrography, which is generally used as a routine method for uranium, activation analysis offers definite advantages for trace elements such as manganese, copper and sodium in cases where the amount of sample is limited or

TABLE II.—RESULTS OF THE APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE DETERMINATION OF SOME ELEMENTS IN URANIUM COMPOUNDS

	Intercomparison sol.		U_3O_8 "nuklearrein"		UO_2 "nuklearrein"		UO_2 "nuclear grade"		Uranyl acetate p.a.	
Element	Added, *ppm*	Found, *ppm*	Certif. upper limit,* *ppm*	Found by actvn. anal., *ppm*	Certif. upper limit,* *ppm*	Found by actvn. anal., *ppm*	Certif. upper limit,* *ppm*	Found by actvn. anal., *ppm*	Certif. upper limit,* *ppm*	Found by actvn. anal., *ppm*
Co	5·00	5·5, 5·6, 5·0, 5·5, 6·2, 5·6	5	0·02, 0·02, 0·02	5	0·05$_2$, 0·04$_4$	<3	0·02$_1$, 0·01$_8$ 0·01$_9$, 0·01$_5$ 0·01$_7$	—	—
Cr	9·82	9·1, 9·0, 10·2, 10·6, 9·8, 11·0	8	0·4$_0$ 0·3$_4$, 0·4$_1$, 0·3$_7$	10	0·9$_9$, 0·7$_0$	<3	1·0$_0$, 1·1$_1$, 0·7$_5$	—	—
Th	—	22·3, 18·9, 22·6, 19·0, 20·7	—	400, 414, 418, 421, 411	—	232, 243, 224, 222, 234	—	4·1$_5$, 3·8$_7$	—	<1 ppm
La	—	—	—	—	—	0·06$_1$, 0·05$_6$	—	0·1$_8$	—	—
Cu	5·00	5·1, 5·4, 4·8, 5·7, 5·2, 5·0, 6·0	5	0·16, 0·18, 0·16, 0·17	5	0·4$_6$, 0·5$_3$ 0·6$_1$, 0·6$_2$	<3	0·12, 0·13 0·11, 0·14	—	—
Mn	9·95	9·9, 10·6, 9·1, 9·8, 10·9	15	0·04, 0·05, 0·04	15	0·45, 0·44 0·46, 0·40	<3	0·12, 0·13, 0·09, 0·12, 0·10	—	0·5
Na	—	—	—	—	—	7·4, 7·8, 7·7, 5·8, 7·5, 8·1	<100	5·6, 5·4, 4·2, 4·3	50	9
W	—	—	—	—	—	—	—	—	—	0·50, 0·50
Mo	5·0	4·0, 5·0, 6·6, 6·0, 4·6, 5·3	—	—	—	—	—	—	—	—

* Figures given by supplier; method of analysis unknown, but probably spectrographic.

where the concentration of these elements is extremely low. This is quite obvious when comparing upper limits reported by spectrography and the values obtained by activation analysis in samples of uranium dioxide and triuranium octoxide.

Using a moderate irradiation time of a few hours and a neutron flux of about 10^{13} n.cm^{-2}.sec.$^{-1}$ the sensitivity for chromium and cobalt is of the order of that of spectrography. The sensitivity can, however, be considerably increased when a longer irradiation time can be tolerated or when higher fluxes are available. In any case, activation analysis represents an independent supplementary technique in addition to spectrography. It also covers a group of elements, such as thorium, tungsten or lanthanum, in concentration ranges which are significant in the analysis of this type of sample but for which spectrography is an insensitive method.

For most elements the precision ranges between 10 and 30% for a single determination at the 95% confidence limit. This is very satisfactory, taking into account the very low concentration levels which would hardly be accessible by spectrophotometry.

The potential of the method described appears to be much broader because there are many more elements which are normally not determined in nuclear grade uranium compounds but which could be of interest in special cases (such as in the analysis of uranium and its compounds originating from processing of ores, alloys or solutions) in which less common elements could be expected to be the main constituents.

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Zusammenfassung—Die Aktivierungsanalyse wird auf die Bestimmung von 9 Spurenelementen in einigen Uranverbindungen angewandt, darunter 3 Proben von "nuklearreinen" Uranoxyden. Die Analysenmethode beruht auf der Vorabtrennung von Uran durch Ionenaustausch mit drei verschiedenen Systemen, je nach den zu bestimmenden Verunreinigungen. In Betracht gezogen werden: Thorium, Lanthan, Chrom, Kupfer, Kobalt, Mangan, Natrium, Wolfram und Molybdän. Ausbeutekorrekturen sind nicht notwendig, da die Methode quantitative Ausbeuten ergibt. Arbeitsbedingungen und Ergebnisse werden diskutiert; es wird gezeigt, daß Blindreagentien kein ernstes Problem darstellen. Die untersuchten Verunreinigungen können in relativ kleinen Probenteilen mit einer Genauigkeit (2σ) von $\pm 20\%$ in Konzentrationsbereichen bis herunter zu wenigen ppb bestimmt werden.

Résumé—On applique l'analyse par activation au dosage de 9 éléments à l'état de traces dans quelques composés de l'uranium, y compris trois échantillons d'oxydes d'uranium de "pureté nucléaire". La méthode d'analyse est basée sur la séparation préalable de l'uranium par échange d'ions, utilisant trois systèmes différents selon les impuretés mises en jeu. On considère les éléments suivants: thorium, lanthane, chrome, cuivre, cobalt, manganèse, sodium, tungstène et molybdène. Des corrections de rendement chimique ne sont pas nécessaires, la méthode fournissant des récupérations quantitatives. On discute des techniques et des résultats et l'on montre que les essais témoins des réactifs ne représentent pas un problème sérieux. On peut doser les impuretés étudiées dans des prélèvements d'échantillons relativement petits, avec une précision (2σ) de $\pm 20\%$, dans des domaines de concentration pouvant descendre jusqu'à quelques p.p.b.

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DETERMINATION OF MAGNESIUM BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY AFTER EXTRACTION

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Summary—A method for the determination of magnesium by atomic-absorption spectrophotometry, after extraction into an organic solvent, has been developed. Magnesium is extracted as an 8-hydroxyquinolate or 8-hydroxyquinaldate complex into methyl isobutyl ketone. The extract is introduced into the flame and the magnesium absorption measured. The 8-hydroxyquinolate extraction method serves to determine trace amounts of magnesium in alkali products such as purified brine, sodium carbonate and sodium bicarbonate. The 8-hydroxyquinaldate extraction method serves to determine small amounts of magnesium in aluminium metal and aluminium alloys.

INTRODUCTION

SEVERAL papers have been published on the determination of magnesium by atomic-absorption spectrophotometry, because of the sensitivity of the method. However, aluminium and silicon have a serious effect on magnesium absorption, because they form acidic oxides which are stable at high temperatures. David[1] demonstrated that the interference from aluminium and silicon in the determination of magnesium is suppressed by the addition of large amounts of strontium. Wallace[2] showed that the addition of 8-hydroxyquinoline solution to aluminium-magnesium solutions counteracts the depressive effects of aluminium on magnesium absorption. However, this technique does not compensate for the interference of silicon. Furthermore, a high salt concentration results in reduced atomiser efficiency and hence low absorption readings. Therefore, in the cases where a comparatively trace amount of magnesium is required to be determined in the presence of a large concentration of salt, it seemed preferable to extract magnesium before determination. It was also felt that the interference from diverse ions could be reduced and an increase in sensitivity obtained by applying an extraction system.

Much has been written regarding the extraction of the magnesium 8-hydroxyquinolate complex before determination by absorption spectrophotometry.[3–5] However, in the authors' experience poor reproducibility was obtained in the absorption spectrophotometric determination.

The work reported here was undertaken to examine the possibilities of applying the extraction of magnesium 8-hydroxyquinolate and 8-hydroxyquinaldate complexes to atomic-absorption spectrophotometry. Furthermore, the work was directed to develop the extraction method for the determination of magnesium in alkali products and in aluminium alloys.

EXPERIMENTAL

Apparatus

Atomic-absorption. A Hitachi photoelectric spectrophotometer EPU-2 was used with the Hitachi atomic-absorption attachment RA-1. An air-acetylene flame was used throughout this work. The 7-cm fish-tail burner was water-cooled. The following operating parameters were employed for analysis.

Air pressure	1.0 Kg. cm^{-2}
Acetylene pressure	0.08 Kg. cm^{-2}
Wavelength	2852 Å
Slit width	0.05 mm
Lamp current	30 mA

Although the highest magnesium absorption was obtained with 0·10 Kg. cm^{-2} of acetylene pressure for fixed air pressure (1·0 Kg. cm^{-2}), it was found that higher than 0·09 Kg. cm^{-2} of acetylene pressure resulted in poor precision of meter readings because of fluctuation of the flame. Therefore, 0·08 Kg. cm^{-2} of acetylene pressure was used in the present work. The absorption with this pressure was about 2·6% lower than that with 0·10 Kg. cm^{-2}.

Reagents

Magnesium solution. Dissolve 1·00 g of pure magnesium metal in the minimum amount of 6*M* hydrochloric acid and dilute to 1 l. with water.

Aluminium solution. Dissolve 1 g of pure aluminium metal in 6*M* hydrochloric acid and dilute to 100 ml.

8-*Hydroxyquinoline solution.* Dissolve 5 g of 8-hydroxyquinoline in 100 ml of ethanol.

8-*Hydroxyquinaldine solution.* Dissolve 5 g of 8-hydroxyquinaldine in 100 ml of ethanol.

Sodium tartrate solution. Dissolve 25 g of sodium tartrate in water and dilute to 100 ml. Adjust the solution to pH 11 and extract with a 5% solution of 8-hydroxyquinoline (or 8-hydroxyquinaldine) in methyl isobutyl ketone to remove magnesium.

Sodium chloride solution. Prepare a saturated solution.

Methyl isobutyl ketone. Purify commercial reagent-grade methyl isobutyl ketone by distillation.

Other reagents were of analytical-grade unless otherwise stated.

Procedure

1. *Extraction of magnesium* 8-*hydroxyquinolate.* Place 10 ml of an acidic solution, containing 3 to 40 μg of magnesium, in a 50-ml separatory funnel. Add 20 ml of sodium chloride solution and 1 ml of sodium tartrate solution. Mix well, and then add 5 ml of 8-hydroxyquinoline solution, followed by 3 ml of ammonia to bring the pH of the solution to greater than 11. Adjust the volume to 40 ml, add exactly 10 ml of methyl isobutyl ketone and shake vigorously for 3 min. Drain off and discard the aqueous phase. Spray the organic phase into the flame and measure the magnesium absorption.
2. *Extraction of magnesium* 8-*hydroxyquinaldate.* Place 10 ml of an acidic solution, containing 3 to 40 μg of magnesium, in a 50-ml separatory funnel. Add 5 ml of sodium chloride solution and 1 ml of sodium tartrate solution. Mix well, and then add 5 ml of 8-hydroxyquinaldine solution, followed by 3 ml of ammonia to adjust the pH of the solution to higher than 11. Dilute to 40 ml with water. Add exactly 10 ml of methyl isobutyl ketone and shake vigorously for 3 min. Extract and spray the magnesium-hydroxyquinaldate complex as in the above procedure.

RESULTS AND DISCUSSION

Extraction of magnesium with 8-*hydroxyquinoline*

Effect of sodium chloride and tartrate. The concentration of sodium chloride played an important role in the extraction of magnesium-hydroxyquinolate complex. Fig. 1 shows the results obtained. The extraction of magnesium-hydroxyquinolate complex was greater at high sodium chloride concentrations, probably because of a salting-out effect. Sodium chloride also served to prevent any emulsification.

Tartrate, which served to prevent hydrolysis of metals at higher pH, had no effect on the extraction of magnesium when present in small concentrations, but decreased the amount extracted when present in larger amounts, as is shown in Table I.

Effect of pH. The extraction of magnesium 8-hydroxyquinolate was investigated over a pH range of 9 to 12. The percentage extracted was constant when the pH was greater than 11.

Effect of reagent concentration. More than 200 mg of 8-hydroxyquinoline was required if the procedure was followed (Fig. 2).

Choice of solvent. Luke and Campbell[3] successfully extracted magnesium-8-hydroxyquinolate complex with chloroform by using Butyl Cellosolve as a supplementary solvent. Jankowski and Freiser[4] studied the extraction of magnesium-hydroxyquinolate complex into mixed organic solvents, *e.g.*, chloroform mixed with Butyl Cellosolve, isopentyl alcohol or ethanolamine. Goto and Kakita[5] investigated the extraction of magnesium-hydroxyquinolate complex into methyl isobutyl ketone.

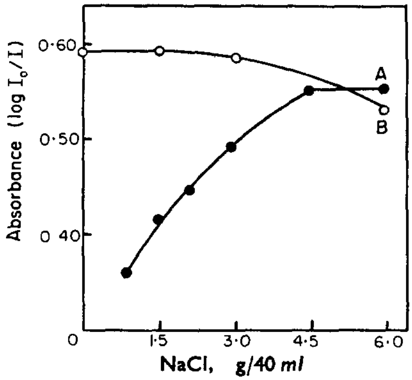

FIG. 1.—Effect of sodium chloride on magnesium extractability:—
A: Hydroxyquinolate complex (25 μg of Mg)
B: Hydroxyquinaldate complex (30 μg of Mg)

In atomic-absorption spectrophotometry with an air-supported flame, the number of solvents that can be successfully burnt is limited. Chloroform gave an unstable flame and noxious gases were produced during the combustion. Esters and ketones behaved satisfactorily in the flame. With these solvents the flames were constantly steady and the combustion was complete. Therefore, the use of esters and ketones was tested by comparing the atomic-absorption signal after extraction. Of all the organic solvents tested, methyl isobutyl ketone was found to be best for extraction. Magnesium-8-hydroxyquinolate complex could also be extracted into esters, but methyl isobutyl ketone was more efficient. An increase in extractability was not found when methyl isobutyl ketone was mixed with Butyl Cellosolve.

TABLE I.—EFFECT OF TARTRATE ON EXTRACTION OF MAGNESIUM 8-HYDROXYQUINOLATE AND 8-HYDROXYQUINALDATE COMPLEXES*

	Decrease in absorbance, %	
Sodium tartrate, *M*	8-Hydroxyquinolate	8-Hydroxyquinaldate
0	0	0
0·0027	0·7	0
0·014	1·2	1·4
0·027	3·6	3·1

* 25 μg of magnesium present in each case.

The extraction efficiency was estimated by extracting with 10-ml portions of methyl isobutyl ketone. It was found that 94% of the magnesium present was extracted in a single pass over the range of magnesium concentration studied. However, the single-extraction technique was used in the present work because of the high reproducibility of extraction. No improvement in extraction was found after shaking vigorously for more than 1 min.

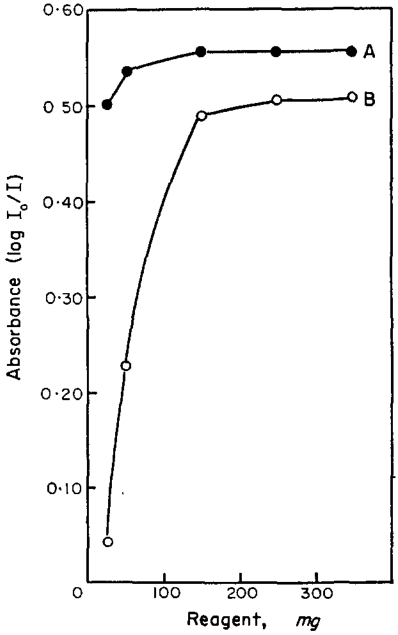

FIG. 2.—Effect of reagent concentration:—
A: 8-Hydroxyquinoline (25 μg of Mg)
B: 8-Hydroxyquinaldine (25 μg of Mg)

Calibration curve. A calibration curve with the concentration of magnesium varying from 4 to 40 μg was prepared by employing the procedure given above. A typical calibration curve is shown in Fig. 3.

Effect of diverse ions. 8-Hydroxyquinoline forms complexes with all metals other than the alkali metals, and these complexes are extractable into methyl isobutyl ketone. Selectivity can be controlled by pH, but aluminium, copper, iron, manganese, nickel, lead and zinc react in the pH range of 11–12. To ascertain the influence of diverse ions magnesium was extracted by 8-hydroxyquinoline from solutions containing diverse ions. The results are summarised in Table II. Most of the metals used were in the chloride form. Chromium(III) was prepared by reducing dichromate with hydrochloric acid. The precipitates remained in the aqueous phase after extraction of copper and calcium as 8-hydroxyquinolate complexes. Aluminium in large amounts also remained without being extracted into 10 ml of methyl isobutyl ketone, and required a larger volume of methyl isobutyl ketone to be completely extracted. Aluminium extracted into the organic phase did not affect the magnesium absorption whereas in aqueous solution it depresses the magnesium absorption. It may be considered that 8-hydroxyquinoline in the extract counteracts the depressive effect of aluminium on magnesium absorption.

Silica, sulphate or phosphate did not interfere with the extraction.

Extraction of magnesium with 8-hydroxyquinaldine

Effect of sodium chloride and tartrate. The effect of sodium chloride on the extraction of magnesium-hydroxyquinaldate complex is shown in Fig. 1. Contrary to the 8-hydroxyquinoline system, the extraction was not enhanced as the sodium chloride concentration increased. The extraction of magnesium appears to be reduced with high concentrations of salt. Therefore, the minimum amount of sodium chloride had to be used for preventing any emulsification in extraction.

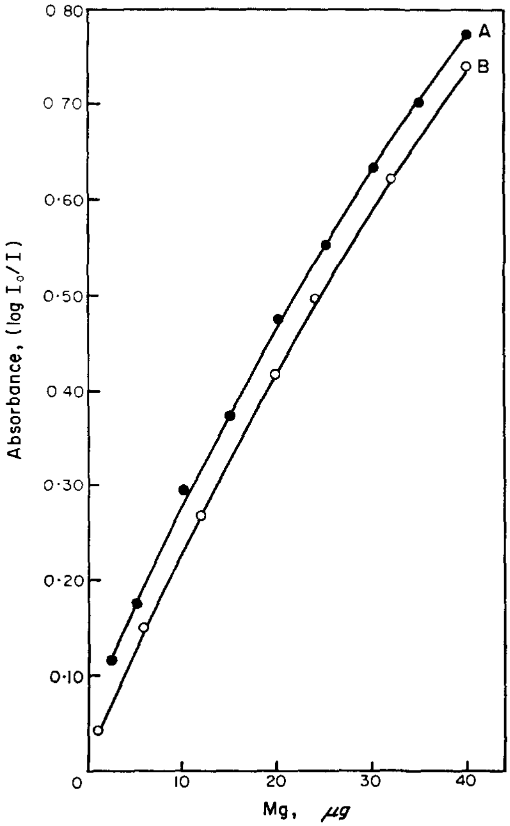

FIG. 3.—Calibration curves for magnesium determination:—
A: 8-Hydroxyquinolate complex
B: 8-Hydroxyquinaldate complex

Large amounts of tartrate lowered the amount of magnesium extracted (Table I). The minimum amount of tartrate needed to prevent the hydrolysis of metals was used.

Effect of pH. It was found that the magnesium-8-hydroxyquinaldate complex was effectively extracted at a pH greater than 11. The pH range of extraction of the magnesium-hydroxyquinaldate complex was not different from that of the hydroxyquinolate complex.

Effect of reagent concentration. As is shown in Fig. 2, more than 200 mg of 8-hydroxyquinaldine was necessary for this procedure.

Calibration curve. A calibration curve of the concentration of magnesium varying from 2 to 40 μg was prepared. A typical calibration curve is shown in Fig. 3.

Magnesium-hydroxyquinaldate complex was also extracted into most esters, but methyl isobutylketone was more suitable for extraction because of the high extractability of the complex.

TABLE II.—EFFECT OF DIVERSE IONS

Foreign ion, μg	Magnesium, μg		
	Present	Found*	
		8-Hydroxyquinolate	8-Hydroxyquinaldate
318 Cu	20·0	19·6	—
532 Cu	20·0	17·5	19·7
500 Ca	20·0	20·0	21·2
454 Fe	20·0	20·8	19·3
300 Mn	20·0	20·0	—
510 Mn	20·0	—	20·0
531 Ni	20·0	20·9	21·2
633 Zn	20·0	21·3	18·4
500 Pb	25·0	25·0	25·5
654 Sn	25·0	—	25·6
311 Cr	25·0	—	25·1
518 Cr	25·0	24·5	22·6
245 Ti	25·0	24·8	—
490 Ti	25·0	23·6	—
490 Ti	30·0	—	30·0
529 Al	20·0	20·0	20·0
1000 Al	20·0	19·2	20·0
3000 Al	20·0	16·4†	20·1
5000 Al	20·0	—	20·0
10000 Al	20·0	—	20·0

* Random error: $\pm 0{\cdot}5$ μg.

† 8-Hydroxyquinolate complexes were not completely extracted.

Effect of diverse ions. 8-Hydroxyquinaldine forms complexes with metals other than the alkali metals, but this reagent does not form a stable aluminium complex.[6,7] However, 8-hydroxyquinaldine has not been used to extract magnesium in the presence of large amounts of aluminium. The effect of aluminium was, therefore, investigated for the determination of magnesium in aluminium. Ten mg of aluminium had no effect, but higher concentrations led to incomplete extraction of magnesium. When the magnesium was extracted from solutions containing more than 10 mg of aluminium, the organic phase had to be washed with a solution of pH 11. However, the effect of 20 mg of aluminium could not be completely overcome.

The effects of other ions are summarised in Table II. Chromium (500 μg) was found to interfere. However, this effect was not encountered when magnesium and chromium were extracted from separate solutions and the extracts were mixed previous to spraying. Therefore, it seemed reasonable to assume that the effect of chromium was encountered in the extraction process.

APPLICATION OF THE METHOD

Determination of magnesium in alkali products

Procedure. Except for brine and sodium chloride, dissolve a suitable weight of sample (43g for sodium bicarbonate and 27 g for sodium carbonate) in about 50 ml of water. Neutralise the solution by slowly adding 45 ml of 12*M* hydrochloric acid and dilute to 100 ml with water. Place 20 ml of the sample solution into a separatory funnel and add 1 ml of sodium tartrate solution. Continue according to *Procedure 1* (p. 990).

Prepare calibration curve by taking standard magnesium solution and 20 ml of sodium chloride solution through the procedure in place of the sample solution.

Some samples of purified brine, sodium carbonate and sodium bicarbonate were analysed by this procedure. The results are given in Table III.

TABLE III.—DETERMINATION OF MAGNESIUM IN ALKALI PRODUCTS AND IN NATURAL WATER

Sample	MgO, *ppm*	
	Added	Found
Purified brine A	—	0·28, 0·28
	0·35	0·62
Purified brine B	—	0·87, 0·84
	0·35	1·24
Sodium carbonate	—	2·78, 2·78
	1·53	4·20
Sodium bicarbonate A	—	0·72, 0·68
	0·97	1·65
Sodium bicarbonate B*	—	41·8, 41·0
Natural water†	—	4·7, 4·7
	1·7	6·3

* 1 g of sample was taken.

† 2·8 ppm of MgO without extraction.

Magnesium in natural water can successfully be determined by this procedure without interference from silica.

Determination of magnesium in aluminium

Procedure A. Dissolve 0·1000 g of sample in 3 ml of hydrochloric acid by the addition of 1 ml of nitric acid. Boil to remove nitrous fumes and allow to cool. Transfer the solution to a 100-ml volumetric flask and dilute to the mark. Take a suitable aliquot of the sample solution into a separatory funnel so as to give about 5–40 μg of magnesium and less than 10 mg of aluminium, and continue according to *Procedure 2* (p. 990).

Prepare a calibration curve, with standard magnesium solution in place of the sample solution, by the above procedure.

Procedure B. To 0·1000 g of sample add 5 ml of 3*M* sodium hydroxide solution. Allow to react without the application of heat until the reaction subsides, and then boil gently until the reaction is

TABLE IV.—DETERMINATION OF MAGNESIUM IN ALUMINIUM ALLOYS

Sample	Magnesium, %	
	Atomic absorption	Certificate value
BCS 182/1*	0·082, 0·086	0·08
NBS 87a†	0·381, 0·389	0·37
BCS 268‡	0·536, 0·532	0·56
BCS 216/1¶	0·738, 0·728	0·74

* Also contains 11·48% silicon, 0·20% copper, 0·44% iron, 0·28% manganese, 0·04% nickel, 0·05% titanium and 0·10% zinc.

† Also contains 6·24% silicon, 0·30% copper, 0·61% iron, 0·26% manganese, 0·57% nickel, 0·18% titanium, 0·16% zinc, 0·11% chromium and 0·10% lead.

‡ Also contains 4·85% silicon, 1·34% copper, 0·39% iron, 0·22% manganese, 0·12% nickel, 0·05% zinc and 0·035% lead.

¶ Also contains 0·74% silicon, 4·42% copper, 0·40% iron, 0·73% manganese, 0·06% nickel, 0·10% titanium and 0·11% zinc.

Sample (BCS 216/1) was analysed by *Procedure A* and others by *Procedure B.*

complete. Cool and add 6*M* hydrochloric acid to acidify the solution. Warm gently and add nitric acid dropwise until the solution becomes clear. Cool and proceed as in *Procedure A*.

Several standard aluminium alloys were analysed by these procedures and the results obtained are shown in Table IV together with the corresponding certified values. One sample was analysed five times to evaluate the reproducibility of the method. The mean value was found to be 0·491 % compared with the certified value of 0·48 % and the coefficient of variation was 2·08 %.

These methods were suitable for samples containing more than 0·05 % of magnesium.

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Zusammenfassung—Es wurde eine Methode zur Magnesiumbestimmung durch atomare Absorptionsspektroskopie nach Extraktion in ein organisches Lösungsmittel entwickelt. Aluminium wird als 8-Hydroxychinolat oder 8-Hydroxychinaldat mit Methylisobutylketon extrahiert, der Extrakt in die Flamme gegeben und die Magnesium-Absorption gemessen. Die Extraktion als 8-Hydroxychinolat dient zur Bestimmung von Magnesium-spuren in alkalireichen Produkten wie gereinigter Sole, Natriumcarbonat und -bicarbonat. Durch Extraktion als 8-Hydroxychinaldat werden kleine Mengen Magnesium in Aluminium und seinen Legierungen bestimmt.

Résumé—On a élaboré une methode de dosage du magnésium par spectrophotométrie d'absorption atomique après extraction en solvant organique. On extrait le magnésium à l'etat de complexe 8-hydroxyquinoléique ou 8-hydroxyquinaldique par la méthyl isobutyl cétone, l'extrait est introduit dans la flamme et l'on mesure l'absorption du magnésium. La méthode d'extraction 8-hydroxyquinoléique sert à doser des traces de magnésium dans des produits alcalins, tels la saumure purifiée, le carbonate de sodium et le bicarbonate de sodium. La méthode d'extraction 8-hydroxyquinaldique sert à doser de petites quantités de magnésium dans l'aluminium métallique et ses alliages.

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SUBSTOICHIOMETRIC SEPARATION USING ION-ASSOCIATION EXTRACTION SYSTEMS

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Summary—A theory of ion-association extraction using tetraphenylarsonium, triphenylsulphonium and tetraphenylphosphonium ions is given, from which these reagents are shown to be suitable for selective substoichiometric separations. From these considerations it follows that the substoichiometric determination of manganese, rhenium and iodine by activation analysis should be possible; however, the use of these reagents for isotope dilution seems to be doubtful.

A PAPER by Tribalat on the extractability into chloroform of perrhenate as an ion-association compound with tetraphenylarsonium[1,2] or tetraphenylphosphonium[3] ion attracted interest, but only recently has a systematic study of the extraction of various anions by means of these reagents been carried out.[4–6] The work of Tribalat gave an exceptional position to the chloride ion amongst the other anions, because the above reagents are commercially available as their chlorides. Bock *et al.*, who have studied the extractability of ion-association compounds of tetraphenylarsonium (TPA),[4] triphenylsulphonium (TPS)[5] and tetraphenylphosphonium (TPP)[6] ions with many anions, pointed out that the formation of an extractable complex can be described by an acid-base reaction, *e.g.*

$$HReO_4 + (C_6H_5)_4AsOH \rightleftharpoons (C_6H_5)_4AsReO_4 + H_2O \tag{1}$$

and they expressed the extractability by means of the distribution ratio

$$\alpha = \frac{\text{total concentration of anion in organic phase}}{\text{total concentration of anion in aqueous phase}} \tag{2}$$

which they measured at various pH, equal and constant volumes of organic and aqueous phases and constant molar ratios of reagent and anion under investigation. Simultaneously, the influence of pH on the partition of TPA, TPS and TPP was studied. It was found that all the reagents are, in the form of their hydroxides, almost fully dissociated in the aqueous phase. Accordingly, the extraction of perrhenate can be described by

$$ReO_4^- + (C_6H_5)_4As^+ \rightleftharpoons [(C_6H_5)_4AsReO_4]_{org} \tag{3}$$

or

$$Z^{n-} + nT^+ \rightleftharpoons (ZT_n)_{org} \tag{4}$$

where *org* denotes the organic phase, Z is the extracted anion, T is the organic reagent and n is the number of molecules of the latter involved in forming the extractable species. In this case the extraction constant can be defined as

$$K = \frac{[ZT_n]_{org}}{[Z^{n-}][T^+]^n} \tag{5}$$

and

$$\alpha = K[T^+]^n \tag{6}$$

For a reproducible substoichiometric separation[7,8] it is necessary that the organic reagent will be consumed completely in forming an extractable species with the element (or its compound) to be separated. Therefore (for $n = 1$)

$$[ZT]_{org} V_{org} \geq 0.99\, c_T V_{aq} \tag{7}$$

where V_{org} and V_{aq} are the volumes of the organic and aqueous phases and c_T is the original concentration of the reagent used. After reaching extraction equilibrium

$$[T]V_{aq} \leq 0{\cdot}01\, c_T V_{aq} \tag{8}$$

and

$$[Z]V_{aq} \leq c_Z V_{aq} - c_T V_{aq} \tag{9}$$

It follows that for there to be 1% (or less) of reagent remaining unreacted in the aqueous phase after reaching extraction equilibrium, the value of the extraction constant must correspond to

$$K \geq \frac{0{\cdot}99\, c_T \dfrac{V_{aq}}{V_{org}}}{(0{\cdot}01\, c_T)(c_Z - c_T)} \tag{10}$$

In practice, normally $V_{aq}/V_{org} = 5/1$ and $c_Z = 2c_T$ (*e.g.*, 50% of element extracted the condition expressed by equation (10) requires $K \geq 5 \times 10^2/c_T$. For the purposes of activation analysis, where milligram amounts of carrier are usually used, c_T is of the order of 10^{-3} to $10^{-2}M$, which means that

$$K \geq 5 \times 10^4 \text{ to } 5 \times 10^5.$$

For isotope-dilution analysis, where c_T is down to $10^{-8}M$, it is only possible to use reagents with extremely high extraction constants. Values of K calculated according to equation (6) from the experimental data of Bock *et al.* are summarised in Table I.

From the above considerations, both TPP and TPA should be suitable for the substoichiometric determination of manganese (as MnO_4^-), rhenium (as ReO_4^-) and probably chromium(VI) by activation analysis. Also, it should be possible to determine iodine (as I^-) using TPA. TPS seems to be less advantageous because of the lower stability of its solution. The use of these reagents for isotope-dilution analysis seems, however, to be doubtful. Only after a determination of α using more dilute reagent solutions, can the question of the determination of manganese, rhenium, iodine, *etc.*, by the latter method be judged.

TABLE I.—EXTRACTABILITY OF VARIOUS ANIONS IN THE FORM OF ION-ASSOCIATION COMPOUNDS WITH TETRAPHENYLARSONIUM, TRIPHENYLSULPHONIUM AND TETRAPHENYLPHOSPHONIUM IONS USING CHLOROFORM AS A SOLVENT

Reagent	TPA		TPS		TPP	
Anion extracted	α	K	α	K	α	K
Chloride	0·20	$3\cdot3 \times 10^1$	0·24	6×10^1	0·18	3×10^1
Bromide	5·0	8×10^2	0·60	1×10^2	3·4	6×10^2
Iodide	>300	$>5 \times 10^4$	15·0	$2\cdot5 \times 10^3$	60	5×10^3
Thiocyanate	34	$5\cdot7 \times 10^3$	$\sim1\cdot0$	$\sim1\cdot5 \times 10^2$	>380	$>6\cdot3 \times 10^4$
Chlorate	>150	$>2\cdot5 \times 10^4$	—	—	>100	$>1\cdot6 \times 10^4$
Bromate	0·9	$1\cdot5 \times 10^2$	0·4	$3\cdot3 \times 10^1$	0·5	8×10^1
Perchlorate	>200	$>3\cdot3 \times 10^4$	>100	$>1\cdot6 \times 10^4$	>200	$>3\cdot3 \times 10^4$
Permanganate	>300	$>5\cdot10^4$	>200	$>3\cdot3 \times 10^4$	>300	$>5\cdot10^4$
Perrhenate	>200	$>3\cdot3 \times 10^4$	>100	$>1\cdot7 \times 10^4$	>600	$>1 \times 10^5$
Nitrate	60*	1×10^4	0·5	8×10^1	5·0	8×10^2
Nitrite	0·2	$3\cdot3 \times 10^1$	0·1	$1\cdot6 \times 10^1$	0·1	$1\cdot6 \times 10^1$
Chromate (pH 2·4)	71	$1\cdot2 \times 10^4$	31·2	$5\cdot2 \times 10^3$	25	4×10^2
Chromate (pH 11·5)	0·03	8×10^2	0·03	8×10^2	0·05	$1\cdot5 \times 10^2$

The extractability of fluoride, iodate, periodate, sulphite, sulphate, thiosulphate, phosphate, pyrophosphate, tungstate, vanadate, borate, arsenite, arsenate, selenite and tellurite is reported[4–6] to below ($\alpha \leq 0\cdot05$) in both an acidic and alkaline medium. Also, the extractability of molybdate in an alkaline medium using TPA and TPS has been found to be very low ($\alpha < 0\cdot005$ and $0\cdot001$, respectively); on the other hand, by analogy with chromate, good extractability of $HMoO_4^-$ (formed in a slightly acidic medium) can be expected.

The values of K listed in the table are calculated from the experimental results of Bock *et al.*,[4–6] assuming that extraction equilibrium has been reached and that the amount of reacting anion corresponds to its analytical concentration.

* In a neutral medium.

Selectivity

It is evident that by this method an extractable anion can be selectively separated from any excess of cations and/or anions not extracted by the reagent used. If there are also present in the extracted solution other anions forming extractable ion-association compounds, then the extraction constant of the test anion must be higher than that of the other anions present in the test solution. The ratio of the concentrations of two anions in the separated organic extract can be calculated according to the relationship

$$\frac{[Z_1T_{n_1}]_{org}}{[Z_2T_{n_2}]_{org}} = \frac{K_1[Z_1][T]^{n_1-n_2}}{K_2[Z_2]} \tag{11}$$

For the simplified case when $n_1 = n_2$ and the original concentration of the two anions is equal ($c_{Z_1} = c_{Z_2}$), a quantitative separation of Z_1 from Z_2, *i.e.*, reaching a ratio of

$$\frac{[Z_1T]_{org}}{[Z_2T]_{org}} > 100, \text{ using } \textit{excess} \text{ of reagent } \left(\frac{[Z_1]}{[Z_2]} < 0\cdot01\right)$$

requires that the ratio K_1/K_2 should be greater than 10^4. Using a substoichiometric amount of reagent, the same degree of selectivity in the separation can be achieved simply if $\frac{K_1}{K_2} \geq 200$ $\left(\text{for } \frac{[Z_1]}{[Z_2]} = 0{\cdot}5\text{, because } 50\% \text{ of unreacted } Z_1 \text{ remains in the aqueous phase}\right)$.

Further increase in the selectivity of the method can be obtained by means of a preliminary separation of the test element from its mixture with foreign ions. For example, manganese could be extracted as its diethyldithiocarbamate in carbon tetrachloride or chloroform, then back-extracted into a solution of dilute mineral acid. Finally, after oxidation, manganese could be extracted as permanganate using a substoichiometric amount of TPP or TPA. Similarly, iodine could be extracted into an organic solvent, back-extracted into the aqueous phase using a reducing agent, then extracted as I^- using TPA.

In contrast with the solvent extraction of metal chelates, the partition of the reagent used cannot be controlled by a change of pH in the case of ion-association extraction systems involving TPP, TPA and TPS. For this reason a preliminary extraction of the test solution by the same reagent to be used for the substoichiometric separation is not possible. An uncontrollable amount of the unreacted reagent remains in the aqueous phase and a reproducible substoichiometric separation cannot subsequently be achieved.

In addition to the anions stated in Table I, other negatively charged species, such as $AuCl_4^-$, $Au(NCS)_4^-$, $PdCl_4^{2-}$, HgI_4^{2-}, *etc.*, can interfere because they are also extracted. Such interferences can be avoided by removing the metal or preventing the formation of its anionic complex. The formation of these complexes, however, permits their use for other substoichiometric determinations. Thus, gold could be determined as $AuCl_4^-$ or $Au(CNS)_4^-$ using TPA. For this purpose not only the extraction constant according to equation (10) must be sufficiently high, but also a very strong chloro complex (in the case of $AuCl_4^-$) must be formed. If not, too great an excess of chloride ions is necessary for the quantitative formation of $AuCl_4^-$ and this excess will interfere in the extraction of $AuCl_4T$ according to equation (8). For

$$\frac{[AuCl_4^-]}{[Au^{3+}][Cl^-]^4} = 10^{20}$$

even a small excess of chloride ions is satisfactory for complete formation of a species extractable as an associate with TPA. The suitability of this system has been recently well demonstrated by Alimarin and Perezhogin[10] in the first paper published on the use of ion-association extraction for substoichiometric determination by activation analysis. From their experimental data it follows that the use of more than $0{\cdot}5M$ hydrochloric acid must be avoided, which observation is in agreement with the above theoretical considerations.

From the theory and extraction data given in this paper, it follows that a substoichiometric separation of manganese, rhenium and probably chromium can be developed using tetraphenylarsonium or tetraphenylphosphonium chlorides as reagents to form extractable species with these metals. Also, the first substoichiometric separation of a non-metal, iodine, will probably be possible in this way. Finally, it should be possible to separate technetium by means of a substoichiometric amount of tetraphenylarsonium chloride using rhenium as a non-isotopic carrier. This separation might be used for the determination of traces of molybdenum *via* ^{99m}Tc by activation analysis.

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Résumé—On présente une théorie sur l'extraction d'associations ioniques utilisant les ions tétraphénylarsonium, triphénylsulfonium et tétraphénylphosphonium, à partir de laquelle on montre que ces réactifs conviennent aux séparations substoechiométriques sélectives. De ces considérations, il résulte que les dosages substoechiométriques du manganèse, du rhénium et de l'iode par analyse par activation devraient être possibles; toutefois, l'emploi de ces réactifs pour la dilution isotopique semble douteux.

Zusammenfassung—Eine Theorie der Extraktion von Ionenassoziaten mit Tetraphenylarsonium-, Triphenylsulfonium- und Tetraphenylphosphoniumionen wird angegeben; dabei wird gezeigt, daß sich diese Reagentien zu selektiven unterstöchiometrischen Abtrennungen eignen. Aus diesen Erwägungen folgt, daß die unterstöchiometrische Bestimmung von Mangan, Rhenium und Jod durch Aktivierungsanalyse möglich sein sollte; die Verwendung dieser Reagentien zur Isotopenverdünnung erscheint jedoch von zweifelhaftem Nutzen.

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GRAVIMETRIC DETERMINATION OF SILICON IN ORGANIC MATERIALS ON THE MILLIGRAM SCALE

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Summary—Samples containing 0.5 mg of silicon are fused with sodium peroxide in a nickel bomb. Silicon is precipitated and weighed as quinoline silicomolybdate. Satisfactory results have been obtained from both solid and liquid samples. Up to 3 mg of fluoride can be tolerated after addition of boric acid; phosphate must be absent.

Because of the poor gravimetric factor involved, the determination of silicon in organic materials by weighing as silica is not very satisfactory. This is particularly so for analysis on the milligram scale. Much improved gravimetric factors can be obtained by the precipitation of the silicomolybdates of organic bases. However, only Schwarzkopf and Henlein[1] appear to have applied this type of method for the micro analysis of organic substances. These authors precipitated and weighed the oxine complex.

During the search for a suitable method for determining silicon in materials also containing phosphorus,[2] very satisfactory results were obtained, in the absence of phosphate,* by precipitation as the quinoline molybdenum blue complex.[3] Previously, Armand and Berthoux[5] had obtained good results for the determination of small amounts of silicon in aluminium alloys by precipitation of the unreduced, yellow complex. Because earlier work in our laboratory[6] had indicated that there was probably no significant advantage in using other organic bases, it was decided to examine the utility of the quinoline complexes for the micro determination of silicon in organic compounds not containing phosphorus.

Conditions for precipitation

Filipov[3] used a rather more acid solution for formation of silicomolybdic acid than Armand and Berthoux.[5] The optimum molybdate concentration and the time required for the complete formation of the complex acid was, therefore, checked by recording the rate of development of the yellow colour. It was similarly established that 0·3 g of boric acid was required to prevent interference in the formation of the complex acid by up to 3 mg of fluoride.

A comparison between the precisions obtained in precipitation of the blue and yellow complexes from standard silicate solutions was made. The results are shown in Table I. In each case, the means and standard deviations are based on 8 determinations. No statistically significant difference in precision was found. Further, the results indicated that the theoretical gravimetric factor (0·0120) could be applied to the yellow complex.

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* It was not clear from the abstract[3] that Filipov's whole procedure, for the analysis of silicon in steels also containing phosphorus, did not allow the formation of phosphate. This only became apparent when we were able to obtain an earlier paper[4] by the same author.

TABLE I.—COMPARISON OF PRECISIONS: BLUE AND YELLOW COMPLEXES

	Blue complex		Yellow complex	
Si taken, *mg*	1·0	0·5	1·0	0·5
Mean wt. of ppt., *mg*	84·06	42·18	83·30	41·56
Standard deviation, *mg*	0·298	0·161	0·341	0·289

TABLE II.—ANALYSIS OF SOLID ORGANIC RESEARCH MATERIALS

	Smaller bombs		Standard bombs		
Compound	Sample wt., *mg*	Si found, %	Sample wt., *mg*	Si found, %	Si calcd., %
Triphenylsilanol	5·320	10·21	5·194	10·27	10·14
	4·807	10·19	5·019	10·07	
			5·288	10·12	
			5·134	10·00	
			4·963	10·15	
			5·309	9·86	
			4·958	10·02	
			5·163	10·18	
			4·863	9·96	
			4·992	10·16	
			5·115	9·98	
			5·114	10·20	
			5·042	10·48	
$C_{21}H_{24}Si_2O$	2·940	16·16	3·082	15·91	16·12
	3·299	16·04	3·250	15·07	
			3·121	15·70	
			3·060	16·01	
			3·235	16·13	
			2·996	16·19	
			2·982	16·91	
$C_{26}H_{26}Si_2O$	3·999	13·50			13·68
	3·729	13·49			
$C_{26}H_{26}Si_2O$			3·964	14·18	13·68
			3·993	13·65	
			3·757	13·61	
			3·805	13·72	
			3·427	13·62	
$C_{31}H_{28}Si_2O$	4·329	12·22	4·158	11·98	11·88
	3·997	11·93	4·202	11·87	
$C_{36}H_{30}Si_2O$	5·840	10·50			10·50
	5·334	10·48			
$C_{21}H_{24}Si_3O_3$	2·667	20·62			20·64
	2·731	20·94			
$C_{28}H_{32}Si_4O_4$	2·647	20·66	2·741	20·98	20·64
	2·460	20·53	2·772	21·98	
			2·714	19·90	
			2·480	20·29	
$(C_7H_{16}SiO)_n$	2·955	19·49			19·45
	3·224	19·45			

Analysis of organic materials

Fusion with 1 g of sodium peroxide had been found an effective mineralisation technique for the analysis of silicon compounds on the semimicro scale.[2] It was decided to use 0·2 g of peroxide for the micro work to ensure complete decomposition of organic materials, particularly because it was anticipated that some liquids might have to be encapsulated. Most of the work has been done using nickel bombs, similar to but smaller than the well-known "fluorine" bombs,[7] with an internal volume of about 0·25 ml.

TABLE III.—ANALYSIS OF LIQUID ORGANIC RESEARCH MATERIALS

Compound	Smaller bombs Sample wt., *mg*	 Si found, %	Standard bombs Sample wt., *mg*	 Si found, %	Si calcd., %
$C_{10}H_{26}Si_2O_3$	3·039	22·41	1·416	21·98	22·44
	2·423	22·37	3·730	21·90	
			1·610	22·21	
			3·314	22·22	
$C_8H_{20}SiO$	5·601	17·21			17·52
$C_{20}H_{34}Si_2O_5$	4·779	13·08	4·085	13·41	13·68
	7·629	13·44	5·372	13·34	
$C_{16}H_{22}Si_2O$	2·567	19·44			19·61
$C_{11}H_{20}Si_2O$	2·340	24·66	10·763*	25·26	25·03
	3·814	24·88	10·187*	25·33	
$C_{21}H_{24}Si_2O$	3·967	16·26	5·629	16·36	16·12
	3·079	16·24	3·805	16·42	
	4·484	16·73	6·813	16·20	
$C_{16}H_{38}Si_3O_2F_2$†	4·894	21·84			21·90
	2·774	21·85			

* All reagent quantities multiplied by 3; 15-μg blank subtracted.
† 0·3 g of boric acid added to the alkaline leach solution.

Solid materials. Samples containing about 1 mg of silicon were used in the initial tests. In order to avoid high and variable blanks,

(i) the copper gaskets used to seal the bombs must not be asbestos filled;
(ii) commercial colloidal graphite could not be used to prevent the copper gaskets sticking to the nickel: a special preparation of carbon black had to be used;
(iii) the furnace had to be lined with metal to prevent dust from the refractory lining falling on the bombs;
(iv) plastic (*e.g.*, PTFE) covers must be used when leaching the bombs in the platinum dishes.

When all these precautions were taken, good results were obtained with no blank correction. However, because relatively large amounts (10 mg or more) of samples were required for analysis of compounds with low silicon contents, trials were conducted with samples containing only 0·5 mg of silicon. Working on this scale, it became apparent that a blank correction (equivalent to 5 μg of silicon) must be subtracted. The results for the analysis of triphenylsilanol and eight research compounds are given in columns 2 and 3 of Table II. The method was tested, by an analyst unfamiliar with the technique, working to the procedure described later and using the commercially available standard "fluorine" bombs. The results obtained are listed in columns 4 and 5 of Table II. When these larger bombs were used for fusion, a blank of 15 μg of silicon had to be subtracted.

Liquid materials. Considerable difficulty was experienced in the analysis of certain liquids, even those not expected to be volatile. Low recoveries were obtained when the sample was dropped directly into bombs, caused mainly, it is thought, by the tendency of the liquids to spread over the surface of the bomb, thus facilitating loss to the atmosphere. The same creeping effect was observed when attempts were made to weigh these samples in shortened Size 4 methyl cellulose capsules. Finally, it was found possible to weigh these samples by allowing them to be absorbed onto filter paper which was then enclosed in a small capsule. The results obtained, using both smaller and standard size bombs, are given in Table III.

EXPERIMENTAL

Reagents

Sodium peroxide. Analytical reagent grade powder.

5% *Ammonium molybdate solution.* Dissolve 50 g of ammonium molybdate in water. Filter through a paper-pulp pad into a 1-litre flask and dilute to the mark.

2% *Quinoline hydrochloride solution.* Dissolve 20 ml of redistilled quinoline in 800 ml of hot water containing 25 ml of concentrated hydrochloric acid. Stir well, allow to cool and dilute to 1 litre.

Quinoline wash solution. Dilute 25 ml of 2% quinoline hydrochloride solution to 1 litre with water.

Weighing of sample

Liquids. Take the cap, or the shortened body, of a Size 4 methyl cellulose capsule, insert a small piece (approximately 10 × 3 mm) of Whatman No. 41 filter paper and weigh. Add a portion of the liquid sample containing about 0·5 mg of silicon from a fine pipette, allowing the liquid to be absorbed by the paper. Now pinch the open end of the capsule together with forceps and bend the flattened section down. Pinch again with the forceps to form a seal and weigh. Place the sealed capsule in the bomb.

Note. The handling of the capsule is conveniently carried out using "surgeon's rubber fingertips" which protect it from the moisture of the hands.

Solids. Weigh a portion of the solid organic sample, containing about 0·5 mg of silicon, in a weighing stick. Empty the sample into the bomb and reweigh.

Fusion and leach

Add 0·2 g of sodium peroxide to the sample in the bomb. Smear a thin layer of carbon black suspension* on the flange of the lid and on the top face of the body of the bomb. Fit an annealed copper washer, close the bomb and tighten the nut.

Heat the sealed bomb in a muffle furnace for 15 min at 500°.

Cool and open the bomb, washing any peroxide adhering to the cap into a platinum dish. Wipe the outside of the bomb with a clean tissue and lay it on its side in the platinum dish. Add water until the bomb is half-covered and cover the dish with a plastic watch glass. Heat the dish on a hot-plate until effervescence ceases and the solution comes to the boil.

Take the dish from the hot-plate, remove the bomb and wash it with water, collecting the washings in the dish.† Add 3·5 ml of 30% sulphuric acid, cover the dish again and heat to boiling to expel carbon dioxide. Cool the solution to room temperature and filter through a paper-pulp pad into a scratch-free 150-ml beaker with a small thermometer as stirrer. Dilute the filtrate to 75 ml.

Precipitation of quinoline silicomolybdate

Add 15 ml of 5% ammonium molybdate solution and allow to stand for 10 min. Add 5 ml of concentrated hydrochloric acid and precipitate yellow quinoline silicomolybdate by adding 5 ml of 2% quinoline hydrochloride solution dropwise from a burette, stirring continuously. Heat to 70–80° to coagulate the precipitate and cool to room temperature. Filter through a tared No. 4 sintered glass crucible, washing 5 or 6 times with the quinoline wash solution. Dry at 150° for 1 hr, cool for 30 min in a desiccator and weigh quickly against a tare crucible.

$$\text{Percentage silicon} = \frac{(\text{weight of precipitate} \times 0{\cdot}0120) - \text{blank}\ddagger}{\text{weight of sample}} \times 100$$

Rapid mineralisation

Fusion, leaching and washing a pair of fluorine bombs by the above procedure takes about 35 min. By using small nickel capsules (15 mm high, 6 mm diameter, 0·5 mm walls) for fusion, this time can be cut to 10–15 min.

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* Prepared by burning analytical reagent grade benzene in a spirit lamp and collecting the carbon smoke on a cold surface. The carbon is mixed with a little wetting agent (*e.g.*, Teepol) and water to form a smooth paste.

† 0·3 g of boric acid should be added to the alkaline solution if the sample contains fluorine (up to 3 mg).

‡ The blank for a given set of apparatus may be obtained by repeat analyses of a standard organic compound or by finding the difference between results found for silicate solution with and without the addition of solution leached from peroxide fusions in the absence of organic material.

The same amount of peroxide was added to the samples, the flanged lid of the capsule fitted and held on by clamping the closed capsule vertically between the jaws of a small vice. The flame from a hand torch was allowed to impinge on the side of the capsule until it glowed red. The capsule was removed, cooled on an aluminium block and leached in a platinum crucible. The normal procedure was then followed.

Results obtained for the analysis of some solids by this method are given in Table IV. No blank has been subtracted. The results tend to be high and are more scattered than those obtained using the other bombs. However, fusion in this type of capsule, which can easily be made out of nickel rod, might be useful where high accuracy is not required, particularly if "fluorine" bombs were not immediately available.

TABLE IV.—ANALYSIS OF SOLID MATERIALS USING RAPID MINERALISATION

Compound	Sample wt., *mg*	Si found, %	Si calc'd., %
Triphenyl-silanol	5·446	10·21	10·14
	5·452	10·09	
$C_{28}H_{32}Si_4O_4$	2·569	19·98	20·64
	2·649	21·23	
$C_{26}H_{26}Si_2O$	5·530	14·07	13·68
	4·280	13·82	
$C_{21}H_{24}Si_3O_3$	3·549	20·95	20·64
	3·216	21·40	
$C_{21}H_{24}Si_2O$	3·788	16·59	16·12
	4·172	16·56	

DISCUSSION

The mean percentage recovery for the 16 solid samples containing about 0·5 mg of silicon, quoted in Table II, mineralised in the smaller bombs is 100·17% (standard deviation 1·02). The results obtained after mineralisation in the standard size "fluorine" bombs are, perhaps, of more general interest because they were found by an analyst unfamiliar with the method working on a routine basis. The mean percentage recovery for these 31 determinations is 99·97% (standard deviation 2·51). The relevant figures for the liquid samples (Table III) are 99·51% (standard deviation 1·89, 13 determinations) for the smaller bombs and 99·21% (standard deviation 1·67, 9 determinations) for the routine method, the two results obtained for the 10-mg (asterisked) samples being omitted. The method is, therefore, entirely adequate for the analysis of organic materials to the accepted limits of accuracy.

Although a sample weight to give about 0·5 mg of silicon was aimed at, it was not always possible to achieve this with the liquid samples. The samples taken were, in fact, such as to give calculated silicon weights varying from 0·3 to 1·1 mg. This illustrates the wide range that can be covered without varying the conditions for precipitation. Two smaller samples, weighing 2·594 and 2·470 mg, of triphenylsilanol were analysed under the standard conditions and gave results of 10·25 and 10·20%, respectively. The method might well be applicable, therefore, to smaller-scale analysis.

We have recommended an encapsulation procedure for weighing liquid samples although it is sometimes possible to obtain good results by weighing samples directly into the cup of the bomb. Until a wider experience of more different types of compound has been gained, it will not be possible to state when it is safe to use the simpler sampling technique.

Only one fluorinated material was available to test the method and good results were obtained. This compound contained a relatively small amount (Si:F = 3:2) of fluorine but, as indicated earlier, it has been found that up to 3 mg of fluoride can be tolerated, after addition of 0·3 g of boric acid, in the determination of 0·5 mg of silicon in standard solutions. This indicates that a silicon:fluorine ratio of 1:9 may be present in an organic molecule without any interference being expected.

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Zusammenfassung—Proben, die 0,5 mg Silicium enthalten, werden mit Natriumperoxyd in einer Nickelbombe geschmolzen. Silicium wird als Chinolin-silicomolybdat gefällt und gewogen. Sowohl mit festen als auch mit flüssigen Proben wurden befriedigende Ergebnisse erhalten. Bis 3 mg Fluorid sind bei Zugabe von Borsäure zulässig; Phosphat darf nicht vorhanden sein.

Résumé—Dans une bombe en nickel, on fait fondre des échantillons contenant 0·5 mg de silicium avec du peroxyde de sodium. Le silicium est précipité et pesé à l'état de silicomolybdate de quinoléine. On a obtenu des résultats satisfaisants à partir d'échantillons solides et liquides. On peut tolérer jusqu'à 3 mg de fluorure après addition d'acide borique; il faut éviter du phosphate.

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POLAROGRAPHIC DETERMINATION OF MAGNESIUM IN CALCIUM CARBONATE

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Summary—Magnesium is determined in calcium carbonate by polarographically reducing the magnesium complex of the dyestuff Solochrome Violet R.S. at pH > 11 using piperidine as buffer. The bulk of the calcium is first removed by means of a precipitation with oxalate; iron, when present at a level above one-tenth of the magnesium content, must be removed by a chloroform extraction of its cupferrate. The method has a coefficient of variation of less than 6% and it is suitable for magnesium levels up to at least 1%. A comparison of the proposed method is made with flame photometry.

INTRODUCTION

THE polarographic technique described by Reynolds and his coworkers[1,2] is here modified for the determination of magnesium in calcium carbonate in the range 0–2,500 ppm of magnesium.

The proposed procedure consists of polarographically reducing the magnesium complex of the dyestuff Solochrome Violet R.S. (C.I. Mordant Violet 5; 5-sulpho-2-hydroxybenzene-2-naphthol). This complex is produced in solutions containing piperidine as buffer and the final solution is adjusted to pH > 11.

In order to avoid interference from calcium, which forms a similar but much weaker complex with the dyestuff, it is necessary first to remove the bulk of the calcium, *e.g.*, by precipitation with oxalate.

Interference from iron (distortion of the polarographic waves) can also be serious when the level of iron is more than one-tenth of the magnesium content. This interference can be removed by extraction with chloroform of the iron complex with cupferron.

EXPERIMENTAL

Removal of calcium

Table I shows the effect of various precipitants investigated for the removal of calcium.

TABLE I

Precipitant	Effect of precipitant
Sulphuric acid, aqueous and ethanolic	Residual soluble calcium sufficiently high to cause interference with subsequent magnesium determination.
Sulphite (by the procedure of Gehrke *et al.*[3])	Residual soluble calcium too high (see immediately above).
Fluoride	Magnesium fluoride coprecipitated with the calcium fluoride.
Oxalate	Satisfactory; no soluble calcium could be found at centrifuge tube stage (see *Method*) when examined by an Evans Electroselenium Ltd. filter flame photometer.*

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* This procedure was independently and simultaneously investigated by Pyburn and Reynolds.[2]

Polarographic procedure

From the findings of Reynolds and his coworkers[1,2] and from our own observations using the K.1000 Cathode Ray Polarograph (Southern Analytical Ltd.) it was found that the quantities of reagents specified under *Method* gave the most reliable and satisfactory working conditions.

Piperidine. The volume of piperidinium chloride buffer solution should be maintained between 0·9 and 1·1 ml. A smaller quantity gave no or very poorly shaped polarographic waves; a larger quantity gave waves with large slopes which were difficult or impossible to synchronise.

Sodium hydroxide. Although the determination can be performed in the absence of sodium hydroxide, the waves exhibit poor peaks and are hence difficult to interpret. The volume of 1*M* sodium hydroxide solution should be greater than 0·5 ml but should not exceed 1·1 ml. A larger quantity gives a calibration relationship with a large negative intercept and also a poorer shaped polarogram.

Solochrome Violet R.S. A smaller quantity of the dyestuff solution than 20 ml produced "tailing" of the calibration curves; a larger quantity tended to give a large preceding dyestuff wave which makes the base of the wave difficult to interpret and to synchronise. Using 15 ml of Solochrome Violet R.S. solution it is possible to determine magnesium down to at least 0·20 μg/ml of the final solution for polarography. For lower amounts of magnesium the quantity of dyestuff solution would need to be decreased.

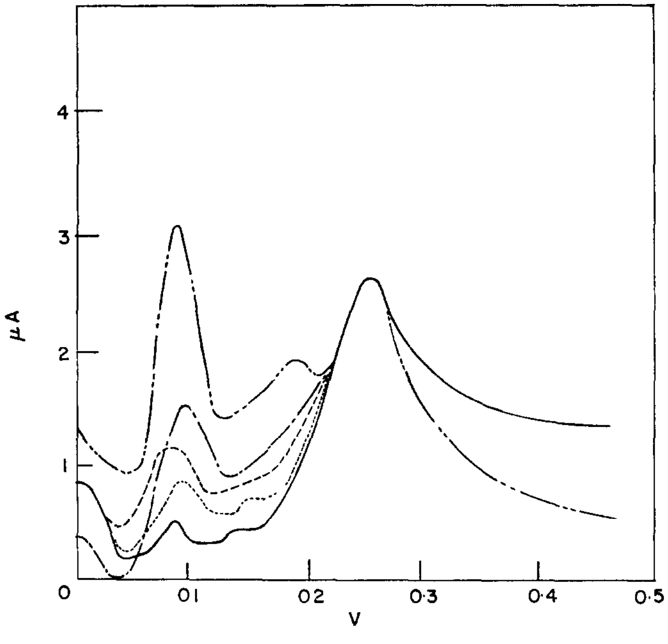

FIG. 1.—Effect of interference of iron on magnesium polarogram:

— · — · · — 1000 ppm of iron,
— · — · — 500 ppm of iron,
- - - - - - - 200 ppm of iron,
· · · · · · · · · · · 100 ppm of iron,
———————— "blank".

Interferences

The effects on the final polarogram of various elements taken through the whole of the method (see p. 1013) are shown in Table II. These effects do not necessarily apply if the oxalate step is omitted.

Barium, calcium and strontium. Experiments indicated that reliable results could not be obtained (either high or wholly non-reproducible) if ratios greater than

calcium/magnesium 10/1
strontium/magnesium 25/1
barium/magnesium 40/1

TABLE II

Element*	Amount of element, *ppm*†	
Aluminium(III)	up to 5,000	Aluminium wave precedes magnesium wave. Above 2000 ppm base of wave is difficult to interpret. However, aluminium content of "Pharmaceutical grade" calcium carbonate is invariably below 500 ppm and interference effects are insignificant.
Antimony(V)	1,000	No interference
Arsenic(III)	1,000	No interference
Barium(II)	see elsewhere	—
Beryllium(II)	1,000	No interference
Bismuth(III)	1,000	No interference
Cadmium(II)	5,000	No interference
Calcium(II)	see elsewhere	—
Chromium(III)	up to 500	Chromium wave precedes magnesium wave. Above 200 ppm difficulties arise in interpreting base of wave. Because chromium level is usually under 10 ppm, chromium interference is of no consequence.
Cobalt(II)	up to 200	Cobalt wave just precedes magnesium wave. Slight interference effects observed with 100 ppm of cobalt and more serious interference effects at 200 ppm and above. Because cobalt level is usually less than 20 ppm, interference effects are of little consequence.
Copper(II)	5,000	No interference
Fluoride	5,000	No interference
Iron(III)	up to 1,000	Serious interference effects found with iron (see Fig. 1) its removal discussed elsewhere. "Pharmaceutical grade" calcium carbonate can contain up to 200 ppm of iron. Interference effects, however, not encountered with analytical reagent grade or luminescent grade calcium carbonate because iron content is below 10 ppm.
Lead(II)	5,000	No interference
Manganese(II)	1,000	No interference
	5,000	Wave appears between dye wave and magnesium complex wave, which makes magnesium wave difficult to interpret.
Molybdenum(VI)	1,000	No interference
Nickel(II)	up to 500	Serious interference effects (wave from nickel complex coalesces with that from magnesium complex) found with 100 ppm of nickel, but these are not likely to be of consequence because "Pharmaceutical grade" calcium carbonate does not contain more than 10 ppm of nickel.
Orthophosphate	500	No interference
Strontium(II)	see elsewhere	—
Thallium(I)	5,000	No interference
Tin(II)	5,000	No interference
Vanadium(II)	1,000	No interference
Zinc(II)	5,000	No interference

* Added to 1 ml of 10% calcium carbonate solution containing 100 μg of magnesium.

† Calculated to solid calcium carbonate.

were obtained in the final solution for polarography. If these ratios are exceeded it is essential to remove the elements by the oxalate procedure.

Iron. To try and eliminate the interference from iron, various complexing agents were added before the addition of ammonium oxalate to a "solution" of calcium carbonate which contained 1,000 ppm of magnesium and 500 ppm of iron. The effects of these reagents are shown in Table III.

TABLE III

Complexing agent	Effect
Acetylacetone (0·1 ml)	Wave form badly distorted
10% Sodium acetylsalicylate (1 ml)	No effect on iron interference
10% Sodium L-ascorbate (1 ml)	Wave form badly distorted
10% Ammonium thiocyanate (1 ml)	Wave form distorted
0·01*M* Cyclohexanediaminetetra-acetic acid (1 ml)	Magnesium wave removed
10% Cupferron (1 ml)	No effect on iron interference
1% Sodium diethyldithiocarbamate (1 ml)	Wave form badly distorted
0·025*M* 4,7-Diphenyl-1,10-phenanthroline (50% ethanolic; 1 ml)	No effect on iron interference*
1% Dithizone (ethanolic; 1 ml)	Wave form badly distorted
0·01*M* Disodium ethylenediaminetetra-acetate (1 ml)	Magnesium wave removed
10% Hydroxylamine hydrochloride (1 ml)	Wave form badly distorted
10% 8-Hydroxyquinoline (50% ethanolic; 1 ml)	Wave form badly distorted
0·25% 1,10-Phenanthroline (1 ml)	Magnesium wave enhanced*
1% Phenyl-2-pyridylketoxime (ethanolic; 1 ml)	No effect on iron interference
10% Sodium rubeanate (1 ml)	Wave form distorted
10% Sodium tannate (1 ml)	Wave form badly distorted
10% Sodium thioglycollate (1 ml)	Wave form badly distorted
50% Triethanolamine (in 1*M* sodium hydroxide; 1 ml)	Iron interference wave removed, but magnesium waves found not to be reproducible

* 1,10-Phenanthroline and 4,7-diphenyl-1,10-phenanthroline used without the addition of reducing agents because these tended to distort the wave forms.

Increasing the pH during the calcium-removal stage by addition of piperidine did not remove the iron interference.

Cupferron was chosen as the most suitable complexing agent with which to try and remove the iron by solvent extraction because it was the only complexing agent which did not have a serious effect on the polarogram of the magnesium-dyestuff complex. This procedure also made the base-line flatter and "cleaned up" any irregularities from the polarogram. Details of the procedure are given under *Method.*

By using a comparison technique the effect of the iron interference could also be overcome. A series of calibration relationships was prepared, containing an equivalent of 0, 50, 100, 150, 200 and 250 ppm of added iron, respectively. The iron is then determined by 1,10-phenanthroline[4] and the result read from the appropriate relationship.

The extraction procedure is preferred for eliminating interference from iron.

Results

Some results obtained by cathode ray polarography are shown in Table IV.

Some of the samples shown in Table IV were also examined by the Unicam S.P. 900 flame spectrophotometer. 0·25% w/v Solutions of the samples in hydrochloric acid were compared with 0·25% w/v "spec-pure" calcium carbonate in hydrochloric acid which contained known amounts of added magnesium. Measurements were carried out using the 285·2-mμ magnesium line; the spectra were scanned from 283·5 to 289·5 mμ.

TABLE IV

Sample	Mg found, *ppm* (average)	Replicate determinations	Standard deviation, *ppm*	Coefficient of variation, %
A*	50	5	7·3	14·6
B*	170	6	9·5	5·5
C*	100	6	8·3	8·3
D*	1200	6	57	4·7
E*	930	6	51	5·5
F*	450	6	21	4·7
G†	990	12	58	5·8
H†	1500	12	33	2·3
H‡	1540	12	79	5·1
I†	4520	12	320	7·0
I‡	4070	12	131	3·2

* Iron content less than 10 ppm.

† Iron content about 150 ppm; comparative method used for eliminating iron interference effects.

‡ Iron content about 150 ppm; cupferrate extraction used for removal of iron.

TABLE V

Sample	Mg found, *ppm* (average)	Replicate determinations	Standard deviation, *ppm*	Coefficient of variation, %
B	105	4	67	64
C	74	5	74	41
D	1100	6	85	7·7
E	880	7	44	5·0
F	260	7	38	14·6
G	980	6	37	3·8
H	1500	5	58	4·0
I	4150	9	150	4·0

Method

Reagents

All reagents should be of recognised analytical grade.

1M Hydrochloric acid

1M Sodium hydroxide

Ammonium oxalate solution (saturated)

4% w/v *Cupferron solution (freshly prepared)*

0·05% w/v *Solochrome Violet R.S. (C.I. Mordant Violet 5) solution*

Chloroform

Piperidinium chloride buffer. Dilute 20 ml of piperidine to 100 ml with water, then adjust the pH to 13·5 with 1*M* hydrochloric acid. Store in a tightly stoppered bottle.

Magnesium stock solution. Prepare from magnesium turnings so that 1 ml = 1000 μg of Mg.

Iron stock solution. Prepare from spectroscopically pure iron so that 1 ml = 1000 μg of Fe.

Calcium carbonate ("spec-pure", Johnson Matthey & Co. Ltd).

Preparation of sample solution

For samples containing less than 20 ppm of iron. Transfer a 1·00-g sample to a 30-ml beaker, dissolve in the minimum quantity of 1*M* hydrochloric acid (*ca.* 22 ml) and evaporate almost to dryness. Transfer to a 10-ml volumetric flask and dilute to the mark with water. Transfer a 1-ml aliquot to a 10-ml graduated centrifuge tube and proceed as described under *Calcium removal and magnesium complex formation stages.*

For samples containing more than 20 ppm of iron. Proceed as described immediately above, but add 1 ml of 4% cupferron solution before diluting to 10 ml in the volumetric flask. Transfer the contents of the volumetric flask, without washing, to a dry 50-ml separatory funnel, add 10 ml of chloroform, shake for 30 sec, allow the phases to separate and discard the chloroform phase. Repeat the extraction with chloroform until the organic extract is colourless. Transfer a 1-ml aliquot to a 10-ml centrifuge tube and proceed as described under *Calcium removal and magnesium complex formation stages.*

Calcium removal and magnesium complex formation stages

To the centrifuge tube containing the 1-ml aliquot, add 4 ml of ammonium oxalate solution and dilute to the 10-ml mark with water; insert a glass rod and mix thoroughly. Place in a boiling water bath for 3 min, then allow to cool. Centrifuge. Transfer 5 ml to a 50-ml volumetric flask. Add 1 ml of piperidinium chloride buffer and mix; add 1 ml of 1*M* sodium hydroxide solution and mix; add 20 ml (15 ml when the magnesium content is less than 500 ppm) of Solochrome Violet R.S. solution and dilute to 50 ml with water. Allow to stand 25–30 min. (If the solution is allowed to stand for longer than 30 min, low results are obtained; if the solution is not allowed to stand for the stated period, erratic results are often obtained.) Transfer about 5 ml of this solution to a polarographic cell and deoxygenate with nitrogen for 5 min. Record the height of the magnesium polarographic wave, using the following conditions:

mercury pool reference electrode
start potential of $-0{\cdot}65$ V.

Read off the results from a calibration graph.

Preparation of calibration graph when magnesium content less than 500 ppm and 20 ppm of iron present

Transfer 1-ml aliquots of 10% w/v calcium carbonate ("spec-pure") solution to a series of six 10-ml graduated centrifuge tubes and add 0, 10, 20, 30, 40 and 50 μg of magnesium (as magnesium stock solution), respectively; add 4 ml of ammonium oxalate solution and proceed as described under *Calcium removal and magnesium complex formation stages.* Plot a calibration graph relating magnesium added and wave height.

Preparation of calibration graph when magnesium content in 500–2500 ppm range and iron content reater than 20 ppm

Transfer 5-ml aliquots of 20% w/v calcium carbonate ("spec-pure") solution to a series of six 10-ml volumetric flasks and add 250 μg of iron (as iron stock solution) to each. Add 0, 500, 1000, 1500, 2000 and 2500 μg of magnesium (as magnesium stock solution), respectively, and 1 ml of 4% cupferron solution, then proceed as described under *For samples containing more than 20 ppm of iron.* Plot a calibration graph relating magnesium added to wave height.

Note. If the magnesium content exceeds 2500 ppm, the initial quantity of sample should be reduced accordingly; the ammonium oxalate should also be reduced in proportion and a calibration graph drawn up using the appropriate quantities.

CONCLUSIONS

The proposed method offers a fairly quick, but reliable procedure for the determination of magnesium in calcium carbonate and it has been used successfully in our laboratories for some months.

The chief interfering elements include aluminium, chromium, cobalt, iron and nickel, of which iron is particularly serious. Interference from iron can, however, be easily overcome by a simple solvent-extraction stage.

The method has also been applied successfully to strontium and barium salts.

Although the procedure is more lengthy than flame spectrophotometry, it is, in general, more accurate as judged by the coefficients of variations shown in Tables IV and V.

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Zusammenfassung—Magnesium in Calciumcarbonat wird bestimmt durch polarographische Reduktion des Magnesiumkomplexes mit dem Farbstoff Solochromviolett R.S. bei pH > 11 mit Piperidin als Puffer. Die Hauptmenge Calcium wird zuerst durch Oxalatfällung entfernt; bei Anwesenheit von Eisen in einer Menge, mehr als ein Zehntel des Magnesiums muß es durch Extraktion seines Kupferronkomplexes mit Chloroform entfernt werden. Die Methode hat einen Variationskoeffizienten von weniger als 6% und ist für Magnesiumgehalte herauf bis wenigstens 1% geeignet. Die vorgeschlagene Methode wird mit der Flammenphotometrie verglichen.

Résumé—On dose le magnésium dans le carbonate de calcium par réduction polarographique du complexe magnésien du colorant Solochrome Violet R.S. à pH > 11 en utilisant la pipéridine comme tampon. La majeure partie du calcium est d'abord éliminée au moyen d'une précipitation à l'oxalate; on doit éliminer le fer par une extraction chloroformique de son cupferrate lorsqu'il est présent en quantité plus que le dixième de la teneur en magnésium. La méthode présente un coefficient de variation inférieur à 6% et elle convient pour des teneurs en magnésium allant jusqu'à 1% au moins. On compare la méthode proposée à la photométrie de flamme.

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TALANTA REVIEW*

SOME RECENT DEVELOPMENTS IN RADIOACTIVATION ANALYSIS

A REVIEW OF IMPROVEMENTS IN THE ANALYTICAL TECHNIQUE

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Summary—The different techniques of activation analysis are considered and recent basic or technical improvements are reviewed. Developments in related fields such as radiochemistry or γ-ray spectrometry are reported only when especially referring to activation analysis. Specific applications of activation analysis to the different fields have not been reviewed, unless they lead to improvements of the technique. Bibliographic references on applications are given.

INTRODUCTION

SINCE the advent of the nuclear reactor, there has been a steady increase in the development and application of activation analysis, which is shown by the continuous increase in the number of papers published in the literature. At the same time, the technique has diversified to such an extent that it is difficult to follow the developments in all the different areas of applied science contributing to activation analysis, which range from chemistry and nuclear physics, to applied mathematics.

In this review the different techniques of activation analysis are considered and an attempt is made to indicate the most recent basic or technical improvements, on the basis of published literature in the last two years. Only papers especially referring to activation analysis are considered. In other fields strictly related to activation analysis, such as radiochemistry and γ-ray spectrometry, only contributions of analytical importance were reviewed.

It is difficult to establish whether analysis based on measurement of the radiation emitted during the nuclear reaction itself is activation analysis or not. Results obtained by detection of immediate radiation are included only when they lead to clearly established analytical methods.

The coverage has not been extended to applications of activation analysis to other fields, unless definite improvements in the analytical technique were obtained. Readers are referred to the excellent bibliographic reports on activation analysis published annually by the A.E.D. Information Service;[1] author, element and matrix indexes are given. This bibliography will soon be published monthly. Other bibliographies on activation analysis have been prepared by Raleigh[2] and Budjoso *et al.*[3] A comparative and critical bibliography on activation analysis applications has also been published.[4] Five hundred examples of activation analysis, chosen for their technical interest, have been collected and are available as a report or in the form of standardised

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cards. The biannual report on nucleonics edited by Leddicotte for *Analytical Chemistry* also covers the field of activation analysis exhaustively to the end of 1963.[5]

BOOKS AND PROCEEDINGS OF INTERNATIONAL CONFERENCES

Since the publication of the book on activation analysis by Schulze in 1962,[6] four more books on activation analysis have been published in about one year.

Albert in a handy booklet[7] summarised the principles of the technique, dealing with the different means by which an element can be activated and a radioisotope determined. Bowen and Gibbons published a comprehensive treatise on the technique, including detailed routine procedures for the chemical separation of radioisotopes from irradiated matrices.[8] Lyon,[9] in a guide to activation analysis, gives the fundamentals and provides typical examples that the beginner may utilise for trial runs. Taylor's book,[10] after illustration of the technique, deals particularly with industrial applications, such as analysis of process streams, activation analysis in prospecting, automated equipment, *etc.*

An International Conference on Modern Trends in Activation Analysis was held in 1961[11] and another followed in April 1965. In this interval of time as many as seven international congresses had sessions which were partially or entirely devoted to activation analysis, thus witnessing the increasing interest in this technique.

In July 1963 at the XIXth International Congress of Pure and Applied Chemistry one section was devoted to trace analysis, in which acitvation analysis was the subject of almost one third of the papers.[12] The third International Symposium of Biology at Saclay was completely devoted to the use of activation analysis in biological sciences. The proceedings[13] show the results which can be obtained in biology and how the technique must be adapted to biological matrices. A particular aspect of activation analysis, *i.e.*, the analytical use of short-lived radioisotopes, was represented by 12 papers of the I.A.E.A. Seminary on practical uses of short-lived radioisotopes.[14] An informal international conference on Recent Advances in Activation Analysis was held in Glasgow during August 1964, following a course of 2 weeks in activation analysis, but only summaries of the papers are available.[15] In the Third United Nations International Conference on Peaceful Uses of Atomic Energy held in Geneva in September 1964 only a limited number of papers on activation analysis were presented, among which was a comprehensive report on advances in activation analysis by Guinn.[16] A complete coverage of activation analysis was obtained during the Symposium on Radiochemical Methods of Analysis held in Salzburg one month later, in which 38 papers on activation analysis were presented.[17] Finally, during the Eighth International Convention of Automation and Instrumentation, held in Milan during November 1964, in a session devoted to automated techniques of physical and chemical analysis, this particular aspect of activation analysis was treated.[18]

SAMPLE PREPARATION AND PRE-IRRADIATION TREATMENT

Handling of specimens

The general practice of avoiding manipulation of the samples before irradiation to minimise the risk of contamination, has been more emphasised in recent years by the requirement of higher and higher sensitivities in trace analysis. Nevertheless, the application of neutron activation to new problems has frequently made it necessary to carry out pre-treatment.

To the best of my knowledge no paper has been published dealing specifically with the problems of pre-irradiation treatment, but quite a number of papers on specific applications of activation analysis devote a part of the paper to demonstrate that no risk of contamination arose during preliminary treatments.

For many analyses of solid samples the problem is reduced to one of general handling. Dust contamination cannot be neglected when dealing with traces. In a laboratory recently constructed[19] the problem is resolved by handling the samples in glove-boxes installed in a "clean room". The air on entry is passed through efficient filters and special clothes must be worn in the room. Surface etching of solid samples after irradiation, when possible, satisfactorily resolves in many cases the problem of external contamination.

Samples are often irradiated as single pieces, thus assuming that the piece is representative of the composition of the bulk material. When non-homogeneity is suspected, many analyses must be carried out to increase the precision, or the material must be homogenised and sampled before irradiation. A simple technique for collecting residues from large amounts of solutions is the freeze-drying technique: the sample is frozen quickly in a rotary evaporator and the water then removed by sublimation. The residue is collected as a finely divided powder, ideally suited for encapsulation and irradiation.[20] An all-plastic homogeniser has been used effectively for the homogenisation of leaf tissues with minimum danger of introducing contaminants.[21]

A difficult problem is the preparation of organic and biological materials in a form which can stand high temperatures and high radiation doses, which can cause decomposition of the materials and build-up of hazardous pressures in the irradiation capsules. An interesting technique for the destruction of organic materials before irradiation is low temperature ashing: the destruction occurs at temperatures below 100°, thus minimising evaporation losses.[22,23] The risk of introducing contaminants is also greatly reduced.

The handling of small samples can also be a problem if the laboratory is not suitably equipped for micro-chemical work. On the other hand and particularly in biology, one of the trends is certainly towards smaller and smaller samples, to trace the pattern of elements down to cell levels or even inside a cell.[24] The potentialities of activation analysis are thus fully exploited. Applications are also expected to increase considerably in the field of forensic science, to identify small samples of different materials, such as paint fragments, soot, soil, *etc.*,[25,26] and to identify persons by the composition of their hair.[26–28] Small fragments of precious objects, such as ancient paintings, can be removed without noticeably damaging the object and used for elemental analysis.[29] Weighing such small samples can be avoided in many cases by relating the weight of the trace element determined to the activity induced in some known component of the sample[29,30] or to a physical property related to the weight and more measurable.[31]

Pre-irradiation procedures

The dangers of pre-irradiation chemical treatment include: introduction of contaminants from reagents and vessels and exchange or adsorption on glassware. Simple chemical treatments before the irradiation can simplify the technique and improve the accuracy when the bulk material is considerably activated by neutrons, or it is highly neutron absorbing. In other cases pre-irradiation treatments are necessary, *e.g.*, when different chemical forms of the same element must be distinguished, or the matrix gives by another nuclear reaction the same radionuclide which is used for analysis, or other nuclides of the same element which make useless the selective chemical separation of the element.[32] In another case pre-irradiation chemistry has allowed the selective separation of iodine from gross amounts of fission products (a spent nuclear fuel element) and the subsequent determination of ^{129}I by neutron activation.[33]

A technique of isotopic dilution before irradiation can be useful to minimise the blank:[34] trace determinations are carried out by dissolving the sample and adding to the solution a radioactive tracer of the element to be measured. Qualitative chemical separations are then carried out with minimum amounts of selected reagents. The residual activity is measured and the weight needed for calculating the specific activity determined by neutron activation.

Washing of the sample must often be done before the irradiation, if the samples are modified by the irradiation itself to such an extent as to impede post-irradiation washing. Sometimes buffer solutions,[35,36] anticoagulants[37] or other solutions must be added as stabilisers. The concentration of the trace elements under study can be affected by these treatments to such an extent as to make uncertain the assessment of the "true" value of the trace concentration. This is the case, for example, with human hair. Its composition is so affected by the kind of preliminary washing used that it is possible to wash off almost all the trace elements of hairs by employing suitable solutions.[38] This particular aspect of the preparation of biological specimens without affecting their trace element content has not been studied in detail up to now, although its importance is recognised.

Pre-irradiation treatments can provide a solution which may be sealed in a quartz vial and irradiated, or the elements under study may be deposited on solid supports and irradiated. Different chemical techniques are used to obtain the required separation with the least danger of contamination from reagents. Concentration on pyrolytic graphite of elements separated by controlled-potential electrolysis has been studied.[39] The electrodes are then irradiated together with a similar electrode for blank subtraction. Elements deposited on the electrodes can also be redissolved and the resulting solution irradiated.[40] Ion exchange has been used for concentrating trace elements from single crystals of alkali metal halides.[41] In biological studies dialysis is used frequently to distinguish between free and protein-bound trace elements.[36] Paper chromatography is also used to distinguish different chemical forms of the same element.[42,43] A technique called "derivative activation chromatography" has been used by Stein and Benson[44] to determine compounds of biological interest which do not possess activatable atoms: derivatives containing covalently-bound bromine or other activatable elements have been prepared, separated by paper chromatography and activated to produce readily detectable and measurable radionuclides.

THE ACTIVATION STEP

Irradiation in a nuclear reactor

Irradiation in a nuclear reactor is still the most commonly used means of activating the elements. Other sources of activating particles have extended the fields of application of activation analysis without limiting the use of the nuclear reactors.

It has been emphasised many times that a nuclear reactor is not simply a source of thermal neutrons, but a source of a large variety of activating particles which can all be used.[45,46] It is true, nevertheless, that thermal neutrons remain the activating particle which offers most advantages of sensitivity, freedom from interference and simplicity of use.

The choice of irradiation times, which is often the simplest means of obtaining selectivity, is made easier by the availability of the necessary data in practical form, such as nomograms, data tables or manuals. Girardi, Guzzi and Pauly,[47] in a manual for sensitivity calculations, choose, among the different (n, γ) reactions occurring in the irradiation of stable nuclides with thermal neutrons, a number of reactions which are most used for activation analysis. They calculate under specified experimental conditions the counting rate of the γ-photopeaks of the radioisotope formed from 1 μg of irradiated element. Plots of saturation and decay curves are also given to help in the comparison of reference conditions with others. Budjoso and Kardos[48] report, in tabular form, saturation and decay factors and saturation activities under reference conditions. Benson and Gleit[49] and Ricci[50] give nomograms for the calculation of neutron induced radioactivities. Isenhour and Morrison[51] have studied a computer programme based on an iterative approximation process to optimise irradiation and decay times for activation analysis of any element in any mixture, regardless of its complexity.

The availability of high flux reactors (neutron fluxes of the order of 10^{14} neutrons . cm^{-2} . sec^{-1}) has brought to attention some possible errors which are typical of high flux reactors. Thus, Ricci and Dyer[52] have studied the interferences of second order reactions. Forty-two cases have been found in which these reactions can interfere significantly. In 23 cases the amount of the interference has been computed and is presented in graphical form. Both resonance and thermal neutron reactions were considered. Maslov[53] has taken into account not only the second order reactions but also the burnout of the stable nuclei during irradiation and the interferences from fast neutron reactions. Corrections are made in terms of auxiliary coefficients which can be computed from a knowledge of the nuclear parameters. Tables of these values are given.

Errors from differences in the neutron dose received by sample and reference because of resonance and thermal neutron absorption have been evaluated by Högdal,[54] Gilat and Gurfinkel[55] and by Reynolds and Mullins.[56] These last authors also take into consideration the enhancement of thermal flux by moderation within aqueous samples. The results support the well known fact that large errors can be made when sample and reference have widely different composition. They also give a means of correcting the results obtained, subject to certain limitations. The use of an internal standard[57,58] can increase the accuracy considerably, or a comparator similar in composition to the unknown must be prepared.[59]

The use of comparators can be avoided by applying absolute methods. These methods have not been used very much in the past, mainly because of lack of accurate knowledge of cross sections and because of the difficulty of doing absolute activity measurements. With the use of γ-ray spectroscopy at least the second difficulty can be overcome. In a study on activation analysis by means of the absolute method it was shown that even in the geometry-counting conditions which are often used in activation analysis, absolute γ-ray counting can be accurate enough in many cases for analytical use. Neutron-flux monitoring is also sufficiently accurate, if the irradiation position is well thermalised. Thus, the major source of error is still the knowledge of activation cross sections. The overall error was found lower than 10% in 11 cases out of 13.[60]

Methods which are intermediate between the absolute and the relative methods are those in which the activation of the elements is determined once for all under specified experimental conditions. A neutron-flux monitor irradiated with the unknown sample is then used to refer the experimental conditions to the reference ones. In neutron-activation analysis the use of these methods is practical when dealing with isotopes with a very short half-life[61] or when a large number of elements is determined in a single irradiated specimen. They are also common routine practice when space in the irradiation capsule is restricted or the flux gradient within the capsule is very high, as is the case of 14 MeV neutron activation or γ or charged particle activation. In a recent study on the application of the single comparator method to thermal neutron activation[62] the effect of the resonance component of the neutron energy spectrum has been investigated. It was shown that considerable variation of the neutron energy distribution can be tolerated in many cases without a prohibitive change in the analytical accuracy. Moreover, an accurate choice of the neutron-flux monitor in relation to the elements analysed can increase considerably the possibilities of the method. The precision attained in a few typical analyses was comparable with that obtained with the relative method.

The resonance component of the neutron-energy spectrum can also be used advantageously to increase the selectivity of the irradiation for elements with high resonance activation integrals. Selective resonance neutron activation, obtained by cutting the unwanted thermal flux with suitable filters, has not been used extensively up to now, although promising results were obtained in some cases.[63,64] The accurate knowledge of the resonance flux of the reactor can simplify considerably the preliminary work. For this purpose sets of resonance neutron monitors which cover the entire resonance region have been proposed and applied.[65,66]

Threshold reactions occurring with the fast neutron component of the reactor flux are also used advantageously in many cases. Again, the accurate knowledge of the neutron spectrum is essential in planning experiments with reactor fast neutrons

The proceedings of the 1963 Congress on Neutron Dosimetry[67] give full information on the measurement of fast neutron fluxes. Graphs of cross sections of threshold reactions *vs.* neutron energy have been published by Liskien and Paulsen.[68]

Fast neutron generators and neutron isotopic sources

Elements with atomic number lower than 10 cannot easily be determined by activation with thermal neutrons. Other activating particles (fast neutrons, charged particles, γ-photons) often afford a simple means of determining these elements.

The determination of oxygen, in particular, has been studied extensively, because of its importance and of the difficulties found by conventional techniques in determining trace oxygen levels. In Table I a summary of different nuclear methods used for this purpose is given. In the case of analysis done by means of 14-MeV neutrons the main advantage is that adequate sensitivity is obtained without the use of expensive installations, such as nuclear reactors or accelerators. With a basic price of $30–50,000 a complete automated system can be set up, capable of determining oxygen down to 10–50 ppm in a few minutes, and available for other analytical uses without additional expenditure.

TABLE I.—ACTIVATION-ANALYSIS METHODS FOR DETERMINATION OF OXYGEN

	Nuclear reaction	Source of activating particles	Half-life of product	Observations
1	$^{6}Li(n, \alpha)^{3}H$ $^{16}O(t, n)^{18}F$	nuclear reactor (tritons from secondary reaction)	112 min	on intimate mixtures of sample and lithium metal or a lithium compound, blank correction is necessary, which limits the sensitivity
2	$^{16}O(n, p)^{16}N$	14-MeV neutron generator	7·3 sec	very simple, non-destructive, sensitivity 1–10 ppm on 10-g samples.
3	$^{16}O(\gamma, n)^{15}O$	particle accelerator (Bremsstrahlung rad.)	2·02 min	sensitivity ~0·05 ppm on 1-g samples
4	$^{16}O(p, \alpha)^{13}N$ $^{18}O(p, n)^{18}F$	particle accelerator (protons)	10·1 min	reaction on ^{18}O is more used; sensitivity 0·01 ppm on 1-g samples
5	$^{16}O(\alpha, 2n)^{18}Ne$ $^{16}O(\alpha, d)^{18}F$ $^{16}O(\alpha, pn)^{18}F$	particle accelerator (α-particles)	112 min 112 min	sensitivity $\sim 10^{-3}$ ppm
6	$^{16}O(^{3}He, p)^{18}F$ $^{16}O(^{3}He, n)^{18}Ne$	particle accelerator (^{3}He ions)	112 min	very small samples are required (1 mg or less), sensitivity ~0·01–0·001 ppm
7	$^{16}O(d, n)^{17}F$ $^{16}O(d, \gamma)^{18}F$	particle accelerator (deuterons)	66 sec 112 min	

Although 14-MeV neutron generators do not have the performances of a nuclear reactor from the standpoint of neutron flux attainable, their low cost, easy operation and maintainance will undoubtedly extend their analytical applications. Problems of considerable industrial interest which have already been studied are, for example, the determination of additives in lubricating oils[69] and the determination of oxygen, carbon, aluminium and silicon in coal.[70] Many firms produce neutron generators and most of them offer complete activation-analysis systems, including neutron generator, neutron-flux monitor, rapid pneumatic transfer and complete counting systems, thus minimising the start-up difficulties. General information can be obtained from the books already mentioned and from the references which follow.

Tables of sensitivity for different elements when activated with 14-MeV neutrons were published by Gillespie and Hill.[71] Schulze[72] in discussing the radionuclides formed by (n, γ), $(n, 2n)$, (n, p) and (n, α) reactions with fast neutrons showed that for most elements, with the exception of 23, there exist some characteristic nuclides which are produced by one element only. He also pointed out that cross sections are known for only one third of the 850 possible reactions, and extrapolated new cross section data for 25 (n, γ) reactions. Cross sections for $(n, 2n)$, (n, p) and (n, α) reactions are also presented, obtained by applying empirical formulae. Experimental and calculated cross sections are tabulated for most stable elements. A collection of all the published data of cross sections for 14-MeV neutrons was also published by Neuert and Pollehn.[73]

An experimental approach was used by Aude and Laverlochere.[74] They irradiated samples of 50 elements with 14-MeV neutrons and measured the γ-spectra obtained under normalised irradiation and counting conditions. A catalogue of spectra and a table of comparative sensitivities were thus obtained. The presentation as a manual makes this catalogue very handy for laboratory use.

The techniques of 14-MeV neutron activation are still under development, because many drawbacks must be overcome to exploit completely the inherent possibilities of these machines. Neutron fluxes attainable at present are approximately 10^9 neutrons. $cm^{-2} . sec^{-1}$ at the irradiation position. Efforts are being made to increase both neutron flux and target life. This last presently finds its limits in the loss of available tritium from the target when high deuteron currents are used to obtain the maximum flux.

An overall view of the problem of accelerator targets designed for the production of neutrons can be obtained from the proceedings of a meeting held in 1964 at Liege under Euratom sponsorship.[75] The simplest means of increasing the target life is an increase of the depth of the tritium layer. The loss of tritium is thus partially compensated by the diffusion of tritium from inside the target. Target systems in which only a small part of the target is exposed to the deuteron beam and is constantly renewed by a rotating device are also used. Target reloading is applied in a commercially produced neutron generator to increase the target life.[76] The reloading is accomplished by changing the ion beam from deuterium to tritium when the generator is not used or by operating the generator with a gas reservoir containing a mixture of deuterium and tritium. In this last mode of operation a constant neutron output is obtained which is roughly one third of that in conventional operation.

The dissociation pressure of rare earth hydrides has been studied as a function of temperature by Redstone and Rowland,[77] who believe that rare earth targets can stand temperatures 200° higher than normal titanium or zirconium targets, thus showing promise of longer-lived targets for high flux production. Another way of increasing the life of the target is to lower the target temperature by improving the characteristics of the cooling system. Rethmeyer and Meulen[78] found that much higher heat dissipation with water cooling can be obtained by improving the contact of the cooling water with the target support. They increased the contact surface and suggested the use of silver as the target support and of filtered cooling water. The use of liquid air or liquid nitrogen both as static coolant or in a flow system increases the heat dispersion respectively by a factor of 10 and 100.[75] Bombarding power of the order of 1000 W should be reached for thin conductive targets by using liquid nitrogen as dynamic coolant.[79] It must be noted also that too low a temperature of the target will slow down the diffusion process which contributes to the maintenance of a longer half-life with thick targets.[75]

Apart from the increase of the neutron flux, other improvements can be introduced to make 14-MeV neutron activation a practical routine analytical tool. A high flux gradient exists at the irradiation position, which can be a considerable source of error when sample and comparator are irradiated simultaneously. The positioning of the irradiation capsule must be accurately reproducible from run to run, if sample and comparator are not irradiated simultaneously. The neutron flux must be monitored accurately in this last case, to check its constancy or to introduce correction factors. A summary of different methods of flux monitoring was given by Iddings.[80] The neutron counting rate can be measured by means of a count rate meter with an R–C integrating time constant equal to the mean life time of the radioisotope measured. Variations of neutron flux during the irradiation of each individual sample are thus compensated.[81] The flux gradient can also be partially compensated by spinning the sample during irradiation with an air jet.[81] The problem of irradiating sample and comparator in exactly the same way has been overcome by Guinn and Steele[82] with a similar spinning technique: sample and comparator are irradiated simultaneously in two parallel pneumatic systems and spun during irradiation. They are then transferred and counted simultaneously in two identical counters. A metal wire inserted along the axis of cylindrical samples has also been used as a flux monitor. Errors from self-shielding for materials with large absorption cross section are thus greatly reduced.[83]

An interesting approach to constant neutron output over long periods of time coupled with simplicity and maintenance-free service are the sealed-tube neutron generators. Studied primarily as low-flux machines for applications where space available was restricted, such as for oil-well logging, their performances are rapidly improving and are approaching those of open tube neutron generators with lower basic price and lower maintenance cost. Tubes with a constant neutron output of 10^{10} neutrons.sec are now commercially available and research is proceeding towards 10^{12} neutrons.sec.[84–86] Fig. 1 shows one of these sealed-off neutron generators.

Operating characteristics

Gas pressure	15 μ
Ion source power	500 w at 20 Mc/s
Target voltage	100 kV
Total tube current	1·5 mA
Suppression voltage	375 V
Neutron output	10^{10} neutrons.sec
Life	100 hr

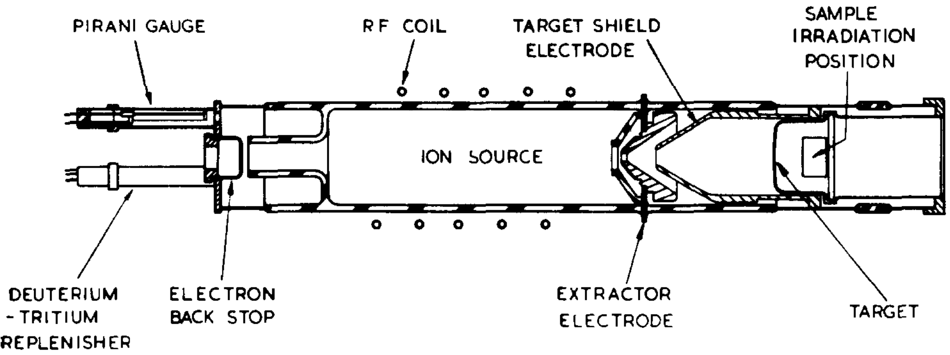

FIG. 1.—Schematic drawing of a sealed-off neutron generator (by courtesy of J. D. H. L. Wood, S.E.R.L. Baldock, U.K.)

Isotopic neutron sources have interesting applications in problems where sensitivity is not the prime factor.[87,88] Summaries of the type of sources available and their analytical applications are given by Strain and Lyon.[89,90]

A promising type of neutron isotopic source is based on the reaction $^{18}O(\alpha, n)^{21}Ne$, obtained by passing ^{18}O as a gas over an α-source. The neutron yield is at present not higher than that of the more conventional neutron isotopic sources, but they have the advantage that the neutron ouptut can be regulated and stopped at will by regulating the flow of ^{18}O. They can, therefore, be positioned and handled safely without any particular care.[90]

Activation with γ-photons

High energy γ-photons obtained as "Bremsstrahlung" radiation from electron accelerators have distinctive advantages over reactor neutrons in a certain number of analytical problems and particularly in the determination of light elements. The use of γ-activation is nevertheless limited, mainly because high energy electron accelerators ready for analytical use are not as readily available as nuclear reactors.

Schweikert and Albert[91] have recently summarised the advantages of γ-irradiation. These are the possibility of selective irradiation, high penetration of the γ-photons and the possibility of resolving problems difficult or impossible with other techniques. They have irradiated, with photons of 18–27 MeV, 24 elements and measured the induced activities under specified experimental conditions. They then calculated the analytical sensitivities, which were below 1 μg for most of the elements studied. It is interesting to note that the sensitivity is low for elements which are highly neutron absorbing, such as boron, cadmium, hafnium, tungsten and manganese, which are, therefore, ideal matrices for γ-activation.

Engelmann[92] has summarised the results of a lengthy experience with routine analysis of oxygen, carbon and nitrogen, particularly for the control of zone-melting purification of beryllium. Sulphur and phosphorus interfere with the determination of oxygen because they give upon (γ, pn) and (γ, n) reaction ^{30}P, which cannot be easily distinguished from ^{15}O, which is used to determine oxygen by (γ, n) reaction on ^{16}O. Because the three reactions have widely different thresholds, the problem can be resolved non-destructively by irradiating sample and comparators with γ-rays of three different energies. The amounts of oxygen and sulphur and phosphorus can be calculated from the activity induced during the three irradiations.

γ-Activation has also been used in the analysis of rocks, ores and concentrates, to determine oxygen, carbon and zirconium.[93]

γ-Isotopic sources can be used in the determination of beryllium by a (γ, n) reaction, and commercial beryllium analysers based on that reaction are available. The method has been modified by Goldstein.[94] The use of enriched ^{123}Sb for the production of the γ-source reduces the useless γ-radiation of ^{122}Sb. The use of large $^{10}BF_3$ neutron counter tubes gives a sensitivity sufficiently great so that a γ-source of only 300 mC of ^{124}Sb is used to determine beryllium with a relative standard deviation of 1 % at the 1·5-mg level.

Activation with charged particles

Charged particles as means of activation have interesting applications particularly in the determination of light elements. Their low penetrating power makes them ideal for surface analysis. When bulk analysis is required, the energy of the impinging particle must be suitably increased.

The increase of the particle energy can be, on the other hand, a source of interference. Thus,[95] if 3-MeV protons are used as bombarding particles the measurement of ^{11}C can be used to determine boron by means of the reaction $^{11}B(p, n)^{11}C$. If the proton energy is increased ^{11}C can also be produced by nitrogen with protons of energy higher than 4·2 MeV[$^{14}N(p, \alpha)^{11}C$] and by carbon with protons of about 19 MeV [$^{12}C(p, pn)^{11}C$, $^{12}C(p, d)^{11}C$, $^{13}C(p, t)^{11}C$].

The sensitivity obtained in the favourable cases is very high, often of the order of parts per billion. Protons with energy of 3–30 MeV have been used by Engelmann[96] to determine oxygen, carbon and fluorine. Fleckenstein and Janke have also used protons to determine ^{18}O added as inactive tracer to biological systems,[97] by measuring the induced ^{18}F activity. Marmier[98] used the same reaction, but he measured directly the energy spectrum of protons which are elastically scattered under a certain angle. Because the energy loss depends on the mass of the scattering nuclei, both qualitative and quantitative analysis can be made by measuring the proton spectrum.

The activation of ^{18}O used as inactive tracer has been made by Amiel with another particle reaction: $^{18}O(\alpha, n)^{21}Ne$. The threshold of the reaction is approximately 6 MeV, sufficiently low to permit the use of α-particles obtained from an isotopic source (thoron in this case). The neutrons emitted are counted with $^{10}BF_3$ proportional counters. This method when applied to the scanning of paper chromatograms leads to an automatic unit which should be of value in many biological studies. The sensitivity obtained, which is not the best attainable, is 35 $\mu g/cm^2$ of paper.[99]

Higher sensitivities in oxygen analysis can be obtained with the use of α-particles from a cyclotron: about 10^{-3} ppm with 10 $\mu A/cm^2$ of 44-MeV particles.[96] The method was applied, for example, to the determination of oxygen in high purity silicon.[100]

Accelerated deuterons have been applied to a study of the corrosion of zirconium alloys by steam.[101] Heavy water steam was used and the deuterium pick-up was measured by the reaction $D(d, n)^3He$. By increasing the deuteron energy, information on the deuterium concentration in different depths of the corrosion layer was obtained. Deuterons as activating particles have also been suggested for the determination of magnesium in nodular cast iron.[102]

^3He ions also show promise as activating particles for the determination of light elements. Very sensitive oxygen determinations were made by means of the reaction $^{16}O(^3He, p)^{18}F$ on actinide metal foils,[103] that could not be analysed by other means. The determination of carbon by the reaction $^{12}C(^3He, \alpha)^{11}C$ and of oxygen in gold and silicon are reported by Markowitz and Mahony[104] and the determination in terbium by Ryan, Green and Lowenkaupt.[105]

Charged particles with sufficiently high energy to cause secondary reactions of analytical interest can be obtained from neutron induced reactions. Among them the reaction $^6Li(n, t)^4He$ has found analytical application in the determination of oxygen. In the analysis of oxygen in gallium-arsenide specimens, Bailey and Ross[106] minimised the blank correction because of the lithium used to produce tritons by irradiating thin wafers of GaAs wrapped in lithium metal. Other reactions for producing charged particles of analytical interest have been proposed.[46]

Secondary reactions have also been produced by knock-on particles obtained from collision of fast reactor neutrons with light nuclides in the irradiated sample. Among them protons[107] and deuterons[108] formed in aqueous solutions have been used to activate ^{18}O and ^2H, used as inactive tracers, by means of the reactions $^{16}O(d, n)^{17}F$ and $^{18}O(p, n)^{18}F$.

RADIOCHEMICAL SEPARATIONS

Radiochemical separations are in many cases necessary to achieve the sensitivity required. There has undoubtedly been in recent years a certain trend towards the elimination of radiochemical separations or at least towards limiting them to the minimum required for an instrumental discrimination, mainly by γ-ray spectrometry. As a result many simple and selective procedures have been developed, which can often be carried out in a few minutes without difficulty by untrained personnel. These separations are based on a large variety of techniques, each of them having their own field of application.

Dissolution of sample

Most radiochemical separations start from dissolution of the sample, although in certain cases some chemical separations can be done directly from the solid state.

Thus, metals with low vapour pressure, such as cadmium, mercury and indium, can easily be vacuum distilled in a matter of minutes with high yields and good radiochemical purity.[109]

Destruction of the solid matrix with gaseous reagents can also be of interest as a simple and safe means of eliminating highly active matrices. Thus, Reuland and Voigt[110] destroyed sodium-tungsten bronzes by heating them in a stream of nitrosyl chloride or bromine trifluoride. They then determined sodium in the residue. The destruction of organic materials by means of excited oxygen has already been mentioned as an interesting new approach to dry-ashing.

The solubilisation of ashes (or of matrices if wet destruction of organic materials is used) is certainly the most critical point of the entire radiochemical procedure. Often it is not easy to demonstrate that the solution obtained is really representative of the solid sample and that the elements are present in the ionic form requested for the steps which follow. Losses by evaporation, exchange or adsorption, formation of residues or colloids can be sources of error not easily controllable. Losses during the attack of samples have already been dealt with in the past[111,112] and more recently.[113,114] Care should be taken in extending the results reported, because variation in temperature, material of the reaction vessel and nature of the matrix can be sources of rather large variations.

Techniques of radiochemistry

The practice of adding carriers in the dissolution step and measuring radiochemical yields at the end of the separation is still the most used means of avoiding the care which is necessary for quantitative separations of trace quantities. In many cases, however, separations can be carried out by techniques, such as ion exchange or partition chromatography, in an essentially carrier-free state, without losses and with a minimum of care, thus avoiding measurement of the chemical yields.[115] The new technique of "substoichiometric" separation developed by Růžička and Starý[116,117] is, in many cases, a very simple means of attaining constant radiochemical yields which suggests several interesting possibilities.

Precipitation techniques after the addition of carriers are still widely employed to obtain the desired selectivity. A precipitation-centrifugation step is often the most rapid means of eliminating a highly active matrix.[118,119]

Ion-exchange techniques with organic ion-exchange resins are now employed very often in activation analysis. They are particularly suitable for the development of sequential separation schemes (see below). Rengan and Meinke[120] applied ion exchange to the rapid separation of neutron-activated rare earths. The separation was accomplished by adsorbing the rare earths on micro cation-exchange columns and eluting with α-hydroxyisobutyric acid. Separations with peak-to-valley ratios between 50 and 100 in the elution curves were accomplished in about 10 min for rare earth elements with atomic numbers differing by 3 or more. The separation of adjacent rare earths in about 16 min was less complete, but adequate when coupled with γ-ray spectroscopy. An advantage of ion-exchange procedures is easy automation, which, coupled with the possibility of obtaining very high decontamination factors in one-step operations, makes it ideal for remotely controlled removal of highly active matrices.[121,122] A new and more complete edition of Samuelson's book on ion exchange in analytical chemistry has been published[123] and is of a great value in planning separations based on ion exchange.

Inorganic ion exchangers, although they are less commonly employed, give in certain cases highly selective separations, which have been used in activation analysis.[122,124]

Isotopic exchange as first used by Sunderman and Meinke[125] also offers many interesting possibilities for rapid and selective radiochemical separations,[126] which should be more fully exploited. Amalgam reduction and exchange, although of more limited application, can lead in a matter of minutes to the separation of elements, such as cadmium, indium, strontium and bismuth.[127]

Solvent extraction is one of the most popular techniques for obtaining selective separations within reasonable amounts of time. It has been applied to separate a large variety of elements [Cu, Zn, Sc, Ag, Hg, Cr, Mn, *etc.*]. The book by Morrison and Freiser gives the necessary information for solvent-extraction applications, including many detailed procedures for the various elements.[128] A technique which combines in many cases the advantages of solvent extraction and ion exchange is the use of liquid ion exchangers. Chromatographic separations on inert supports impregnated with liquid ion exchangers have been dealt with by Cerrai.[129]

Paper chromatography has often been used in post-irradiation chemical treatments. Techniques for both specific and non-specific colour development of spots have been studied particularly for activation-analysis applications.[130,131] Coulomb and Schiltz have applied paper chromatography to the simultaneous determination of many trace elements in geological specimens.[132] The elements were partitioned in bands which were then analysed by γ-ray spectroscopy.

Distillation has gained much popularity in recent years in activation-analysis applications. Some elements [Hg, Cr, Os, As, Sb, Ge, Se, Ru and Mn] can be distilled from various media with high yields. Major advantages are simplicity and relative lack of contamination hazards. A clear-cut separation between distillable and non-distillable elements can be a simple preliminary step to more complex separations.[133]

Electroanalytical methods give the required analytical purity of the separated fractions only in favourable cases, although the use of controlled-potential electrolysis can greatly increase the selectivity.[134] They are, on the contrary, extremely useful to eliminate unwanted radiation in easily remote-controlled, one-step operations.

Sequential separation of many elements

In many cases the determination of more than one element or a complete survey of all possible trace elements is required. Sequential separation schemes can be applied in these problems with considerable saving of time. They are also necessary when the amount of sample available for analysis is at a minimum.

The development of separation schemes for activation analysis can be pursued in two major directions: the first is to attain the separation of individual radioisotopes of the highest radiochemical purity, and use the selectivity of the activity detector as a control of radiochemical purity. The other is to separate the isotopes in groups and leave to the activity detector the job of the ultimate separation. While the second way is certainly time-saving, a well-balanced mixture of isotopes must be present in each group, as one intense activity can completely mask the others. An approximate knowledge of the composition of the sample is required and the scheme cannot be used for different matrices. The sensitivity obtained is also generally lower.

The solutions for the problems of sequential separation are widely different, depending on the nature of the problem under study.

The chemical separation of trace elements from activated high-purity metals has been studied by Albert. In his most recent scheme[135] the systematic use of solvent extraction, resin chromatography and electrolysis techniques has made the scheme simpler, faster and more automatic. Fifty elements are determined on 1-g samples, with detection limits which are always better than 0·1 ppm. Smales[136] separates 10 long-lived elements in 200-mg samples of iron meteorites with a separation scheme based on precipitation, distillation and extraction after carrier addition. The 10 elements are next purified separately to obtain the highest radiochemical purity, which is then controlled by γ-ray spectroscopy. Samsahl[133,137] has set up a scheme in which the elements are firstly split into two groups by distillation. Further separation is obtained within the two main groups by ion-exchange procedures. A total of 15 groups containing more than 40 elements is obtained, which are then analysed by γ-ray spectroscopy. Schemes based on anion exchange have been studied by Girardi and Pietra for aluminium[115] and by El Shamy, Rassoul and Bishay[138] for aluminium and lead. A general scheme completely based on ion-exchange resins was studied by Auboin and Laverlochere[139] for the separation of approximately 30 elements. The elements are separated almost completely and the scheme has been studied in such a way that adaptation to different matrices is easy. Ross[140] has studied a scheme for the determination of 62 possible impurities in aluminium, beryllium and iron. Thirteen of them are determined non-destructively with 10-sec and 20-min irradiations. The other 49 are activated with a 16-hr irradiation, then divided into six groups by a series of rapid radiochemical separations. The final selection within the groups is made by γ-ray spectroscopy. Techniques for the determination of 11 trace metals in petroleum, including sequential radiochemical separations, were studied by Colombo, Sironi, Fasolo and Malvano.[141]

Automation of radiochemical separations

The development of automated radiochemical separations, has been strongly advocated.[126]

Comar and LePoec are studying the automated radiochemical separation of iodine and other elements from biological fluids. The best results[142,143] were obtained with automated equipment in which the following sequence of chemical operations is carried out: adsorption of I^- on anion-exchange resin, washing-out of Cl, Na and Br, elution of I^-, oxidation to I_2, extraction with CCl_4, distillation of I_2, dissolution in NaOH and final counting. Fig. 2 shows a schematic diagram of the equipment. The overall time of the separation is 10 min and 40 samples/day can be dealt with automatically.

Girardi, Merlini, Pauly and Pietra[122] are studying the automation of radiochemical separations of different elements by employing ion-exchange resins, inorganic ion exchangers and partitioning agents on inert supports. A machine to perform a series of elutions from columns connected initially in series, then automatically disconnected to continue the elution separately was developed. The main advantage of the machine is its modular conception, which facilitates the adaptation to different problems.

Samsahl[144] has developed an ingenious and simple machine for fast separation on ion-exchange resins, in which instead of adsorbing on one column and eluting with eluting agents of different concentration, the separation is carried out by adsorbing the elements from different concentrations of the same medium on different columns connected in series. The variation of concentration is obtained by introducing, between one column and the next, a stream of eluting agent of appropriate concentration, which is thoroughly mixed with the active solution to obtain the desired final concentration.

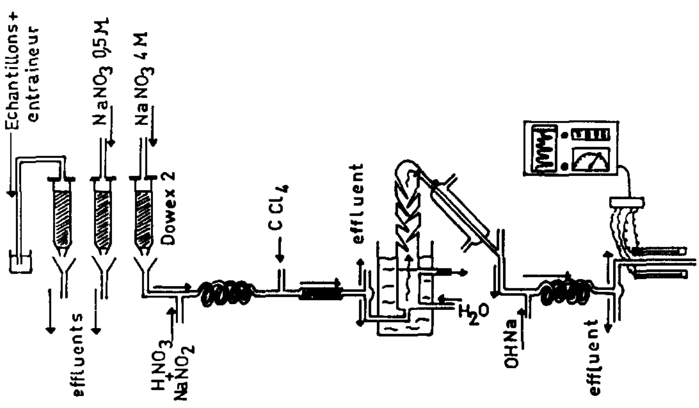

FIG. 2.—Schematic drawing of the apparatus for automated radiochemical separation of ^{128}I from irradiated biological fluids

(by courtesy of D. Comar, CEA Saclay, France)

Automated radiochemistry is a possible solution of one major problem in biological applications, *i.e.*, the analysis of a high number of similar samples to obtain biologically significant data on concentration and distribution of trace elements in natural samples. The activation of minor constituents, such as manganese, sodium or chlorine, sometimes makes impossible direct instrumental analysis, so that lengthy and hazardous manual radiochemical separations are necessary. Extensive applications of automated radiochemistry depend on the solution of many practical problems, such as development of versatile machines, easy decontaminations, *etc.* These problems are still far from being solved on a general basis, although the first results obtained on specific problems are promising.

RADIOACTIVITY MEASUREMENTS

The measurement of radioactivity has improved in sensitivity, precision and selectivity, more through a number of small refinements in the existing techniques than through spectacular new detectors or instruments.

γ-Ray scintillation spectroscopy

γ-Ray scintillation spectroscopy is certainly the most used technique for the radioactivity measurement. General information on the technique, including a catalogue of γ-spectra obtained with a 4 × 4 in. NaI(Tl) detector, are given in the book on applied γ-ray spectroscopy by Crouthamel.[145]

Recently, two congresses have dealt with the technique of γ-ray spectrometry: the Second Meeting of the Society for Applied Spectroscopy (SAS) and the Ninth Scintillation and Semiconductor Counter Symposium. Only summaries of the papers of the first symposium are available,[146] while full proceedings of the second are published.[147] The applications to activation analysis in the SAS meeting were reviewed by Guinn.[148] The use of electronic computers in nuclear and radiochemistry has been dealt with in a symposium in 1962 at Gatlinburg; full proceedings are available.[149]

Heath has recently published the second edition of his γ-ray spectrum catalogue.[150] The catalogue has been completely revised. In addition to the graphs representing the response of a 3 × 3 in. detector, the data are presented in digital form for the preparation of punched cards, perforated tape or magnetic tape libraries for data analysis. Neutron-deficient isotopes are included. Much useful information, such as tables of detector efficiency, photopeak efficiency, discussion of spectrometer design, electronics, *etc.*, is included in the catalogue. Catalogues of γ-spectra have also been prepared by Anders,[151] Aude and Laverlochere[74] and Girardi, Guzzi and Pauly.[47] All three referred particularly to activation analysis and the determination of sensitivities in different neutron-energy spectra: 14-MeV neutrons,[74] well-thermalised neutrons[47] and the neutron spectrum obtained with the reaction $^{9}\text{Be}(d, n)^{10}\text{B}$ by means of a 2-MeV Van de Graaff, moderated with a 2-ft paraffin cube.[151]

The γ-ray scintillation detector has not been substantially improved recently. The 3 × 3 in. NaI(Tl) detector is still the most used, but larger crystals are employed more often as the technology of the preparation of NaI(Tl) crystals improves, and because the use of electronic computers for the unscrambling of complex γ-spectra makes less imperative the necessity of high resolution detectors. The use of pure and europium-activated calcium iodide detectors was reported by Hofstadter, O'Dell and Schmidt.[152] The advantage over the NaI(Tl) detector is a higher light-output signal, and therefore a higher resolution [5·19% fwhm* for ^{137}Cs as compared with the 7·5% obtained with a similar NaI(Tl) detector]. Difficulties in preparation of the scintillation units limit the thickness of calcium iodide detectors produced up to now, to approximately 6 mm.

In recent years the application of electronic computers to γ-spectroscopy has grown spectacularly. The least squares fitting of a set of library spectra with the unknown spectrum as proposed by Salmon is the most widely used technique.[153] In a recent paper[154] Salmon describes a general computer programme written for the IBM 7030. The programme is designed for maximum flexibility and enough subroutines are included to meet almost any desire of a customer. Least squares fitting programmes have been recently developed especially for activation-analysis problems by Auboin, Junod and Laverlochere,[155] Münzel[156] and Coulomb and Schiltz.[132] Other principles less frequently used for the analysis of complex spectra are iterative spectrum stripping[158] and solution of simultaneous equation systems.[158] A simplified programme based on the determination of photopeak surfaces is used by Borella and Guzzi.[159] Least squares fitting is also used for the analysis of multicomponent radioactive decay curves.[160,161]

The precision of the results obtained by computer techniques is largely affected

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* Full width at half maximum.

by drifts of detectors, amplifiers and pulse-height analysers, because of large variation of the γ-counting rate or to temperature changes. Also, drifts of the zero setting of the analyser cannot be neglected in many cases. Much effort was, therefore, spent in recent years in stabilising the γ-ray spectrometers, both by improving the characteristics of detectors and associated electronics and by developing subsidiary drift control units.

The requirements of γ-ray spectrometers for spectrum stripping or computer calculations have been dealt with by Guinn and Lash,[162] who indicate a number of possible sources of error and how to control them, within certain limits. The detector stability has been studied by Covell and Euler,[163] who have measured the amplification drift *vs.* counting rates of many commercial photomultipliers. Detectors which are guaranteed for a stability better than 1 % for changes of the counting rate from 1,000 to 10,000 cps are now commercially available. Crouch and Heath[164] report a series of tests developed and used to evaluate and calibrate performance parameters of analysers, such as analogue-to-digital converter accuracy, stability, integral and differential linearity and zero and bias shifts. Covell[165] has described a technique of periodic quality controls for both establishing and maintaining instrument stability over long periods of time. The use of periodic control tests is of great value to keep the performances of nuclear instrumentation to the level required for analytical use.

It is thus demonstrated that a careful choice and use of the γ-spectrometer system is essential to obtain γ-ray spectra of the quality required for computer calculations. The presence of a drift control unit in the γ-spectrometer is also of great help. Many solutions of this problem have been proposed. All of them are based on the control of the position of a reference peak, which may be a γ-peak in the spectrum under study or from a radioactive source counted simultaneously with the unknown, an electronic pulse or a light pulse. A correction signal is obtained, which is used to modify in the appropriate direction the zero or amplification controls. The stabilisation of γ-ray spectrometers against zero and gain drifts was discussed in detail by Dudley and Scarpatetti[166] who also give complete references to previous works. The drift control system proposed by these authors assures a constancy of peak-to-channel numbers to a few hundredths of a channel out of 200 channels, which approaches the theoretical limit set by statistical fluctuations.[167] Drift control units are also commercially available.

The electronic computer itself affords a simple means of normalising a spectrum which was obtained under slightly different conditions from those of the reference spectrum.[168,169] In a recent commercial multidimensional analyser, provisions to change the baseline and gain of the γ-spectra recorded are included.[170]

One of the problems, which also is of considerable importance in activation-analysis applications, is the reduction of the Compton continuum. The method originally proposed by Pierson[171] has been considerably improved by DeSoete and Hoste[172] by using a plastic detector provided with a lead grating and mounted perpendicular to the γ-ray detector, instead of the anthracene detector mounted at a 180° angle used by Pierson. By this means the compensation is adequate up to 2·7 MeV γ-rays, the backscatter is considerably reduced and the decrease of efficiency is limited to 14%.

The method of using an annular detector mounted in anticoincidence with the central principal detector, to count any escaped photon, has the additional advantage of decreasing the background counting rate. Plastic scintillators or NaI(Tl) crystals are used as the annular guard detectors. Perkins[173] uses 4 × 6 in. detectors surrounded by a 11–1/2 × 12 in. NaI(Tl) annular guard detector. A background reduction of 5–10 times is obtained. With two 4 × 6 in. detectors mounted in coincidence within the guard annulus he is able to detect by γ–γ coincidence extremely small amounts of radioactivity with a high selectivity. A multidimensional analyser is used to obtain in one measurement the concentration of ^{46}Sc, ^{60}Co, ^{64}Cu, ^{72}Ga, ^{106}Ru, ^{124}Sb, ^{140}Ba and ^{140}La which could not be measured by simple γ-ray spectrometry.

β-Counting

The great advantages of γ-counting and γ-spectroscopy over β-counting have limited the application of β-counting in activation analysis to those cases in which the radiochemical purity of the source is certain. The high efficiency of β-counting also make this technique preferable in many cases when the highest sensitivity is required. Liquid scintillation β-counting, for example, can lead to almost 100% efficiency. A review on developments in liquid-scintillation counting was made by Rapkin.[174]

The counting of high energy β-particles by means of a Cerenkov detector has recently received attention as a simple means of discriminating low amounts of high energy β-particles in a highly radioactive field of low energy β- and γ-particles. It is thus possible, for example, to use the fast flux of a nuclear reactor to induce the reaction ^{16}O(n, p)^{16}N and measure the 10·3-MeV β-particles of ^{16}N even if the induced activity of the samples is considerable.[175]

Neutron counting

Neutron counting has received attention in recent years as a radiation detector for activation analysis in certain problems. Its use has been outlined by Amiel.[176,177] Counting delayed neutron emission from fission products is a simple and selective means of measuring fissionable elements. If the sample is of natural origin and it is irradiated with thermal neutrons, the concentration of ^{235}U can thus be measured. Irradiation with and without cadmium screens can lead to the determination of both ^{235}U and ^{238}U.

The delayed neutron precursor ^{17}N can be produced from ^{17}O and ^{18}O by (n, p) and (n, d) reactions induced by a fast neutron flux. When ^{6}Li is present the tritions produced by (n, α) reaction can lead to ^{17}N through other reactions: ^{18}O(t, α)^{17}N and ^{15}N(t, p)^{17}N. The measurement of ^{17}N can then lead to the analysis of lithium, ^{18}O or ^{15}N with different and controlled experimental parameters. Both ^{18}O and ^{15}N are important stable tracers for oxygen and nitrogen.

Neutrons can also be produced by (γ, n) reaction on beryllium and deuterium with γ-rays with energy higher than 1·67 and 2·23 MeV, respectively. The emission of photoneutrons can then lead to the determination of beryllium or deuterium, or alternatively of γ-emitting isotopes, if the unknown γ-source is surrounded by a beryllium block or a deuterated compound in which the neutron counters are embedded. Among the γ-emitting isotopes which can be measured by this technique are ^{24}Na, ^{56}Mn, ^{37}S, ^{49}Ca, ^{38}Cl and ^{28}Al. Neutrons induced by (γ, n) reaction on ^{18}O with an α-isotopic source can lead, as has been said already, to a simple means of measuring ^{18}O.

Semiconductor detectors

Semiconductor detectors have entered the field of nuclear detection quite recently with very promising results. Properties and applications of these detectors were discussed by Goulding.[178] The methods and problems related to the construction of silicon and germanium lithium-drifted detectors were described by Bertolini, Cappellani and Restelli.[179] A survey of commercially available detectors and preamplifiers was recently published by *Nucleonics*.[180]

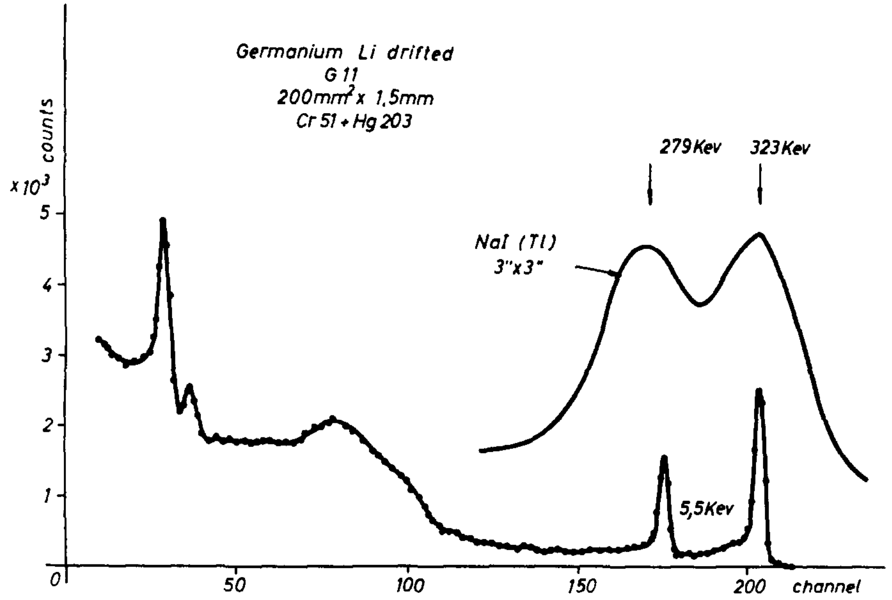

FIG. 3.—Comparison of resolution of a NaI(Tl) scintillation γ-ray detector and a lithium-drifted germanium semiconductor detector for the 279-KeV γ ray of ^{203}Hg and the 323-KeV γ-ray of ^{51}Cr
(by courtesy of G. Restelli, Euratom, Ispra, Italy)

The most interesting use of semiconductor detectors in activation-analysis problems is γ-ray spectroscopy, where the lithium-drifted germanium detector has a resolving power much higher than the NaI(Tl) scintillator. A resolution of 7 keV for 2·75-MeV γ-rays has been obtained by Tavendale,[181] whereas a good 3 × 3 in. NaI(Tl) detector has a resolution of only 100–120 keV for the same γ-ray energy. Fig. 3 shows a comparison of the separation obtained between the 279-keV γ-ray of ^{203}Hg and the 323-keV γ-ray of ^{51}Cr, by a 3 × 3 in. NaI(Tl) detector and by a germanium lithium-drifted detector.

Drawbacks of semiconductor detectors are at present the necessity of operating them in vacuum at liquid nitrogen temperature and their low efficiency for high energy γ-rays, resulting from the small size of the detectors. In the case outlined in Fig. 3 the efficiency was, respectively, 0·25 and 25 % for the germanium and the NaI(Tl) detectors. As a consequence of their small dimensions Compton scattering is the prevailing effect (above approximately 150 keV) and a high Compton continuum is present in the γ-spectra. The small size of the detectors also makes single and double escape peaks from high energy γ-rays particularly evident over the high Compton scattered background. Tavendale[181] reduced the background by three orders of magnitude with the use of a triple-crystal spectrometer in which two NaI(Tl) scintillators detect the escape of 511-keV annihilation quanta in coincidence with a pair event occurring in a central germanium detector.

Applications of semiconductor detectors to activation analysis are still few. Their use as a practical analytical tool is largely conditioned by the availability of larger detectors, and to a smaller degree by the availability of semi-conductor materials that could be operated at room temperatures, *e.g.*, gallium arsenide.

AUTOMATED SYSTEMS OF ACTIVATION ANALYSIS

A certain degree of automation has already been reached in the different steps of the activation-analysis line: activation, γ-spectrometry and computer calculation of results and, to a minor extent, radiochemical separations. The automation of the entire activation-analysis sequence is, therefore, feasible and in many cases it should lead to a highly economical exploitation of the technique.

Automated activation-analysis systems for the determination of oxygen are now produced commercially and the application of similar systems to a wide range of analyses of industrial interest should increase considerably.

A unique example of a completely automated system capable of handling more than 4000 samples/day has been developed at the Texas A. & M. University. In the Mark II system[182] different sources can be used for activation: a nuclear reactor, a 14-MeV neutron generator or a 88-in. cyclotron. The samples are then measured non-destructively by γ-ray spectroscopy by means of three 4×4 in. NaI(Tl) detectors which are drift-stabilised and coupled with 400-channel analysers, while a fourth detector dynamically subtracts the background. Magnetic tape read-out and an IBM 709 computer make possible the calculation of weights in a few seconds. The system should be capable of resolving those many important problems which require that thousands of similar samples be elementally analysed rapidly and accurately at reasonable cost.

Automation is the essential requirement for lunar and planetary surface compositional analysis, and work is under way to set up the necessary equipment in many laboratories in the U.S.A. The complete activation-analysis system should be essentially constituted of a 14-MeV neutron generator, a scintillation detector, a multichannel analyser and the necessary read-out and telemetering units. For general description of the status of the problem the reader should refer to references 183–186.

Another field where automation is essential is process-stream monitoring. Although nuclear methods based on absorption or scattering of radiation have the evident advantage of immediate answer, neutron activation can be employed in those cases in which the half life of the radioisotope formed is short enough not to cause an unacceptable delay on the production line. A method for plant stream monitoring was proposed by Anders,[187] who also indicated a number of elements which produce by fast or thermal neutron activation radioisotopes which are sufficiently short-lived for stream analysis. A technique for stream analysis and preconcentration of copper minerals was proposed by Ramdohr.[188]

Zusammenfassung—Es werden die verschiedenen Arbeitsweisen der Aktivierungsanalyse erörtert und eine Übersicht über neuere Verbesserungen in den Grundlagen oder der Methodik gegeben. Über Entwicklungen auf verwandten Gebieten wie der Radiochemie oder der γ-Spektrometrie wird nur berichtet, wenn sie sich speziell auf die Aktivierungsanalyse beziehen. Besondere Anwendungen der Aktivierungsanalyse auf verschiedenen Gebieten wurden nur berücksichtigt, wenn sie zu Verbesserungen der Methodik führen. Literatur über Anwendungen wird angegeben.

Résumé—On considère les différentes techniques d'analyse par activation et passe en revue les récents perfectionnements fondamentaux et techniques. On ne mentionne les développements dans les domaines s'y rattachant, tels la radiochimie et la spectrométrie γ, que lorsqu'il y a référence spéciale à l'analyse par activation. On n'a pas passé en revue les applications spécifiques de l'analyse par activation aux différents domaines, à moins qu'elles ne conduisent à des améliorations de la technique. On donne des références bibliographiques sur les applications.

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SHORT COMMUNICATIONS

Polarography in neutral fluoride solution with particular reference to lead

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TRACE amounts of lead have a detrimental effect on the creep-resisting properties of nickel-base[1] and other high-temperature alloys and it is desirable to know the lead content of such alloys. Lead can be determined spectrophotometrically in many of these alloys after a solvent extraction separation, but a fast, direct method for lead would be attractive. This paper outlines a direct polarographic method, which should be suitable for the determination of trace amounts of lead in high-temperature alloys of low iron content.

EXPERIMENTAL

Apparatus

Polarograph. A Sargent model XV polarograph was used. The micro-range extender for this instrument was occasionally employed.

Dropping mercury electrode. This was constructed from a 15-cm length of "Veridia" Pyrex glass capillary tubing of 60-μ bore obtained from Chance Brothers Limited, Birmingham, England.

Polarograph cell. This was a Meites-type H-cell with a saturated calomel electrode in the electrode compartment and an agar-saturated potassium chloride bridge. Fifty ml of solution were used in the solution compartment. The cell was immersed in a tank thermostatically controlled at 25·0°. Oxygen-free nitrogen was used to free the solution from dissolved oxygen.

Reagents

Hydrofluoric and nitric acids, ammonium fluoride and aqueous ammonia were of analytical-reagent grade.

Standard lead solution. This was exactly $10^{-2}M$, prepared from the appropriate weight of analytical-reagent grade lead nitrate crystals, of which the lead content had been previously determined by complexometric titration with standard EDTA solution. The lead solutions used in obtaining the calibration graphs were prepared from this standard lead nitrate solution by dilution with $5M$ neutral ammonium fluoride solution and water.

RESULTS AND DISCUSSION

Previous polarographic investigations for 28 metallic ions in $0{\cdot}1M$ hydrofluoric acid–$0.1M$ ammonium fluoride[2] had shown that lead ions produced a reversible reduction wave at $-0{\cdot}402$ V *vs.* the saturated calomel electrode. Metallic species, which were reduced in the vicinity of the lead and which would, therefore, interfere with a lead determination, were thallium(I) $E_{\frac{1}{2}} = -0{\cdot}455$ V, uranium(VI) $E_{\frac{1}{2}} = -0{\cdot}51$ V, iron(III) $E_{\frac{1}{2}} = -0{\cdot}52$ V and molybdenum(VI) $E_{\frac{1}{2}} = -0{\cdot}53$ V. Because ions of metals in the +3 and higher oxidation states are complexed strongly by fluoride, while most singly- and doubly-charged ions are only slightly complexed,[3] it was decided to investigate the polarographic properties of metallic ions in a more strongly complexing solution, namely $1M$ ammonium fluoride at pH 7; it was expected that in such a base electrolyte the half-wave potential for the reduction of iron(III)—iron being a common constituent of high-temperature alloys—would be moved to a considerably more negative potential, while the half-wave potential for lead would be only slightly more negative than before. The half-wave potentials for molybdenum(VI) and uranium(VI) in $1M$ ammonium fluoride at pH 7 were also expected to be considerably more negative than the values quoted above because of the increase in pH from 3·2 for $0{\cdot}1M$ hydrofluoric acid–$0{\cdot}1M$ ammonium fluoride, to 7·0.

In practice, these hopes were realised and polarographic data for 35 ions in $1M$ ammonium fluoride at pH 7 are given in Table I. Another advantage of $1M$ ammonium fluoride at pH 7 as base electrolyte is that polarograms can be recorded using a dropping mercury electrode (D.M.E.) constructed from a Pyrex glass capillary, which is not attacked by fluoride ions at pH 7. With $0{\cdot}1M$ hydrofluoric acid–$0{\cdot}1M$ ammonium fluoride, glass capillaries are attacked immediately and satisfactory polarograms cannot be produced with them. The data previously reported for 0·1*M* hydrofluoric acid–0·1*M* ammonium fluoride were obtained with a Teflon dropping mercury electrode constructed according to the method of Raaen.[4] Although such a D.M.E. is perfectly satisfactory for acidic fluoride solutions, its construction demands considerable manipulative skill and most analytical chemists would prefer to buy glass capillaries rather than construct their own Teflon capillary.

TABLE I

Element	$E_{1/2}$, V	$E_{1/4} - E_{3/4}$, *m*V
Silver	>0	—
Copper(II)	Overlapping double wave, about +0.02; −0.16	Waves cover 0·35 V; incomplete separation of first wave from mercury wave.
Iron(II)	(1) about −0·06†	Incomplete separation from mercury wave
	(2) −1·44	63
Vanadium(V)	(1) About −0·12; small wave with maximum.*	Wave covers range −0·06 to −0·60 V.
	(2) −0·79; small wave	140
	(3) −1·40	100
Bismuth	−0.265	35(19)
Tin(II)	(1) −0·412†	−34(−28)
	(2) −0·703	29(28)
Lead	−0·453	30(28)
Thallium(I)	−0·463	54(56)
Tellurium(IV)	−0·52	140
Cadmium	−0·614	27(28)
Antimony(III)	−0·74	95(19)
Iron(III)	(1) −0.77(III → II)	160(56)
	(2) −1·47(II → 0)	100
Uranium(VI)	Overlapping double wave, −0·80; −1·11	Waves cover range −0.5 to −1·4 V.
Nickel	−1·05	71
Zinc	−1·148	54(28)
Tellurium(VI)	−1·24	85
Selenium(IV)	−1·28	100
Cobalt(II)	−1·32	110
Titanium	−1·37	95(56)
Arsenic(III)	About −1·40; maximum present.*	Wave covers range −1·1 V to final rise at −1.8 V.
Rhenium(VII)	About −1·44; Maximum present.*	Wave covers range −1·2 V to final rise
Vanadium(IV)	Overlapping double wave, −1·45; about −1·68	Waves cover range −1·2 V to final rise
Gallium	−1·50	About 120(19)
Manganese(II)	−1·55	About 40(28)

† Oxidation wave.

* This maximum was not completely suppressed with the maximum permissible concentration of Triton X-100 or gelatine, namely 0·004% w/v and 0·1% w/v, respectively.

The reduction waves for antimony(V), chromium(III), niobium(V), tin(IV) and tungsten(VI) started just before the ammonium ion wave. There were no reduction waves for arsenic(V), indium, molybdenum(VI), selenium(VI), tantalum(V) and zirconium.

The concentration of all ions was 2 × 10^{-4}*M* except for bismuth where a saturated solution (<2 × 10^{-4}*M*) was used.

The figures shown in parenthesis are the $E_{1/4} - E_{3/4}$ values expected for reversible reductions.

In 1*M* ammonium fluoride at pH 7, reduction waves for vanadium(V), thallium(I), tellurium(IV) and uranium(VI) interfere with the lead wave as does the oxidation wave for tin(II). Equal molar amounts of copper, bismuth, cadmium, antimony(III) and iron(III) have no interfering effect on the lead wave, but appreciably larger amounts of copper and bismuth will cause difficulty in the determination of lead using a d.c. polarograph. Interference from cadmium, antimony(III) and iron(III) occurs when the molar ratios of these elements to lead exceed 10:1, 4:1 and 4:1, respectively. There is no interference from the other 24 ions.

Thallium and uranium are unlikely to be present in high-temperature alloys and it may be possible to arrange for vanadium, tellurium and tin to be in the +4, +6 and +4 oxidation states, respectively, where they no longer interfere.

In $1M$ ammonium fluoride at pH 7, the diffusion current was found to be directly proportional to lead concentration, as expected, in the ranges 10^{-5} to $10^{-4}M$ and 10^{-6} to $10^{-5}M$. In the range 10^{-5} to $10^{-4}M$, the standard deviation of the error in diffusion current was 0·0059 μA, which corresponds to a relative standard deviation of 0·9% at a lead concentration of $10^{-4}M$. In the range 10^{-6} to $10^{-5}M$, where the micro-range extender was employed, the standard deviation of the error in diffusion current was 0·0014 μA, corresponding to a relative standard deviation of 2·0% at a lead concentration of $10^{-5}M$. The error in diffusion current is expressed by i_d(measured) − i_d(calculated), where the values of i_d(calculated) are points exactly on the straight-line calibration graph of diffusion current *vs.* concentration.

Lead in high-temperature alloys often occurs in amounts less than 50 ppm and the authors' instrument was not sufficiently sensitive to determine such small amounts of lead. One nickel–titanium addition alloy containing 92 ppm of lead, was, however, analysed by the method described below, where the micro-range extender was employed on the Sargent recording polarograph. A lead content of 86 ppm with a standard deviation of 11 ppm was obtained. This corresponds to polarographing a lead solution of concentration $1{\cdot}65 \times 10^{-6}M$. A much more precise result would have been obtained with a more sensitive polarograph.

The lead content of the alloy (92 ppm) had been originally determined by solvent extraction of the lead from an ammoniacal cyanide–tartrate solution at pH 9·5 with a solution of dithizone in carbon tetrachloride, followed by spectrophotometric measurement of the lead dithizonate complex.

Method for analysis of the nickel-titanium alloy

Dissolve 0·2 g of alloy in 5 ml of concentrated hydrofluoric acid plus 1 ml of concentrated nitric acid. Evaporate the solution just to dryness and dissolve the residue in 5 ml of concentrated hydrofluoric acid. Re-evaporate the solution just to dryness. Dissolve the residue in 25 ml of $2M$ hydrofluoric acid and add concentrated ammonia solution until the pH is 7·0 when determined with a pH meter. Dilute the solution to 50 ml in a graduated flask. Record a polarogram for this solution over the range of 0 to −1·0 V against the saturated calomel electrode and measure the diffusion current of the lead wave in microamps. Determine the concentration of lead in the solution from a suitable calibration graph and hence calculate the amount of lead in the alloy.

CONCLUSION

The authors are of the opinion that this work performed with a d.c. polarograph indicates that direct polarography in $1M$ ammonium fluoride adjusted to pH 7, in association with a differential cathode ray or pulse polarograph, could be employed for the precise determination of lead in high-temperature alloys in amounts greater than 1 ppm. Parts per million of trace metals in alloys have already been determined using a square wave polarograph.[5] With such instruments it is reasonable to expect that a much greater iron(III):lead ratio could be tolerated.

Acknowledgements—We are indebted to Riyadh University, Saudi Arabia, for providing one of us (A. G. H.) with a maintenance grant. We thank Jessop-Saville Ltd. for supplying us with a nickel–titanium alloy of known lead content.

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Summary—The polarographic behaviour of 35 ions in $1M$ ammonium fluoride solution adjusted to pH 7 has been investigated. In this base electrolyte lead is reduced reversibly and, except for considerably larger amounts of copper, bismuth, cadmium, antimony(III) and iron(III), the only ions interfering with the d.c. polarographic determination of lead are vanadium(V), thallium(I), tellurium(IV), uranium(VI) and tin(II). By arranging for vanadium, tellurium and tin to be in the +4, +6 and +4 oxidation states, respectively, interference from these elements could be eliminated and a selective polarographic method for lead is available.

Résumé—On a étudié le comportement polarographique de 35 ions en solution dans le fluorure d'ammonium 1 *M* ajusté à pH 7. Dans cet électrolyte de base le plomb est réduit réversiblement et, sauf lorsqu'il y a des quantités considérablement plus élevées de cuivre, bismuth, cadmium, antimoine(III) et fer(III), les seuls ions qui interfèrent dans le dosage du plomb par polarographie en courant continu sont le vanadium(V), le thallium(I), le tellurium(IV), l'uranium(VI) et l'étain(II). En amenant le vanadium, le tellurium et l'étain aux degrés d'oxydation +4, +6 et +4 respectivement, on peut éliminer l'interférence de ces éléments et disposer d'une méthode polarographique sélective du plomb.

Zusammenfassung—Das polarographische Verhalten von 35 Ionen in 1 M Ammonfluoridlösung bei pH 7 wurde untersucht. In diesem Trägerelektrolyten wird Blei reversibel reduziert. Außer beträchtlich größeren Mengen Kupfer, Wismut, Cadmium, Antimon(III) und Eisen(III) stören die gleichstrompolarographische Bestimmung von Blei nur Vanadin(V), Thallium(I), Tellur(IV), Uran(VI) und Zinn(II). Bringt man Vanadin, Tellur und Zinn auf die Oxydationsstufen +4, +6 und +4, ist die Störung durch diese Elemente beseitigt und Blei kann selektiv polarographisch bestimmt werden.

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Determination of aluminium by homogeneous precipitation of basic aluminium benzoate

(*Received* 16 *June* 1965. *Accepted* 5 *August* 1965)

HOMOGENEOUS methods of precipitation are well established and their uses and advantages have been thoroughly reviewed by Gordon, Salutsky and Willard.[1]

To give a readily filterable form of aluminium hydroxide Willard and Tang carried out the precipitation in the presence of succinate ion, claiming that this gave the densest precipitate of several anions chosen.[2] There is, however, the disadvantage that the basic aluminium succinate forms a tenaciously adherent film on the walls of the beaker and this must be dissolved in hydrochloric acid and reprecipitated with aqueous ammonia.

The modification described in this paper, namely, the use of benzoate rather than succinate buffer, overcomes this objection and enables the aluminium to be precipitated quantitatively as basic aluminium benzoate in a single operation. The crystalline precipitate is not as dense as the basic succinate but it can be filtered rapidly and washed efficiently; furthermore, any deposit on the walls of the beaker is easily removed mechanically.

EXPERIMENTAL

Reagents

Standard aluminium solution. Pure aluminium (0·8848 g) was dissolved in dilute hydrochloric acid and this solution was diluted to 1 litre.

Benzoate buffer. Ammonium chloride (48 g) and benzoic acid (18 g) were dissolved in 2 litres of water.

Résumé—On a étudié le comportement polarographique de 35 ions en solution dans le fluorure d'ammonium 1 *M* ajusté à pH 7. Dans cet électrolyte de base le plomb est réduit réversiblement et, sauf lorsqu'il y a des quantités considérablement plus élevées de cuivre, bismuth, cadmium, antimoine(III) et fer(III), les seuls ions qui interfèrent dans le dosage du plomb par polarographie en courant continu sont le vanadium(V), le thallium(I), le tellurium(IV), l'uranium(VI) et l'étain(II). En amenant le vanadium, le tellurium et l'étain aux degrés d'oxydation +4, +6 et +4 respectivement, on peut éliminer l'interférence de ces éléments et disposer d'une méthode polarographique sélective du plomb.

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Procedure

pH of precipitation of basic aluminium benzoate. To 350 ml of the buffer solution were added 3 g of urea and 50 ml of the standard aluminium solution which had been neutralised by adding aqueous ammonia until there was a faint permanent precipitate, followed by just enough dilute hydrochloric acid to redissolve the precipitate. The solution was brought rapidly to boiling point, then kept on a steam bath for the duration of the experiment. Samples (20 ml) were taken at intervals, cooled rapidly and the pH determined at 25° with a glass-electrode system. After filtration the aluminium remaining in solution was determined with Aluminon.[3]

Determination of aluminium. To 350 ml of the benzoate buffer were added 3 g of urea and the standard aluminium solution containing 0·01–0·05 g of aluminium (made just acid). The solution was brought rapidly to the boil, kept on a steam bath for 1·5–2 hr, filtered through a medium paper and the precipitate washed thoroughly with 1% ammonium nitrate solution. The paper and precipitate were then ignited to constant weight at 1250° in a platinum crucible and the product weighed as Al_2O_3.

RESULTS AND DISCUSSION

As a result of several experiments it was found that precipitation of aluminium was invariably complete at pH 3·7 and that there was a sufficiently slow increase of pH with time. In a series of experiments using the same volume of solution, the pH after 60 min was remarkably constant. There was some variation depending on the amount of aluminium present: pH 3·7 for 0·08 g of aluminium oxide to pH 4·1 for no aluminium.

The results of a typical experiment are given in Table I.

TABLE I

Time, *min*	pH at 25°	Aluminium in solution, *mg of* Al_2O_3/400 *ml*
30	3·15	6
50	3·63	0·2
55	3·70	<0·01
60	3·80	<0·01
90	4·00	<0·01
120	4·08	<0·01

Similar experiments were carried out using phthalic acid and monosodium phosphate buffers but, although the aluminium could be precipitated quantitatively, there were other disadvantages compared with the benzoate method.

A comparison of the well-established ammonia method,[4] the succinate method and the benzoate method was carried out. Any precipitate which could not be mechanically removed from the walls of the beaker was ignored, because it was felt that the complication introduced by dissolving and reprecipitating was not warranted. The error occasioned by this procedure was so great with the succinate method with amounts of aluminium less than 0·05 mg of aluminium oxide that the method became useless. The precipitates were ignited to constant weight at 1250°.[5]

TABLE II

Al taken, *g of* Al_2O_3	Al_2O_3 found, *g*		
	Ammonia	Succinate	Benzoate
0·0836	0·0835	0·0834	0·0840
	0·0833	0·0827	0·0835
	0·0838	0·0810	0·0841
			0·0834
0·0337	0·0332		0·0337
	0·0331		0·0337
	0·0335		0·0339
			0·0338
0·0167	0·0150		0·0168
	0·0160		0·0169
	0·0166		0·0165

The results given in Table II show that the benzoate method is at least as reliable as the ammonia method and is much faster.

Effect of beryllium

It was hoped that the close control of pH obtainable by the hydrolysis of urea in the presence of the benzoate buffer would permit the determination of aluminium in the presence of beryllium, because the figures quoted by Britton[6] show that beryllium hydroxide is precipitated at a higher pH than aluminium hydroxide.

Using the method described for aluminium it was found that even at pH 4·3 no beryllium hydroxide was precipitated in the presence of benzoic acid and because aluminium hydroxide was completely precipitated at pH 3·7 it seemed possible to effect a separation. Using 330 ml of the benzoate buffer solution, 3 g of urea, 50 ml of standard aluminium solution, 20 ml of standard beryllium chloride solution (equivalent to 0·0360 g of beryllium oxide) and boiling gently for 90 min, the pH rose to 4·0. The precipitate was filtered, washed with 1% ammonium nitrate solution, adjusted to pH 4·0 and ignited to constant weight at 1250°. Beryllium remaining in the filtrate was determined by precipitation with aqueous ammonia and igniting to BeO.

The ignited aluminium precipitate was fused with sodium carbonate, in which beryllium oxide is insoluble. In this way it was shown that 0·0038 g of beryllium oxide coprecipitated with the aluminium. Treatment of the beryllium precipitate in the same way showed that no aluminium was coprecipitated, *i.e.*, all the aluminium had been precipitated at pH 4·0.

A series of experiments was carried out using various quantities of aluminium and beryllium, but keeping the total volume at 400 ml by taking the appropriate volume of buffer solution.

The results are given in Table III.

TABLE III

Amount taken, g			Amount found, g		
Al as Al_2O_3	Be as BeO	Total	Al_2O_3	BeO	Total
0·0834	0·0360	0·1194	0·0867	0·0327	0·1194
0·0834	0·0360	0·1194	0·0872	0·0325	0·1197
0·0834	0·0360	0·1194	0·0854	0·0338	0·1192
0·0834	0·0360	0·1194	0·0869	0·0327	0·1196
0·0834	0·0180	0·1014	0·0864	0·0179	0·1043
			0·0854	—	—
0·0334	0·0900	0·1234	0·0363	0·0871	0·1234
0·0334	0·0360	0·0694	0·0350	0·0342	0·0692
0·0167	0·0900	0·1067	0·0184	0·0891	0·1075

These results show that, in every case, beryllium is coprecipitated with aluminium and that the benzoate and also, of course, the succinate method cannot be used for the determination of aluminium in the presence of beryllium.

It is difficult to explain this coprecipitation of beryllium because the quantity involved appears to bear no simple relationship either to the amount of aluminium or beryllium originally present in solution but it is reasonably constant at 3 mg.

Britton found that the titration curve for beryllium sulphate had two distinct curves in the acid zone, and that precipitation did not occur until pH 5·7, the start of the second zone, *i.e.*, when more than one equivalent of base had been added. The first zone showed little change of pH as the amount of base was increased. This zone corresponds to the formation of $BeSO_4.(BeOH)_2$ and the pH during this state does not rise much above 4. Because the weight of beryllium coprecipitated with aluminium is virtually constant, it is felt that this is a pH rather than an adsorption effect and that for some reason which is not readily explicable, beryllium hydroxide starts to precipitate as low as pH 3·7, *i.e.*, without the formation of the soluble $Be^{2+}.Be(OH)_2$ species, in the presence of aluminium hydroxide.

It seems, therefore, that these two elements cannot be separated by any method which relies on the precipitation of their hydroxides.

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Summary—Aluminium can be determined gravimetrically by the homogeneous precipitation of basic aluminium benzoate. The benzoate method is more rapid and has other advantages over the basic succinate and ammonia methods. It is concluded that aluminium can never be separated from beryllium by any method which relies on precipitation of their hydroxides or basic salts.

Zusammenfassung—Aluminium kann durch homogene Fällung von basischem Aluminiumbenzoat gravimetrisch bestimmt werden. Die Benzoatmethode geht schneller und hat noch andere Vorteile vor den Bernsteinsäure- und Ammoniakmethoden. Aluminium kann von Beryllium auf keine Art getrennt werden, die auf der Fällung von Hydroxyden oder basischen Salzen beruht.

Résumé—On peut doser l'aluminium gravimétriquement par précipitation en milieu homogène du benzoate basique d'aluminium. La méthode au benzoate est plus rapide, et a d'autres avantages par rapport aux méthodes au succinate basique et à l'ammoniaque. On conclut que l'aluminium ne peut jamais être séparé du béryllium au moyen d'une méthode reposant sur la précipitation de leurs hydroxydes ou sels basiques.

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Sur un principe de colorimétrie en milieu non aqueux—IV: L'emploi du 2,4-dinitrophénol pour le dosage des acides carboxyliques

(*Reçu le* 8 *Juillet* 1965. *Accepté le* 8 *Aout* 1965)

Les esters *p*-nitrophénylés d'acylamino-acides ont précédemment été obtenus[2] par condensation du carboxyle sur le *p*-nitrophénol en présence de dicyclohexylcarbodiimide. Selon nos essais,* on accède de même aux esters 2,4-dinitrophénylés par action du 2,4-dinitrophénol sur les acides carboxyliques.

La présence des deux groupes nitrés en *méta* permet par ailleurs une identification colorimétrique en milieu non aqueux. Sur un principe précédemment énoncé,[3] il est en effet possible, à partir de l'acide carboxylique, de procéder à la formation de l'ester puis, par l'emploi de solvants convenables, de développer d'emblée une coloration, sans isolement préalable de l'ester ni élimination de l'excès de réactif. Après acylation par le 2,4-dinitrophénol en nitrométhane, et en présence de dicyclohexylcarbodiimide, l'addition d'hydroborure de potassium† en diméthylformamide développe une coloration rouge (560 mμ) qui n'est pas observée en l'absence de carboxyle. La loi de Beer étant satisfaite, des dosages sont possibles sur des prises d'essai de l'ordre de quelques centièmes de milligramme (Tableau I).

La réaction est négative avec l'acide formique. Avec les acides essayés, l'intensité de la coloration obtenue est inversement proportionnelle au poids moléculaire.

Réactif

Mélange à volumes égaux, préparé extemporanément, de solution à 0,5 p. cent de 2,4-dinitrophénol dans le nitrométhane et de solution à 5 p. cent dans le même solvant de *N,N'*-dicyclohexylcarbodiimide préparé selon Amiard et Heymès.[1]

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* Effectués avec la collaboration de Melle M. Pépin.

† Le même réactif a été utilisé pour la colorimétrie des groupes 2,4-dinitrophénylaminés.[4]

Summary—Aluminium can be determined gravimetrically by the homogeneous precipitation of basic aluminium benzoate. The benzoate method is more rapid and has other advantages over the basic succinate and ammonia methods. It is concluded that aluminium can never be separated from beryllium by any method which relies on precipitation of their hydroxides or basic salts.

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TABLEAU I

Acides dosés	Prise d'essai, en μg, pour obtenir une densité optique de 0,3 en cuve de 1 cm
Acétique	19
Benzoïque	36
Butyrique	29
Déhydrocholique	124
Palmitique	85
Propionique	24

Mode opératoire

A la prise d'essai en solution dans 0,5 cm^3 de nitrométhane, on ajoute 0,3 cm^3 de réactif puis, après homogénéisation et repos pendant 15 mn à température ordinaire et à l'obscurité, on ajoute 3,5 cm^3 de solution à 0,1 p. cent d'hydroborure de potassium dans le diméthylformamide. Lecture immédiate à 560 mμ par rapport à un témoin sans acide carboxylique (ce témoin est coloré en vert).

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Résumé—Les tests d'identification en milieu non aqueux qui ont été précédemment décrits (*Talanta*, 1960, **5**, 216; 1961, **8**, 556; 1961, **8**, 619) ont été étendus au dosage des acides carboxyliques sous forme d'esters 2,4-dinitrophénylés. Ces esters développent, en effet, sans extraction préalable ni élimination de l'excès de réactif, une coloration rouge par action d'hydroborure de potassium en solvant nitrométhane-diméthylformamide. Les prises d'essai sont à l'échelle de quelques centièmes de milligramme.

Summary—The quantitative tests in non-aqueous media which have been previously described (*Talanta*, 1960, **5**, 216; 1961, **8**, 556; 1961, **8**, 619) have been extended to the determination of carboxylic acids in the form of their 2,4-dinitrophenyl esters. Without either extraction or elimination of the excess of reagent, a red colour is developed in nitromethane-dimethylformamide by using potassium borohydride. Determinations are possible on the hundredths of a milligram scale.

Zusammenfassung—Die früher beschriebenen (*Talanta*, 1960, **5**, 216; 1961, **8**, 556; 1961, **8**, 619) quantitativen Bestimmungen in nichtwäßrigen Medien wurden auf die Bestimmung von Carbonsäuren als Dinitrophenylester ausgedehnt. Ohne Extraktion und Entfernung des überschüssigen Reagens entwickelt sich mit Kaliumborhydrid in Nitromethan-Dimethylformamid eine rote Farbe. Hundertstel Milligramme können bestimmt werden.

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Coulometric reduction of iridium(IV) in perchloric acid media

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One of us has previously reported on the coulometry of iridium[1] and noted that fuming of iridium(IV) with perchloric acid before coulometry yielded high results when calculated on the basis of a one-electron reduction. The results were consistent with the postulate that fuming gave a partial oxidation to a state higher than iridium(IV). A later communication to this Journal,[2] and also published elsewhere,[3] has implied that this conclusion is erroneous, and has postulated on the basis of experimental work on an unfumed solution that the initial electrolysis product, iridium(III), reacted with perchlorate ion in the bulk electrolyte to regenerate iridium(IV). The high results on coulometry were then explained on the basis of a secondary reduction process involving this regenerated iridium(IV).

We are currently investigating the nature of the iridium species produced by fuming in perchloric acid and we have evidence, supported by other workers,[4-6] that fuming gives partial oxidation to a state higher than iridium(IV). In the course of this investigation we have carried out a large number of coulometric reductions in the presence of perchlorate ion, never observing steady-state currents of the relatively high value upon which the postulate of the secondary reduction process was based. We have, therefore, repeated and enlarged upon the work involving this postulate and wish to report the results of our experiments.

EXPERIMENTAL

Electrolyses were carried out using either a Wenking 61 R Potentiostat or the potentiostat previously employed[1] and patterned after that of Kelley, Jones and Fisher.[7] Electrolysis currents were measured with a precision meter. The electrolysis cell was an H-type double diaphragm cell similar to that described by Meites.[8] The working electrode compartment was stirred in as reproducible a fashion as possible and a continuous stream of nitrogen was passed through the solution being electrolysed. The working electrode was either a mercury pool (25 ml, 19·0 cm^2) or a cylindrical platinum gauze (40 mm × 33 mm diameter) cathode. The reference electrode was a Metrohm (Type EA 402 A) calomel electrode filled with saturated sodium chloride solution. It had a potential of +5 mV *vs.* the usual saturated potassium chloride-calomel electrode at 25°. All potentials reported, in V, are relative to this saturated sodium chloride-calomel electrode. The central and counter electrode compartments of the cell were filled with 0·20M perchloric acid electrolyte and a platinum gauze counter electrode was employed.

Two iridium(IV) stock solutions were used. One solution was prepared by dissolving Na_2IrCl_6 (Engelhard Lot 873) in 0·10M hydrochloric acid. Coulometric titration of this solution showed it to contain 0·526 mg of iridium/ml. Spectrographic analysis of the salt showed no appreciable amounts of other platinum or base metals. The other stock solution was prepared by dissolving $(NH_4)_2IrCl_6$ (Johnson, Matthey and Company Batch 8) in 0·20M perchloric acid and was found to contain 0·486 mg of iridium/ml. This solution corresponded closely to that used in the previous steady-state experiment.[2] The perchloric acid electrolyte was prepared directly from Baker Analysed Reagent (72%). Linde nitrogen (less than 10 ppm of oxygen) was purified by passage over hot (500°) copper turnings, then saturated with water vapour by passage through 0·20M perchloric acid. All other chemicals used were of reagent-grade quality.

For each electrolysis, 80 ml of 0·20M perchloric acid electrolyte were first deaerated, then pre-electrolysed at the appropriate potential. The electrolysis was interrupted, a 10-ml aliquot of the appropriate stock solution added and deaeration continued. Electrolysis was commenced when deaeration was deemed complete. If a mercury cathode was employed, the mercury was withdrawn from the cell during periods of deaeration when current was not flowing.

The final currents obtained, both on pre-electrolysis and iridium(IV) reduction, were sensitive to impurities, but if normal precautions were taken (double-distillation of mercury, purification of nitrogen and careful deaeration of the working electrode solution) they were consistently very small (<10 μA).

Absorption spectra of the electrolysed iridium solutions were recorded in the wavelength range 200–650 mμ on a Bausch and Lomb Spectronic 505 using matched 1- and 10-cm quartz cells.

RESULTS AND DISCUSSION

Duplicate electrolyses using the iridium(IV) stock solution prepared with perchloric acid were carried out on a mercury cathode at −0·35 V. Pre-electrolysis gave background currents of 6 and 2 μA. Initial electrolysis currents were ~1·5 mA and the electrolysis current, i_t, decayed smoothly over 230 min to steady background currents, i_b, of 6 and 3 μA. Plots of log ($i_t - i_b$) *vs.* time were linear down to i_t of 11 and 7 μA indicating a diffusion controlled process. The mass transfer coefficient, λ ($i_t = i_0\, 10^{-\lambda t}$), determined from the slope of the plot had values of $2{\cdot}18 \times 10^{-4}$ and $1{\cdot}88 \times 10^{-4}$ sec^{-1}. Similar results were obtained using the iridium(IV) stock solution prepared with hydrochloric acid.

Electrolyses carried out on a mercury cathode at 0 V gave results similar to those obtained at $-0{\cdot}35$ V, with either stock solution.

Duplicate electrolyses using the iridium(IV) stock solution prepared with perchloric acid were carried out at a platinum gauze cathode at 0 V. Pre-electrolysis gave background currents of 2 and 1 μA. The initial current of $\sim$5 mA decayed to steady background currents of 2 and 1 μA within 70 min. Plots of log ($i_t - i_b$) *vs.* time were linear down to i_t of 2 and 1 μA. The mass transfer coefficient had values of $9{\cdot}00 \times 10^{-4}$ and $8{\cdot}98 \times 10^{-4}$ sec^{-1}. Similar results were obtained using the iridium(IV) stock solution prepared with hydrochloric acid.

In the complete series of electrolyses no final steady-state current of the magnitude previously reported (160 μA) was observed although the mass transfer coefficients were similar. All background currents were small, reproducible and probably from reduction of the acid electrolyte or trace impurities in the electrolyte.

If there was substance to the claim of a secondary reaction between iridium(III) and perchlorate ion, one would expect this reaction to continue in the electrolysed solution on standing. Accordingly, spectra of each of the reduced solutions were recorded immediately upon conclusion of the electrolysis and at weekly intervals of standing in the dark in the presence of air. The initial spectrum showed that iridium(III) was present and indicated none of the strongly absorbing iridium(IV). The changes observed in the spectrum on standing were similar to those reported by Jørgensen[9] and are solely from the hydrolysis of iridium(III).

From the above results one may conclude that the reported secondary reduction process does not occur and no steady-state current of the magnitude reported[2,3] exists.

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Summary—A previous report that high results for the coulometry of iridium(IV) could be explained on the basis of a secondary reduction process is shown to be incorrect.

Zusammenfassung—Es wird gezeigt, dass ein früherer Bericht nicht richtig war, der zu hohe Ergebnisse bei der Coulometrie von Iridium(IV) mit sekundären Reduktionsprozessen erklärte.

Résumé—On montre qu'un rapport antérieur, selon lequel des résultats élevés trouvés lors de la coulométrie de l'iridium(IV) peuvent s'expliquer en se basant sur un processus de réduction secondaire, est incorrect.

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PRELIMINARY COMMUNICATIONS

Titration of acidic cations in molten nitrates with electrolytically generated oxide ions

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It is known that a number of metal oxides are sparingly soluble in molten alkali nitrates.[1] Therefore, the corresponding cations must possess acidic properties, according to the Lux definition,[2] acting as oxide ion acceptors as follows:

$$Me^{n+} + n/2\,O^{2-} \rightleftharpoons MeO_{n/2} \tag{1}$$

While the acidic properties of non-metallic oxides and oxy-anions have been extensively investigated by Shams El Din and coworkers (see, for example, references 3 and 4), the only study of acidic cations is that of Lyalikov *et al.*,[5] who titrated cadmium and lead ions dissolved in molten potassium nitrate by adding weighed quantities of solid potassium hydroxide and following the titration potentiometrically with a glass electrode as indicator.

A study of the properties of acidic cations in molten alkali nitrates has been undertaken. In the present preliminary investigation, in order to test the feasibility of their acidimetric titration, the following cations were examined: Al^{3+}, Be^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}.

An approximately 10^{-3} molal solution of each cation was prepared by dissolving a weighed amount of the appropriate nitrate in about 70 g of a molten equimolecular mixture of sodium nitrate and potassium nitrate at 240°. The titration assembly was similar to the one previously described.[6] The indicator electrode was a piece of platinised platinum foil, over which oxygen was bubbled. The reversibility of the oxygen electrode in nitrate melts has been questioned,[4,7] but because it gives steady and reproducible potential values, it is well suited for analytical purposes. The reference electrode was a silver wire contained in a thin-walled Pyrex-glass bulb filled with a sodium nitrate-potassium nitrate-silver nitrate mixture.[8]

The solutions were titrated with oxide ions produced by constant current reduction of the solvent on a platinum electrode according to the reaction:[9]

$$NO_3^- + 2e \rightleftharpoons NO_2^- + O^{2-} \tag{2}$$

The anode was contained in a separate compartment.[6] It should be noted that, because all the cations to be titrated (except lead ions) were introduced to the solution as hydrated nitrates, and because no effort was made to eliminate water from the melts, the effective titrant is probably hydroxyl ion, because the equilibrium of the reaction

$$H_2O + O^{2-} \rightleftharpoons 2OH^- \tag{3}$$

probably lies well over to the right.[4] The efficiency of the production of base according to reaction (2) was tested by passing a known amount of electricity into a cell containing pure solvent and titrating the alkalinity produced after dissolution in water; it was found to be 100 ± 2%. The nitrite ions apparently do not interfere in the titrations.

The potential of the oxygen electrode was either measured by a Knick model 35 valve voltmeter or recorded by a Sargent model MR recorder; steady potential values were obtained within 3–4 min, except near the equivalence point, when much longer waiting times were needed.

Among the cations examined, those of aluminium, bismuth and iron(III) appeared to be very strong acids, and partially decomposed the solvent with the production of nitrogen dioxide.[10] Apparently, they were neutralised in stages, but the titration curves were poorly reproducible; the (negative) titration errors were always very large. Beryllium, chromium(III) and copper ions appeared to be less strongly acidic, but still gave some solvent decomposition and negative titration errors. The remaining cations produced little or no solvent decomposition, and gave well-defined titration curves, with equivalence points in approximate agreement with the quantities introduced. All the cations gave insoluble oxides (or hydroxides), with the exception of chromium(III) and magnesium, the basic forms of which were soluble. Aluminium ions gave a precipitate which redissolved in excess base.

Some more quantitative results were obtained for zinc and cadmium ions. Solutions of these cations in sodium nitrate–potassium nitrate were prepared by accurately weighing $Zn(NO_3)_2.6H_2O$ and $Cd(NO_3)_2.4H_2O$, which had been recrystallised from water and the composition of which had been checked by EDTA titration. The results are summarised in Table I.

Table I

Cation	Number of titrations	Concentration range (molality)	O^{2-}/Me^{2+} ratio	Standard deviation
Zn^{2+}	5	$2 \times 10^{-4} - 2 \times 10^{-3}$	0·945	0·013
Cd^{2+}	5	$2 \times 10^{-4} - 1 \times 10^{-3}$	1·008	0·008

Cadmium ion is a relatively weak acid, giving a total potential drop of about 450 mV in the titration of a 10^{-3} molal solution, while zinc ion is a stronger acid (potential drop about 700 mV); the negative error in the titration of zinc is, therefore, probably caused by a slight decomposition of the solvent. Because of their different acidity, zinc and cadmium can also be titrated when present together; even in this case, the results obtained were satisfactory for cadmium and low for zinc.

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Summary—The feasibility of the titration of acidic cations in molten sodium nitrate-potassium nitrate with electrolytically generated oxide ions has been tested. Quantitative data are given for the titration of zinc and cadmium ions.

Zusammenfassung—Die Möglichkeit der Titration von sauren Kationen in Natriumnitrat-Kaliumnitrat-Schmelze mit elektrolytisch erzeugten Oxydionen wurde geprüft. Über die Titration von Zink- und Cadium-ionen werden quantitative Angaben gemacht.

Résumé—On examine la possibilité de dosage des cations acides en nitrate de sodium—nitrate de potassium fondus au moyen d'ions oxyde produits électrolytiquement. On présente des données quantitatives pour le dosage des ions zinc et cadmium.

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Dichloramine-T in anhydrous acetic acid as an oxidimetric titrant

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REDOX titrations in non-aqueous media have attracted only limited attention.[1] In this preliminary communication, we wish to report on the use of dichloramine-T (*N,N*-dichloro-*p*-toluene sulphonamide, hereafter abbreviated as DCT) as a new oxidimetric titrant in a non-aqueous medium. This seems to be the first time that a metal-free organic compound is being used as a titrant. The use of DCT in non-aqueous media was suggested by the successful use of chloramine-T as an oxidimetric titrant in an aqueous medium.[2,3]

A 0·2*N* solution of DCT in anhydrous acetic acid, containing 10% of its volume of acetic anhydride, is employed for titrimetric work. This solution is found to be stable when kept in a dark-coloured bottle with attached automatic burette and precautions for the exclusion of moisture.

Preliminary work has shown that the DCT solution can be used to determine, simply and accurately, such diverse reductants as I^-, Fe^{2+}, Sn^{2+}, ascorbic acid, thioglycollic acid, *etc.*, under suitable conditions, employing electrometric and visual indicator methods for detection of the equivalence point. A systematic study is under way and the details will be published later. Other solvents than anhydrous acetic acid, such as acetonitrile, are also being examined as to their suitability.

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Summary—Dichloramine-T in anhydrous acetic acid is proposed as a new oxidimetric titrant in a non-aqueous medium.

Zusammenfassung—Dichloramin-T in wasserfreier Essigsäure wird als neues oxydimetrisches Titriermittel in nichtwäßrigem Medium vorgeschlagen.

Résumé—On propose la dichloramine T en solution dans l'acide acétique anhydre comme nouvelle solution titrée oxydante en milieu non aqueux.

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LETTER TO THE EDITOR

Stability of acidified aqueous solutions of chloramine-T

SIR,

I wish to report some observations on the stability of *acidified* aqueous solutions of chloramine-T, a reagent that has recently commanded some interest in titrimetric analysis.[1-3] Although the stability of "neutral" aqueous solutions (stock solutions) of this reagent has been extensively examined,[1] no quantitative studies seem to have been carried out on the stability of the solutions in acid media. Such a study was, therefore, undertaken, especially in view of the several oxidimetric back-titration procedures which have been carried out employing chloramine-T in acid media.

It is found that decinormal aqueous solutions of chloramine-T may be acidified with sulphuric acid (up to an overall acidity of even $3N$) and may be kept in *tightly-stoppered* vessels for periods as long as 48 hr with only slight deterioration (less than 0·3%). In a typical experiment, when 2·400 mmole of chloramine-T in a $2{\cdot}70N$ sulphuric acid medium was kept aside for 48 hr, the deterioration was only 0·21%. When the acidified mixture is kept in *open* vessels, there is appreciable deterioration, especially when the atmosphere above the liquid is continually renewed by sweeping with an inert gas like carbon dioxide, making the vessel "most open". Under the latter conditions, the deterioration on keeping 2·400 mmole of chloramine-T in a $2{\cdot}70N$ sulphuric acid medium amounted to as much as 3% in only 4 hr. When hydrochloric acid is used instead of sulphuric acid, there is appreciable decomposition even on keeping the acidified mixture in closed vessels.

This relative stability of chloramine-T is in sharp contrast to the instability of hypochlorites in acid media. The present findings are explicable in terms of the equilibria existing in acidified chloramine-T solutions as discussed by Bishop and Jennings.[1]

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16 *August* 1965

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PROFESSOR JAROSLAV HEYROVSKÝ

FOREWORD

The Editorial Board and Publisher of TALANTA take pleasure in honouring the seventy-fifth year of

JAROSLAV HEYROVSKÝ

by presenting this special issue, which is comprised entirely of invited contributions from his former students and associates.

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J. HEYROVSKÝ AND THE DEVELOPMENT OF POLAROGRAPHY

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THE introduction of new techniques often results in sudden changes in the development of scientific disciplines; new techniques open quite unexpected possibilities and vistas. The introduction of a new technique is rarely a consequence of an isolated observation, of the events of a single day, or even of a week. A new technique has its roots, its predecessors, in related techniques and often undergoes development at some stage after its introduction. However, here the generalities and similarities between the fates and progress of various methods come to an end. Some techniques were developed in a hurried succession of events, rapidly became important and remained of importance—even after the original enthusiasm had somewhat deteriorated. Other methods, after initially becoming popular, later slowly (or rapidly) lost this popularity. Still others developed only slowly, in a series of successive steps. There are some techniques where it would be difficult to name a single originator, and others where the author is evident.

This shows that not only "libelli habent sua fata", but also techniques. Amongst all of these histories, that of polarography is probably unique in one respect, namely in the relationship between the method and its originator.

After making their fundamental discovery, some originators of important techniques lost either the interest or the energy for further development, which was left to others. After they developed the technique in question, others turned to further, unrelated projects.

In contrast, Professor Heyrovský, who discovered polarography more than forty years ago, has never lost an active interest in his method. His personal enthusiasm and his choice of similarly enthusiastic coworkers have resulted in the fact that he and his research school have been among the leading groups in the field for the whole of the time from 1922 onwards. His published work, reviews and lectures have reflected the steady growth of interest in the method. Professor Heyrovský early and clearly realised that if he personally did not try to disseminate a knowledge of his method, nobody else was likely to do it for him. Thus, because of his unceasing efforts, polarography is now rated among one of the five most frequently used analytical methods. It can be assumed that, without his determined scientific publicity, polarography would possibly be one of the "Sleeping Beauties" from the analytical point of view—as are, indeed, several other promising physical methods.

Another reason for the broad acceptance of polarography as an analytical method was the fact that Professor Heyrovský always stressed the importance of an understanding of the physical principles involved. His main interest was to explain the observed phenomena, then he let his coworkers work out a quantitative treatment of the theoretical problems. Thus, it would seem that the interest of Professor Heyrovský was more or less academic, but such a contradiction between this academic or "pure science" point of view and the practical, applied aspects is only superficial. It was just this profound understanding of the basic principles and processes governing polarographic currents, which resulted in the wide practical application of the method. Applications were more readily predicted and worked out when the necessary information regarding the fundamental factors was theoretically based than had it been based on empirical observations alone. However, while stressing the importance of fundamental research for his immediate coworkers, Professor Heyrovský clearly realised that perhaps the most important role of polarography in the future was to be played by analytical and other practical applications. Even though he himself rarely worked experimentally on an applied analytical problem, Professor Heyrovský stressed the analytical aspects of polarography in many of his lectures, reviews and books. Hence, polarography gives a good illustration of the now well-established rule that sound development of an analytical method must always be based on an understanding of the underlying principles.

When we are looking for other reasons for the wide acceptance of polarography, we find yet a further contribution by Professor Heyrovský. In the thirties he had started to collect and publish a bibliography of papers dealing with polarographic methods. The work is still continued under his guidance; during the last few years it has been mainly carried out by his wife, Marie. This huge systematic work has made it possible for polarographers all over the world to obtain information about the present state of published work on this method much more easily than for most other methods. With the increasing volume of the chemical literature during the last decade, such a bibliography also plays an important psychological role: it frees the polarographer from the fear that he has missed some important papers concerning his own work. In this respect polarography with its carefully collected bibliography represents a sheltered haven in the present choppy sea of chemical documentation.

In one other aspect of his work Professor Heyrovský has shown a foresight which has also contributed to the wide acceptance of his method. Nowadays, automatically recording instruments are so much a part of the routine equipment of the analytical laboratory that we take them for granted and are not at all surprised that the result of our analysis is recorded. One of the remarkable qualities of the human mind seems to be the tendency to retain only the pleasant memories and to forget the bad ones. It would, therefore, seem necessary to recall the situation before World War II, when recording instruments were rare in analytical laboratories. At that time, when absorption spectra were recorded either by time-consuming photographic methods or measured point by point, the polarograph supplied automatically recorded curves. It was perhaps the first method to illustrate the first steps towards the ultimate in analytical instrumentation, *i.e.*, a black box into which the solution to be analysed is poured at one end and a printed result obtained at the other. The ingenuity of Professor Heyrovský and his first coworker Shikata is shown by the fact that their basic design, used for the first series of five polarographs produced in 1925, remains practically unchanged in all the photographically recording polarographs produced nowadays.

The seventy-fifth year is a time in human life for celebration and expression of feelings. Polarographers all over the world think of Professor Heyrovský with feelings of gratitude and deep respect at this time. Respect for a life full of enthusiasm, for seeing clearly his goal, for a life full of modesty, for the valour to resist the evil: gratitude for the method he has given us, for his example in scientific life, in relations, and in readiness to help others. Those of us who have been fortunate enough to work for some time with him will bear the stamp of his personal influence for the rest of our lives.

It was to express the feelings of at least some representatives of the huge family of polarographers that this volume was gathered. In order to differentiate the reviews included from others which have been published recently, the subject matter of the papers has been centred mainly on a discussion of the kinds of substance which are amenable to polarographic analysis. Applications of polarography to various groups of inorganic and organic species, of low and high molecular weight, are discussed. Special attention is paid to the application of organic solvents both to inorganic and organic compounds, and to applications in molten salts and studies at high pressures; some theoretical papers are also included.

Last, but not least, let us look forward and express all our best wishes to Professor Heyrovský for the remaining quarter of his century.

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POLAROGRAPHY OF ALIPHATIC COMPOUNDS

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Summary—A review of the polarography of aliphatic compounds is presented.

INTRODUCTION

A MAJOR advantage of the polarographic method is its selectivity, which often makes the determination of a compound in a mixture possible without prior separation. The selectivity of the polarographic determination is based on the differences in electrode potential necessary for the occurrence of different electrode reactions. In order to judge which compounds may be polarographically active and which substances may interfere with their determination, a knowledge of the electrode reactions, and the factors which influence these reactions, is necessary.

In the following discussion of the polarography of aliphatic compounds emphasis is laid on the nature of the electrode reactions, and examples of compounds undergoing these reactions are mentioned. In some of the more important applications the merits of the polarographic determination compared to other methods are discussed. Often, however, no one of several applicable analytical methods is clearly preferable, and the choice will depend on the special circumstances or the personal preference of the analyst.

ELECTRODE REACTIONS

A polarographic reduction consists of a transfer of electrons from the cathode to the reducible system coupled with the uptake of the appropriate number of hydrogen ions. The high potential gradient,[1] about 10^8 V. cm^{-1}, in the immediate vicinity of the electrode polarises the reducible molecule and makes the attack of one or more electrons on the reactive centre possible. Although the reaction results in a reduction at a certain place in the molecule it is the properties of the whole molecule which determines the energy necessary for the transfer of the electrons, *i.e.*, the reduction potential. The presence of multiple bonds makes the system more easily reducible, and aliphatic compounds are, therefore, generally more difficult to reduce than aromatic and heteroaromatic compounds.

Under fixed conditions the electrode potential determines the course of the electrode reaction; a more negative potential may make further reduction possible. Other factors, however, also influence the electrode reaction and the necessary reduction potential.

REACTION CONDITIONS

Hydrogen ions are involved in most organic electrode reactions and pH may influence not only the reduction potential but also the course of the reaction. The change of electrode reaction with pH may be drastic as in the case of isonicotinic amide[2] (in acid solution the amide group is reduced to the aldehyde, whereas the pyridine nucleus is reduced in alkaline solution) or slight as in the reduction of androsta-1,4-dien-17β-ol-3-one,[3] which forms different stereoisomeric pinacols in acid and alkaline solution. Sufficient buffer capacity is, therefore, necessary to ensure that the consumption of hydrogen ions in the electrode reaction does not change the pH in the immediate vicinity of the electrode. In non-aqueous, aprotic media the scarcity of protons may change the reduction path. The reduction of carbon tetrachloride in acetonitrile[4] thus yields dichloromethylene, whereas chloroform is formed in most media.

The change in the electrode reaction with pH is often caused by a change in the species reduced. If the molecule has protolytic properties the form reduced in acid solution will carry more protons than the one reduced in alkaline solution. The protonated form is always more easily reducible than the unprotonated one.

The pH around which the reaction changes from a reduction of the protonated to a reduction of the unprotonated form is often not at the pK of the reducible acid. In the acid-base equilibrium the more easily reducible acid is removed from the equilibrium at the electrode by reduction and the conjugate base combines with hydrogen ions to form the acid, which is then reduced. The height of the wave, *i.e.*, the rate of the electrode reaction, is thus in a certain pH region determined partly by the rate of the recombination reaction at the electrode between the base and protons.[5]

This is a special case of the general one where the electroactive species is formed in the vicinity of the electrode by a chemical reaction slow enough to be the rate controlling step for the over-all reaction.[6] Such waves are called kinetic waves and they can be identified as such by their independence of the height of the mercury reservoir and their high dependence on the temperature. This heavy dependence of the height of the wave on temperature and pH makes, in general, kinetic waves less suited for use in a quantitative determination than a diffusion controlled wave.

The concentration of the electroactive compound may influence the electrode reaction. In some instances the reaction involves a slow step before a further reduction, and the intermediate may either be further reduced or react otherwise. The non-electrochemical reaction is often a dimerisation. The rate of the dimerisation would as a second-order reaction increase faster with concentration than the first-order reduction.[7] The polarographically visible result is that the height of the wave grows less with concentration than required by the Ilkovič equation.[8,9]

The course of an electrode reaction should preferentially be proved by a preparative electrolytic reduction at controlled potential, where the products can be identified by conventional means. Often the occurrence or absence of further reduction waves reveals the reduction path, but such evidence is not always reliable. For instance, a slow chemical step in the reaction may result in a diffusion from the electrode of a product which is then transformed to a reducible compound, which would have yielded a further wave in the polarogram if it had remained at the electrode.[10,11]

In the following survey of types of polarographically reducible, aliphatic compound these are classified according to the type of bond suffering reduction in the electrode reaction.

CARBON–CARBON BONDS

Carbon–carbon triple bonds

Only few compounds containing the carbon–carbon triple bond are polarographically reducible. Some derivatives of acetylene-dicarboxylic acid are reduced in two steps, and from the half-wave potential of the second wave the reduction product from the diethyl ester was identified as diethyl fumarate.[12] This means that a trans addition of hydrogen to the triple bond has taken place. In the reduction of the acid a dimerisation occurs and from a preparative reduction racemic dimethylsuccinic acid can be isolated.[12]

Unconjugated acetylenes are not polarographically reducible, but acetylene can on reaction with bromine in acetic acid be transformed into the reducible tetrabromoethane.[13]

Carbon–carbon double bonds

The isolated carbon–carbon double bond is not polarographically reducible under ordinary conditions, but by suitable conjugation a reducible system may be formed. Conjugation with an electron-withdrawing group, *e.g.*, the cyano, carboxamide, carbethoxy, carboxyl or carbonyl group, renders the system reducible in a convenient potential region, whereas electron-donating groups, *e.g.*, an alkyl group, make the reduction more difficult. Thus, derivatives of α,β-unsaturated acids, aldehydes and ketones can generally be determined polarographically. This includes compounds such as acrylonitrile,[14,15,16] acrylamide,[17] acrylates[18] and homologues thereof, derivatives of unsaturated dicarboxylic acids, such as maleic and fumaric acids,[19,20] α,β-unsaturated carbonyl compounds, such as acrolein,[21] citral,[22] α- and β-ionone[22] and methyl vinyl ketone.[23]

The electrode reaction of unsaturated acid derivatives is in general a two-electron reduction of the double bond to the saturated acid. In some cases, *e.g.*, acrylamide[17] and acrylonitrile,[24] the number of electrons in the electrode reaction, *n*, is found to be about 0·2. This low value is explained by a polymerisation of unreduced acrylonitrile, in the vicinity of the electrode, initiated by the initial reduction product, the carbanion, $CH_3\bar{C}HCN$. Under certain conditions a reductive dimerisation of acrylonitrile to adipic nitrile takes place.[25]

The reduction of dimethylmaleic anhydride to racemic dimethylsuccinic acid and dimethylfumaric acid to meso dimethylsuccinic acid show that in both cases a trans addition of hydrogen to the double bond takes place.[12]

The determination of dissolved acrylonitrile in mixtures, *e.g.*, with unsaturated hydrocarbons and saturated nitriles, is faster and more selective than an oxidative titration or a hydrolysis followed by a determination of ammonia and just as accurate. For an analysis of monomeric acrylonitrile in polymeric material the use of *N*,*N*-dimethylformamide as a solvent and tetrabutylammonium bromide as supporting electrolyte is very convenient[15] because of the high solubility of the organic compounds in this solvent.

The polarographic determination of a mixture of maleic and fumaric acid is in many cases preferable to other methods because it is more selective than the oxidative [$KMnO_4$, Ce(IV), Br–Cl], conductometric and acidimetric methods, more accurate than the paper chromatographic one and demands less time and material than a method based on chemical separation. The polarographic method requires, however, a rather strict pH control.[20] In the presence of interfering electroactive substances it may be necessary to precipitate the acids as their barium salts before the determination.[19]

The electrode reaction of α,β-unsaturated carbonyl compounds is a one-electron reduction to a radical which preferentially dimerises at the β-carbon atom to a saturated diketone, but may form a pinacol when a dimerisation at the β-carbon is sterically unfavourable. In methyl vinyl ketone the radical reacts with mercury, thus forming di(3-ketobutyl) mercury.[26]

When considering the method of choice for analysis of these compounds it must be remembered that some of them, *e.g.*, methyl vinyl ketone, are rather volatile, and a deaeration cannot be performed without special precautions.[23] With the polarographic method for instance, a simultaneous determination of pseudo and β-ionone and citral[22] in a mixture is possible, but if the special specificity of this method is not required a bromometric titration may be preferable.

Carbon–carbon single bonds

A carbon–carbon single bond is cleaved by reduction only under special circumstances. The only reported case is in the reduction of 4-cyanopyridine[2,27] in alkaline solution, where cyanide and pyridine are formed. Here the stability of the cyanide ion and the electron-attracting properties of the pyridine ring may be responsible for the cleavage.

CARBON–OXYGEN BONDS

Carbon–oxygen double bonds

The carbon–oxygen double bond is found in several polarographically reducible compounds, such as formaldehyde,[28,29] acetaldehyde,[30] butyraldehyde,[31] glyoxal,[32] sugars,[33,34] pyruvic acid,[35] diacetyl[36] and dehydroascorbic acid.[37]

Two properties of the carbon-oxygen double bond are of major interest in the polarography of carbonyl compounds, *i.e.*, the reducibility and the ease with which it adds nucleophilic reagents. Roughly speaking the two properties are modified in the same direction by a substituent, which is understandable because the electron can be regarded as a nucleophilic reagent and a reduction thus as an addition of a nucleophilic reagent.

The reduction of formaldehyde proceeds easily with a half-wave potential in alkaline solution at −1·6 V *vs.* S.C.E. Substitution of one of the hydrogen atoms with an alkyl group, which is electron donating, lowers the half-wave potential to about −1·8 V *vs.* S.C.E. Substitution of both hydrogen atoms in formaldehyde with alkyl groups lowers the half-wave potential to about −2·3 V *vs.* S.C.E., which can only be measured in a solution containing tetralkylammonium ions as supporting electrolyte. An electron-attracting group, such as the carboxyl or carbonyl group α to a carbonyl group, raises the reduction potential, as in pyruvic acid or diacetyl. A hydroxyl group at the same carbon atom as the carbonyl group makes the compound unreducible unless an electron-attracting group, *e.g.*, carboxyl, is substituted at the carbonyl group, as in oxalic acid.

Additions to the carbonyl group influence the polarographic behaviour of carbonyl compounds in two ways. One is the reversible addition of water or an alcohol to the carbonyl group, thus forming a hydrate or a semiacetal, which is non-reducible. Formaldehyde is very much hydrated, acetaldehyde less, and acetone is practically unhydrated in aqueous solution. In sugars the semiacetal formation is very pronounced. The presence of electron-attracting groups, *e.g.*, chlorine or carboxyl groups, favours hydration of the carbonyl group as in chloral and glyoxylic acid.[38] The reduction wave of a hydrate-forming carbonyl compound is a kinetic wave, where the wave-height is partly determined by the rate of the dehydration.

Another addition reaction is the acid and base catalysed aldol condensation, which is of importance for all aldehydes containing an α-hydrogen atom. The visible result of the condensation is a gradual diminishing of the wave-height of the aldehyde; in acid solution a wave of an α,β-unsaturated aldehyde may be formed because of a dehydration of the primarily formed condensation product.

A further possible complication in the polarography of carbonyl compounds is enolisation.[39] The enol-form is more difficult to reduce than the keto-form.

The electrode reaction of saturated aldehydes is in most instances[31] a two-electron reduction to the alcohols; in some cases a pinacol formation is suspected.[32] Reduction of oxalic acid[40] gives glyoxylic acid, which is partly protected against further reduction by the formation of a hydrate. Similarly, diethyl oxalate is reduced to the semiacetal of glyoxylic acid ethyl ester.[41]

The determination of formaldehyde by polarography has been found preferable in some cases, *e.g.*, in acetic acid[29] or in the reaction mixture after the periodate oxidation of glycols,[42] but in many instances the colorimetric determination with chromotropic acid has advantages.[43]

Pyruvic acid is often preferentially determined by polarography; the choice between this method and a photometric one, using the 2,4-dinitrophenylhydrazone in alkaline solution or after reaction with salicylic aldehyde, depends on the kind of interfering compound present.

The more difficultly reducible or highly hydrated carbonyl compounds are with advantage determined polarographically through their azomethine derivatives.

Carbon–oxygen single bonds

The reduction of a carbon–oxygen single bond has been found in aromatic and steroidal α-hydroxy- and α-acetoxyketones[44,45,11] and in certain compounds such as *o*-benzoylbenzoic acid pseudo ethylester.[46]

CARBON–SULPHUR BONDS

Carbon–sulphur double bonds

The carbon–sulphur double bond is more easily reduced than the carbon–oxygen double bond. Of aliphatic compounds, carbon disulphide,[47,48] dithio-oxamide,[49] dithioformic acid[41] and cyanothioformamide[50] have been found to be polarographically reducible.

Carbon disulphide yields in alkaline solution two polarographic waves; the electrode reaction of the first wave is a two-electron reduction to dithioformic acid[41] and the second one a two-electron reduction of this compound to hydrogen sulphide and an unidentified polymeric material.[41] In acid solution a single four-electron wave is found. The electrode reactions of dithio-oxamide and cyanothioformamide have not been reported.

The polarographic determination of carbon disulphide, as such, is impracticible because the compound is too volatile for a deaeration of the solvent without loss. It is more feasible to let the compound react with a secondary amine and to determine the resulting dialkyldithiocarbamate by anodic polarography[51] or by spectrophotometry.[52]

Carbon–sulphur single bonds

The carbon–sulphur single bond is reducible in some aromatic thiocyanates,[53,11] where the electrode reaction is a reductive cleavage with the formation of cyanide ions[53] or thiocyanate ions[11] and in phenacylsulphonium salts.[54] In the latter case the carbon–sulphur bond was cleaved before the reduction of the carbonyl group. In aliphatic compounds this kind of reduction occurs at too negative a potential to be of analytical value.

CARBON–NITROGEN BONDS

Carbon–nitrogen triple bonds

The carbon–nitrogen triple bond is more difficultly reducible than the carbon-nitrogen double bond. No aliphatic nitrile has been reported to be reduced in the cyanide group, and the only proved example of a polarographic reduction of a nitrile group is the reduction of 4-cyanopyridine to 4-aminomethyl pyridine in acid solution.[2,27]

Carbon—nitrogen double bonds

The carbon–nitrogen double bond is generally reduced at a less negative potential than the carbon–oxygen double bond, which makes it possible to determine many carbonyl compounds through their azomethine derivatives. Unconjugated ketones, for instance, are not normally reducible in the common supporting electrolytes, but they can be determined as their azomethine derivatives. Such derivatives are semicarbazones,[55] different kinds of hydrazone,[56,57,58] oximes[59,60] and imines formed from ammonia,[61] n-butylamine,[62] ethylenediamine[63] or hexamethylenediamine.[63]

The transformation of a carbonyl group into a stable azomethine compound also traps the carbonyl group in a derivative, which is somewhat less apt to hydration, ring formation or condensation.

The electrode reaction of imines is a simple two-electron reduction of the carbon-nitrogen double bond to an amine. The oximes and most hydrazones and semicarbazones are reduced in a four-electron reduction, where the first step is a reductive cleavage of the nitrogen–oxygen or nitrogen–nitrogen single bond.[65,66]

Carbon–nitrogen single bonds

The reductive cleavage of a carbon–nitrogen single bond is only possible under special conditions where two electron-attracting groups are bonded to the same carbon atom. In aliphatic compounds this type of reduction is found in trimethylaminoacrolein perchlorate[67] and 2,2-dinitropropane.[68] In the latter case the reduction in alkaline solution produces 2-nitropropane and nitrite ion, which also is the first step in acid solution. The reaction is here complicated by the reaction between 2-nitropropane and nitrite which forms a reducible "pseudonitrolic acid".

CARBON–HALOGEN BONDS

The reduction of a carbon–halogen bond is important in organic polarography because it occurs in polyhalogenated compounds, *e.g.*, carbon tetrachloride,[69] chloro-, bromo-[70] and iodoform, 2,3-dibromobutane,[69] 1,1,1-trichloro-2-methyl-2-propanol[71] and in α-halogenated carbonyl compounds, such as bromacetic acid[72] and chloral.[73,74] Unsaturated compounds may be transformed into reducible derivatives on addition of bromine.[13]

The ease of reduction of a carbon-halogen bond can be judged from its bond-energy, the carbon-iodine being the easiest and the carbon-fluorine bond the most difficultly reducible. The latter has only been found reducible when it is α to a carbonyl group[75,76] or in an activated trifluoromethyl group.[77] When placed in a ring with fixed conformation, a carbon-chlorine bond in the more stable equatorial position is more difficult to reduce than when placed in the axial position.[76,78] The presence of more halogens at the same carbon atom lowers the reduction potential, and often a step-wise reduction of the carbon–halogen bonds is found.

A double bond in an allylic position favours a reduction, whereas a vinylic halogen is more difficult to reduce than the saturated halogen compound. This parallels the reactivity of the halogen in a polar substitution reaction; in a reduction the electrode may be regarded as the attacking nucleophilic reagent.

The electrode is a "bulky" attacking reagent, and steric hindrance of the attack on the reactive centre makes the reduction more difficult, *i.e.*, requires a more negative reduction potential.[79] The attack of one electron results in the formation of a halide ion and a radical which may dimerise[80] or take up one further electron forming a carbanion. The carbanion can be stabilised in different ways.

The most common way is to abstract a proton from the medium. Such is the case in the reduction of methyl iodide to methane,[69] of allyl bromide to propylene[69] and of carbon tetrachloride to chloroform and this further to methylene chloride.[69] Another possibility for the carbanion is to expel a stable anion, which in a polyhalogenated compound may be done by elimination of a β-halogen as halide ion. The less negative reduction potential generally found for trans vic-dihalogenethylenes compared to the cis-compounds[81,82] reflects the easier trans-elimination. A similar behaviour is found in polar elimination reactions. This kind of reduction is common in vicinal halogen compounds and results in the formation of a double bond; 2,3-dibromobutane is thus reduced to butylene,[69] dibromomaleic acid to acetylenedicarboxylic acid[12] and meso-α, α -dibromosuccinic acid to fumaric acid.[12] Also, in the reduction of carbon tetrachloride in acetonitrile[4] the lack of available protons forces the carbanion, formed initially, to expel a chloride ion in an α-elimination, thus forming dichloromethylene. In some instances competition between an elimination of halogen and a substitution with hydrogen may be expected.

A third kind of reduction route has been found in certain trihalogenmethyl derivatives, which in a six-electron reduction form a methyl compound.[74,77]

The polarographic analysis of the components in a mixture of organic halogen compounds will often be preferable to the less selective methods, *e.g.*, the determination of the halide ions obtained by alkaline hydrolysis or reduction of the halogen compounds, which require a separation of the components before the determination.

OXYGEN–OXYGEN BONDS

Compounds containing an oxygen–oxygen single bond are generally polarographically reducible. Thus, hydroperoxides,[83,84] peracids[85,86] acylperoxides,[87] ozonides, aldehyde and ketone peroxides[88] can be determined polarographically. The electrode reaction is a reductive cleavage of the peroxide bond to two hydroxyl groups.

A convenient medium for the polarographic determination of water-insoluble peroxides is a 1:1 methanol-benzene mixture containing lithium chloride.[89] The dialkyl peroxides are reduced at the most negative potentials with $E_{\frac{1}{2}}$ more negative than $-1{\cdot}0$ V *vs.* S.C.E. in the above mentioned medium. The presence of many alkyl groups shifts the half-wave potential to more negative potentials because of the electron-donating power of these and their shielding of the reactive centre; di-tert-butyl peroxide is thus not reducible in the accessible potential region. Hydroperoxides are reduced in the interval $-0{\cdot}6$ to $-0{\cdot}9$ V *vs.* S.C.E., and the presence of electron-withdrawing groups, *e.g.*, the acyl group, makes diacyl peroxides reducible in the region 0 to $-0{\cdot}2$ V *vs.* S.C.E. The half-wave potential of an organic peroxide is thus valuable in the elucidation of its structure.

The polarographic technique is often the method of choice for a qualitative and quantitative analysis of a mixture of peroxides.[87,90–92] A comparison[93] of this method with the commonly used iodometric and stannous chloride determinations in the analysis of some hydroperoxides showed that the three methods yielded the same results when applied to pure materials, but with impure products the polarographic technique probably gave more reliable results because it is more specific than the chemical methods.

OXYGEN–SULPHUR DOUBLE BONDS

The oxygen–sulphur double bond is reducible in some sulphones[94] and sulphoxides where the electrode reaction is, respectively, a four-electron or two-electron reduction to a sulphide. This kind of reduction is unimportant in aliphatic polarography.

OXYGEN–NITROGEN BONDS

Oxygen–nitrogen double bonds

The oxygen–nitrogen double bond is important in organic polarography, because it is easily reducible without requiring further conjugation. In aliphatic compounds it is found in mononitroalkanes and -alkenes,[95–97] dinitroalkanes,[98] esters of nitric[99] and nitrous acid,[100] *N*-oxides, *N*-nitrosamines[101–103] and nitro- and nitroso derivatives of urea[104] and related compounds.[105–107] All these compounds may be determined polarographically; a reduction of the oxygen–nitrogen double bond takes place in all the compounds, except in the nitrates,[99] the *N*-nitrosamines[103] in alkaline solution, and in some dinitroalkanes.[68] The electrode reaction of alkyl nitrites is not known; they are hydrolysed too rapidly for a preparative reduction.[41]

Nitroalkanes, in acid solution, are reduced in a four-electron reaction to alkylhydroxylamines.[95] This wave is well-defined and very suitable for a quantitative determination of such compounds. The half-wave potentials are in slightly acid solution about $-0{\cdot}8$ V *vs.* S.C.E. The hydroxylamine formed in the first reduction is in slightly acid solution reduced further at a more negative potential to alkylamines. In strongly alkaline solution primary and secondary nitroalkanes are transformed into the non-reducible aci-form, and no polarographic wave is thus seen in this medium.

The polarographic determination of aliphatic nitroalkanes requires little or no separation before the measurement because only a few types of compound are reduced at the same potential. Polarography has thus been found advantageous in the determination of the toxic constituent of "creeping indigo", 3-nitropropanoic acid,[108] because an extract from the plant material could be used directly. Possibly the non-reducibility of nitroalkanes in strongly alkaline solution may be useful in their determination in a mixture containing interfering compounds.

The polarographic method does not, however, distinguish primary nitroalkanes from secondary ones as some of the colorimetric methods are able to do.

Compounds with a nitro group at a double-bonded carbon atom are reduced somewhat differently.[97] The four-electron reduction in acid solution produces an oxime of a saturated aldehyde. At a more negative potential a two-electron wave occurs, which was found to yield an alkylhydroxylamine. Generally, an oxime would be expected to yield an amine in a four-electron reduction.

The polarographic behaviour of components with two nitro groups at the same carbon atom depends on whether or not a hydrogen atom is bonded to the same carbon atom. 1,1-Dinitroethane[98] shows in most solutions two waves; the over-all reduction in alkaline solution requires eight electrons and produces acetamide oxime. In chloropicrin the reduction probably involves both the nitro group and one or more of the carbon-chlorine bonds.

N-Nitrosamines, in acid solution, are reduced polarographically in a four-electron reduction to unsymmetric dialkylhydrazines; in alkaline solution the electrode reaction consumes two electrons and an amine and nitrous oxide are formed by a reductive cleavage of the nitrogen–nitrogen single bond.[103] The wave in acid solution, which at pH 1 is found at about −0·9 V *vs.* S.C.E., is preferable for a quantitative determination of *N*-nitrosamines.

Because secondary amines can be transformed quantitatively into *N*-nitrosamines the polarographic determination of these furnishes a convenient and selective method of determining secondary amines in the presence of aliphatic primary and tertiary amines.[101] Tertiary amines do not interfere, and some nitroalkane or nitrolic acid, resulting from a reaction between nitrite and a carbonium ion formed by reaction between the primary amine and nitrous acid, can be destroyed by dithionite. Compounds such as *N*,*N*-dialkylanilines may be nitrosated at carbon, but such nitroso derivatives are reduced at less negative potentials than aliphatic *N*-nitrosamines.

N-Nitrosamines have also been determined by ultraviolet spectroscopy and by volumetric gas analysis after reduction to hydrazine followed by oxidation to nitrogen; however, the polarographic method has been found to be the most convenient.[102]

With respect to selectivity the polarographic determination of secondary amines through their *N*-nitrosamines compares well with other methods, *e.g.*, the determination through the dithiocarbamates formed on reaction with carbon disulphide; most methods require a prior removal of primary amines by reaction with, for example, salicylaldehyde.

Oxygen–nitrogen single bonds

Polarographically reducible compounds containing an oxygen–nitrogen single bond include alkyl nitrates,[99] such as butyl nitrate, nitroglycerine,[109,110] pentaerythritol trinitrate,[111] and derivatives of hydroxylamine like alkylhydroxylamines, oximes,[59] amidoximes[65,112] and hydroxamic acids.[113]

The alkyl nitrates are reduced to nitrite ion and alcohol in a two-electron reduction.[99] The amidoximes are reduced to amidines,[65] which may be further reducible, and the first step in the reduction of ald- and ketoximes is also a cleavage of the nitrogen–oxygen bond.[65,66] The electrode reaction of aliphatic hydroxamic acids has not been proved, but because *p*-cyanobenzhydroxamic acid and isonicotinichydroxamic acid are both reduced to the amide,[41] which is then further reduced, the aliphatic hydroxamic acids are included in this section.

Alkyl nitrates are reduced at about −0·7 V *vs*. S.C.E. in neutral, aqueous ethanol; the most likely interference would thus be from nitro compounds. The polarographic method has, for example, been found advantageous in the determination of butyl nitrate in diesel oil,[112] where a 2:1 mixture of benzene-methanol with dissolved lithium chloride was used as medium, and, combined with spectrophotometry, in the determination of pentaerythritol trinitrate in a mixture containing nitroglycerine, 2-nitrodiphenylamine and dibutylphthalate.[111]

The determination of aliphatic esters as their hydroxamic acids by polarography seems, in most instances, less preferable than other methods. The alkylhydroxylamines are reducible only in a narrow pH interval and their determination through this wave is unlikely to be widely used. Hydroxylamine and *N*-methylhydroxylamine, however, exhibit an anodic wave at different potentials in alkaline solution,[41] and such anodic waves are more likely to be of value for analytical purposes.

SULPHUR–SULPHUR SINGLE BONDS

A sulphur–sulphur single bond is generally reducible, and compounds such as di-, tri- and tetrasulphides,[115] thiolsulphonates[116] and disulphones[94] can be determined polarographically. Important examples from this group are cystine[117] and its disulphoxide,[118] tetramethylthiuram disulphide,[119] thioethanolamine disulphide[120] and dithioglycolic acid.

The electrode reaction is in all cases a simple cleavage of the sulphur–sulphur bond with the formation of mercaptans and sulphinic acids. The latter are formed from disulphones[94] and thiolsulphonates.[116]

The polarographic method is used as a routine together with other methods in the qualitative and quantitative analysis of different kinds of sulphur compound in naphtha.[121] The polarographic determination of a disulphide is especially valuable, when the mercaptan is also present.[120]

It is less suited for secondary and tertiary disulphides,[122] because their reduction potentials are rather negative, so the diffusion plateau of the waves are poorly developed.

SULPHUR–NITROGEN BONDS

Sulphur–nitrogen double bonds

A reduction of a sulphur–nitrogen double bond occurs in sulphilimines. The electrode reaction is a two-electron reduction to a sulphide and a sulphonamide, which were isolated from a preparative reduction.[41]

Sulphur–nitrogen single bonds

A sulphur–nitrogen single bond, *e.g.*, in sulphonamides, is generally not reducible. However, 4,4′-dithiodimorpholine is polarographically reducible,[41] and the products isolated from a preparative two-electron reduction, in slightly acid solution, are morpholine and sulphur. Probably a reduction of the sulphur–sulphur bond occurs primarily, and the thus formed nitrogen-sulphhydryl compound decomposes. Such an instability may explain that no nitrogen-sulphhydryl compound has ever been isolated.

SULPHUR–HALOGEN BONDS

A sulphur–halogen bond is reducible in sulphochlorides.[123] In some instances the electrode reaction is reported to be a two-electron reduction to sulphinic acid,[123,124] but in other cases a more complicated route involving dimerisation and further reduction has been claimed.[125,126]

NITROGEN–NITROGEN BONDS

Nitrogen–nitrogen double bonds

Aliphatic compounds containing a nitrogen–nitrogen double bond are not as common as the corresponding aromatic ones. Azomethane, prepared by anodic oxidation of *N,N'* -dimethylhydrazine in alkaline solution, is reducible in a two-electron reduction to *N,N'* -dimethylhydrazine.[41] The two compounds do not form a reversible system at the dropping mercury electrode, as their aromatic counterparts do, because there is a difference of about 1 V between the reduction potential of azomethane and the oxidation potential of *N,N'*-dimethylhydrazine.[41] In alkaline solution diazirines are reduced to diaziridines.

Nitrogen–nitrogen single bonds

The nitrogen–nitrogen single bond is often reducible when a neighbour to a double bond. The reduction is thus found in *N*-nitrosamines in alkaline solution[103] and as the first step in the four-electron reduction of phenylhydrazines, semicarbazones and possibly other types of hydrazone in acid solution.[65] In some cases, *e.g.*, the dimethylglycylhydrazone of α,β-unsaturated steroids,[57] the height of the wave, which is twice that of the one-electron wave of the parent steroid, points to a two-electron reduction. The nitrogen-nitrogen bond of diaziridines is reducible in acid solution.[41]

ANODIC WAVES

The dropping mercury electrode is less suited for oxidations than for reductions because the accessible potential region in the positive direction is limited by the potential at which mercury dissolves. The oxidation of the mercury anode occurs at a less positive potential when the medium contains anions forming insoluble salts with mercury.

An extension of the accessible potential interval can be made by using a platinum electrode; the oxidation of the water is then the limiting process. By working in suitable non-aqueous solvents the useful potential region can be extended considerably in a positive direction; for example, compounds as difficult to oxidise as benzene[127] yield voltammetric waves at a platinum electrode in acetonitrile containing sodium perchlorate.

Below, only compounds giving anodic waves at the dropping mercury electrode are discussed. These may be divided into classes according to the functional groups responsible for the electrode reaction. Here a division into oxygen-, nitrogen-and sulphur-containing compounds is made.

Oxygen-containing compounds

The presence of an "enediol" group, -C(OH)═C(OH)-, makes a molecule subject to anodic oxidation. Enediols include compounds such as ascorbic acid,[128] reductone,[129] dihydroxyfumaric acid and dihydroxyacrylic acid. Two electrons per molecule are involved in the electrode reaction in which is produced an α-diketone. This diketone is often hydrated, and the hydrated form is not polarographically reducible. The system enediol-α-diketone is thus not polarographically reversible as is the corresponding aromatic system catechol-*o*-benzoquinone.

The most important member of this group is ascorbic acid and because few compounds are oxidised as easily as ascorbic acid this compound can be determined in the presence of many different kinds of compounds without prior separation. The method is in general more specific than the colorimetric method which responds to many kinds of reducing compound. The sensitivity of a colorimetric method is, however, often higher than the polarographic one.

Nitrogen–containing compounds

Many nitrogen compounds, such as ammonia[130] and some amines,[130] show anodic waves, where the electrode reaction is a formation of a mercurous salt. Many other compounds forming insoluble mercury salts interfere with such a determination.

Hydroxylamines and some hydrazines and hydrazides, aliphatic and aromatic, can be oxidised at the dropping mercury electrode. Phenylhydroxylamine and nitrosobenzene form a reversible system, and the anodic oxidation of *N*,*N*-dibenzylhydroxylamine produces *N*-benzylbenzaldoxime and some benzaldehyde.[65] The electrode reactions of aliphatic hydroxylamines have not yet been proved.

The anodic reaction of hydrazine at a mercury or oxide-coated platinum electrode is dependent on the concentration and produces nitrogen[6] and ammonia. A similar concentration dependence is found in the anodic reaction of isonicotinic hydrazide.[2] *N*,*N*′-dimethylhydrazine is oxidised to azomethane,[41] but the electrode reaction of *N*,*N*-dimethylhydrazine has not yet been proved.

Both hydroxylamine and *N*-methylhydroxylamine can be determined polarographically in a mixture, because their half-wave potentials differ by 0·15 V.[41] Similarly *N*,*N*-dimethylhydrazine or *N*,*N*′-dimethylhydrazine can be determined in the presence of hydrazine, but the waves of the two dimethylhydrazines overlap too much for a determination of the one in the presence of the other. More investigation is needed in order to evaluate the possibilities of the polarographic method compared with other methods in the determination of hydroxylamines and hydrazines.

Sulphur–containing compounds

Molecules containing a thiol group or an enolisable thiocarbonyl group give anodic waves at the dropping mercury electrode and compounds such as mercaptans, *e.g.*, cysteine,[131] glutathion[132] and 2,3-dimercaptopropanol,[133] dithiocarbamates,[119] derivatives of thiourea,[134] including thiobarbiturates[135] and some thioamides,[136] may be determined polarographically. Carbon sulphide can be determined as a dithiocarbamate after reaction with a suitable amine.[51]

The electrode reaction consists of an oxidation of the mercury electrode with the formation of a mercurous salt. Part of the mercurous salt may be adsorbed on the electrode with the occurrence of an adsorption wave. Further complications may arise at higher concentrations.

At a platinum electrode mercapto compounds are oxidised to disulphides at a considerably more positive potential. At this electrode, also, sulphides yield a voltammetric wave; sulphoxides result from the oxidation.[137]

A polarographic determination of thiol compounds is faster than most methods, but may be less accurate; a higher accuracy may be obtained by a polarometric (amperometric) titration. When a determination of both the mercapto compound and the disulphide is wanted, the direct polarographic method is often the method of choice.

Summarising it can be said that the polarographic method is useful in the quantitative and qualitative determination of many compounds and its proved and potential applications are in general not fully appreciated. Polarography is also valuable in the study of reaction rates,[6] as a tool in determination of structures, and for the establishment of the optimum conditions for electrosynthesis.

Zusammenfassung—Es wird eine Übersicht über die Polarographie aliphatischer Verbindungen gegeben.

Résumé—On présente une revue sur la polarographie des composés aliphatiques.

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APPLICATIONS OF POLAROGRAPHY IN HETEROCYCLIC CHEMISTRY

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Summary—A review of the applications of polarography in heterocyclic chemistry is presented.

INTRODUCTION

HETEROCYCLIC chemistry is of the greatest practical importance because it deals with many substances playing an important role in biochemical or pharmacological processes, such as vitamins, alkaloids, antibiotics or chemotherapeutics. Consequently, the group of heterocyclic organic compounds must be rather heterogeneous; this fact brings about serious complications when attempting a systematic approach to the whole group in a textbook or in a review. This is also true with the electrochemical or polarographic behaviour of heterocyclics. In the present review the author will use the classification of heterocyclic compounds as outlined by Albert.[1]

In the late fifties it was the general opinion that the polarographic behaviour of heterocyclic compounds is parallel to that of other organic substances, either aliphatic or aromatic, and is modified only by the presence of the heterocyclic ring. Essentially this conception is not incorrect, and excellent results have been obtained when using it. However, the present state of our knowledge points to the fact that, in addition to the above concept, two important factors are operative with most heterocycles: the first is the adsorbability of heterocyclic substances on the mercury drop, either of the depolariser itself, or of the reaction intermediates and of the reaction products. This property is here more conspicuous than with other organic compounds, and it results in deforming and complicating of the polarograms. The hindrance of the electrode process by the adsorption of the electrode-process participants[2–4] will be shown later. The other factor that affects the wave-form and the value of the limiting current is especially characteristic of nitrogen-containing heterocyclics (not necessarily depolarisers). It is their function as adsorbed proton donors taking part in the kinetics of protonation preceding the electrode process proper.[5,6] The recombination of depolarisers of this type occurs thus almost entirely in a heterogeneous manner.

CLASSIFICATION OF HETEROCYCLES

According to Albert[1] the heterocycles are divided into heteroparaffinic, heteroaromatic and heteroethylenic compounds. The heteroparaffinics, *i.e.*, completely saturated heterocycles are not very important from the standpoint of polarographic investigation, and polarographic reducibility is here rather an exception than a rule. For this reason the group will not be the object of the present article, although at least the interesting case of polarographic reduction of cytostatic ethyleneimino-*p*-benzoquinones should be mentioned.[7] The heteroaromatics, *i.e.*, completely unsaturated compounds, may be divided into two groups: π-deficient heteroaromatics (with nitrogen as the sole heteroelement and a deficit of π-electrons elsewhere) and π-excessive heteroaromatics (with either nitrogen as the sole heteroelement and an excess of π-electrons elsewhere, or with oxygen or sulphur as a heteroelement (with or without nitrogen and with an excess of π-electrons elsewhere). The π-deficient heterocycles (*e.g.*, pyridine, quinoline, acridine, pyrazine, *etc.*) are strongly polarised and react more readily than benzene or the parent aromatic hydrocarbon with nucleophilic reagents (*i.e.*, the electron uptake is easier). The π-excessive substances—mostly five membered nuclei—contain the electron-releasing system =CH—NH—CH=. This group comprises pyrrole, furan, thiophen, *etc.* In pyrazole and imidazol the π-excessive effect prevails, as well as in the five-membered rings with both sulphur or oxygens atoms and nitrogen (for instance thiazole). The heteroethylenics are non-aromatic, unsaturated systems, such as various partially reduced di- and tetrahydroderivatives of heteroaromatic systems on the one hand and six-membered oxygen or sulphur-containing compounds (γ-pyrones, flavones, chromones., *etc.*) on the other. Regardless of the above adsorption effects the kind of heterocyclic ring exerts an essential influence on the polarographic behaviour of the substance under investigation.

POLAROGRAPHIC ACTIVITY AND REVERSIBILITY

The polarographic activity is due either to the heterocyclic ring itself or to an external substituent. In some cases such a separation is rather difficult or even impossible, because the whole system is subject to the electrode process: this may be illustrated by the reduction of 1,2 di(4-pyridyl)ethylene,[3] 1,4-bis[pyridyl-4-vinyl]benzene,[8] cyanine dyes[9] and similar compounds bearing chains of conjugated double bonds in conjugation with the heterocyclic ring. Regardless of this uncertainty, conclusions may be drawn from the reaction products if they are known or have been isolated.

As with the polarographic activity of organic substances in general, four possibilities exist: reducibility, oxidisability, formation of salts or complexes with mercury (*e.g.*, with pyridoxthiol,[10] with barbituric acid derivatives[8,11] and uracils[9,12]) and finally formation of catalytic waves of hydrogen evolution.[13,14] This last effect is characteristic of nitrogen-containing heterocycles bearing a free electron pair on the nitrogen atom which facilitates the reduction of hydrogen ions from the supporting electrolyte. Consequently, the quaternary *N*-alkyl derivatives should be catalytically inactive, but before the formation of the catalytic hydrogen wave they are reduced by a single electron, yielding a catalytically active product.[15] The main subjects of this article are, however, the oxidation and reduction processes.

The ease of reduction of the heterocyclic ring depends on whether it is π-excessive or π-deficient. No reports exist on the reducibility of a π-excessive five-membered ring. In contradistinction to this the π-deficient six-membered rings are readily reducible, often in the absence of electron-attracting substituents or without annelation with benzene rings.

The behaviour of pyridine, the simplest compound among the π-deficient substances, is not quite clear. Although the reduction at negative potentials has been proved, in experiments with periodically changed square-wave voltage, according to Kalousek (oxidisable products[16] are obtained) no convincing reduction-wave of pyridine has been published as yet. Unfortunately, no comparable data obtained under identical conditions can be found in the literature that would reflect the influence of annelation with further benzene rings, of the increase in the number of nitrogen atoms and their mutual position in the ring. A partial insight into the influence of annelation may be obtained from Table I (certain differences in the reaction mechanisms of, for example, acridine and quinoline, *etc.*, must be taken into account). Other proofs are also available. For instance, among the heterocycles containing two nitrogen atoms in the same nucleus, the half-wave potential of quinoxaline[18] with one more benzene ring is about 40 mV more positive than that of pyrazine.[19] The position of the nitrogen atom in the ring is also very important for the ease of reduction: thus at pH 4·9 pyrazine is reduced at —0·74 V, whereas pyrimidine is not reduced sooner than at —1·09 V; unfortunately, no comparable data are available for pyridazine.

TABLE I—POLAROGRAPHIC DATA FOR PYRIDINE-LIKE HETEROCYCLES[17]

Compound	$E_{1/2}$	$\frac{2{\cdot}303\ RT}{\alpha nF}$, *mV*	k_{-1} (β)
Acridine	−1·24 V	188	−0·325
Phenanthridine	−1·64 V	136	−0·518
Quinoline	−1·69 V	160	−0·527
Benzo[f]quinoline	−1·70 V	145	−0·536
Benz[f]isoquinoline	−1·41 V	76	−0·603
	−1·78 V	102	
Isoquinoline	−1·84 V	175	−0·576
Pyridine	−2·07 V	191	−0·841

$n = 2$; 5×10^{-2} *M* $N(C_2H_5)_4$ in 95% dimethylformamide

In addition to activity the concept of reversibility in the electrode processes of heterocycles will now be considered.

Pyrazine and quinoxaline are the simplest heterocyclic depolarisers, having two nitrogen atoms in a single ring, that behave reversibly at the dropping mercury electrode. Their reversibility is in accordance with the general chemical rules on electrochemical reversibility.[20] In reversible systems there is no great difference between the geometrical structure of the oxidised and reduced forms. This is the case with sufficiently long systems of conjugated double bonds. The proton transfer, forming a part of the reaction, leads to the formation of OH or NH double bonds that very easily undergo exchange with the solvent. Before localisation of the electrons, a hydrogen bond between H^+ and the free electron pair of the heteroatom of the heterocyclic ring may occur. The fission of δ-bonds, which do not readily exchange (C–Hal, C—N, N—O, O—O), is irreversible, as is also the formation of the kinetically stable bond C—H or C—C in dimerisations, because these require the localisation of electrons.

Thus, only quinones and, among heterocycles, oxazines, thiazines, *etc.*, are reduced reversibly. In some other heterocycles,[8] there is an additional condition of symmetry of the whole system.* Consequently, for example, only the isomers with at least one 4-substituted pyridine nucleus behave in a reversible manner. The reversibility becomes

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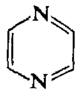
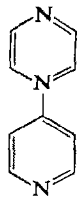
* The only exception known as yet is the reversible reduction of 1,1′-ethylene-2,2′-dipyridylium dibromide.

more pronounced with two 4-substituted pyridine rings. Similarly, pyrazine and quinoxaline are reversible depolarisers, whereas pyrimidine and phthalazine are not:

Reversible depolarisers

Irreversible depolarisers


(I)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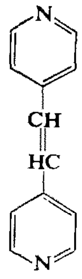
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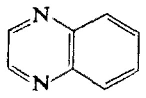
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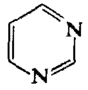
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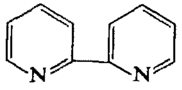
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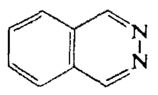
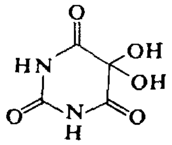

(VII)

I pyrazine
II 4,4'-bipyridine
III 1,2-di(4-pyridine)ethylene
IV quinozaline

V pyrimidine
VI 2,2'-bipyridine
VII phthalazine

A rather peculiar, most probably reversible system[43] is represented by alloxan (VIII), alloxantin (IX) and dialuric acid (X). Recent observations confirm the fact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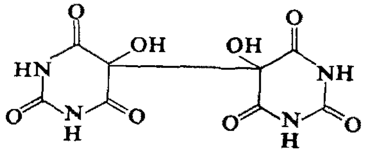
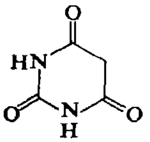

(IX)


(X)

that the $E_{1/2}$-values of the reduction and oxidation waves of the above three species are essentailly identical and agree with the potentiometric E_0-values. However, the reduction waves of (VIII) and (IX), the heights of which are but a fraction of the oxidation wave of (X), are fully under kinetic control. The rate-controlling reaction is probably the dehydration of the hydrated carbonyl at C-5 of alloxan.

Several polarographic criteria must be taken into account when considering the polarographic reversibility of a given system: (*a*) the half-wave potentials of both forms $[(E_{1/2})_{ox} = (E_{1/2})_{red}]$ must be equal; (*b*) the polarographic overvoltage $\eta_{1/2}$ must be equal to zero $(\eta_{1/2} = E_0 - E_{1/2} = 0)$; (*c*) the slope of the $\log \bar{\imath}/\bar{\imath}_d - \bar{\imath}$ *vs.* E plot must give the number of electrons consumed in the electrode process.

(*b*) is verified by comparing the potentiometric and polarographic data on (*a*) by comparison of the half-wave potentials of the polarographic waves for the reduced and oxidised form and their mixture, respectively. Polarisation by a periodically changed square-wave voltage,* single-sweep methods and constant-current oscillographic polarography may be useful when the products of oxidation or reduction are

---

* In evaluating these commutator experiments extreme care is necessary because with respect to the numerous adsorption and especially capacity effects strong currents may appear after commutation that do not correspond to an electrolytical process.[22]

unstable. However, the only unambiguous proof of reversibility is given by measuring the instantaneous currents (i-t curves) on single drops. In the Ilkovič equation[21] the dependence of instantaneous current on time is given by a sixth-order parabola $i = \text{const.}\, t^{\beta}$ ($\beta \approx 1/6$). In irreversible processes this relation is fulfilled on the limiting current only; in reversible processes β remains constant on any part of the wave and

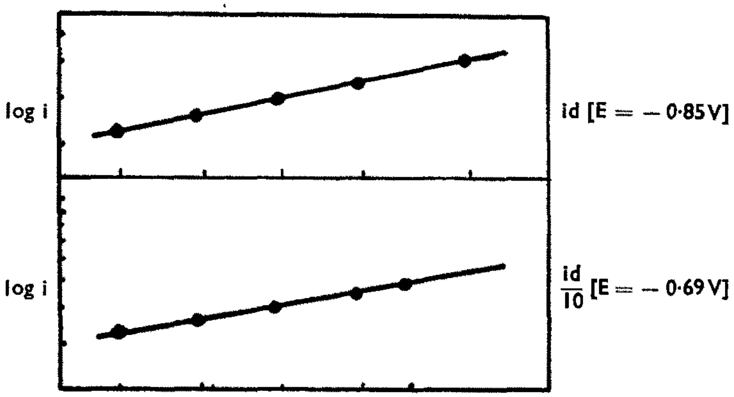
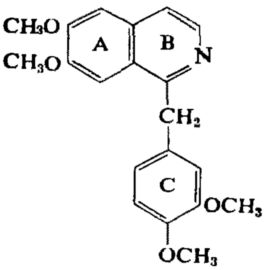


FIG. 1.—Log plot of the current-time curve for 4,4′-bipyridine at pH 3·18. (C = $2{\cdot}5 \times 10^{-3}$ *M* for id and 5×10^{-3} *M* for id/10).

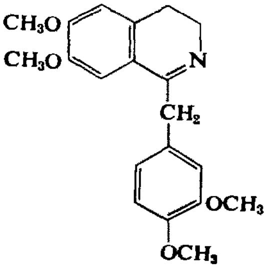
equals 0·192 (1/6 + correction for spherical diffusion). In heterocyclic compounds this test has been applied for the reduction of pyrazine, 4,4′-bipyridine (Fig. 1) and 1,2-di(4-pyridyl)ethylene.[8] Because of the adsorption phenomena clear-cut curves without adsorption prewaves and deformation are seldom obtained.

In some cases inactive heterocyclic nuclei are made reducible, only their originally difficult reducibility is facilitated by introducing a new substituent. This happens for example in pyridine-3-carboxylic (nicotinic) acid,[23] its esters and amide; in such a case the effect is observed with electron-attracting substituents.

The conditions for the polarographic activity of heteroethylenes are the same as those for the reducibility of organic substances in general. This means that in partially reduced aromatic heterocycles the remaining double bonds (especially >C=N—) under consideration must be conjugated with an aromatic nucleus (*e.g.*, benzene), with a sufficient number of conjugated double bonds, or finally with an electron-attracting group. Such a reduction can be exemplified with papaverine (XI) and 3,4-dihydropaverine (XII):[24]

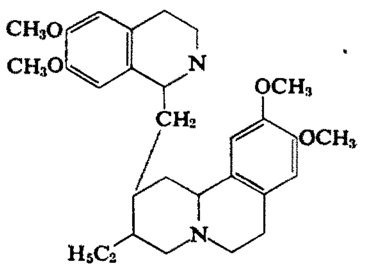


(XI)

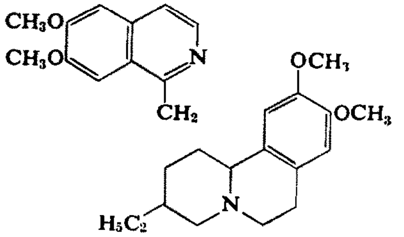


(XII)

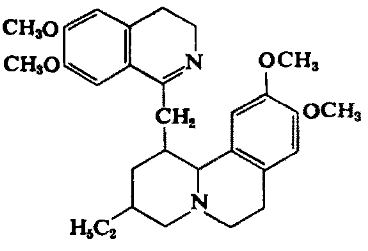
Whereas in (XI) the reduction of the isoquinoline nucleus B occurs under the uptake of four electrons not earlier than at −1·95 V [2% $N(CH_3)_4OH$ in 50% ethanol] and a 1,2,3,4-tetrahydroisoquinoline derivative is formed, 3,4-dihydropapaverine (XII) must be looked upon as a cyclic imine derived from desoxybenzoin. That is why a relatively positive two-electron reduction wave results at −1·52 V in the same medium. A similar system concerns the following three alkaloids: emetine (XIII), emetamine (XIV) and *O*-methylpsychotrine (XV):



(XIII)



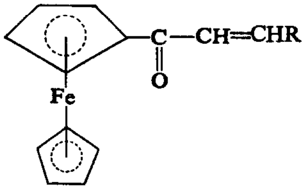
(XIV)



(XV)

In this particular case emetine (XIII) corresponds to 1,2,3,4-tetrahydropapaverine and yields no wave, even in solutions of tetralkylammonium hydroxides. Emetamine (XIV) is reduced at −2·00 V; this is in accord with papaverine (−1·95 V). Finally *O*-methylpsychotrine (XV) gives a two-electron reduction wave at −1·57 V under the same conditions (3,4-dihydropapaverine at −1·52 V).

The second main group of polarographically active compounds among heterocycles is formed by the substances in which an external substituent attached to the aromatic heterocyclic ring is subject to the electrochemical reaction at the electrode whereas the nucleus itself remains unchanged. Essentially, the same types of active group can be observed here as in the benzenoid series, with the same conditions for reducibility (conjugated double bonds, *etc.*). However, the ease of reduction (*i.e.*, the value of $E_{1/2}$) and the general behaviour is in most cases strongly influenced by the heterocyclic ring. The differences from the general polarographic behaviour of analogous benzene derivatives often result from the existence of protonated and basic forms in heterocycles (their mutual ratio changing with pH). In the π-deficient heterocycles, there is a deficit of π-electrons on the reducible group as compared to the corresponding benzene derivative. Consequently, the electron uptake is rendered easier with π-deficient nuclei and made difficult with π-excessive rings. For various formyl derivatives with different heterocyclic nuclei the result of this influence is shown in Fig. 2. In a buffered solution of pH 6–7 all three isomeric formylpyridines are reduced at considerably more positive potentials than that of benzaldehyde, this being in accord with the π-deficient character of pyridine. The π-excessive 2-formylthiophen and 2-formylfuran are reduced approximately over the same $E_{1/2}$-area as benzaldehyde. The most negative half-wave potentials were observed with 2-formylpyrrole. It is known that the relative order of π-electron densities in the ring is as follows: benzene < thiophen < furan < pyrrole. In 2-formylthiazole, which shows the most positive half-wave potential among all derivatives under consideration, the nucleus has areas of both π-deficiency and π-excess. The 2-position is most probably π-deficient. In 2-formylimidazole the insertion of a further nitrogen atom reduces the π-excessive nature of the nucleus, but the half-wave potential of this compound is only slightly less negative than that of 2-formylpyrrole. A very similar sequence is obtained with chalcones resulting from the reaction of acetylferrocene with various heterocyclic aldehydes(XVI):[26]



R = pyridine, thiazole, thiophen, pyrrole, *etc.*

(XVI)

The individual positions on the heterocyclic ring are, of course, not equivalent as regards the deficiency or the excess of π-electrons; thus, for example, in pyridine the 4-derivative is reduced at a slightly more positive potential than the 2-derivative (very often their $E_{1/2}$ are virtually equal) and both these exhibit by far more positive waves than that of the 3-derivative.[27] In a similar manner the half-wave potential of 2-formylthiophen is more positive than that of 3-formylthiophen. However, just the opposite is true for their aldoximes.[28]

In the usual qualitative treatment[29] of six-membered nuclei the nitrogen atom in the pyridine nucleus may be looked upon as a strong external substituent and in agreement with this concept the 2- and 4-derivatives are reduced at more positive potentials than the 3-derivatives. The external substituents attached to an aromatic benzene ring exert the following well-known influence : a shift of $E_{1/2}$ to more positive values is caused by —T or —I substituents (COOH, NO_2 or Cl, Br, I) and to more negative values by +T and +I substituents (OH, NH, OCH_3 or CH_3). This effect is more pronounced in the ortho (2) and para (4) positions than in the meta (3) position. A quantitative treatment by means of empirical equations of organic chemistry will be shown later. In contradistinction to Fig. 2, Fig. 3 represents the regions of reduction for most pyridine derivatives (pH 4–5). This graph could be applied for the identification of an unknown reducible group on the pyridine ring from its $E_{1/2}$-value. It is evident that, for a known ring, several active groups must be considered. The final decision is obtained from further characteristics of the wave, *i.e.*, $\Delta E_{1/2}/\Delta pH$, n, number of waves, *etc.*

The third possibility of polarographic activity in heterocycles is the formation of

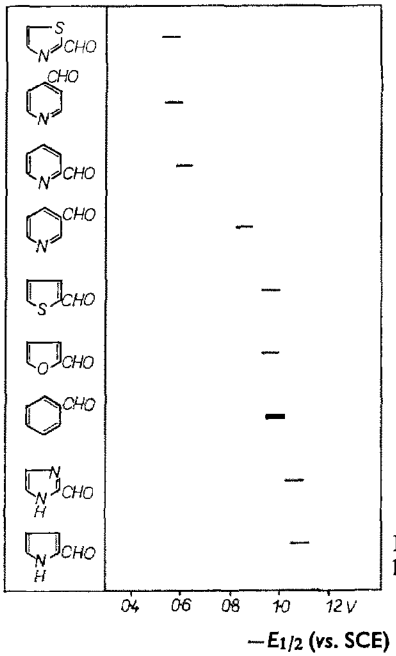


FIG. 2.—Half-wave potentials of various heterocyclic aldehydes under identical conditions (pH 4–5).

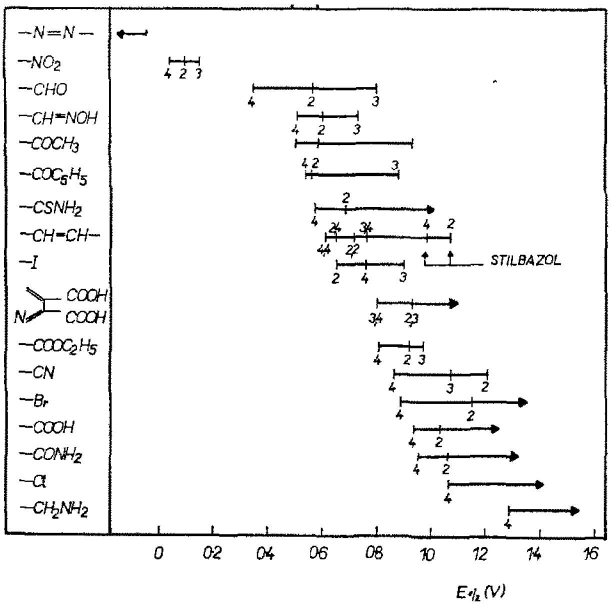


FIG. 3.—Reducibility of various external substituents ($E_{1/2}$) attached to a pyridine ring (pH 4–5).

insoluble salts and complexes with mercury. This may be through external SH-groups (*e.g.*, SH in thiamine) or to some groupings in the heterocyclic ring: NH—CO—NH in barbituric acid or in uracil, NH—CS—NH in thiobarbiturates and 4-methylthiouracil, and NH—CS—S in mercaptobenzthiazole.[30]

The catalytic reduction of hydrogen ions in the presence of heterocycles is ascribed to nitrogen-containing compounds alone,[14] although certain data are available which point to the fact that oxygen-containing heterocycles (chromones)[31] also give catalytic hydrogen waves.

Catalytic waves, similar to those obtained with cystine in ammoniacal solutions of cobalt(II) ions, were found with 5,5-diphenyl-2-thiohydantoin, 5,5-diphenyl-2,4-dithiohydantoin, 2-thiocytosine and 2,4-dithiopyrimidine.[74]

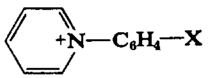
EMPIRICAL EQUATIONS

The effects of substituents described, qualitatively, in the above paragraphs on the reducibility and oxidisability can be expressed quantitatively by means of empirical equations[32] of organic chemistry (LFER). The effects of substitution on the free energy change of activation or on the standard free energy change are resolved into contributions of polar, resonance and, sometimes, steric effects that are believed to be independent of each other. Empirical constants characteristic of these effects for each substituent are obtained by comparing the logarithms of rate and equilibrium constants of suitable reactions under the influence of substitution. The differences in standard redox-potentials of reversible systems are proportional to the standard free energy change, and the half-wave potentials of irreversible systems to the change in free energy of activation. This enables the use of the above-mentioned constants for the polarographic half-wave potentials. The empirical equation in its simplest form, denoted as the Hammett equation, reads as follows (only the polar effect is accounted for):

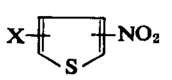
$$E_{1/2} = \rho_{\pi,R} \cdot \sigma_X = P \qquad (1)$$

This form is used for benzene derivatives with an active group and with a *p*- or *m*-substituent; σ_X is the total polar constant. It is characteristic of the nature of the substituent and its orientation or of the type of the aromatic system; $\rho_{\pi,R}$ is the reaction constant (in volts) typical for the electroactive group on the nucleus under consideration. It is a measure of the $E_{1/2}$ shift caused by a given substituent [the difference between the half-wave potential of the substance with the substituent X and the reference substance with a hydrogen atom instead of X: $\Delta E_{1/2} = (E_{1/2})_X - (E_{1/2})_R$]. The positive sign of $\rho_{\pi,R}$ points to the electron-uptake as the potential-determining step and a negative sign is characteristic of an S_N1-like or of a radical mechanism. The latter reaction type, however, is only seldom encountered. The following types of heterocycles fit the above Hammett equation:

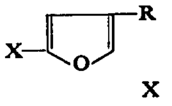
1. Het—C_6H_4—X; the heterocycle itself is reducible (Fig. 4).
   Example:



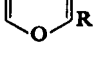
2. R—Het—X; substituent on heterocyclic ring reducible.
   Example*:



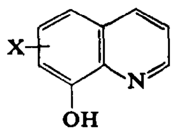
* In five-membered heterocyclic rings some authors use either σ_p or σ_m values, or their arithmetic mean. Later papers[32] recommend the application of σ_{p-X} for five-membered heterocycles with a reducible group in the side chain R, *e.g.* and σ_{m-X} for the following two cases:



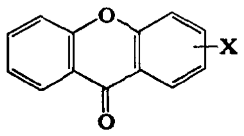
and



3. X—Ar—Het; substituent on benzene ring condensed to reducible heterocycle.
   Example:



4. X—Ar—Het—R; substituent on benzene ring condensed to heterocyclic ring with reducible group.
   Example:



A further equation is the so-called Taft equation:

$$\Delta E_{1/2} = \sigma^{*}_{\pi,R} \cdot \sigma_{X}^{*} . \qquad (2)$$

The meaning of the symbols is analogous with the exception that the reference X is CH_3. The electroactive group is here not separated from the substituent and the steric effects are regarded as constant for the series.

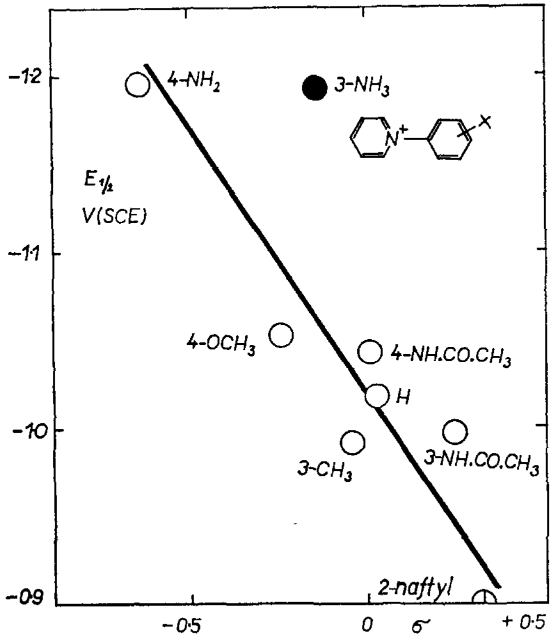
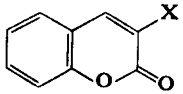


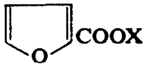
FIG. 4.—The $E_{1/2}$-σ_I plot for various substituted N-phenylpyridinum salts (σ_I total polar substituent constant) (no correlation for 3-aminoderivative, 2-naphthyl only taken from polarographic measurements).

The two following types are known for heterocycles:

1. Het—X; substituent on reducible heterocyclic ring.
   Example:



2. Het—R—X; substituent in reducible chain on heterocyclic ring.
   Example:



The values of σ have been tabulated.[32,44]

The above relationships enable both the determination of the heterocyclic ring bearing a known electroactive group, and the nature of the substituent on a known heterocyclic ring. The second possibility will probably be encountered more often.

In the application of these empirical relationships to heterocycles (in particular those with nitrogen atoms) in addition to the normal restrictions (identical experimental conditions, the same transfer coefficient α and the same number of electrons and protons) the adsorptivity of the depolariser and of the reaction products must be accounted for. This often results in considerable shifts of half-wave potentials that are thus not an accurate measure of the factor in the empirical equations.

The $E_{1/2}$ *vs.* δ plots are primary relationships. Similar relationships may be obtained between $E_{1/2}$ and other quantities, such as frequencies in infrared and ultraviolet absorption spectra, and perhaps dissociation constants. The $E_{1/2}$ of the reduction waves of thiocyamines are a linear function of the longest absorption bonds[33] and the $E_{1/2}$ *vs.* pK plot of 1-hydroxy-2-methyl-1,2,3,4-tetrahydroxyisoquinolines is also linear.[34]

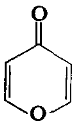
CORRELATION OF POLAROGRAPHIC BEHAVIOUR WITH PHYSICAL CONSTANTS

During the last 15 years a number of papers have appeared where the correlations between the polarographic half-wave potentials and physical properties, calculated by quantum-chemical methods, have been investigated. The major part of these publications is based on the statement of Maccoll[35] and Lyons[36] that a linear correlation exists between the energies of the lowest vacant π-molecular orbitals of aromatic hydrocarbons and their $E_{1/2}$-values. Recently, this method has been extended to heterocycles of the pyridine type[17,7] and to sulphur-containing heterocycles. Earlier, the treatment proved useful in benzenoid hydrocarbons, α,ω-diphenylpolyenes, polyenes and fluoranthenes. The energies were calculated by means of the HMO approximation. Some of the nitrogen compounds and their half-wave potentials are tabulated in Table I. The correlation is expressed by the following equation:[38]

$$E_{1/2} = 2{\cdot}127\,k_{-1} - 0{\cdot}555, \qquad (2)$$

(or, in reference 39, $E_{1/2} = 2{\cdot}12\,k_{-1} - 0{\cdot}484$).

The energy of the lowest vacant orbital is expressed by the value of the coefficient k_{-1} (Fig. 5). The accord of the two independent papers is satisfactory. A similar treatment has been attempted[39] in γ-pyrone (XVII), γ-thiapyrone (XVIII), γ-thiopyrone (XIX), γ-thiothiapyrone (XX) and α-thiothiapyrone (XXI). No correlation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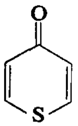
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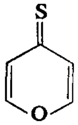
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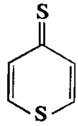
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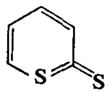

(XXI)

has been found between $E_{1/2}$ and the energy of the lowest vacant orbital in this case. However, there is some correlation between $E_{1/2}$ and the energy of the first intense maximum in the electronic spectrum. The disagreement in the former case is quite comprehensible, because the whole group of substances under investigation are not electrochemically related compounds in contrast to the pyridine-like compounds.

In addition to the above recent results there are earlier papers dealing with the theoretical treatment of relationships between $E_{1/2}$ and the structure. The basic concept is similar to that given above. The investigation was a success in the case of aldehydes[39] of the type $C_4H_3O(CH{=}CH)\varepsilon$ CHO derived from furan (n = 0, 1, 2), and with methoxyanthones[40] and aminoacridines.[41] However, a complete failure has been observed with pyridine-aldehydes[42] in acid media because of upsetting the proportionality by the formal positive change on the nitrogen atom in the pyridine nucleus. Maccoll's relation is only valid in alkaline media.

MECHANISM OF THE ELECTRODE PROCESS

In correlating the polarographic behaviour of organic substances with their physical constants, in determining the rate constants of the electrode process, or in deciding about the reversibility of an electrode process, the mechanism of the electrode

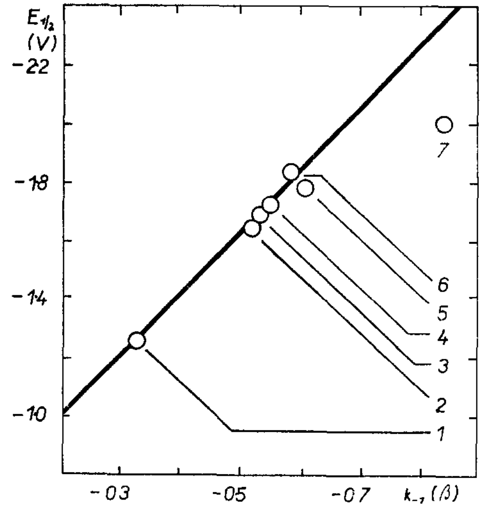


FIG. 5.—Dependence of the half-wave potentials of pyridine-like heterocycles on the energy of the lowest free-molecular orbital (k_1).
Experimental data and substances 1–7 as in Table I. Point 7 deviates.

reaction must be studied. This analysis is based on a log $i/i_d - i$ *vs.* E plot,[45,46] on the determination of E_0, and of number of electrons. The experimental facts enable the the determination of the transfer coefficient α or, possibly, of the rate constant for the electrode process. Because of the adsorption of the participants in an electrode process caused by heterocycles the dependence of the wave-height and the wave-form on the depolariser concentration is of utmost importance.

The determination of the products formed in the electrode reaction is helpful in elucidating the course of a reduction or oxidation process. If the products of the polarographic reduction are polarographically active either they can yield waves at more negative potentials which make the proof of their formation possible, or if the products are unstable or only active at more positive potentials the switch technique with periodically changed square-wave voltage (Fig. 6a, b) can be applied. Recently, many[47] authors have carried out preparative electrolyses with large-area mercury electrodes at a constant potential. The conditions are chosen so as to simulate the situation at the surface of the dropping mercury electrode in classic polarography. The foundations of this technique were laid by Pasternak[48] and Lingane[49] between 1940 and 1950, but it came into general use in the late fifties. Essentially, the method is extremely successful and a number of heterocyclic reductions and oxidations have been elucidated[50] in this way. The present author was able to solve the mechanisms of the 4-cyanopyridine[51] and 1,2-dipyridylethylene reduction.[3,52] In 4-cyanopyridine (and, recently, also in 2-cyanopyridine) two different mechanisms were found for acid and alkaline solutions, respectively. In acid media the reduction proceeds with the uptake of four electrons and the corresponding aminomethylpyridine is formed:

$$[C_6H_4N.CN]H^+ + 4e + 4H^+ \rightarrow [C_6H_4N.CH_2NH_2]H^+.$$

In alkaline solutions reductive fission of the C—CN-bond takes place:

$$C_6H_4N.CN + 2e + H_2O \rightarrow C_6H_5N + CN^- + OH^-$$

and a two-electron wave results. The reducibility of cyanopyridines in contradistinction to benzonitrile is rendered possible by the π-deficit in the pyridine nucleus caused by the presence of the heterocyclic nitrogen.

Nevertheless, there may be differences between polarography and preparative electrochemical reduction. This is because of different concentrations employed in the two methods and to the duration of the electrolysis.

Thus, the cation of isonicotinic acid[53] is reduced up to pH 4 in a single two-electron wave and 4-formylpyridine is formed. A dihydro-compound with a partially reduced nucleus results at pH-values between 4 and 8. The constant-potential reduction gives the same results, but if the reduction is allowed to proceed at pH below y pyridine-4-carbinol is obtained. A similar case is the reduction of isonicotinoyl amide in which the resulting 4-formylpyridine is partially protected by hydration against a further reduction to the carbinol. The oxidation wave of isonicotinyl-hydrazide[54] in alkaline media corresponds to a four-electron uptake probably under formation of isonicotinic acid. At pH 11·2 the preparative reduction with n = 2 yields mainly 1,2-di(isonicotinoyl)-hydrazine. In this case the higher concentration of depolariser facilitates the reaction of the isonicotinyl hydrazide anion with OH^- and with the isonicotinoyl cation.

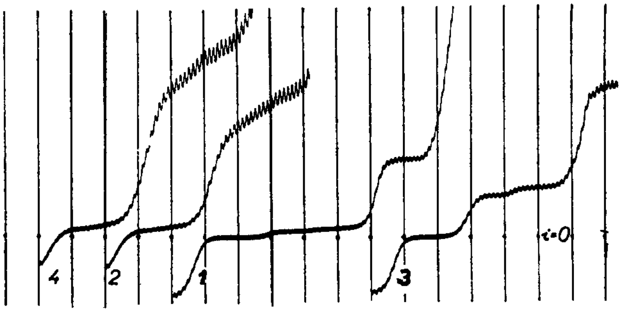


FIG. 6*a*.—Proof of electrochemical oxidation of 2,2′-pyridoin to 2,2′-pyridyl by means of periodically changed square-wave voltage.

Phosphate buffer pH 7.5 (50% ethanol); Curves 1 and 2: 1,3 × 10^{-3} *M* 2,2′-Pyridoin Curves 3 and 4: 1·3 × 10^{-3} *M* 2,2′-Pyridoin + 9·8 × 10^{-4} *M* 2,2′-pyridyl; Curves 1 and 3: normal d.c. polarograms; Curves 2 and 4 with periodically square-wave voltage (auxiliary potential 0,0 V). Each curve starts at 0,0 V; 200 mV/absc; *vs.* S.C.E.; s = 1:100; frequency 32 Hz; cathodic polarisation. The cathodic wave on curve 2 corresponds to the reduction of 2,2′-pyridyl formed by the oxidation in the anodic wave of 2,2′-pyridoin. The wave on curve 4 results from the reduction of 2,2′-pyridyl both add to the solution and formed in the oxidation at the electrode.

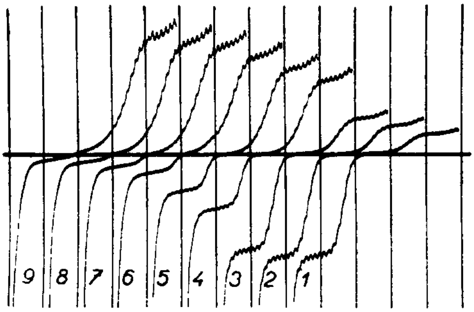
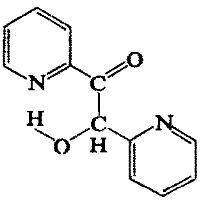


FIG. 6*b*.—Proof of chemical oxidation of 2,2′-pyridoin to 2,2′-pyridyl. Samples taken after certain intervals (in 96% ethanol) and mixed with the same volume of barbital buffer (pH 7·0); final concentration: 9·4 × 10^{-4} *M* depolariser.

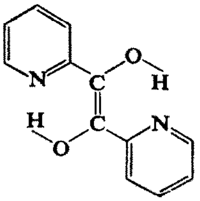
Curve 1: after 15 min.
Curve 2: after 30 min.
Curve 3: after 45 min.
Curve 4: after 75 min.
Curve 5: after 95 min.
Curve 6: after 120 min.
Curve 7: after 140 min.
Curve 8: after 160 min.
Curve 9: after 180 min.

DETERMINATION OF VARIOUS FORMS IN SOLUTION

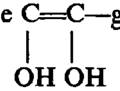
The equilibria of two or more forms of a substance present in solution are very often the subject of polarographic investigations. Sometimes the decision about the form that prevails in the solution is based on the general behaviour of the depolariser, on its comparison with known substances, and is usually empirical. Such a case may be exemplified with 2,2′-pyridoin.[47] The substance can exist in solution either in its ketonic (XXII) or its endiolic form (XXIII).

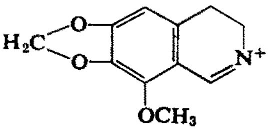


(XXII)

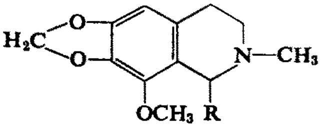


(XXIII)

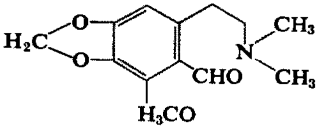
It has been shown that the equilibrium is strongly shifted to the right-hand side (in accord with the infrared spectra). This results in the formation of an anodic oxidation wave, characteristic of the  $\underset{\mathrm{OH}}{\mathrm{C}}=\underset{\mathrm{OH}}{\mathrm{C}}$—group but not observable with (XXII). It follows from this observation that 2,2′-pyridoin is not a true analogue of benzoin. In other cases model substances must be prepared; for instance, in the determination of the cotarnine form prevailing in aqueous solutions. The similar reduction of cotarnine (XXIV) and of 1-anilinohydroxotarnine (XXV) [R = NHC_6H_5] on the one hand, and of substituted benzaldehydes and *N*-benzoylcotarnine (XXVI) [R = COC_6H_5] on the other hand leads to the conclusion that only the cyclic forms are present in the solution. An analogy exists only between benzaldehyde and *N*-benzoylcotarnine.[55]



(XXIV)



(XXV)



(XXVI)

The greatest number of cases where the existence of a special form of the depolariser in the solution has been proved are based on reactions preceding the electrode reaction. A considerable number of heterocycles are present in the solution in a form that is inactive at a given potential. This species has to be transformed to the depolariser proper before the reduction (exceptionally also the oxidation) takes place. Under favourable conditions kinetic currents appear enabling us to detect protonation, dehydration and formation of cyclic forms. It is a well known fact among polarographers that this happens with weak acids, reducible at the dropping mercury electrode. In heterocyclic polarography such a phenomenon has been observed not only with a number of heterocyclic carboxylic acids, such as isonicotinic,[56] picolinic,[56] cinchomeronic[57] and quinolinic[57] acids, but for instance also with halogenopyridines;[27] in such a case only the protonation of the nitrogen atom in the pyridine ring must be assumed. In addition one can prove the existence of such systems even when they are undetectable by the other chemical or physicochemical methods. Protonated forms whose unknown pK-values lie at very high acidities have been found, for example, with isoflavones,[58] 3-phenylsydnones[59], *etc.*

A further case of a reaction preceding the electrode process is the dehydration of hydrated substances, *e.g.*, the carbonyl groups of numerous heterocyclic aldehydes such as all three isomeric pyridine-aldehydes[60,61] (as well as their quarternary *N*-methyl derivatives), imidazol-2-aldehyde,[26] thiazol-2-aldehyde[26] and alloxan[73] (the last compound has been described already among reversible depolarisers). The hydration protects the carbonyl group against reduction which takes place only after dehydration. Because the equilibrium between the two forms is mobile the polarographic current is governed by the finite rate of dehydration. Equations, similar to those for the recombination of weak acid anions, have been derived. The pH-dependence of the current is the result of general acid-base catalysis of dehydration. In heterocyclic compounds this simple mechanism is further complicated by acid-base equilibria between the protonated and the basic forms, which differ in their degree of hydration (Fig. 7). In general, the cation, because of its unit positive charge, is more strongly hydrated than the free base. From the kinetic currents the rate constants of dehydration have been computed and from the linear dependence of the expression log $K_{hydr}.k$, and on the acidity function H_0, the mechanism of the acid catalysis as below has been proposed:

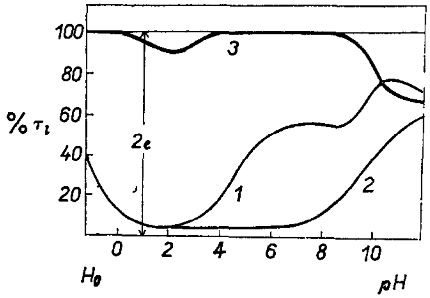
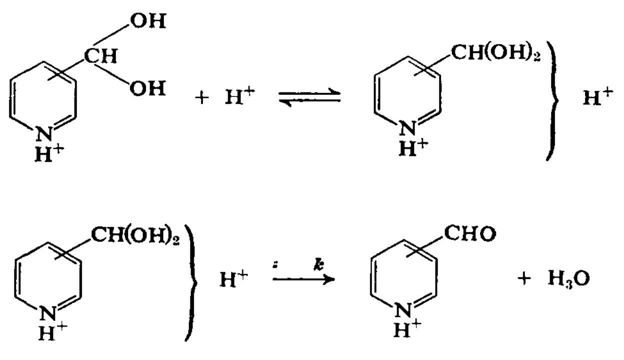
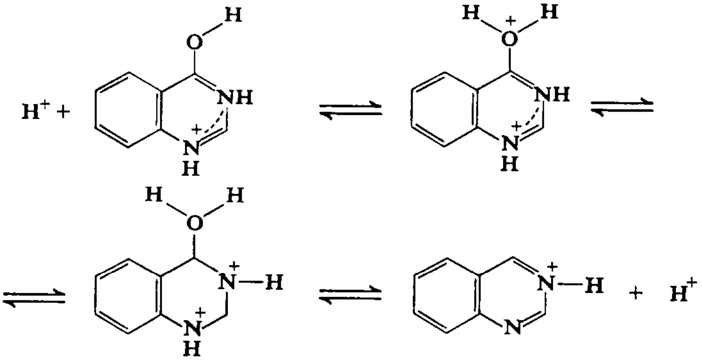


FIG. 7.—Polarographic limiting currents of pyridine-aldehydes as a function of pH:—
curve 1. pyridine-4-aldehyde;
curve 2. *N*-methyl-pyridinium-4-aldehyde;
curve 3. 3-acetylpyridine;



The hydration constants defined as $K_{hydr} = C_{CHO}/C_{CH(OH)_2}$ may be determined by eliminating the kinetic component of the current in impulse polarography (single-sweep); the voltage is applied here at a considerable speed (100 V/sec instead of approximately 0·003 V/sec as in classic polarography).

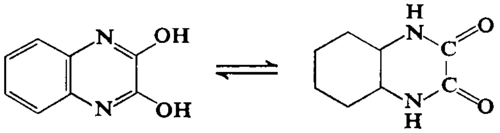
A recent contribution to the problem of hydration of heterocycles solved by polarography is based on an entirely different phenomenon. In quinazoline[62] the protonated nucleus itself is hydrated. Specific acid catalysis is operative in the dehydratiation reaction:



In this case the rate constants of dehydration have also been computed.

The formation of a depolariser from inactive cyclic forms may again be described by similar equations to the above dehydration and the rate and equilibrium constant are obtained. Such a reaction is assumed to take place in pyridoxal[63,64] and is hindered, possibly sterically, in pyridoxal-5-phosphate.[10] The hydration of the aldehydic group in pyridoxal, however, cannot be ruled out.

An example of lactam-lactim tautomerism has been found with hydroxy-substituted quinoxalines.[65] Whilst the unsubstituted ring is reduced, probably reversibly, a distinct irreversibility is to be observed with 2,3-dihydroxyquinoxaline (XXVII) because this compound is present as a dioxo substance (XXVIII) in solution:



XXVII XXVIII

ADSORPTION EFFECTS

Adsorption effects, which recently have become one of the most frequently investigated topics of theoretical polarography, are extraordinarily pronounced with heterocycles, and especially those containing nitrogen. Essentially, adsorption effects from the adsorption of the depolariser, of the reaction intermediates or of the final products may be observed on the one hand, and those of other surface-active agents on the other. The latter phenomenon will only be dealt with in the next paragraph in connection with nitrogen-containing non-depolarisers. For the present we are going to discuss the adsorption of the depolariser itself, of the electrode reaction intermediates, or of the final products on the surface of the dropping mercury electrode. A very feeble surface excess may in some special cases facilitate the electrode process,[66] but as yet no processes of such a type have been reported for heterocycles. Much more frequent is a strong adsorption which results in an inhibition of the electrolytic process and in a deformation of the polarographic current-potential curves, the appearance of adsorption prewaves, shift of the wave to more negative potentials, discontinuities on the polarogram, or even irregularities on the limiting current. All this reveals the fact that in the absence of surface-active substances one of the three forms mentioned above is adsorbed. On the other hand little information is obtained as to which species is adsorbed. In order to find this, auxiliary methods must be used. The i-t curves on single drops which are a valuable tool in the investigation of the effect of surface-active substances[67] on polarographic waves are of little use here; mostly they only prove that adsorption has taken place. The distinction is made more easily by means of electrocapillary curves and of polarograms with superimposed alternating voltage (according to Breyer[68]). The electrocapillary curve (obtained by measuring the time necessary for the formation of a certain number of mercury drops) passes below the curve of the supporting electrolyte alone if adsorption occurs—*i.e.*, the drop-time is shorter—over the potential region where the adsorption occurs. The comparison of the electrocapillary curve with the polarogram gives evidence whether the depression on the electrocapillary curve takes place before the reduction sets in, or on the limiting current where no depolariser can be present at the electrode surface. Even the eventual discontinuity observed on the i-E curve appears on the electrocapillary curve (Figs. 8 and 9). This method lead to the proof of depolariser adsorption, *e.g.*, in 2-benzoylpyridine,[4] or of 1,2-di(4-pyridyl)ethylene,[2] to the determination of the adsorption of

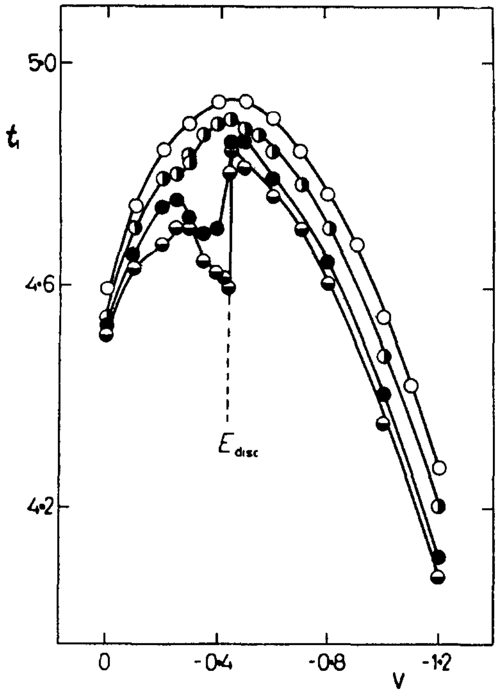


FIG. 8.—Electrocapillary curves of 2-benzoylpyridine in 0·1*M* H_2SO_4:
○ 0·1*M* H_2SO_4;
◑ 10^{-4} *M* 2-benzoylpyridine;
● 7 × 10^{-4} *M* benzoylpyridine;
◒ 10^{-3} *M* benzoylpyridine; E_{disc} potential of discontinuity on the current-voltage curve.

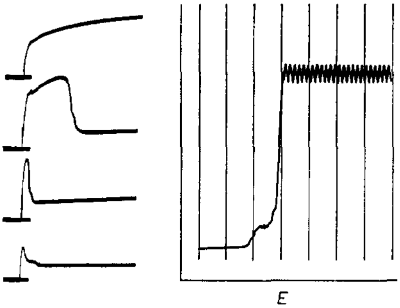


Fig. 9.—Current-time curves of 2-benzoylpyridine in 0·1*M* H_2SO_4 at different potentials 10^{-3} *M* 2-benzoylpyridine (1% ethanol); the current-potential curve (right) recorded from −0·1 V at 1/30 full sensitivity; 100 mV/absc., the current-time curves recorded at

curve 1. −0·330 V (s = 1/1); curve 2. −0·357 V (s = 1/1);
curve 3. −0·363 V (s = 1/1·6); curve 4. −0·366 V (s = 1/2·5).

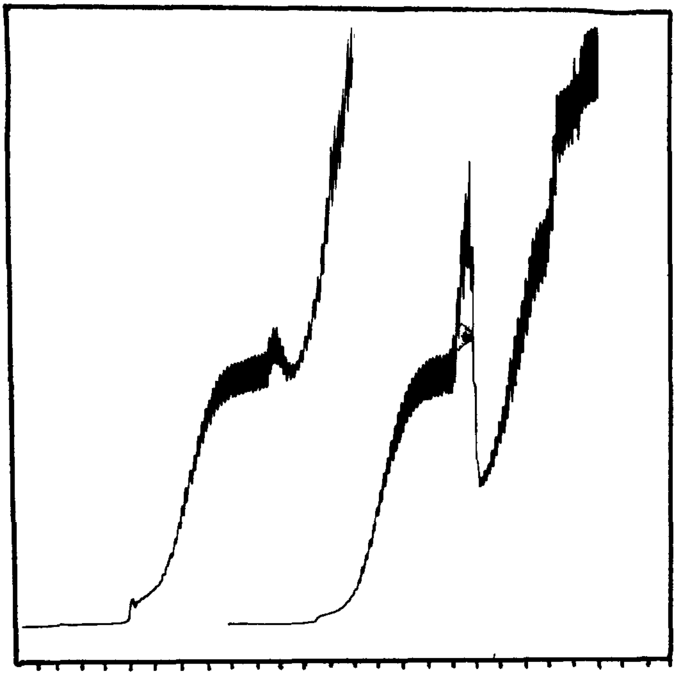


Fig. 10.—Deformations of the current-voltage curves because of adsorption of the reduction product:

curve 1. 10^{-3} *M* 4,4′-bipyridine; 50 mV/absc.; from −0·4 V; s = 1/100;
curve 2. 3·33 × 10^{-3} *M* 4,4′-bipyridine; 50 mV/absc.; from −0·4 V; s = 1/300.

the reduction intermediate in 2,3,5-tri-iodoimidazol,[2] to that of the product in 3-acetylpyridine[2] and 4,4′-bipyridine (Figs. 10 and 11). In an analogous method due to Breyer, both the drop-time (in electrocapillary curves) and the alternating current (in Breyer's a.c. polarography) are proportional to the electrode capacity and are lowered by adsorption. The method has been applied in benzoylpyridines[4] and the results agree with those by means of the electrocapillary curves. The curves obtained by oscillopolarographic measurements[4] (constant current according to Heyrovský[69]) in general agree with the two aforementioned methods, but their diagnostic value and evaluation is rather limited. The situation is still worse with curves obtained with a stationary mercury drop.[4] The instantaneous currents on single drops give in some cases, in spite of the above reservations, characteristic patterns if the depolariser is adsorbed (Fig. 9). The Kalousek switch (as for the investigation of reversibility) is sometimes useful. Here the currents influenced by adsorption, and also those due to capacity changes,[22] give much larger commutated currents of opposite sign than normal faradaic currents controlled by diffusion only. For quantitative evaluation of adsorption, the surface excess may be best computed from the electrocapillary curves (the surface tension must be expressed in absolute units instead of using t_1). The method is encumbered with a rather poor reproducibility in counting the number of drops over a certain period of time. The interpretation of most adsorption inhibitory effects is essentially based on the concept that the reduction through the adsorbed layer (regardless of its origin—depolariser or product) is stopped or proceeds at a smaller rate than at blank mercury. Consequently, after the original increase in current, either the further reduction proceeds at more negative potentials—the wave is shifted—or the substance is reduced only after the potential of desorption of the given substance has been reached—a discontinuity appears

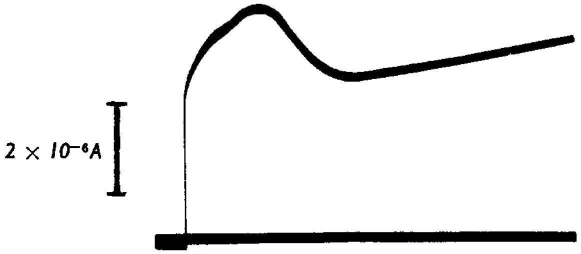


FIG. 11.—Current-time curve for 4,4′bipyridine at pH 3·18. ($C = 2{\cdot}5 \times 10^{-3}\,M$; $E = -0{\cdot}95$ V; recorded on the foot of the second wave).

In the preceding paragraph the influence of adsorption on the electrode process proper was described. However, to a large extent the electrode processes of organic substances are preceded by chemical reactions, mostly protonations. With regard to the nitrogen atoms of many heterocycles the protonation must be typical of this group of substances. Here again two cases may occur. (*a*) The substance is a depolariser. In this case the kinetic currents due to recombination with protons[70] are much higher than would correspond to the pH-value of the solution, the pK value of the substance and the maximum admissible value of the recombination rate constant k_r.[71,5] This is because the concentration of the free base at the electrode is increased by adsorption and the recombination reaction proceeds in a heterogeneous manner. Consequently, the pK′ values of heterocyclic *N*-containing compounds are shifted to larger pH-values with increasing depolariser concentration.[5] (*b*) The *N*-containing heterocycle is polarographically inactive. Such a substance reacts again as a proton donor (at a suitable pH with respect to its pK) and because of its excess at the electrode it either increases the kinetic current of recombination with heterocyclic depolariser (Fig. 12) or shifts the half-wave potential of the reduction wave of, for example, α-bromocarboxylic acids,[71] or of α-ketocarboxylic acids,[5] to more positive values. A quantitative treatment of the former case, the *N*-containing heterocyclic base as a depolariser, was attempted by Mairanovskii.[6]

ANALYTICAL APPLICATIONS

For solving analytical problems of heterocyclic chemistry by means of polarography certain rules may be recommended:

(*a*) With respect to adsorption and the complications arising from it the work at rather low concentrations ($2 - 3 \cdot 10^{-4} M$) is advantageous. Thus, even adsorption prewaves are still concentration proportional and the concentration limits given by the solubility product are possibly not attained (however, *cf* reference 72).

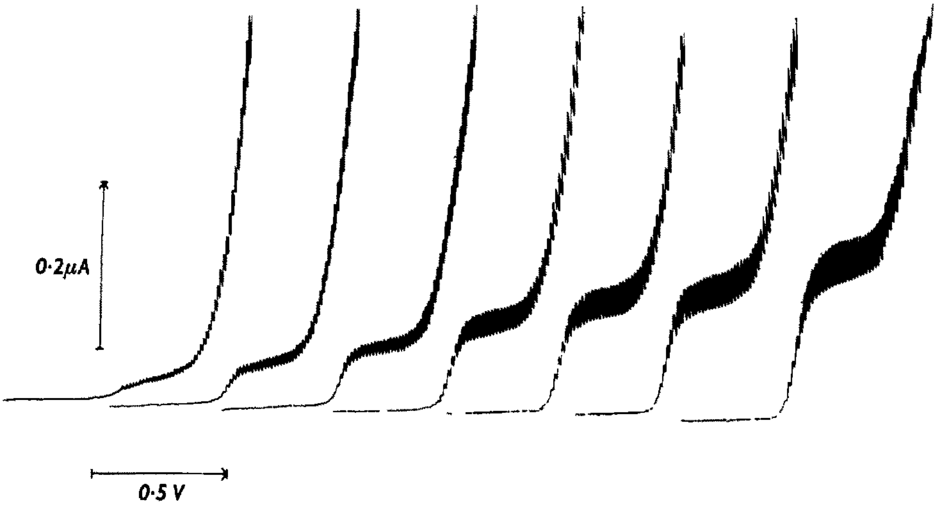


FIG. 12.—The influence of 4-aminopyridine on the kinetic current of isonicotinic acid (10^{-3} *M* isonicotinic acid; borate buffer pH 10·8; each curve starts at −1·0 V);

curve 1. 0;
curve 2. 0·75 × 10^{-3} *M*;
curve 3. 1·5 × 10^{3} *M*;
curve 4. 2·25 × 10^{-3} *M*;
curve 5. 3 × 10^{-3} *M*;
curve 6. 3·75 × 10^{-3} *M*;
curve 7. 4·5 × 10^{-3} *M*.

(*b*) The adsorption effects may be eliminated by using non-aqueous solvents, such as alcohols, *N,N'*-dimethylformamide, dioxan, *etc.* On the other hand, the addition to the solution of surface-active agents as maximum suppressors, even of gelatin, may be dangerous because of the above influence of *N*-containing bases.

(*c*) The possible mutual influencing of the respective waves of two heterocycles must be accounted for.[60] For this reason separate calibration curves must be plotted for each concentration of the other component.

(*d*) The distinction of more heterocycles and their quantitative polarographic determination in the presence of each other is a difficult task and the use of oscillopolarography [dE/dt = f(E)] and of derivative curves [(di/dE = f(E)] is only a partial success. It proved useful for example, with isomers.[73]

(*e*) In most cases it is easier and more reliable to separate the components before polarographic analysis. In the case of pharmaceuticals paper or thin-layer chromatography has proved extremely useful.

Zusammenfassung—Es wird eine Übersicht über die Polarographie in der Chemie der Heterocyclen gegeben.

Résumé—On présente une revue sur la polarographie dans la chimie des hétérocycles.

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POLAROGRAPHIE DES COMPOSES AROMATIQUES

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Résumé—On présente une revue sur la polarographie des composés aromatiques.

GENERALITES

La rédaction d'une mise au point exhaustive sur la polarographie des composés aromatiques apparaît au départ assez illusoire, car les recherches polarographiques dans ce domaine sont particulièrement nombreuses. Les raisons de cette abondance tiennent évidemment à l' intérêt général de la découverte de Heyrovský, mais, dans le cas envisagé, elles doivent être également attribuées à l'importance naturelle et synthétique de la série et à la multiplicité des variantes structurales possibles.

Notre étude se limitera strictement aux composés présentant au moins un cycle benzénique. Nous en excluerons les quinones et les composés aromatoïdes (hétérocycles, métallocènes dérivés du cyclopentadiène, tropolones, *etc.*), bien que ces dérivés présentent souvent un comportement très voisin de celui des composés benzéniques correspondants. Par contre nous y incluerons les métallocènes dont l'un des anneaux de la structure "sandwich" est un cycle benzénique.

L'activité polarographique d'un composé aromatique peut résulter de plusieurs possibilités:

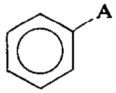
(a) Réduction ou oxydation du noyau benzénique lui-même.
(b) Réduction ou oxydation des fonctions latérales.
(c) Formation de vagues cinétiques, catalytiques ou d'adsorption liées à la présence de la fonction latérale.

La possibilité (*a*) se limite en fait à l'étude des carbures aromatiques.

La possibilité (*c*) ne peut apparaître que dans des cas d'espèce qui seront signalés au cours de l'étude des fonctions.

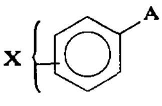
Par contre l'étude de l'électroactivité des chaînes latérales apparaît très vaste.

Si l'on accepte un schéma conventionnel, une discussion générale peut envisager les deux aspects suivants:



(I)

1. Quelles seront les caractéristiques apportées par le groupement phényle sur l'électroactivité de A dans le dérivé (I)?



(II)

2. Quelles seront les caractéristiques apportées par X sur l'électroactivité de A dans le dérivé (II)?

La réponse à la première question revient à comparer un composé C_6H_5A à toute structure RA. Bien qu'aucune règle générale ne puisse être avancée a priori, les mécanismes, donc la morphologie des vagues, ne diffèrent pas essentiellement en série aliphatique et en série aromatique.

Si l'on considère la position de la vague dans l'échelle des potentiels, la réponse doit être beaucoup plus nuancée. En effet l'influence du noyau peut avoir des effets opposés selon la nature de la liaison intéressée. La réduction des dérivés halogénés (qui entraîne une rupture C-Halogène) sera plus difficile en série aromatique qu'en série aliphatique. La réduction des groupes NO_2, CHO, COR, *etc.* (qui intéresse des chaînes latérales) sera par contre en général facilitée par l'électronégativité du groupe phényle.

Les séquences relatives des $E_{1/2}$ sont nettement plus concordantes si l'on envisage des séries voisines telles que les divers noyaux aromatoïdes.

On a en effet montré[1] que, pour des dérivés de formule générale RX et pour X = Br, CHO, $COCH_3$, CH=CHCOR, NO_2 et quelques autres fonctions complexes, les $E_{1/2}$ de réduction croissent (en valeur absolue) dans l'ordre:

$$\text{Thiazole-2} < \text{Pyridine-4} < \text{Pyridine-2} < \text{Pyridine-3}$$

$$< \text{Thiophène-2} < \text{Thiophène-3} < \text{Benzène} < \text{Pyrrole-2}.$$

Toutefois de telles séquences apparaissent fréquemment inversées, soit par suite de changement de mécanisme à l'électrode, soit par suite de l'influence du support fonctionnel sur les caractéristiques acidobasiques de l'entité réactive.

L'influence d'un substituant sur une fonction latérale électroactive est par contre actuellement beaucoup mieux connue. Son étude a fait l'objet de très nombreux travaux au cours de la dernière décennie, et on pouvait d'ailleurs prévoir, a priori, l'allure générale des lois qui régleraient l'évolution de l'électroactivité de A en fonction de X, puisque, dès 1950, on connaissait déjà les influences qualitatives des substituants $\pm$ I $\pm$ M sur les $E_{1/2}$.

Une constatation générale s'impose d'ailleurs pour toutes les corrélations entre grandeurs physico-chimiques: quand on étudie deux grandeurs voisines dans une série donnée, la corrélation des deux grandeurs reste toujours excellente si le site réactionnel ne subit pas de modifications immédiates (par exemple nucléophilicité et basicité de la série des ions phénates); par contre toute corrélation s'évanouit souvent si on modifie profondément la structure du site réactionnel (l'ion phénate et l'ion Br^- ont une "nucléophilicité" comparable, mais diffèrent par un facteur de l'ordre de 10^7 pour leur basicité).

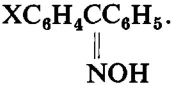
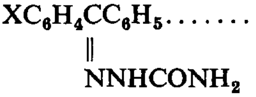
Remarquons tout d'abord que la présence de X peut parfois entrainer des effets chimiques secondaires influant profondément sur la nature du site électroactif. On a montré par exemple que le groupe CHO de l'*o*-nitro-benzaldéhyde était partiellement hydraté (donc non réductible), et que, par contre coup, la morphologie de la vague de réduction du NO_2 apparaissait nettement modifiée.[2] En dehors de ces cas extrêmes, la prévision de l'influence d'une substitution sur le $E_{1/2}$ revient à discuter cette influence sur des grandeurs thermodynamiques (pour les systèmes réversibles) et sur des grandeurs cinétiques (pour les systèmes irréversibles). Dans tous les cas la discussion doit tenir compte des facteurs polaires, des facteurs de résonance et des facteurs stériques.

Dans le cas des processus *irréversibles*, toute étude de corrélations et toute conclusion ne restent valables que si on s'est, au préalable, assuré que les mécanismes d'électrode étaient strictement comparables.[3] Parmi ces corrélations la corrélation de Hammett:

$$\Delta E_{1/2}X = E_{1/2}(X - C_6H_4 - A) - E_{1/2}(H - C_6H_4 - A) = \rho'\sigma_X$$

a été vérifiée sur de très nombreuses séries.

Des mises au point nombreuses et détaillées,[4–7] sont parues sur ce sujet au cours de la dernière décennie. Dès 1958 l'un des auteurs[4] pouvait réunir 13 séries de composés aromatiques étudiées sous l'angle de la corrélation de Hammett. Les valeurs expérimentales des ρ' pour quelques séries caractéristiques sont indiquées ci-après:

	ρ'(volts)		ρ'(volts)
XC_6H_4CHO	0,35	Azobenzènes	0,13
$XC_6H_4CH = N\ NHCSCH_3$	0,17	Dérivés iodés	0,40
$XC_6H_4COCH_3$	0,35	Phtalimides	0,24
$XC_6H_4COC_6H_5$	0,25	Phtalimides N. substituées	0,26
 $XC_6H_4\underset{\underset{NOH}{\Vert}}{C}C_6H_5$	0,08	Phtalonimides	0,14
 $XC_6H_4\underset{\underset{NNHCONH_2}{\Vert}}{C}C_6H_5$	0,13	Phtalonimides N. substituées	0,18
$XC_6H_4NO_2$	0,16		

La constante de réaction ρ' varie évidemment un peu avec le pH et le solvant et on devra se reporter aux publications originales pour connaître les conditions expérimentales.

Il est d'ailleurs possible de relier la constante ρ', mesurée par polarographie, à la constante conventionnelle ρ utilisée dans la relation liant deux constantes cinétiques. On a:[1] $\rho' = 2{,}3\rho \times RT/\alpha n_\alpha F$. En supposant $n_\alpha = 1$; $\rho = 2$ and $\alpha = 0{,}5$ on trouve $\rho' = 0{,}24$ volt.

Le caractère général de la corrélation de Hammett en polarographie a été signalé plus particulièrement par Zuman qui notait en 1960, que plus de 500 valeurs de potentiels de demi-vague vérifiaient cette loi.[5]

Il est curieux de constater que, si on compare les données cinétiques aux données polarographiques, celles-ci sont particulièrement "favorisées" à cet égard malgré les conditions imposées théoriquement pour la vérification d'une telle corrélation (identité des coefficients de diffusion et des coefficients de transfert pour toute la série). Ceci tient vraisemblablement au fait que, lorsqu'on passe d'une série cinétique à une autre série, la nature du réactif varie, alors que, pour toutes les séries polarographiques, le "réactif" (électron ou électrode) reste identique pour toutes les séries.

L'intérêt d'une telle généralité est évident: prévision des $E_{1/2}$, détermination des constantes σ inconnues, séparation des différents effects structuraux et étude des processus à l'électrode. A ce dernier point de vue, une valeur de ρ' positive peut en effet être considérée comme un argument pour un processus nucléophile déterminant (transfert d'électron).

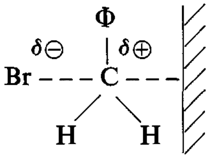
Une valeur de ρ' négative suggérerait au contraire un mécanisme où le transfert d'électron ne serait pas le processus déterminant.

La généralité de la corrélation de Hammett souffre toutefois quelques exceptions. Deux cas peuvent être signalés: celui des sels de phényl diazonium *p*-substitués[8] et celui des bromures de benzyle substitués[9]. Dans le premier cas les substituants —I ou —M (CO_2H ou Br) et les substituants +I ou +M (tels que CH_3 et OCH_3) diminuent tous le $E_{1/2}$.

Ce résultat doit d'ailleurs être rapproché d'une anomalie analogue observée au cours de la décomposition des sels de diazonium.[10]

Dans le deuxième cas on observe de même que les $E_{1/2}$ sont abaissés par les deux catégories de substituants —I ou —M et +I ou +M. Selon Klopman ce résultat peut s'interpréter en faisant intervenir deux facteurs déterminants dans la facilité de réduction des dérivés halogénés.

1. Formation de la "liaison" entre le carbone et l'électrode. Ce phénomène, analogue à la formation d'une liaison entre réactif et nucléophile, dépendra de la charge du centre attaqué et sera directement fonction du pouvoir capteur ou donneur d'un substituant éventuel.



(e)

2. Rupture de la liaison C—Br. Ce phénomène dépendra de la nature de la liaison considérée et également du pouvoir capteur ou donneur d'un substituant éventuel, mais, cela, d'une façon inverse à celle envisagée ci-dessus.

Dans une telle éventualité la relation de Hammett n'est linéaire que dans le cas d'un mécanisme limite: ρ' est négatif si la rupture de la liaison est prépondérante, ρ' est positif si le transfert de charge est déterminant.

Le cas particulier de l'effet *ortho* a fait l'objet d'une mise au point détaillée de Zuman.[11] Cet auteur a tenté de définir un "*glissement polarographique ortho*" général et a discuté les manifestations de *l'inhibition de résonance* en polarographie.

Dans ce qui suit, nous envisagerons successivement l'électroactivité des différentes chaînes latérales greffées sur un reste benzénique.

Nous ne discuterons pas le cas des carbures benzéniques eux-mêmes. Le comportement cathodique des différents carbures aromatiques a en effet été résumé par Hoijtink[12] et un travail d'ensemble sur l'oxydation de ces mêmes carbures a été publié récemment par Pysh et Yang.[13] D'autre part nous insisterons plus particulièrement sur les fonctions qui, à notre connaissance, n'ont pas encore fait l'objet d'une mise au point particulière.

DERIVES HALOGENES

La réduction d'un composé aromatique halogéné donne lieu généralement à une seule vague à 2*e*. Lorsque la molécule ne porte pas de substituant acide ou basique, le potentiel de demi-vague est indépendant du pH.

Le mécanisme suivant[14,15] permet de rendre compte de cette invariance:

$$R-X+e\xrightarrow{\text{lent}}R\cdot+X^-$$

$$R\cdot+e+H^+\xrightarrow{\text{rapide}}RH.$$

Pour des composés analogues, la difficulté de réduction croît dans l'ordre normal $I < Br < Cl$.[14] Les dérivés fluorés juxtacycliques ne sont pas réductibles, même dans un électrolyte support à base d'ions ammonium quaternaires. On a cependant observé une vague de réduction du fluor pour les trifluorométhylbenzènes dans la diméthylformamide[16] et en milieu aqueux.[29]

L'influence des substituants a surtout été examinée systématiquement pour les dérivés iodés, en raison de leur facilité de réduction. *Lorsque la molécule porte un substituant acide ou basique* (CO_2H, NH_2, OH), $E_{1/2}$ n'est indépendant du pH qu'en milieu acide et basique. Il varie dans la zone intermédiaire[17,18] et cette variation est vraisemblablement attribuable à la recombinaison forme basique-proton.[19,20]

Les iodo-benzènes substitués vérifient l'équation de Hammett[21] et des corrélations ont été établies entre les potentiels de demi-vague et diverses grandeurs de la chimie théorique.[22–24]

L'effet des substituants sur le potentiel de demi-vague a également fait l'objet de recherches dans les séries des polychloro et polybromobenzènes,[25] des naphtalènes monohalogénés[26] et du *p*-fluoroiodobenzène.[27] Lors de la réduction de l'*o*-dibromo et de l'*o*-chlorobromobenzène,[28] on a suggéré la formation intermédiaire du benzyne. La polarographie des dérivés halogénés aromatiques a fait l'objet d'une mise au point par Zuman.[30]

L'étude de la réduction polarographique de sels de diphényliodonium substitués a conduit à proposer le mécanisme:[31,32]

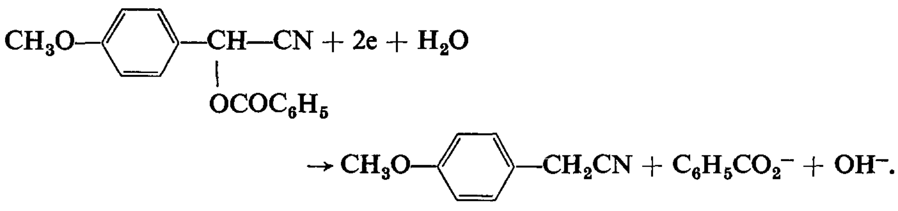
$$1^\circ \text{ vague:}\quad R\overset{\oplus}{I}R + e \rightleftarrows R\overset{\bullet}{I}R$$

$$2^\circ \text{ vague:}\quad R\overset{\oplus}{I}R + 2e + H^+ \rightarrow RH + RI$$

$$3^\circ \text{ vague:}\quad R\overset{\oplus}{I}R + 4e + 2H^+ \rightarrow 2RH + I^-.$$

ALCOOLS AROMATIQUES ET DERIVES

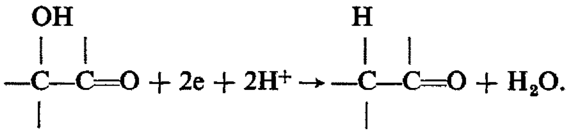
La *réduction* polarographique de la fonction alcool ne peut en général apparaître dans la région accessible. Toutefois quelques exemples d'électroactivité ont été signalés dans des cas bien particuliers. Cette possibilité est toujours attribuable à des conditions structurales favorables. Par exemple, on a signalé[33] la réduction d'un ester dérivé du *p*-methoxymandelonitrile (I) selon:



(I) (II)

Cette activité résulte probablement de l'influence cumulative de l'effet (—I —M) du CN qui facilite l'attaque "nucléophile" de l'électron et de l'effet du groupe *p*-méthoxy qui stabilise la structure benzylique intermédiaire.

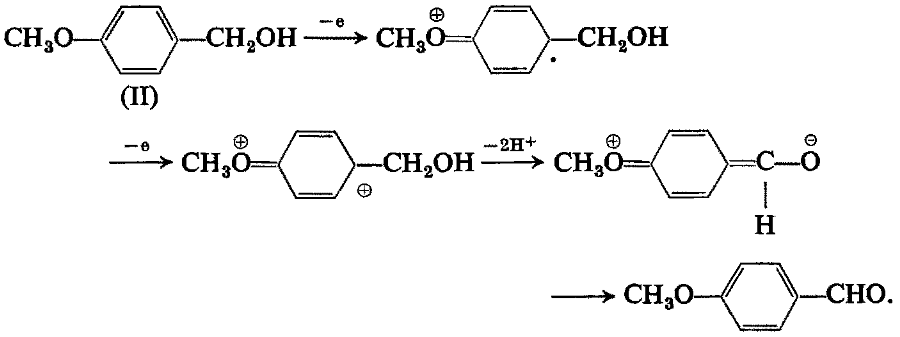
On a également suggéré[34] que la réduction anormale du phénylacétylcarbinol[35] pouvait s'interpréter selon le mécanisme admis pour les hydroxycétones:



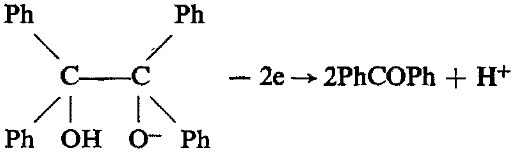
$$-\overset{\overset{\displaystyle OH}{|}}{\underset{|}{C}}-\overset{|}{C}{=}O + 2e + 2H^+ \rightarrow -\overset{\overset{\displaystyle H}{|}}{\underset{|}{C}}-\overset{|}{C}{=}O + H_2O.$$

L'influence de la stabilité des carboniums sur l'électroactivité apparaît dans le cas du triphénylcarbinol. Wawzonek *et al.*[36] ont en effet montré que les triphénylcarbinols, en solution dans l'acide méthane sulfonique anhydre, donnent des sels de triphénylcarbonium réductibles en triphénylméthanes.

L'oxydation anodique de nombreux alcools benzyliques a été étudiée par Lund[37] sur microélectrode de platine dans l'acétonitrile en présence de perchlorate de sodium. Le dérivé *p*-méthoxylé (II) présente deux vagues (−1,22 et −1,64 V) et la deuxième vague apparaît à un potentiel très voisin de celui présenté par l'aldéhyde anisique (−1,63 V) correspondante. D'autre part il est possible d'isoler l'aldéhyde anisique à l'état de dinitro-2,4 phénylhydrazone dans les produits d'oxydation de II mais uniquement en présence d'un accepteur de proton tel que la pyridine. Ces constatations ont conduit à proposer le mécanisme suivant pour la première vague:



La seconde vague correspond vraisemblablement à l'oxydation ultérieure du dérivé carbonylé. Un exemple particulièrement intéressant d'oxydation d'un glycol a été observé par Kemula *et al.*[38] A pH > 8 le benzopinacol est oxydé en benzophénone sur l'électrode à goutte ($E_{1/2} = -0{,}58$ V dans NaOH 0,12*N*). Le mécanisme proposé fait intervenir l'ion benzopinacolate:



et l'auteur a mis en évidence la benzophénone formée. C'est un des rares exemples connus d'oxydation polarographique avec rupture d'une liaison C—C.

DERIVES ORGANOMETALLIQUES ET ORGANOMETALLOIDIQUES

Les dérivés phénylmercuriques présentent deux vagues à 1*e* chacune. La première vague conduit au radical $C_6H_5Hg^{\cdot}$ qui est dimérisable en $(C_6H_5)_2Hg$ et Hg et reste adsorbé à l'électrode en provoquant des irrégularités sur le palier de diffusion. Ce phénomène a été étudié par observation microscopique et tracé des courbes i — t. Le deuxième stade a été attribué à la rupture de la liaison C—Hg:[39]

$$C_6H_5Hg^+ \xrightarrow{+e} C_6H_5Hg^{\cdot} \xrightarrow{+e+H^+} C_6H_6 + Hg.$$

L'importance des phénomènes d'adsorption a été confirmée par le tracé des courbes électrocapillaires de l'hydroxyde de phénylmercure[40] et on a montré récemment que la morphologie de la première vague du *p*-chloromercuribenzoate s'interprète facilement dans l'hypothèse d'une autoinhibition.[41]

La décroissance de la vague de l'acide *p*-chloromercuribenzoïque et de ses dérivés a été utilisée pour la détermination des groupes SH[42–47]. Plusieurs travaux ont également étudié les dérivés arylmercuriques: sulfures de bisalcoyl et bisarylmercure,[48] *o*-chloromercuriphénol[49] et phénylmercuriamides.[50]

Les chlorures de triphénylselenonium et telluronium et les chlorures de tétraphénylstibonium, arsonium et phosphonium ont été étudiés par Matsuo.[51,52] Le chlorure de triphényltelluronium présente en particulier un polarogramme à 2 vagues ($E_{1/2} = -0{,}77$ et $E_{1/2} = -1{,}10$). La hauteur de la première vague varie linéairement avec la concentration et sa position est indépendante du pH. Le processus de la réduction est d'ailleurs compliqué par des phénomènes d'adsorption.[51]

Le dibenzyl et le diphénylsélénoxide (en solution dans un mélange benzène, eau, méthanol) ont été polarographiés par Evans et Woodbridge[53] qui proposent un processus à 2*e*:

$$Ph_2SeO + H_2O + 2e \rightarrow PhSePh + 2OH^-.$$

L'acide phénylarsonique a été étudié par Maruyama et Furuya.[54]

Des études polarographiques et chronopotentiométriques sur électrode de platine ont montré que l'ion tétraphénylborate présente une vague d'oxydation à 2*e* dans l'acétonitrile.[55] Le nombre apparent d'électrons trouvé par coulométrie sous potentiel contrôlé varie de 1,02 ($c = 1{,}0 \times 10^{-2}$) à 1,8 ($c = 8{,}9 \times 10^{-5}$). Cette variation indique qu'un processus chimique secondaire utilisant l'un des produits de la réduction consomme de l'ion tétraphénylborate et les auteurs ont proposé le mécanisme suivant:

$$(C_6H_5)_4B^- - 2e \rightarrow (C_6H_5)_2B^+ + C_6H_5C_6H_5 \qquad (A)$$

$$(C_6H_5)_2B^+ + H_2O \rightarrow (C_6H_5)_2BOH + H^+ \qquad (B)$$

$$(C_6H_5)_4B^- + H^+ \rightarrow (C_6H_5)_3B + C_6H_6 \qquad (C)$$

$$(C_6H_5)_3B + 0{,}5O_2 \rightarrow (C_6H_5)_2BOC_6H_5 \qquad (D)$$

Le déficit observé pour la valeur de *n* provient de la disparition de l'ion $(C_6H_5)_4B^-$ selon (C) sous l'action des ions H^+ formé en (B). L'analyse critique des différents résultats confirme cette hypothèse.[55,56]

Dans la série des métallocènes du type arène on a signalé[57–59] que le dibenzènechrome donne une vague anodique réversible:

$$(C_6H_5)_2Cr^+ + e \rightleftharpoons (C_6H_5)_2Cr.$$

Un substituant méthyle déplace la vague vers les potentiels négatifs.

Une étude polarographique comparée[60] des cétones dérivées du benzènechrometricarbonyle (BctH), du ferrocène (FcH) et du benzène a montré que les $E_{1/2}$ se classaient (en valeur absolue) dans l'ordre:

$$\text{Bct COR} < C_6H_5COR < \text{Fc COR}.$$

Cette séquence montre que le radical Bct· est plus électronégatif que le radical phényle et ce résultat est en bon accord avec les propriétés chimiques connues du benzènechrometricarbonyle.

PHENOLS—ANILINES ET DERIVES

Les premières observations systématiques sur *l'oxydation* polarographique des phénols ont été faites par Gaylor *et al.*[61] sur électrode de graphite et Hedenburg et Freiser[62] sur électrode de platine. Le $E_{1/2}$ anodique se situe en effet au-delà de + 0,3 volt (Hydroquinone + 0,4 V, phénol + 0,9 V, environ, à pH 1,2) et la vague anodique ne peut être observée sur le mercure.

Le courant de diffusion est proportionnel à la concentration totale de phénol et l'analyse de la vague donne $n = 1$. On a proposé[62] le mécanisme:

$$C_6H_5OH \overset{\text{rapide}}{\rightleftharpoons} C_6H_5O^- + H^+$$

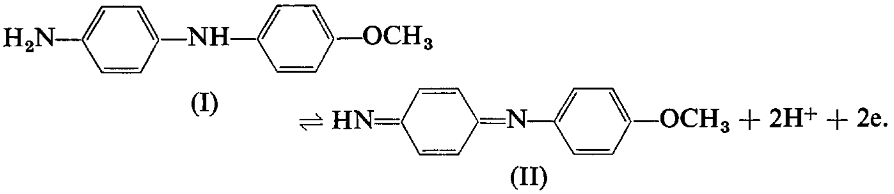
$$C_6H_5O^- - e \xrightarrow{\text{lent}} C_6H_5O.$$

Les $E_{1/2}$ anodiques des phénols et des anilines substitués en méta et en para vérifient convenablement la corrélation de Hammett et il y additivité des σ,[63] mais on observe les déviations habituelles pour les dérivés disubstitués ortho.

L'oxydation anodique des amines et des phénols aromatiques a également été étudiée par chronopotentiométrie.[64] Dans le cas des anilines la courbe $E_{1/4} = f(pH)$ présente une cassure correspondant au pK_A. Plusieurs autres types d'électrodes ont été utilisés pour l'étude de l'oxydation des amines.[65–67]

Walker et Adams ont signalé l'utilisation de la polarographie à courant alternatif pour l'étude de diverses anilines.[68] La méthode facilite l'étude des mécanismes à l'électrode en autorisant la détection de faibles quantités de produits réactionnels.

La nature des produits d'oxydation des amines a été précisée dans le cas du dérivé I qui conduit à la diimine II[69]



(I)

(II)

Les sels de Wurster (HX, RN $= C_6H_4 =$ NR, HX) qui sont en général les produits intermédiairies d'oxydation des *p*-phénylènediamines ont été étudiés eux-mêmes sur divers types d'électrodes. Ces dérivés doivent être stabilisés en solution aqueuse par addition de méthanol et d'acide acétique. Le dérivé tétraméthylé à l'azote présente deux vagues à 1*e*.[70]

Signalons enfin que les sels d'anilinium ont été polarographiés dans l'acétonitrile ($E_{1/2} = -1{,}00$ V pour le 2,5-dichloroanilinium).[71]

DERIVES SULFURES

Acides sulfoniques et dérivés

L'acide benzènesulfonique et l'acide méta-benzène disulfonique ne sont pas réductibles à l'électrode à gouttes,[72] mais les acides naphtalènes sulfoniques donnent *une vague de réduction du noyau*[72] dont la nature cinétique a été discutée par Levin.[73] Les chlorures d'arènesulfonyles ont été étudiés par Mairanovskii et Neiman,[74] Urabe et Yasukochi,[75] Čerňák et Blažej,[76] Umano[77] et Horner et Nickel.[80] Mairanovskii et Neiman ont proposé le mécanisme:

$$RSO_2Cl + 2e^- \rightarrow RSO_2^- + Cl^-.$$

Urabe et Yasukochi ont montré que, en solution aqueuse et sous atmosphère d'azote, l'hydrolyse du groupe SO_2Cl est négligeable si l'on fait la mesure immédiatement après la mise en solution. Il indique l'influence des substituants sur les $E_{1/2}$ et propose les mécanismes:

$$RSO_2Cl + 2H^+ + 2e \rightarrow RSO_2H + HCl$$

$$RSO_2Cl + 3H^+ + 3e \rightarrow 0{,}5RSO_2SR + HCl + H_2O$$

$$RSO_2Cl + 5H^+ + 5e \rightarrow 0{,}5RSSR + HCl + 2H_2O.$$

Umano a pu isoler dans les produits de réduction l'acide sulfinique, le disulfure et le thiosulfonate. Les valeurs suivantes indiquées par Horner et Nickel montrent l'influence de la structure sur $E_{1/2}$ (volts E.C.S.; dioxane 75%)

$PhSO_2R$

R =	F	Cl	Br
$E_{1/2}$	−1,57	−0,13	−0,07

RSO_2Cl

R =	C_6H_5	*p*-MeC_6H_4	*o*-MeC_6H_4	*p*-ClC_6H_4	*p*-$AcNHC_6H_4$
$E_{1/2}$	−0,13	−0,135	−0,125	−0,10	−0,11

Les esters des acides sulfoniques $PhSO_3R$ donnent une seule vague à 2*e*, mais l'introduction d'un atome de chlore dans le noyau produit une scission de la vague de l'ester.[78]

Sulfones et sulfoxydes

Les sulfones sont réductibles mais les mécanismes de réduction proposés dans la littérature ne concordent pas. Mairanovskii et Neiman[78] ont signalé que les sulfones présentant un groupe aryle donnent un polarogramme à deux vagues. Ils attribuent la première vague à une réduction à 4*e*:

$$RSO_2R + 4e + 2H_2O \rightarrow RSR + 4OH^-$$

et la deuxième à la décharge de l'hydrogène provenant du sulfonium formé dans la réaction:

$$RSR + H_2O \rightarrow [RSHR]^+ + OH^-.$$

Par contre Levin et Shestov[72] et Drushel et Miller[79] admettent une réduction à $2e$ avec formation d'acide sulfinique et de benzène ($n = 1{,}85$ par coulométrie sous potentiel contrôlé)

$$C_6H_5SO_2C_6H_5 + 2H_2O + 2e \rightarrow C_6H_5SO_2H + C_6H_6 + 2OH^-.$$

Ce mécanisme est semblable à celui présenté dans la réduction par le sodium métallique dans le toluène bouillant:

$$2C_6H_5SO_2C_6H_5 + 2Na \rightarrow 2C_6H_4SO_2Na + C_6H_5{-}C_6H_5.$$

Une vague de réduction a été observée pour le diphénylsulfoxyde, Ph_2SO, à $-2{,}2$ V.[80]

Sulfures, disulfures et sels de sulfonium

Les sulfures mixtes d'alcoyle et d'aryle donnent des *vagues anodiques* sur électrode de platine dans le mélange nitrobenzène–méthanol.[81] On a également étudié la vague de réduction de $(C_6H_5S)_2Hg$.[86]

Les disulfures aromatiques ArSSAr se réduisent irréversiblement en thiophénols[82]

$$ArSSAr + 2H^+ + 2e \rightarrow 2ArSH.$$

Les $E_{1/2}$ indiqués en milieu hydroalcoolique à pH O sont les suivants ($E_{1/2}$ E.C.S., alcool isopropylique à 40%):

ArSSAr

Ar=	C_6H_5	p-$C_6H_4CH_3$	p-C_6H_4Cl	p-$C_6H_4NH_2$	p-C_6H_5-C_6H_4
$E_{1/2}$	$-0{,}108$	$-0{,}111$	$-0{,}22$	$-0{,}10$	$-0{,}21$

Shinagawa *et al.*[83] ont proposé une réduction à $4e$ ($E_{1/2}$: $-1{,}5$ V) pour l'ion triphénylsulfonium. Ce résultat n'est pas en accord avec la nature des produits isolés antérieurement dans une réduction macroscopique.[84]

Thiocyanates et thiobenzamide

L'étude de divers thiocyanates a montré que seuls les thiocyanates aromatiques sont polarographiquement actifs dans un domaine facilement accessible (C_6H_5SCN, $-1{,}50$ V; $C_6H_5CH_2SCN$, $-1{,}52$ V en solution hydroalcoolique de LiCl *N*).[85]

La discussion de la valeur expérimentale trouvée pour n ($n = 1{,}26$ pour C_6H_5SCN) a conduit les auteurs à proposer le mécanisme:

$$PhSCN + e \rightarrow PhS\cdot + CN^-$$

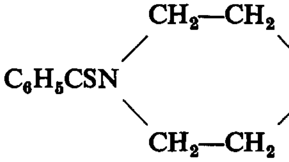
$$2PhS\cdot + Hg \rightarrow (PhS)_2Hg$$

$$(PhS)_2Hg + 2e \rightarrow PhS^- + Hg.$$

Le thiobenzamide (I), le thiobenzanilide (II) et le thiobenzomorpholide (III)

$C_6H_5CSNH_2$ (I)

$C_6H_5CSNHC_6H_5$ (II)

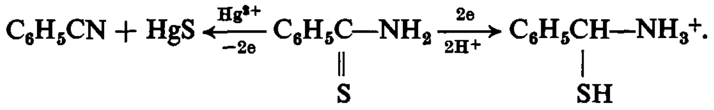


(III)

présentent des vagues *cathodiques* et *anodiques* étudiées par Lund.[87]

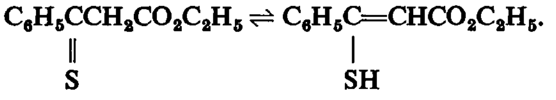
	I	II	III
$E_{1/2}$ cat. (pH: 3,55)	−1,22	−1,14	−1,23
$E_{1/2}$ an. (pH: 10,6)	−0,33	−0,33	−1,54

L'analyse des produits obtenus par réduction ou oxydation sous potentiel contrôlé a permis d'établir le mécanisme:



$$C_6H_5CN + HgS \xleftarrow[-2e]{Hg^{2+}} \underset{\underset{S}{\|}}{C_6H_5C}—NH_2 \xrightarrow[2H^+]{2e} \underset{\underset{SH}{|}}{C_6H_5CH}—NH_3^+.$$

Nous signalerons enfin, dans le domaine des dérivés sulfurés, que la méthode polarographique a été utilisée pour étudier l'équilibre entre le thiobenzoylacétate (IV) et la forme thioénol (V)[88]



$$\underset{\underset{S}{\|}}{C_6H_5C}CH_2CO_2C_2H_5 \rightleftharpoons \underset{\underset{SH}{|}}{C_6H_5C}{=}CHCO_2C_2H_5.$$

(IV) (V)

DERIVES CARBONYLES

Les aldéhydes et les cétones aromatiques se réduisent généralement en deux stades. Le premier stade, qui correspond en milieu acide ou alcalin à une vague à $1e$ conduit à un radical libre susceptible de se dimériser ensuite en pinacol:[89,90,95,100]

$$C_6H_5COR + e + H^+ \rightarrow C_6H_5\dot{C}HOR \xrightarrow{\text{dim.}} \text{pinacol (milieu acide)}$$

$$C_6H_5COR + e \rightarrow C_6H_5\dot{C}OR^- \xrightarrow{\text{dim.}} \text{pinacol (milieu alcalin).}$$

Le radical peut d'ailleurs se réduire en donnant naissance en milieu moyennement acide à une seconde vague à $1e$:

$$C_6H_5\dot{C}HOR + e + H^+ \rightarrow C_6H_5CH_2OR.$$

Les deux vagues sont confondue en milieu neutre.

Divers travaux[91,92] ont conduit à préciser le mécanisme de la protonisation. L'étude de l'influence de la dimérisation du radical sur les vagues polarographiques a permis de conclure en particulier à la réversibilité du premier stade de la réaction.[93–96]

L'influence des substituants a été étudiée systématiquement.[97,98,104,105] En général, l'équation de Hammett est applicable aux potentiels de demi-vague.[99,101] Certains substituants (OH, NH_2, CN) modifient profondément le polarogramme: la réduction se fait alors en un seul stade à 2*e* pour tous les pH.[98] Dans plusieurs cas (phtalaldéhyde[102] et *o*-nitrobenzaldéhyde[103]) on note des anomalies typiques attribuables à des phénomènes d'hydratation du carbonyle.

Le comportement polarographique d'aldéhydes et de cétones aromatiques a également été étudié dans la diméthylformamide.[91,107,108]

La réduction polarographique de cétones substituées sur le carbone en α s'effectue généralement avec rupture de la liaison substituant-carbone:

$$C_6H_5COC(RR')Y + 2e + H^+ \rightarrow C_6H_5COCRR'H + Y^-.$$

On observe systématiquement ce mécanisme lorsque Y est un halogène, un groupe cyané ou un substituant de la forme OR, OCOR, ONO_2, SR ou SCN.[109] Ce mécanisme est d'ailleurs généralisable au cas de la réduction des ω-piperidino et pyridinoacétophénones.[110]

La méthode polarographique a été employée, parallèlement à la spectrophotométrie ultra-violette, pour préciser la structure de l'Amphenone B.[111] Signalons enfin dans cette série une étude systématique des thiobenzophénones.[106]

DERIVES DE CARACTERISATION DU CARBONYLE

(dérivés azotés du type RR'C=NA)

En milieu acide, les oximes,[112,113,114,117,131] les phénylhydrazones,[115,117,131] les semicarbazones[115,117,131] et thiosemicarbazones[115,117] dérivées des aldéhydes aromatiques se réduisent généralement en une vague à 4*e*:

$$RR'C{=}NA + H^+ \rightleftarrows [RR'C{=}NA]H^+$$

$$[RR'C{=}NA]H^+ + 4e + 3H^+ \rightarrow RR'CH{-}NH_2 + AH.$$

Certains résultats ont d'ailleurs conduit à proposer une réduction en deux stades, avec formation intermédiaire de l'imine:[120,131]

$$[RR'C{=}NA]H^+ + 2e + 2H^+ \rightarrow [RR'C{=}NH]H^+ + AH$$

$$[RR'C{=}NH]H^+ + 2e + 2H^+ \rightarrow RR'CH{-}NH_3^+.$$

En milieu neutre, la hauteur de cette vague décroît et le polarogramme présente une allure caractéristique en forme de S renversé.[112] Cette morphologie singulière peut s'interpréter en faisant appel à une modification des conditions interface-solution.[112] On peut envisager en particulier une réaction de protonisation en surface, la forme neutre étant adsorbée.[115,116]

En milieu alcalin, la réduction porte sur la forme basique de la molécule et dans les électrolytes supports usuels, les oximes présentent encore une vague à 4*e*. Par contre les thiosemicarbazones se réduisent alors en une vague à 2*e*, avec formation d'une hydrazine substituée.[115] Pour les phénylhydrazones et les semicarbazones. la vague n'apparaît pas avant la réduction de l'électrolyte support.

Pour les semi et thiosemicarbazones dérivées d'acétophénones substituées, la réduction a toujours lieu avec intervention de 2*e*.[119] Certaines oximes substituées se réduisent en deux vagues à 2*e*, la première vague correspondant à la réduction en imine.[120]

En milieu ammonium quaternaire, les polarogrammes des formes *syn* et *anti* des oximes sont différents.[121–125]

Les polarogrammes de diverses phényhydrazones, semi et thiosemicarbazones aromatiques en milieu alcalin ont été interprétés dans l'hypothèse d'un équilibre entre plusieurs formes tautomères.[126–130]

ACIDES AROMATIQUES ET DERIVES

Dans la série des acides aromatiques ne présentant pas d'autres fonctions réductibles que la fonction acide, quelques auteurs ont étudié l'électroactivité de l'acide benzoïque et de ses dérivés substitués. Seul l'acide salicylique semble donner une vague définie ($E_{1/2} = -2{,}39$ V).[133]

Les données relatives à l'acide benzoïque lui-même ne sont pas concordantes[132,133] et la vague de réduction éventuelle semble difficilement accessible dans les conditions habituelles. Par contre, l'acide phtalique a fait l'objet d'études détaillées. Cet acide peut présenter plusieurs vagues observables en faisant varier la valeur du pH de la solution. La première vague présente un caractère cinétique. L'origine du courant cinétique a été discutée par divers auteurs. Le travail de Furman et Bricker[134] suggérait le mécanisme:

$$\mathrm{HPh^- + H^+ \rightleftarrows H_2Ph}$$

$$\mathrm{H_2Ph + 2e + 2H^+ \rightarrow H_2Chd}$$

(H_2Ph = acide *o*-phtalique, H_2Chd = acide *trans* cyclohexadiène-3,5 dicarboxylique-1,2).

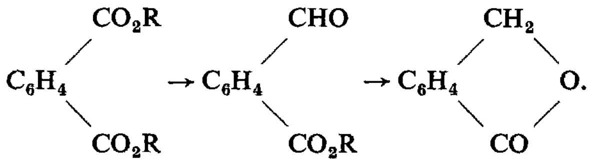
Mais les données de Ryvolová et Hanuš[135] militent plutôt en faveur d'une préréaction faisant intervenir un "superacide" phtalique H_3Ph^+:

$$\mathrm{H_2Ph + H^+ \rightleftarrows H_3Ph^+}$$

$$\mathrm{H_3Ph^+ + 2e + H^+ \rightarrow H_2Chd.}$$

Buck[136] a déterminé par spectroscopie la constante de "superacidité" $K = [H_2Ph].[H^+]/[H_3Ph^+]$. Il a de plus montré que la variation, par rapport à la force ionique, de la constante de vitesse apparente de protonisation indiquait que la charge de l'entité réductible était positive, ceci en analysant l'effet ψ selon Gierst et Hurwitz et Matsuda (résultats polarographiques et chronopotentiométriques).

La plupart des dérivés phtaliques sont eux-mêmes électroactifs. Cette électroactivité a été signalée tout d'abord sur le phtalimide.[137] Dans ce cas la facilité anormale de réduction doit être attribuée à la structure cyclique (*cf.* dérivés orthocondensés). Mais les dérivés non cyclisés sont également facilement réductibles. En particulier le diamide phtalique, l'acide amide et son ester[138] et les ester phtaliques[139] présentent des vagues facilement accessibles. Dans ce dernier cas on observe une vague à 4*e*:



On trouve d'ailleurs dans la littérature de nombreuses applications analytiques de l'électroactivité des dérivés phtaliques: caractérisation et dosage des phtalates,[140–142] des esters des dérivés phtaliques d'amino acides[143] et surtout des phtalimides.

Le cas des acides aromatiques nitrés et des acides cétones aromatiques est signalé dans l'étude des fonctions correspondantes.

NITRILES—AMIDINES—AMIDOXIMES

Le mécanisme de la réduction des nitriles aromatiques a été étudié en détail par Rieger et ses collaborateurs.[144] Cet auteur indique les $E_{1/2}$ suivants pour quelques dérivés caractéristiques (solvant: DMF, sel de fond: perchlorate de tétra-n-propylammonium, polarographe à 3 électrodes):

	Première vague		Deuxième vague	
	$E_{1/2}$	n	$E_{1/2}$	n
C_6H_5CN	−2,74	1	—	—
$C_6H_4(CN)_2o$	−2,12	1	−2,76	2
$C_6H_4(CN)_2m$	−2,17	1	—	—
$C_6H_4(CN)_2p$	−1,97	1	−2,64	1
FC_6H_4CNp	−2,69	3/2	—	—
$HO_2CC_6H_4CNp$	−1,19	1	−2,53	1

La discussion des données polarographiques et des spectres E.S.R. des radicaux organiques obtenus par réduction a conduit les auteurs à proposer les mécanismes:

$$C_6H_5CN + e \rightleftarrows [C_6H_5CN]^{\dot{-}}$$

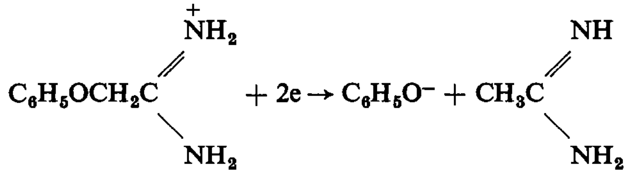
$$\left\{\begin{array}{l} C_6H_4(CN)_2o + e \rightleftarrows [C_6H_4(CN)_2o]^{\dot{-}} \text{ (1 ère v.)} \\ [C_6H_4(CN)_2o]^{\dot{-}} + e \rightleftarrows [C_6H_4(CN)_2o]^{-} \text{ (2 ème v.)} \\ [C_6H_4(CN)_2o] \xrightarrow{SH} C_6H_5CN + S^- + CN^-. \end{array}\right.$$

Les influences structurales ont été étudiées sur les trois séries $(C_6H_5)(R')C{=}C(CN){-}CO_2C_2H_5$, $(C_6H_5)(R')C{=}C(CN)_2$ et $(C_6H_5)(R')C{=}CHCN$. Les dérivés diphénylés $R' = C_6H_5$ présentent deux vagues à 1*e*. Pour les autres dérivés, on n'observe qu'une seul vague définie.[145]

Les amidines aromatiques correspondant aux acides conjugués (I) et (II) sont électroréductibles.

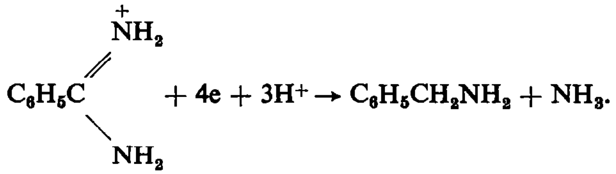
Par électrolyse sous potentiel contrôlé, on a obtenu respectivement le dichloro-2-4 phénol à partir de la dichloro-2-4 phénoxyacetamidine et la benzylamine à partir de la benzamidine.[146] Ces deux résultats suggèrent deux mécanismes différents:

(I)

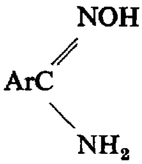


$$C_6H_5OCH_2C\begin{array}{l}\diagup\!\!\!\diagup \overset{+}{N}H_2\\ \diagdown NH_2\end{array} + 2e \rightarrow C_6H_5O^- + CH_3C\begin{array}{l}\diagup\!\!\!\diagup NH\\ \diagdown NH_2\end{array}$$

(II)



$$C_6H_5C\begin{array}{l}\diagup\!\!\!\diagup \overset{+}{N}H_2\\ \diagdown NH_2\end{array} + 4e + 3H^+ \rightarrow C_6H_5CH_2NH_2 + NH_3.$$

Les benzamidoximes aromatiques  $ArC(=NOH)NH_2$ sont également électroréductibles. Elles donnent une vague à 2*e* ($E_{1/2} = -1{,}25$ V pour le dérivé non substitué à pH 4) mais le mécanisme de réduction n'a pas été précisé.[147]

DERIVES NITRES

Les dérivés nitrés aromatiques présentent en général les deux vagues de réduction classiques correspondant respectivement à la formation de phénylhydroxylamine et d'amine.[148] L'oscillopolarographie à variation linéaire de tension a permis de mettre en évidence la formation de composés intermédiaires.[168] Le nitrobenzène a également fait l'objet d'études par polarographie à tension alternative surimposée.[169,170]

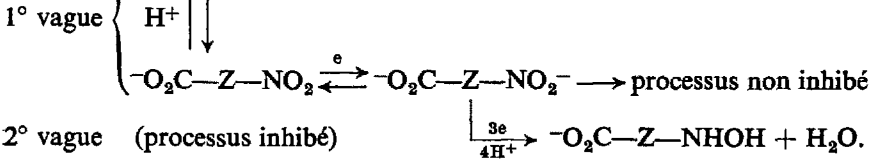
Le mécanisme de la réduction correspondant à la première vague a donné lieu à de nombreux travaux. Ces études ont permis de mettre en évidence, en présence de substances tensioactives, un premier stade de réduction conduisant à la formation réversible d'un anion radicalaire:[151–157]

$$C_6H_5NO_2 + e \rightarrow [C_6H_5NO_2]^-.$$

Ce mécanisme permet de rendre compte de l'apparition d'une vague à 1*e* dans la diméthylformamide et l'acétonitrile.[158,159] La présence du radical a été vérifiée dans ce dernier milieu par résonance paramagnétique électronique.[160,161]

L'influence des substituants sur la réduction du NO_2 a été très étudiée; les potentiels de demi-vague obéissent en général à l'équation de Hammett.[161–164]

Dans certains cas, la présence du substituant se traduit par une anomalie du polarogramme. En particulier, la *p*-nitraniline et l'*o*- et le *p*-nitrophénol ne suivent pas le mécanisme habituel et se réduisent en une seule vague à 6*e*. Ce comportement particulier est dû à la transformation de la phénylhydroxylamine formée au premier stade en une forme quinoïde facilement réductible.[148] Ce mécanisme a été vérifié par chronopotentiométrie,[150] et l'expression mathématique du courant polarographique a été calculée récemment.[149] Le comportement particulier du trinitrobenzène est lié à l'apparition de formes acinitrées.[165] La scission de la vague à 4F de l'*o*-nitrobenzaldéhyde a été attribuée à une hydratation du carbonyle et a fait l'objet d'une étude chronopotentiométrique.[166] La scission de la vague des acides nitrobenzoïques en milieu alcalin ne peut être identifiée à une vague cinétique classique de recombinaison ion–acide. Cette impossibilité a été signalée tout d'abord lors d'une discussion sur la valeur des $E_{1/2}$.[163] L'origine de la scission a été précisée récemment.[167] La scission correspond à une inhibition du stade irréversible de la réaction par une substance tensioactive (alcool, gélatine); cette inhibition n'est sensible que sur la base conjuguée de l'acide[157]



$$\text{1° vague}\left\{\begin{array}{l} HO_2C{-}Z{-}NO_2 \overset{e}{\rightleftarrows} HO_2C{-}Z{-}NO_2^- \xrightarrow[4H^+]{3e} HO_2C{-}Z{-}NHOH + H_2O \\ H^+ \uparrow\downarrow \\ {}^-O_2C{-}Z{-}NO_2 \overset{e}{\rightleftarrows} {}^-O_2C{-}Z{-}NO_2^- \longrightarrow \text{processus non inhibé} \end{array}\right.$$

$$\text{2° vague (processus inhibé)} \qquad \xrightarrow[4H^+]{3e} {}^-O_2C{-}Z{-}NHOH + H_2O.$$

La vague normale de dissociation due à la recombinaison ion–acide n'apparaît que dans le cas de l'acide *o*-nitrobenzoïque[157,167] et des acides nitrophtaliques.[174]

Plusieurs composés nitrés aromatiques ont été étudiés dans l'acide acétique[171] et dans SO_4H_2[172] et on doit noter enfin dans cette série une revue d'ensemble de Stradins.[173]

DERIVES C ET N NITROSES

Le nitrosobenzène et les nitrosonaphtalènes forment avec les hydroxylamines correspondantes des systèmes redox réversibles. La vague polarographique de réduction du dérivé nitrosé ou d'oxydation de l'hydroxylamine correspond à 2*e*:[175–177]

$$C_6H_5NO + 2e + 2H^+ \rightleftharpoons C_6H_5NHOH.$$

Le produit de la réduction est donc l'hydroxylamine comme pour les dérivés nitrés.

L'introduction de certains substituants (OH, NH_2) en position ortho ou para modifie le polarogramme. La réduction du *p*-nitrosophénol[177,178] ou de l'α-nitroso-β-naphtol[179] conduit directement à l'amine correspondante avec consommation de 4*e*. Ce comportement est dû, comme en série nitrée, à la transformation de l'hydroxylamine en une forme quinoïde facilement réductible;[177] l'expression mathématique du courant cinétique résultant a pu être calculée.[180]

L'α-nitroso-β-naphtol a été particulièrement étudié, en raison de son emploi en analyse[179,182,183] et la littérature indique également une étude sur la *N*-nitroso 1-naphtylhydroxylamine (néocupferron).[186]

Les dérivés N-nitrosés des amines aromatiques secondaires présentent, selon le milieu, une vague irréversible à 4*e* ou 2*e*.[184,185] La réduction a lieu selon le mécanisme:[185]

$$RR'NNOH^+ + 4e + 4H^+ \rightarrow RR'NNH_3^+ + 2H_2O \quad \text{(milieu acide)}$$

$$2RR'NNO + 4e + 3H_2O \rightarrow 2RR'NH + N_2O + 4OH^- \quad \text{(milieu neutre ou basique).}$$

La polarographie des dérivés nitrosés a fait l'objet d'une mise un point.[181]

DERIVES AZOIQUES ET DIAZOIQUES—PHENYLHYDRAZINES

Le système *trans*-azobenzène-hydrazobenzène est réversible à l'électrode à goutte entre pH 2 et 6.[187] La réversibilité du système dépend de la concentration et ce résultat paraît lié à des phénomènes d'adsorption.[189] Il existe une différence sensible entre les potentiels de demi-vague du *cis* et du *trans*- azobenzène[197] et la cinétique de la transformation d'une forme en l'autre a été étudiée polarographiquement.[188]

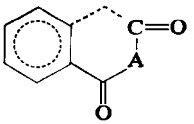
L'influence des substituants a fait l'objet de divers travaux;[190–193] l'équation de Hammett's applique aux $E_{1/2}$.[194,195] Divers colorants azoïques ont été étudiés.[196] La réduction de l'Erichrome Violet B consomme 4*e* et conduit à des anilines substituées.[197]

Les sels de diazonium dérivés d'amines aromatiques présentent 2 vagues de réduction.[198–201] La première vague correspond à une réduction à 1*e*, avec formation d'un radical libre qui réagirait avec le mercure.[200–202] Les résultats concernant la deuxième vague ne sont pas concordants. Certains auteurs[198] indiquent un processus à 1 faraday, d'autres un processus à plusieurs faradays.[199,202] Les phénomènes d'adsorption doivent d'ailleurs jouer un rôle prépondérant dans ce cas.[202]

La phénylhydrazine et ses dérivés *p*-méthylé, *p*-chloré et *p*-nitré donnent une vague *anodique* bien définie. On a trouvé pour n une valeur de 3,6 et les auteurs ont suggéré que l'oxydation ne conduit pas au sel de diazonium ou à la diimine mais correspond à la formation d'un composé complexe avec le mercure. La vague est d'ailleurs compliquée par des réactions avec le mercure mais les potentiels de demi-vague des dérivés substitués vérifient l'équation de Hammett.[203]

CYCLES ORTHO—CONDENSES SUR UN NOYAU BENZENIQUE

Cette rubrique mérite d'être citée dans une analyse d'ensemble sur la polarographie des composés aromatiques car l'analyse polarographique a été utilisée systématiquement et avec succès pour suivre de nombreuses cinétiques chimiques, plus particulièrement les cinétiques de cyclisation ou d'ouvertures de cycles ortho-condensés. L'effet de la cyclisation a souvent été signalé en spectroscopie. En polarographie le seul effet de la cyclisation n'est pas suffisant pour déplacer sensiblement le potentiel de demi-vague. Mais si la cyclisation entraîne une tension ou une conjugaison la différence entre le composé linéaire et le composé cyclique peut devenir considérable. Le cas du phtalimide est particulièrement typique. Le phtalimide donne en effet des vagues nettement définies pour des potentiels respectifs de $-0{,}67$ V (pH $= 0$) et $-1{,}33$ V (pH $= 12$) alors que la vague du benzamide n'apparaît qu'à $-1{,}86$ V dans l'iodure de tétrabutylammonium. Des études systématiques[204] portant sur les succinimides, les maléimides, les phtalimides, les phtalonimides, les homophtalimides et leurs produits de condensation ont montré que:



(I)

(a) Les composés β-dicarbonylés hétérocycliques du type I sont réductibles dans le domaine accessible si les deux carbonyles sont conjugés avec une double liaison ou liés à un cycle aromatique soit directement soit par l'intermédiaire d'un carbone non saturé (conjugaison directe ou croisée).

(b) En général la vague disparaît après ouverture du cycle.

Le mécanisme de la réduction du phtalimide a été discuté par Tirouflet *et al.*[205] et Ryvolova.[206] L'électrolyse sous potentiel contrôlé conduit à l'hydroxyphtalimidine[204c] et l'évolution de la morphologie de la vague en fonction du pH milite en faveur du mécanisme:

$$\begin{tikzcd}
\text{Phtalimide} + e + H^+ \arrow[r] & \text{radical libre} \arrow[r, "+e+H^+"] \arrow[d, shift right, "H^+"'] & \text{Hydroxyphtalimidine} \\
& \text{radical protonisé} \arrow[u, shift right] \arrow[r, "+e"] & \text{Hydroxyphtalimidine}
\end{tikzcd}$$

Les dérivés N-substitués du phtalimide présentent un comportement analogue et les $E_{1/2}$ des dérivés substitués dans le cycle sont justiciables de la corrélation de Hammett.[205]

Les possibilités d'analyse polarographique dans les différentes séries signalées ont été utilisées pour étudier la cinétique de l'hydrolyse des phtalimides N et C-substitués.[208,209] Elles ont permis de déceler et d'analyser systématiquement le phénomène "isocinétique".[207]

Tous les cycles ortho-condensés présentant un groupe carbonyle et un oxygène directement branchés sur le cycle aromatique sont également électroactifs. Les premières données systématiques sur ces dérivés ont été rassemblées par Kolthoff et Lingane.[210] Depuis cette publication, des études systématiques ont permis de préciser l'influence des données structurales et les mécanismes. Ces études concernent les aurones,[211] les isoflavones,[212] les xanthones,[213] les chromannones[214] et les chromones.[214,215] La série des chromannones doit d'ailleurs être mise en parallèle avec celle des *o*-hydroxychalcones par suite de la transformation réciproque de ces composés. Les $E_{1/2}$ apparaissent toujours (en valeur absolue) dans l'ordre:

$$o\text{-hydroxychalcone} < \text{chromone} < \text{chromannone}$$

Le dosage des *o*-hydroxychalcones en présence de chromannones se fait au mieux par polarographie classique. Par contre pour déceler la chromannone en présence de chalcone, il est souvent avantageux de s'adresser à la polarographie oscillographique à courant imposé.[216,217] L'influence des incréments de structure est nettement plus marquée pour les *o*-hydroxychalcones que pour les chromannones et, si l'on utilise l'analyse polarographique pour séparer deux chromannones, on aura toujours intérêt à transformer au préalable la chromannone en chalcone pour dilater la gamme des incréments.[216] C'est d'ailleurs l'analyse polarographique qui a permis de faire l'étude thermodynamique et cinétique de l'équilibre *o*-hydroxychalcone $\rightleftarrows$ chromannone en fonction du pH et des paramètres chimiques.[216,218]

Summary—A review of the polarography of aromatic compounds is presented.

Zusammenfassung—Es wird eine Übersicht über die Polarographie von Aromaten gegeben.

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POLAROGRAPHIE CHINOIDER VERBINDUNGEN

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Zusammenfassung—Es wird eine Übersicht über die Polarographie von Chinonen und ähnlichen Substanzen gegeben.

Eingehendere polarographische Untersuchungen über Chinone sind erst seit etwa 20 Jahren erfolgt, obwohl dieses Gebiet durch potentiometrische Analysen vorbereitet war. Zunächst schien es, daß seitens der Polarographie keine wesentlich neuen Erkenntnisse zu erwarten wären, doch zeigte sich in den letzten Jahren, daß über die bekannten bielektronigen "Normal-Chinone" hinaus spezielle Chinonderivate mit besonderen Eigenschaften existieren. Welche Aussagemöglichkeiten die moderne Polarographie hierüber machen kann, soll in der folgenden Übersicht an charakteristischen Beispielen erläutert werden.

CHINONE IN WÄSSRIGEN LÖSUNGEN

Normal-Chinone und ihre Substituentenabhängigkeiten

Typisch für chinoide Gruppierungen in Normal-Chinonen ist im allgemeinen der reversible Austausch von zwei Elektronen und zwei Protonen. Die Erfahrung lehrt, daß reversible Redoxreaktionen an das Vorhandensein von konjugierten Heteroatomen (N;O)[1] gebunden sind. Das Chinonmethan $O{=}C_6H_4{=}CH_2$ z.B. verhält sich irreversibel, weil ein Wasserstoffatom an einem C-Atom angelagert werden muß, ähnlich wie bei Ketonen oder Aldehyden.

Zwischen der oxidierten und reduzierten Form liegt der Oxidationsstatus des Semichinons. Die Semichinonbildungskonstante K_s resultiert nach

$$K_s = \frac{[\dot{Q}H]^2}{[QH_2][Q]} \tag{1}$$

worin Q die chinoide Komponente, $\dot{Q}H$ das Semichinon und QH_2 die reduzierte Form bedeuten.

Der Maximalgehalt von $\dot{Q}H$ in Prozent (S_M) beim Halbstufenpotential ist nach dem Massenwirkungsgesetz mit K_s verknüpft nach:

$$S_M = \frac{100 \cdot \sqrt{K_s}}{2 + \sqrt{K_s}} \tag{2}$$

Bei $K_s = 1$ ($\dot{Q}H = 33{,}3\,\%$) fallen beide Halbstufenpotentiale zusammen. Erst ab $K_s = 16$ (entsprechend 66,7% $\dot{Q}H$) beginnt die deutliche Aufspaltung der Kurve in zwei einelektronige Teilstufen mit $E_{1/4}$ und $E_{3/4}$. $K_s < 1$ bedeutet, daß das Potential der Reaktion $Q \rightarrow QH_2$ bereits positiver liegt, als das der Reduktion $Q \rightarrow \dot{Q}H$, und die ideale Stufe wird registriert.

Die pH-abhängigen Redoxpotentiale (*bzw.* Halbstufenpotentiale) der beiden Teilsysteme weisen daraufhin, daß basische Semichinone in saurer Lösung und umgekehrt, daß Semichinone saurer Natur in alkalischer Lösung, als Salze in höheren Konzentrationen zu finden sind.

Weitere Substitution der H-Atome am *p*-Benzochinonkern z.B. mit Methylgruppen, vergrößert den Wert von K_s. Beim Durochinon (Tetramethylbenzochinon-(1,4)) liegen bereits nennenswerte Konzentrationen an Semichinonen im Gleichgewicht vor. Stabilisierenden Einfluß auf die Semichinonbildung zeigen im besonderen organische Lösungsmittel, die sorgfältig von Wasserspuren befreit worden sind. Hierauf wird im Abschnitt *Chinone in nichtwässrigen Lösungsmitteln* eingegangen werden.

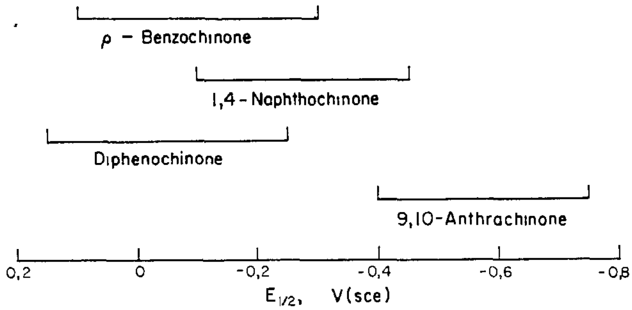


ABB. 1.—Potentialbereiche der Halbstufenpotentiale substituierter Chinone; Halbstufenpotentiale (gegen gesät. Kalomelelektrode) bei pH ≈ 7.

Kinetische Untersuchungen von Vetter[2] auf der Grundlage von Überspannungsmessungen an Festelektroden klärten, daß die beiden Durchtrittsreaktionen nacheinander ablaufen. Hierbei ist es ohne Bedeutung, ob das Semichinon $\dot{Q}H$ in nachweisbaren Gleichgewichtskonzentrationen auftritt. In jüngster Zeit wurden diese Ergebnisse an der Tropfelektrode bestätigt.[3]

In sauer Lösung (pH $<$ 5) vollziehen sich nach Vetter beim *p*-Benzochinon z.B. die Durchtrittsreaktionen mit den protonisierten Formen (QH^+ und $\dot{Q}H_2{}^+$), im neutralen und alkalischen Milieu tauschen die nichtprotonisierten Formen (Q und $\dot{Q}H$) die Elektronen an der Elektrode aus.

Betrachtet man den ersten Schritt der Reduktion, so erfolgt chemisch gesehen eine Aufspaltung der C=O π-Bindung, die auch bei der Ketonreduktion zu gleichartigen Zwischenprodukten (C-Radikalen) führt. Die elektrochemische Reaktionsarbeit, die gleich der freien Enthalpie ist, liegt um so niedriger, je schwächer die π-Bindung durch Mesomerie- und Induktionseinflüsse ist und je höher die Mesomerieenergie der entstehenden Verbindung liegt.[4] Verlängerte Konjugationssysteme, wie sie in den Dipheno- und Stilbenchinonen der Fall sind, verkleinern die π-Bindungsenergien der C=O Gruppe, d.h. die Halbstufenpotentiale weisen positivere Werte auf (größere Redoxpotentiale), als die entsprechenden Benzochinonderivate (s. Abb. 1).

Wird eine C=C Doppelbindung des Benzochinonkerns durch Anellierung in das benzoide Konjugationssystem des zweiten Ringes einbezogen, so erhöht sich die Bindungsordnung an der Ketogruppe. Wiederholt man die Anellierung, gelangt man zu den Anthrachinonen, deren HSP wiederum kleiner (negativer) sind als entsprechende Derivate der Naphthochinone. Diese Wechselwirkungsänderungen erklären teilweise die Lage der Reduktionsbereiche im Schema der Abb. 1. Die Ausdehnung der Zonen über die Potentialwerte bestimmen die Wechselwirkungseffekte der Substituenten. Bei der Aufklärung von Konstitutionsformeln, z.B. in der Antibiotikaforschung, ist eine polarographische Untersuchung besonders dann vorteilhaft, wenn aus dem chemischen Verhalten Hinweise auf eine Chinonstruktur existieren.[5]

Neben der IR-Aufnahme ist die Potentiallage eine Stütze für die Struktur des Grundkörpers, wenn die elektrochemische Methode unter einigermaßen normalen Lösungsmittel- und pH-Bedingungen eingesetzt werden kann.

Ausführliche theoretische Berechnungen am π-Elektronensystem von Chinonen auf der Grundlage der LCAO-MO-Methode wurden von Koutecký und Mitarbeitern[6] durchgeführt. Die Redoxpotentiale ließen sich gut mit den sogenannten "bizentrischen Lokalisierungsenergien" (Atomlokalisierungsenergien der beiden sauerstoffbindenden Zentren) korrelieren. Aber auch die den Resonanzenergien entsprechenden Werte, sowie die Differenzen der π-Elektronenenergien der Chinone und Hydrochinone[7] zeigen die erwartete Proportionalität.

Es wurden auch eine ganze Reihe Beziehungen zwischen Halbstufenpotentialen von Chinonen und experimentellen oder berechneten spektroskopischen Daten gefunden,[4,6,8,46] so z.B. zu den langwelligsten Anregungsenergien, den untersten vakanten Energieniveaus, den Orbital-Energiedifferenzen, sowie den Wellenzahlen der Charge-transfer-Komplexbanden (Abb. 2) und den Wellenzahlverschiebungen bei Ausbildung von Wasserstoffbrückenkomplexen.

Substitution der Chinongrundkörper beeinflußt je nach Art und Stellung der Substituenten die Elektronenverteilung im Molekül und damit auch an den polarographisch aktiven Zentren, was eine Halbstufenpotentialverschiebung zur Folge hat. Systematische Durchmusterung vieler Halbstufenpotentialwerte durch Zuman[9] führten zu linearen Freien-Enthalpie-Beziehungen.

Die Verschiebung des Redoxpotentials E_0 oder Halbstufenpotentials $E_{1/2}$ ist proportional der Änderung der Logarithmen der Gleichgewichtskonstanten der substituierten (K_X) und nichtsubstituierten Verbindung (K_H):

$$\Delta E_{1/2} \sim \ln K_X/K_H \tag{3}$$

wobei ln K mit der Freien Enthalpie ΔG durch die bekannte Beziehung: $\Delta G = -RT \ln K$ verknüpft ist.

Die modifizierte Hammettgleichung für p-chinoide Systeme formuliert Zuman[9] folgendermaßen:

$$\Delta E_{1/2} = \rho_{\pi,\mathrm{p-Ch}}\, \sigma_X \tag{4}$$

Hierin bedeutet $\rho_{\pi,\mathrm{p-Ch}}$ die Reaktionskonstante, die die Empfindlichkeit der π-Elektronen des p-chinoiden Systems gegenüber den Substituenteneffekten ausdrückt, und σ_X die Substituentenkonstante nach Taft, die eine Maßzahl für den Einfluß des Substituenten auf die Elektronendichte am Reaktionszentrum darstellt. Ungesättigte Verbindungen, wie es die Chinone sind, enthalten in der Substituentenkonstante

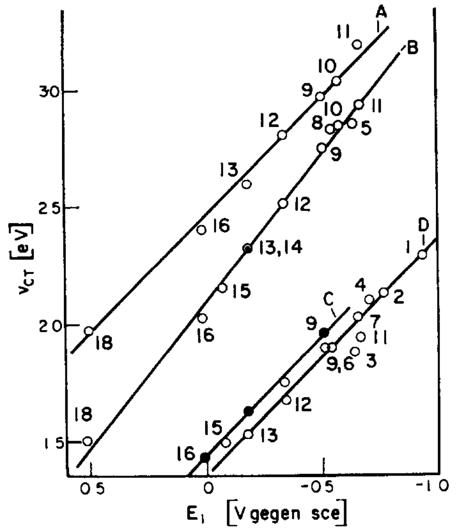


Abb. 2.—Abhängigkeit der Energie der langwelligsten Charge-transfer-Bande bei Chinonkomplexen von den Redoxpotentialen der Chinone (in Acetonitril gemessen). Komplexe mit: (*A*) Hexamethylbenzol in CCl_4; (*B*) Pyren in CH_2Cl_2; (*C*), (*D*) Tetramethyl-*p*-phenylendiamin (*C*) in Cyclohexan, (*D*) in CH_2Cl_2. Vgl. [8]. (*1*)–(*3*) 9,10-Anthrachinon substituiert mit: (*1*) H; (*2*) 1-OH; (*3*) 1,8-diOH; (*4*)–(*6*) 1,4-Naphthochinon substituiert mit: (*4*) H; (*5*) 2-OH; (*6*) 5-OH; (*7*) 9,10-Phenanthrenchinon; (*8*) 1,2-Naphthochinon; (*9*)–(*18*) 1,4-Benzochinon substituiert mit: (*9*) H; (*10*) CH_3; (*11*) 2,5-diCH_3; (*12*) Cl; (*13*) 2,6-diCl; (*14*) 2,5-diCl; (*15*) triCl; (*16*) tetraCl; (*17*) tetraBr; (*18*) (2,3-diCl, 5,6-diCN).

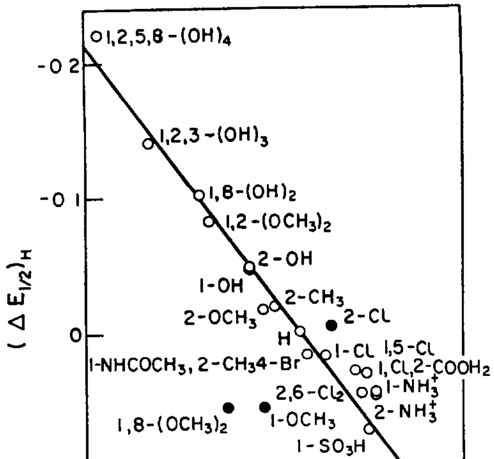


Abb. 3.—Abhängigkeit der Halbstufenpotentiale substituierter 9,10-Anthrachinone von der Summe der Substitutionskonstanten ($\Sigma\sigma_p$). Die Halbstufenpotentiale wurden unter Verwendung von 10%iger H_2SO_4 in Eisessig gemessen und als relative Verschiebungen gegenüber der nichtsubstituierten Verbindung aufgetragen ($(\Delta E_{1/2})_H$). Reaktionskonstante $\rho_{\pi,p\text{-}OH} = +0{,}14$ V (die schwarzen Punkte sind nicht mit zur Ermittlung von ρ herangezogen worden). Vgl. [9].

neben dem induktiven Effekt, mesomere Anteile und man muß genauer schreiben

$$\Delta E_{1/2} = \rho^{\mathrm{I}}_{\pi,\mathrm{p-Ch}}\sigma_{\mathrm{X}}{}^{\mathrm{I}} + \rho^{\mathrm{M}}_{\pi,\mathrm{p-Ch}}\sigma_{\mathrm{X}}{}^{\mathrm{M}} \tag{5}$$

Nimmt man an, daß $\rho^{\mathrm{I}}_{\pi,\mathrm{p-Ch}} = \rho^{\mathrm{M}}_{\pi,\mathrm{p-Ch}}$ ist, vereinfacht sich Gleichung (5) zu:

$$\Delta E_{1/2} = \rho_{\pi,\mathrm{p-Ch}}(\sigma_{\mathrm{X}}{}^{\mathrm{I}} + \sigma_{\mathrm{X}}{}^{\mathrm{M}}) \tag{6}$$

In erster Näherung kann man den $\sigma_{\mathrm{p-X}}$ -Wert verwenden, weil dieser (im Gegensatz zum $\sigma_{\mathrm{m-X}}$ -Wert) den mesomeren Effekt der Aromaten mit enthält. Damit können wir Gleichung(6) dahingehend vereinfachen, daß wir nun schreiben

$$\Delta E_{1/2} = \rho_{\pi,\mathrm{p-Ch}}\,\sigma_{\mathrm{p-X}} \tag{7}$$

Übereinstimmende Ergebnisse wurden hin und wieder auch gefunden, wenn für einen ortho-Substituenten ein Wert eingesetzt wird, den man aus $(\sigma_{\mathrm{p-X}} + \sigma_{\mathrm{m-X}})/2$ ermittelt hat.

Der Effekt mehrerer gleichartiger oder verschiedener Substituenten läßt sich in den meisten Fällen durch Summation der einzelnen Substituentenkonstanten erfassen. Vladimircev und Stromberg[10] haben etwa 50 Naphthochinonderivate polarographisch untersucht, die in 2- und 3-Stellung jeweils substituiert waren. Aus der sehr umfangreichen Arbeit geht unter anderem hervor, daß in der Regel die Additivität der Substituentenkonstanten im Bezug auf die Korrelation zu den Halbstufenpotentialen gültig ist.

In oben erwähnter Arbeit[10] fehlen jedoch die quantitativen Beziehungen, wie sie später von Zuman aufgestellt wurden,[9] doch geht aus den Werten und der Diskussion bereits hervor, in welcher Weise Substituenten über den induktiven Effekt als Elektronendonator oder-acceptorgruppen die Reduktion entsprechend erschweren oder erleichtern.

Abbildung 3 zeigt eine graphische Darstellung der von Starka und Mitarbeitern[11] gemessenen Halbstufenpotentialverschiebungen in Abhängigkeit von der Summe der Substituentenkonstanten ($\Sigma\sigma_{\mathrm{X}}$).

In Tabelle I ist die Halbstufenpotentialverschiebung substituierter Anthrachinone gegenübergestellt, wenn z.B. anstelle von Wasser als Lösungsmittel 50%iges Äthanol verwendet wird. Die Änderung der Acidität des Mediums geht in die Reaktionskonstante $\rho_{\pi,\mathrm{p-Ch}}$ ein, so daß die Abweichungen durch die geänderten polaren Effekte des Lösungsmittels resultieren (Solvatationseinflüsse).

TABELLE I.—VERSCHIEBUNG DER HSP SUBSTITUIERTER ANTHRACHINONE IN 0,1N NaOH/H_2O UND IN 50% ÄTHANOL/H_2O (vgl. [9])

Substituent	$(E_{1/2})_H$, V	
	Wasser	50% Äthanol
1-SO_3^-	$+0{,}01_2$	+0,01
2-SO_3^-	$+0{,}07_0$	+0,01
1-O^-	$-0{,}03_7$	−0,05
2-O^-	$-0{,}13_7$	−0,19
1,2-di O^-	$-0{,}19_3$	−0,23
1,4-di O^-	$-0{,}06_2$	—
1,8-di O^-	$-0{,}09_2$	—
2,6-di O^-	$-0{,}28_0$	−0,42

Substitution am Benzolring bei bi-, tri- und polycyclischen Systemem hat in der Regel einen kleineren Einfluß auf die Verschiebung des Potentials.

Neuere Bestimmungen von Aktivierungsenthalpien und-entropien haben gezeigt, daß die Annahme konstanter Aktivierungsentropien innerhalb einer Verbindungsklasse selten zutrifft. Wahrscheinlich sind hier Solvatationseffekte im Spiel, die bei einer Änderung des Substituenten sehr beträchtlich beeinflußt werden können. Darin sind Abweichungen und Nichtadditivität von Substitutionskonstanten zu einem nicht geringen Teil begründet.

Ein der Gleichung(3) entsprechender Zusammenhang zwischen Halbstufenpotentialen und Reaktionsgeschwindigkeitskonstanten:

$$B \, \Delta E_{1/2} = \Delta \log k \tag{8}$$

konnte mehrfach bei verwandten chinoiden Substanzreihen experimentell bestätigt werden (vgl. Kapitel *Katalytische Hydrierungen*).

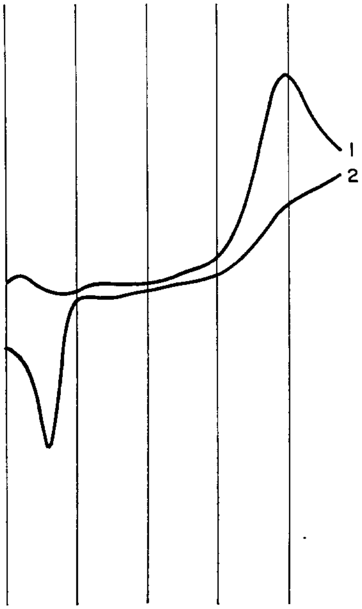


ABB. 4.—Strom-Spannungs-Kurve der Anthrachinon-1,5-disulfonsäure mit Hilfe der stationären Quecksilbertropfelektrode nach Vogel registriert. 4 · 10^{-4} M Depolarisator, 40% Isopropylalkohol, pH 7. (*1*) Kurve von 0,0 V bis −1,0 V; (*2*) Kurve von −1,0 V bis 0,0 V. NCE; 200 mV/Absz., Empf. 1 : 3. Vgl. [37].

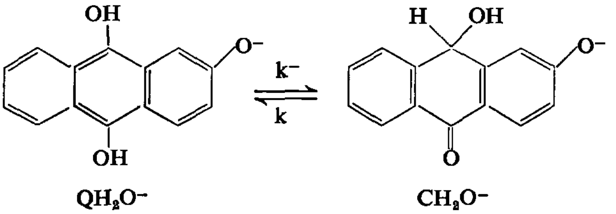
Chinone mit besonderen Adsorptionseigenschaften

Im allgemeinen macht sich auch bei schwerlöslichen Chinonen keine auffallende Deformation der zweielektronigen Stufe bemerkbar. Bisher kennen wir nur einige in 1-Stellung substituierte Anthrachinone, die sich in saurer Lösung durch unregelmäßige Vorstufen[12,13] von denen mit gleichen Substituenten in 2-Stellung beträchtlich unterscheiden. Wegen der Form ihrer zyklischen Polarogramme am stationären Tropfen (Abb. 4), muß man sogar von "irreversiblen Chinonen" sprechen, da der Oxidationspeak sich um *ca.* 0,5 V positiver ausbildet. Nach unserer Vorstellung liegt die Ursache in den besonderen Adsorptionseigenschaften des Hydrochinons, in welchem die benachbarten Substituenten $—SO_3^-$, —OH, $—NH_2$ durch Wasserstoffbrücken fixiert werden. In diesen quasi Vier- oder Fünfring-Systemen verläuft die Reoxidation gegenüber freien Hydrochinongruppen erschwert, wozu auch die schwerlösliche Deckschicht des Hydrochinons beiträgt.

Chinone im Gleichgewicht

Hierunter sollen Chinone oder Hydrochinone verstanden werden, die in Lösung im Gleichgewicht mit einer anderen Form, etwa einem Tautomeren, stehen.

Tautomerie-Gleichgewicht: 2-Hydroxy-Anthrahydrochinonanion und 2-Hydroxy-Oxanthronanion. Da die Gleichgewichtseinstellung nur in alkalischer Lösung[14] zu verfolgen ist, sind Dissoziationsformen daran beteiligt:

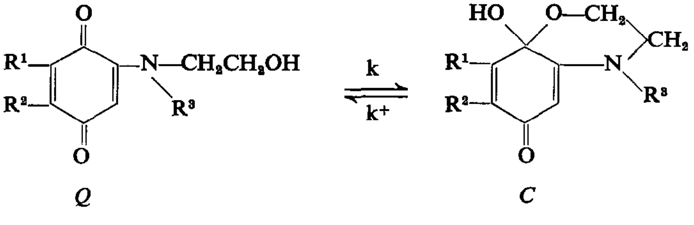


(9)

Der Reaktionsstart erfolgt durch rasche pH-Erhöhung einer 2-Hydroxy-Anthrahydrochinonlösung oder nach schneller katalytischer Reduktion (Pd-Sol-Wasserstoff[15]) des 2-Hydroxy-Anthrachinonanions im gewünschten pH-Bereich. Die Gleichgewichtseinstellung(9) erfolgt so langsam, daß Diffusionsströme von QH_2O^- und CH_2O^- gemessen werden bei einer Halbstufenpotentialdifferenz von etwa 0,66 V (Abb. 5). Die Änderung der Stufenhöhen erfolgt symmetrisch und das Tautomerie-Gleichgewicht zwischen den Hydroxyanthronformen und den Hydrochinonen erreicht bei pH 10 (etwa dem pK_1-Wert des Dissoziationsgleichgewichtes $QH_2OH \rightleftharpoons QH_2O^-$) ein Maximum (Abb. 6).

Obwohl bei diesem Tautomerie-Gleichgewicht keine kinetischen Grenzströme auftreten, ist seine vollständige Analyse nur mit Hilfe der Absorptionsspektroskopie möglich.

Kette-Ring-Gleichgewicht bei 2-[Hydroxyäthylamino]-benzochinonen. Ein interessantes Betätigungsfeld für polarographische Untersuchungen aller Spezialrichtungen[16–20] bieten die Gleichgewichts-Chinone, von denen nahezu 20 Vertreter vom Typ *Q* bekannt sind, die im mittelschnellen Gleichgewicht mit den Chinolformen *C*



(10)

stehen. Charakteristisch für diesen Typus ist die positive reversible Stufe der Form *Q* und die um 0,8 V negativere irreversible Stufe der Form *C*. Bei kleiner Gleichgewichtskonstante $K_1 = [Q]/[C]$ z.B. im Falle $R^1 = R^2 = H$, $R^3 = CH_3$, weist die

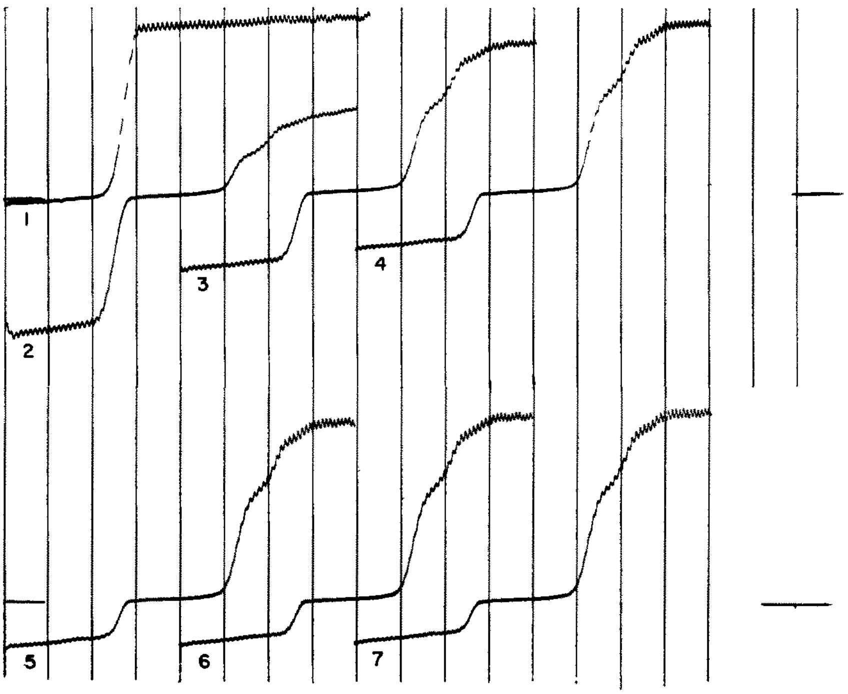


Abb. 5.—Polarographische Verfolgung der Gleichgewichtseinstellung zwischen dem Anthrahydrochinon-Anion und dem Oxanthron-Anion. $2 \cdot 10^{-4}$ M 2-Hydroxyanthrahydrochinon, Britton-Robinson-Puffer pH 8, 20% Isopropylalkohol, 40°. (*1*) Reduktionsstufe des Anthrachinons; (*2*) nach Reduktion durch Palladiumsol, Kurve registriert nach: (*2*) O; (*3*) 10 Min.; (*4*) 20 Min.; (*5*) 30 Min.; (*6*) 40 Min.; (*7*) 50 Min. (5–7 bei nahezu erreichtem Gleichgewicht). Galvanometernullinie eingezeichnet. Kurven von 0,0 V, 200 mV/Absz., NCE., Empf. 1 : 15 Vgl. [15].

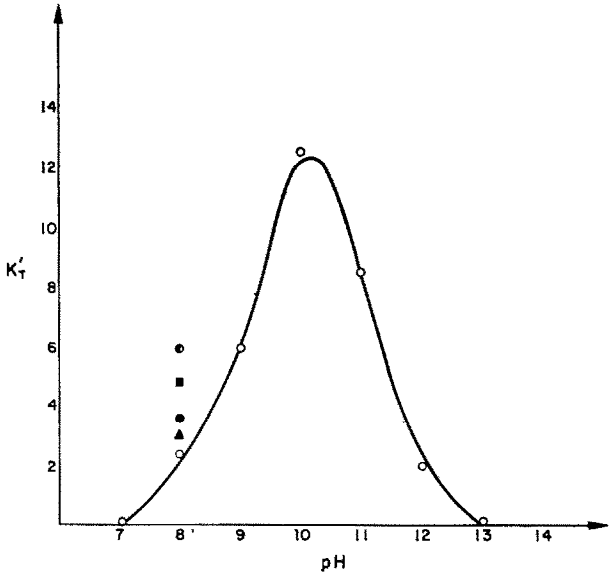


Abb. 6.—Abhängigkeit der Tautomerisierungskonstante K_T = Oxanthron/Anthrahydrochinon vom pH-Wert. Für pH 8 Werte bei: ○ 25°; ▲ 35°; ● 45°; ■ 55°; ◐ 65°. Vgl. [15].

niedrige Stufe der Form Q einen kinetischen Grenzstrom auf, dem sich in wäßriger Lösung ein (nichtwirbelndes) kinetisches Maximum überlagern kann (Abb. 7). Die Analyse dieser vorgelagerten Reaktion ist nicht nur mit Hilfe der Absorptionsspektroskopie zur Bestimmung der K_1-Werte möglich, sondern auch aus der Frequenzabhängigkeit der Peakhöhe von Wechselstrompolarogrammen nach Breyer läßt sich ein $\tilde{K}_1$-Wert ermitteln, z.B.:

	K_1	$\tilde{K}_1$	$\Delta G \left[\frac{kcal}{Mol}\right]$	$\Delta H \left[\frac{kcal}{Mol}\right]$	ΔS [Cl]
$R^1 = R^2 = H, R^3 = CH_3$	$2{,}8 \cdot 10^{-2}$	$3{,}3 \cdot 10^{-2}$	2,1	5,9	12
$R^1 = R^2 = H, R^3 = CH_2CH_2OH$	$50 \cdot 10^{-2}$	$40 \cdot 10^{-2}$	0,3	4,2	12

Aus den Gleichungen für kinetische Ströme bei vorgelagerten Reaktionen resultiert das Produkt kK_1 und nach Einsetzen erhält man Tautomerisierungsgeschwindigkeitskonstanten der Größenordnung

$$k^{+} \approx 1 s^{-1} \text{ und } k \approx 100 s^{-1}, \text{ d.h.}$$

es handelt sich um eine mittelschnelle Reaktion (Abb. 8). Die fluoreszierende Komponente C ermöglicht eine zweite unabhängige Bestimmung von K_1[21] und darüber hinaus Rückschlüsse auf das Halbstufenpotential des angeregten Moleküls.[22] Es handelt sich hier also um ein Beispiel eines Problemes, das man vorteilhaft kombiniert polarographisch und spektroskopisch untersuchen kann.

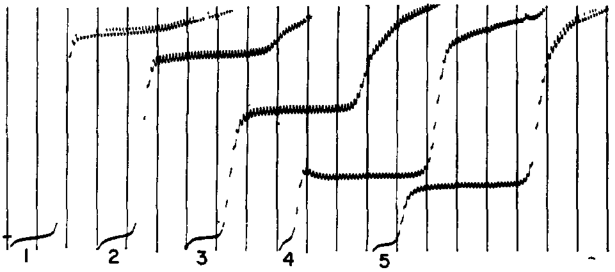
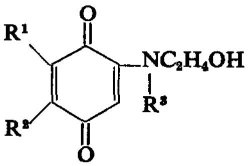


Abb. 7.—Strom-Spannungs-Kurven verschiedener Gleichgewichts-Chinone $4 \cdot 10^{-4}$ M 2-[Hydroxyäthylamino]-benzochinon, Britton-Robinson Puffer pH 7, 40% Isopropylalkohol

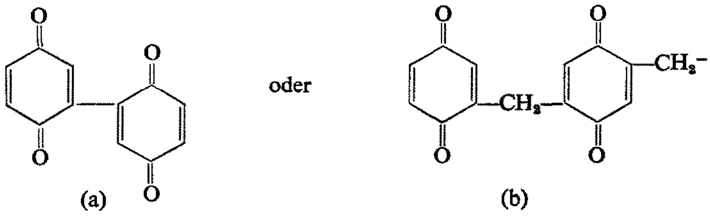


(*1*) $R^1 = R^2 = CH_3, R^3 = H$; (*2*) $R^1 = R^2 = R^3 = CH_3$; (*3*) $R^1 = H, R^2 = R^3 = CH_3$; (*4*) $R^1 = R^2 = H, R^3 = C_6H_5$; (*5*) $R^1 = R^2 = H, R^3 = CH_3$. Kurven ab 0,0 V, NCE, 200 mV/Absz., Empf. 1 : 20 Vgl. [15].

Chinone mit mehreren Akzeptorgruppen

Neben einer Chinongruppe die einer zweielektronigen Elektrodenreaktion entspricht, können weitere Chinongruppen im Molekül vorhanden sein (in Polychinonen) oder andere elektroaktive Gruppen, die ihrerseits Elektronen austauschen können.

Polychinone. Mehrere Benzochinonkerne sind miteinander verknüpft in (11a) oder (11b) und können vier oder mehr Elektronen aufnehmen.[23] Das Dichinon (11a)



(11)

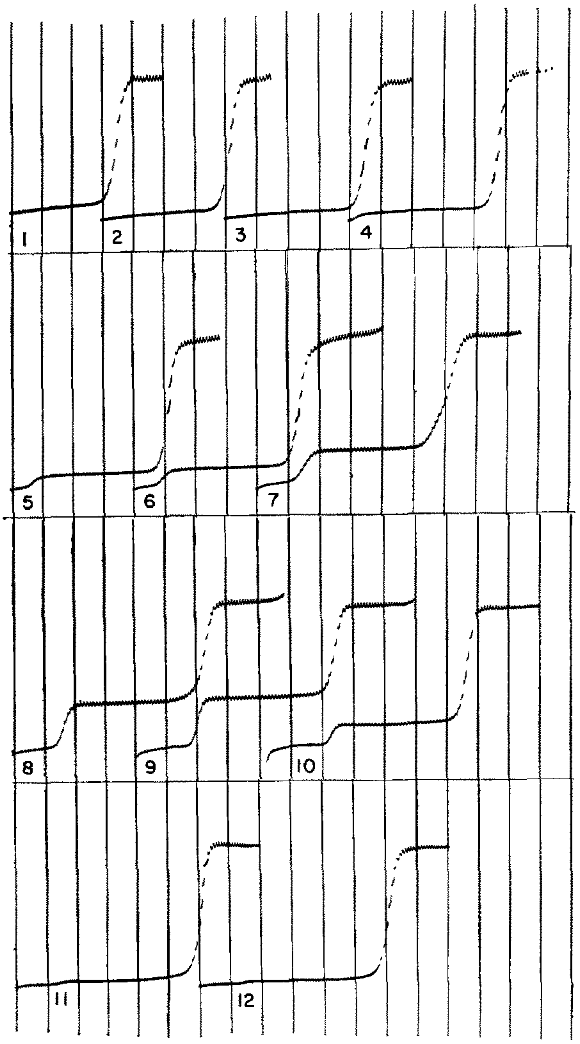
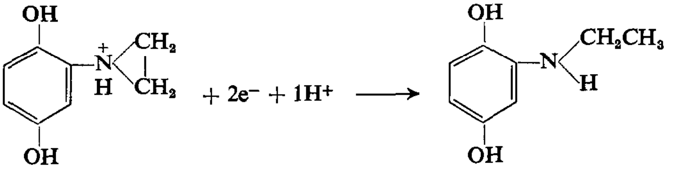


Abb. 8.—pH-Abhängigkeit der Strom-Spannungs-Kurven des 2-[Dihydroxyäthyl-amino]-benzochinons.

$4 \cdot 10^{-4}$ M Benzochinon, Britton-Robinson-Puffer, pH: (*1*) 2; (*2*) 3; (*3*) 4; (*4*) 5; (*5*) 6; (*6*) 7; (*7*) 8; (*8*) 9; (*9*) 10; (*10*) 11; (*11*) 12; (*12*) 0,1 M NaOH. Kurven (*1*)–(*10*) ab 0,0 V, (*11*) und (*12*) ab −0,2 V, NCE, 200 mV/Absz., Empf. 1:30. (*1*)–(*4*), (*11*) und (*12*) nur die Chinonstufe vorhanden, (*5*)–(*10*) die kinetisch begrenzte Chinonstufe geht durch ein Maximum. Vgl. [15].

verursacht in wäßrigen Pufferlösungen nach eigenen Erfahrungen zwei gleichgroße Stufen. Polychinone vom Typ (11b) weisen mehrstufige Polarogramme auf, die zu einem Teil durch stabile "Multiradikale" bedingt sind. Potentialverschiebungen rühren von der gegenseitigen Beeinflussung der Ringsysteme her, wobei Wasserstoffbrücken zu den Karbonylgruppen eine Rolle spielen.

Äthylenimino-Chinone. An einem Chinonkern können bis zu vier Äthyleniminogruppen vorhanden sein, von denen jede nach dem gleichen Schema irreversibel gespalten wird:[24]



(12)

Ab pH < 10 zeigt sich bei etwa -1 V die katalytische Welle dieses Vorganges auf dem Polarogramm und erreicht bei vollständiger Protonisierung einen Grenzwert (Abb. 9). Gleichzeitig macht sich eine zeitliche Abnahme ihrer Höhe bemerkbar infolge hydrolytischer Spaltung der Ringe[25] (vgl. Abschnitt *Hydrolysen*), was mit einer ausgeprägten cytostatischen Wirkung im Zusammenhang steht.

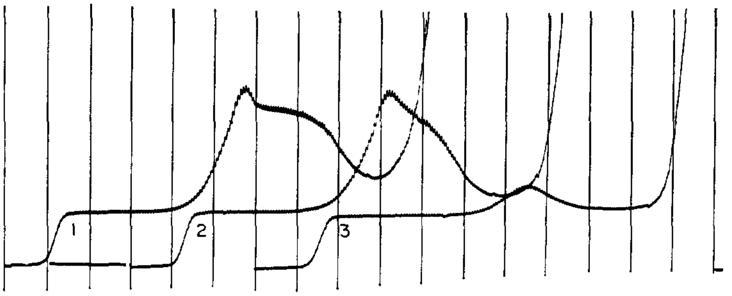
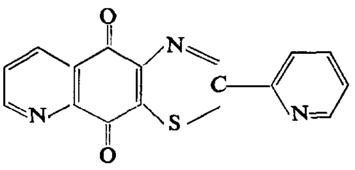


Abb. 9.—Die Stufen von 2,5-Bis-(äthylenimino)-3,6-bis-(n-propoxy)-benzochinon-(1,4) bei höheren pH-Werten.
$4 \cdot 10^{-4}$ M Chinon, Britton-Robinson-Puffer pH: (*1*) 7; (*2*) 7,5; (*3*) 8,9. Kurven ab 0,0 V, NCE, 200 mV/Absz., Empf. 1:20. Die Äthyleniminostufe sinkt ab. Vgl. [15].

Chinolin-Chinone. Die als Cytostatika neuerdings bekannten Chinolin-Chinone vom Typ (13) weisen nach der reversiblen Chinonstufe eine irreversible Stufe bei 1,02 V auf und häufig daran anschließend noch katalytische Wellen (Abb. 10). Die



(13)

Ursache der mehrelektronigen irreversiblen Stufe dürfte in der Elektronenaufnahme an dem heterozyklischen Fünfring zu suchen sein.[26]

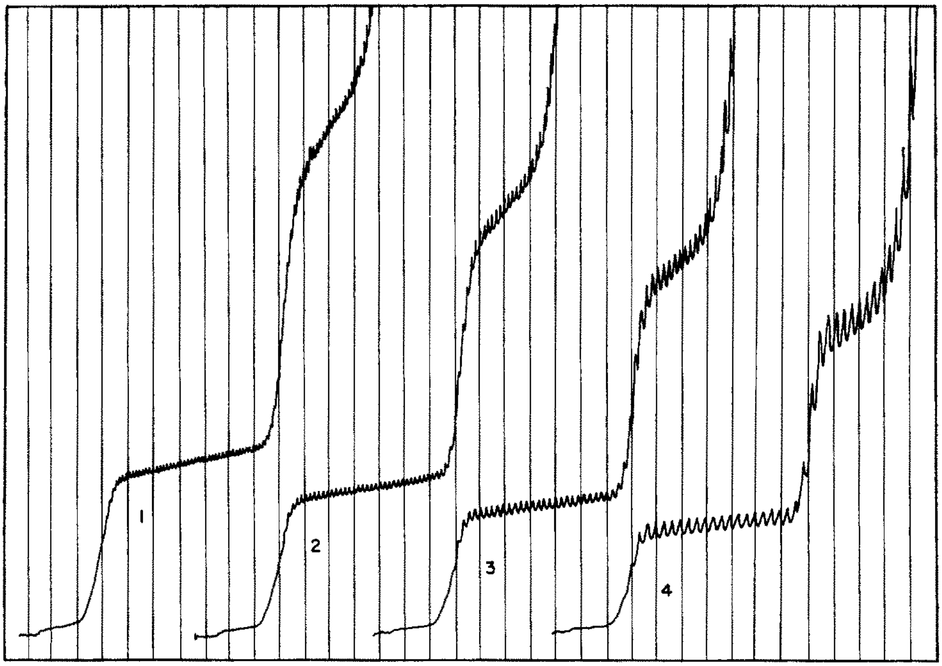


ABB. 10.—Strom-Spannungs-Kurven von 2-(2'-Pyridyl)-8-aza-naphthothiazol-4,9-chinon.
$3 \cdot 10^{-4}$ M Chinon (13) in Phosphatpuffer pH 7,0 bei Quecksilberbehälterhöhe H = (*1*) 89 cm; (*2*) 64 cm; (*3*) 49 cm; (*4*) 36 cm. Kurven ab. 0,0 V, NCE, 100 mV/Absz., Empf. 1:50, 20° (nach Horn).

CHINONE IN NICHTWÄSSRIGEN LÖSUNGSMITTELN

Auf Grund besonders guter Lösungseigenschaften einiger organischer Lösungsmittel nimmt die Zahl der Untersuchungen in reinen organischen Lösungsmitteln allgemein und zum Zwecke der Klärung von Elektrodenprozessen im Speziellen ständig zu.

In den meisten Fällen ist das Solvens eine schwächere Säure, als das Wasser und für Pufferungszusätze ungeeignet, d.h., daß elektrochemische Redoxreaktionen mit Protonenaustauschvorgängen unkomplizierter ablaufen werden, als in wäßrigen oder teilwäßrigen Systemen.

Die am häufigsten benutzten organischen Lösungsmittel sind Acetonitril, *N,N*-Dimethylformamid und das Dimethylsulfoxid. Als wasserähnliche Lösungsmittel finden auch Ameisen-oder Essigsäure Verwendung.

Als Grundelektrolyten werden in der Hauptsache sehr leicht lösliche Salze wie Tetraalkyl-ammonium-perchlorate oder Alkaliperchlorate verwendet.

Nach Hoijtink[27,28] unterscheiden sich die Reduktionsmechanismen in protonenreicheren Medien grundsätzlich von denen in protonenarmen. Für zweielektronige

Reduktionen diskutiert Hoijtink[27,28] zwei Mechanismen, die Given, Peover[29,30] und Kolthoff[31] an Chinonen bestätigten. In wasserähnlichen Solventien gilt folgendes Schema:

$$Q + e^- \rightarrow \dot{Q}^- \tag{14}$$

$$\dot{Q}_- + HD \rightarrow \dot{Q}H + D^- \tag{15}$$

$$\dot{Q}H + e^- \rightarrow QH^- \tag{16}$$

$$QH^- + HD \rightarrow QH_2 + D^- \tag{17}$$

Kann das Produkt $\dot{Q}^-$—das Radikalion des ersten Reduktionsschrittes—protonisiert werden, dann findet die weitere Reduktion des Radikalzwischenproduktes beim gleichen Potential statt, weil die Elektronenaffinität des Radikals $\dot{Q}H$ im allgemeinen größer ist, als die des Ausgangschinons Q.

Um den Einfluß von Wasserstoffionen auf den Redoxvorgang studieren zu können, gibt man saure organische Substanzen, wie Phenol oder Benzoesäure, als Protonendonatoren hinzu.[29]

Die Merkmale der Änderungen von Polarogrammen mit Erhöhung der Protonenkonzentration sind in 5 Hauptgruppen zusammengefaßt worden:

(a) die 1. Stufe wächst auf Kosten der 2. bis diese verschwindet,
(b) eine neue Stufe entsteht zwischen der 1. und 2. Stufe und wächst auf Kosten der 2.,
(c) die Stufenhöhe wächst an, begleitet von Potentialverschiebungen,
(d) die 1. Stufe bleibt unverändert, die 2. verschiebt sich nach positiveren Potentialen,
(e) eine neue positivere Stufe entsteht und wächst auf Kosten der beiden anderen.

Die Deutung aller Erscheinungen ist mit dem angegebenen Mechanismus möglich.

In Acetonitril, *N,N*-Dimethylformamid oder Dimethylsulfoxid ohne Protonendonator vereinfacht sich das Schema:

$$Q + e^- \rightarrow \dot{Q}^- \quad \text{(1. Stufe)} \tag{18}$$

$$\dot{Q}^- + e^- \rightarrow Q^{2-} \quad \text{(2. Stufe)} \tag{19}$$

Weiterhin spielen sich eventuell folgende langsame Reaktionen ab:

$$Q^{2-} + HA \rightarrow QH^- + A^- \tag{20}$$

$$QH^- + HA \rightarrow QH_2 + A^- \tag{21}$$

Die den ersten Reduktionsschritt zum Teil begleitende geringe Protonisierung von $\dot{Q}^-$ durch das Lösungsmittel und seine Disproportionierungs- und Dimerisierungsreaktionen bewirken, daß die 1. Stufe größer als die zweite im Polarogramm erscheint. Außerdem wurde die 2. Stufe als irreversibel gefunden,[31] wenn man z.B. in Dimethylsulfoxid mit $0{,}1M$ Tetraäthylammoniumperchlorat polarographiert. Gibt man successiv einen Protonendonator, wie $0{,}01M$ HCl oder Wasser hinzu, dann verschiebt sich die 2. Stufe nach positiveren Potentialen, bis nur noch eine Stufe mit einem Maximum beobachtet werden kann. Die resultierende Stufenhöhe entspricht der Summe der beiden Einzelstufen vor der Zugabe eines Protonendonators.

Durochinon z.B. gibt in Dimethylsulfoxid zwei Stufen mit $(E_{1/2})_1 = -0{,}73$ V und $(E_{1/2})_2 = -1{,}53$ V gegen SCE, von denen die erste als reversibel identifiziert wurde.

Die zweite Stufenhöhe war kleiner als die 800 mV positivere und ihr Grenzstrom nahm mit Negativierung des Potentials ab.

Eine Chinon/Hydrochinon-Elektrode reagiert nur in Solventien reversibel, welche sauer genug sind, um eine schnelle Reaktion der konjugierten Säure mit dem Semichinonradikal zu garantieren. In Dimethylsulfoxid ist die Chinhydronelektrode nicht mehr als pH-Elektrode zu verwenden.

Vom Hydrochinon ist im Dimethylsulfoxid keine anodische Stufe zu erhalten. Wawzonek und Mitarbeiter[32] nehmen an, daß eine Oxidation an der tropfenden Quecksilberelektrode nur stattfinden kann, nachdem das Hydrochinon ionisiert vorliegt.

Als Bezugselektrode wird auch in reinen organischen Lösungsmitteln meistens die wäßrige gesättigte Kalomelelektrode verwendet, wobei am günstigsten eine 1*N* KNO_3-Agar-Brücke dazwischengeschaltet wird (weniger gut eignet sich eine gesättigte KCl-Brücke). Man kann mit einer 1*N* KNO_3-Brücke in Dimethylformamid auf 1 mV reproduzierbar über Stunden und Tage messen, nachdem die Drift in der Anfangsperiode beendet ist.[30]

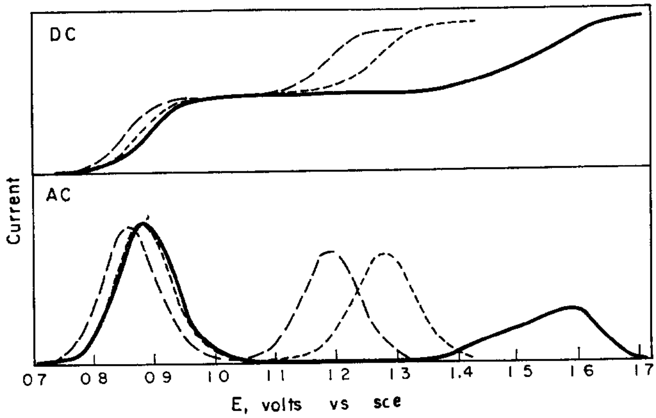


ABB. 11.—Strom-Spannungs-Kurven von Anthrachinon bei Gleichspannung (DC) und Wechselspannung (AC).
Anthrachinon in Dimethylformamid bei 25°. Grundelektrolyt:
——— 0,1 M $N(C_2H_5)_4ClO_4$; - - - - - 0,03 M $LiClO_4$ mit 0,07 M $N(C_2H_5)_4ClO_4$;
- - - - 0,1 M $LiClO_4$.

Interessant ist der Einfluß des Leitelektrolyten auf die Potentiallage der Stufen in wasserfreien Solventien. Polarographiert man z.B. Anthrachinon bei 25°C in Dimethylformamid mit 0,1*N* $(C_2H_5)_4NClO_4$ als Leitsalz, so erhält man zwei um etwa 700 mV auseinanderliegende Stufen (s. Abb. 11). Hält man die Ionenstärke konstant, indem man einen Teil des Ammoniumsalzes durch LiCl ersetzt (0,03*N* LiCl + 0,07*N* $(C_2H_5)_4NClO_4$), so positivieren sich beide Halbstufenpotentiale, wobei die Verschiebung für das doppelt negativ geladene Hydrochinonanion wesentlich größer ist, als für das Semichinonanion. Verwendung von 0,1*N* $LiClO_4$ bewirkt erneute Positivierung der Stufen, wobei die zweite durch den Lithiumionenzusatz reversibel wird, wie aus den AC-wechselstrompolarographischen Kurven hervorgeht. Es muß eine Komplexbildung zwischen Hydrochinonanionen und Lithium-Kationen eingetreten sein, die jene weitgehenden Änderungen bedingt. Es zeigte sich eine signifikante Abhängigkeit der Halbstufenpotentialverschiebung vom Kationenradius.

Die Neigung zur Ionenassoziation ändert sich mit der Struktur der Chinone. Das schwach basische Chloranil z.B. assoziiert nicht als Semichinon mit Li-Ionen. Die Ladungsdichte des Chinon-Anions konzentriert sich in der Hauptsache am O-Atom und es findet nur dann Komplexbildung statt, wenn durch starke elektrostatische Wechselwirkung mit Alkali-Ionen die Solvathülle aufgebrochen werden kann. In Acetonitril-Lösungen ist die Komplexbildungstendenz größer, als im Dimethylformamid, was aller Wahrscheinlichkeit nach auf die niedrigere Solvatation der Kationen zurückzuführen ist.

Die Gleichgewichtskonstante K für den Anthrasemichinon-Ionen-Komplex:

$$\mathrm{Li}^+ + \dot{\mathrm{Q}}^- \rightleftharpoons \mathrm{Li}^+\dot{\mathrm{Q}}^- \qquad (22)$$

in Dimethylformamid liegt etwa bei 39 und deutet auf ein schwaches 1:1 Assoziat hin.

Das doppelt negative Anion ist mit drei Li-Kationen zu einem starken 1:3-Komplex assoziiert. Die Neigung zur Komplexbildung sinkt in folgender Reihe $\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{N(C_2H_5)_4} > \mathrm{N(C_4H_9)_4}$.[30]

Aten und Hoijtink[33] fanden an aromatischen Kohlenwasserstoffanionen dann reversible Reduktion in der ersten Stufe, wenn das Potential nicht negativer als −1,5 V lag. Entsprechendes kann für Chinonreduktionen gesagt werden, wobei Peover −1,4 V gegen SCE als Grenze angibt.

Donator-Akzeptor-Komplexe werden in reinen organischen Lösungsmitteln, und deshalb vor allem auf spektroskopischem Wege untersucht. Die Elektronendonatoren: Hexamethylbenzol, Pyren, Benzpyren *usw.* zwingen dazu, als Solvens für Donator-Akzeptor-Komplexe mit Chinonen die bereits erwähnten Lösungsmittel sowie Dichlormethan, Cyclohexan und Tetrachlorkohlenstoff einzusetzen. Es ist von großem Interesse, die Elektronenaffinität der Chinon-Akzeptoren unter ähnlichen Bedingungen angeben zu können. Die Ionisationspotentiale der Donatoren sind relativ gut untersucht worden, während experimentelle Parameter der Elektronenaffinitäten weniger bekannt sind.[34]

Ihre Kenntnis ermöglicht das Verständnis für die Stabilität der Komplexe, wenn eine quantitative Aussage in dieser Beziehung gemacht werden soll. Intramolekulare H-Brückenbindungen, wie sie z.B. bei einigen α-Hydroxy-Chinonen auftreten, bewirken eine erhöhte Elektronenaffinität.[35]

Eine Abhängigkeit der einelektronigen Reduktionspotentiale $(E_{1/2})_1$ von den Energien der berechneten untersten freien Molekülorbitale zeigt Abb. 12.

Es kann abschließend festgestellt werden, daß die Polarographie eine bequeme Methode zur Messung der 1-Elektronen-Potentiale in nicht-protonenaktiven Lösungsmitteln darstellt. Gestützt werden können die Ergebnisse der Gleichstrom-Polarographie bequem durch Anwendung der Wechselstrommethode.

CHINON-REAKTIONEN

Katalytische Hydrierungen

Als polarographisch weitgehend indifferenter Wasserstoffdonator eignet sich Platin- oder Palladiumsol mit Schutzkolloid in Wasserstoffatmosphäre.[36] Nach eingehendem Studium der Mikroheterogenkinetik in Abhängigkeit von der Katalysatorkonzentration, dem Lösungsmedium und der Temperatur wurde die lineare Freie Enthalpie-Beziehung

$$\log k_j' - \log k_i' = \mathrm{B}(\Delta E_j - \Delta E_i) \qquad (23)$$

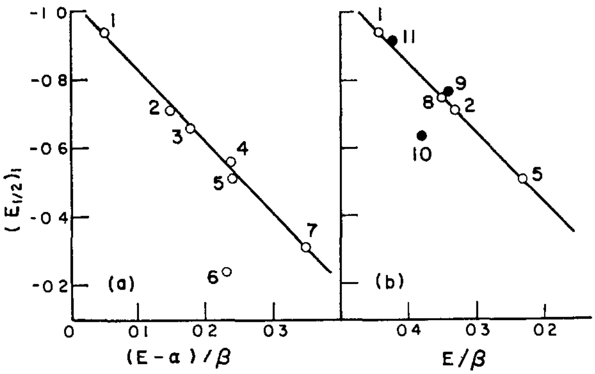


ABB. 12.—Abhängigkeit des Halbstufenpotentials der ersten Chinonsstufe in Acetonitril von der Energie des untersten unbesetzten Molekülorbitals, berechnet nach (a) Kuboyama und (b) Pullman.

(*1*) 9,10-Anthrachinon; (*2*) 1,4-Naphthochinon; (*3*) 9,10-Phenanthrenchinon; (*4*) 1,2-Naphthochinon; (*5*) *p*-Benzochinon; (*6*) 1,8-Diphenochinon; (*7*) 1,2-Benzochinon; (*8*) 1,4-Anthrachinon; (*9*) 2-Methyl-naphthochinon; (*10*) 2-Hydroxy-naphthochinon (in Dimethylformamid); (*11*) 2-Amino-1,4-naphthochinon (vgl. [35]).

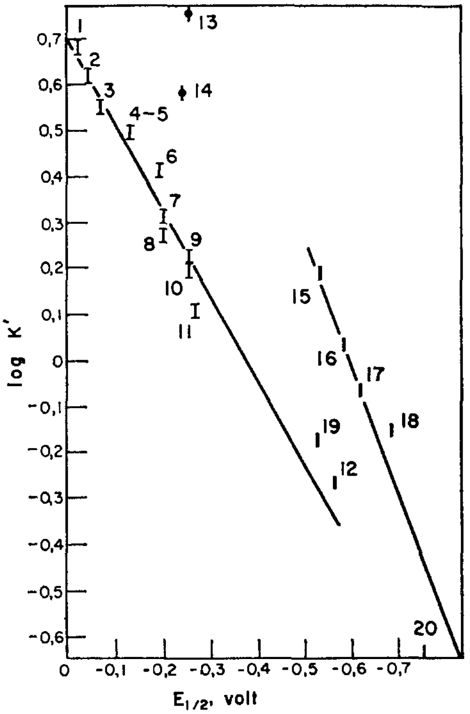


ABB. 13.—Abhängigkeit der Reduktionsgeschwindigkeit von der Konstitution ($4 \cdot 10^{-4}$ M Akzeptor, $3{,}9 \cdot 10^{-4}$ M Pd, Phosphatpuffer pH 7, bei 25°).

(*1*) Benzochinon; (*2*) Phenylbenzochinon; (*3*) Toluchinon; (*4*) *o*-Xylochinon; (*5*) *p*-Xylochinon; (*6*) 2,5-Bis(methyl-β-oxyäthyl)amino-benzochinon; (*7*) Morpholino-5-methyl-benzochinon; (*8*) 2-Benzyl-(β-oxyäthyl)aminobenzochinon; (*9*) Durochinon; (*10*) 2-Methyl-(β-chloräthyl)amino-5-methylbenzochinon; (*11*) Diäthoxybenzochinon; (*12*) 2,5-Bis-(β-oxyäthyl-amino)-benzochinon; (*13*) Phenanthrenchinon; (*14*) Naphthochinon; (*15*) Anthrachinon-2-sulfonsäure; (*16*) 1-Hydroxyanthrachinon; (*17*) 2-Hydroxyanthrachinon; (*18*) Anthrachinon-2,6-disulfonsäure; (*19*) Anthrachinon-1-sulfonsäure; (*20*) Anthrachinon-1,5-disulfonsäure. (Vgl. [37]).

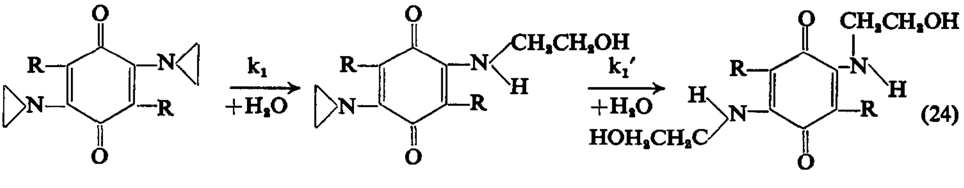
untersucht.[37] In Gl.(23) bedeuten $k' = k_1$ [Pd] summarische Reduktionsgeschwindigkeitskonstanten und B eine Symmetriekonstante, $\Delta E = E_{1/2} - E_{\text{Pd}}$. Die Potentialdifferenz zwischen dem Halbstufenpotential des Chinons und dem Oberflächenpotential des Palladiumsolpartikels ändert sich am stärksten mit dem pH-Wert. Das wirkt sich im Diagramm log k' über $E_{1/2}$ häufig im Steigungsmaß der Kurve aus. Für den Vergleich der Substituenteneinflüsse müssen daher alle Akzeptoren einer Reihe das gleiche Steigungsmaß aufweisen. Abgesehen von reversiblen Farbstoffen wurden bisher zwei Chinon-Reihen (E_{Pd} = const.) untersucht (Abb. 13):

Die Benzochinonreihe mit $B = 1{,}9\ \text{V}^{-1}$ weist die kleineren Reduktionsgeschwindigkeiten im vergleichbaren Potentialbereich auf. Stärkere Abweichungen können von den komplizierteren Teilvorgängen (Adsorption) bei der mikroheterogenen Katalyse gegenüber der Homogenreduktion herrühren. Die Anthrachinonreihe wird gekennzeichnet durch $B = 2{,}7\ \text{V}^{-1}$. Ausnahmen bilden stark adsorbierbare Chinone mit Substituenten in 1 und- 1,5-Stellung.

Der Aussagewert von Gleichung (23) besteht in folgendem: Die Reduktionsgeschwindigkeit weiterer Akzeptoren läßt sich nach ihren Halbstufenpotentialen voraussagen. Signifikante Abweichungen deuten auf Besonderheiten in Konstitution oder Reaktion.

Hydrolysen

Hydrolytische Veränderungen in der Seitenkette können nur das Halbstufenpotential der Chinongruppe und in geringem Maße die Stufenhöhe verändern. Als typisches Beispiel soll die der polarographischen Reduktion ähnliche Ringspaltung eines 2,5 Bis-Äthylenimino-Benzochinons (1,4)(vgl. *Äthylenimino-Chinone*) geschildert werden. Allgemeine Säure-Basen-Katalyse löst die Folgereaktion:



(24)

aus, wobei (B) und (C) negativere Stufen als (A) verursachen (Abb. 14). Aus ihren zeitlichen Änderungen errechnen sich k_1 und k_1', welche eine Analyse des Misch-Absorptionsspektrums ermöglichen.[25]

Die Chinone mit Drei- und Vierringen lassen sich nicht mehr in ihren Stufenreaktionen verfolgen. Dennoch vermag die Polarographie ihre Reaktionsfähigkeit (Reduktion und Hydrolyse) auch in Zellsuspensionen zu studieren. Die Instabilität der Ringe mit steigender Protonenkonzentration ist nicht ohne Bedeutung für den cytostatischen Mechanismus,[38] da die Krebszelle einen niedrigeren pH-Wert aufweist. Während der Ringspaltung in der Zelle können Enzymgruppen blockiert werden. Das Produkt (C) zeigt eine relativ hohe Stabilität und erst in stark saurer Lösung werden die N-Bindungen am Kern hydrolysiert.[39]

Photochemische Veränderungen

Photochemische Veränderungen von Chinonen sind spektrophotometrisch verfolgt worden, jedoch wurden Untersuchungen in dieser Richtung sehr selten unter Anwendung der polarographischen Methode publiziert.

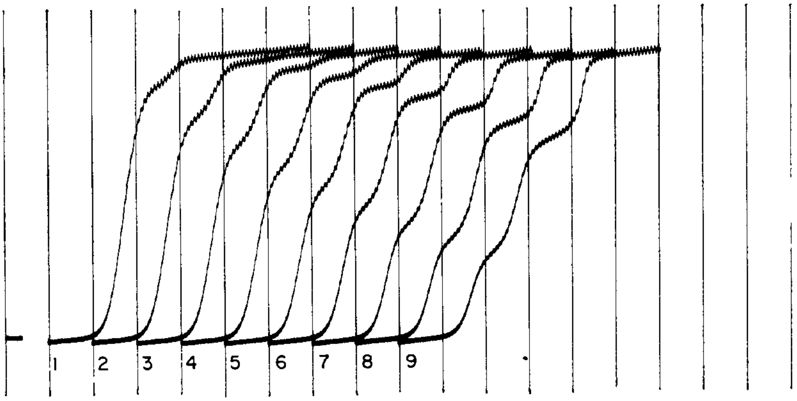
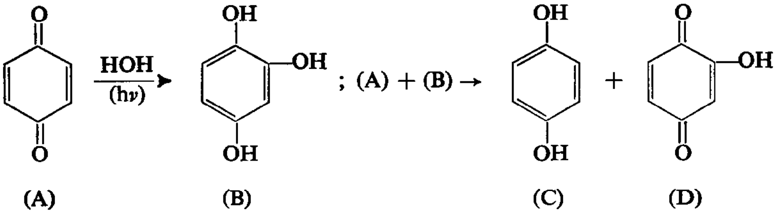


Abb. 14.—Hydrolyse der Äthyleniminoringe von 2,5-Bis-(äthylenimino)-3,6-bis-(n-propoxy)-benzochinon-(1,4).
$5 \cdot 10^{-4}$ M Äthyleniminochinon, Acetatpuffer pH 5,6, bei 25°. Registrierbeginn nach: (*1*) 50; (*2*) 115; (*3*) 180; (*4*) 240; (*5*) 300; (*6*) 360; (*7*) 420; (*8*) 480; (*9*) 540 Minuten. Kurven ab −0,2 V, Mercurosulfatelektrode; 100 mV/Absz., Empf. 1:30. Vgl. [25].

Poupě[40] beschäftigte sich mit den Reaktionsmöglichkeiten des *p*-Benzochinons und fand, daß diese Substanz, im Tageslicht polarographiert, im mereine geringe Menge Hydrochinon enthält. Diese Photolyse stellte er bei Modellexperimenten zu photodynamischen Untersuchungen fest. Folgende Reaktion setzt ein:

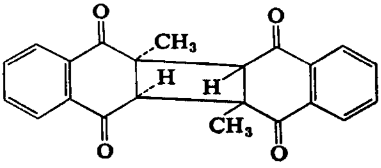


(25)

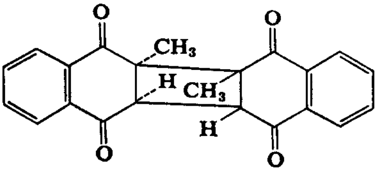
Das Hydroxybenzochinon-(1,4) verbirgt sich zuerst im oberen leicht schrägen Anstieg der Chinonstufe und wird erst nach längerer Bestrahlung als wenig negativere Stufe sichtbar.

Mit dem 2-Methylnaphthochinon führte Asahi[41] eine Reihe Bestrahlungsversuche mit Licht zwischen 300–450 nm durch. Ohne Sauerstoff reagiert es, wie bereits am *p*-Benzochinon-Beispiel gezeigt, zum 2-Methyl-1,4-Naphthohydrochinon mit geringer H_2O_2-Bildung als Nebenprodukt.

In Gegenwart von O_2 entsteht aus dem Reduktionsprodukt wieder das Ausgangschinon (als Nebenprodukt erneut H_2O_2), doch läuft die Reaktion dann weiter zum 2,3-Epoxy-Chinon, welches einmal photochemisch zum Phthiocol isomerisieren kann (entsprechend dem 2-Hydroxy-*p*-benzochinon) und andererseits zu zwei isomeren Dimeren (26A) und (26B) zu polymerisieren vermag:



(A)



(B)

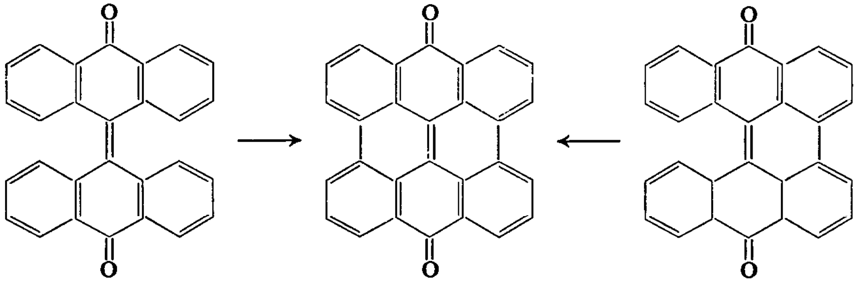
(26)

Die beiden Produkte wurden wie alle anderen in kristalliner Form gewonnen und eindeutig identifiziert.

Besonders die dimeren Formen dienten erneut als Ausgangssubstanz zu weiteren photochemischen und polarographischen Experimenten.

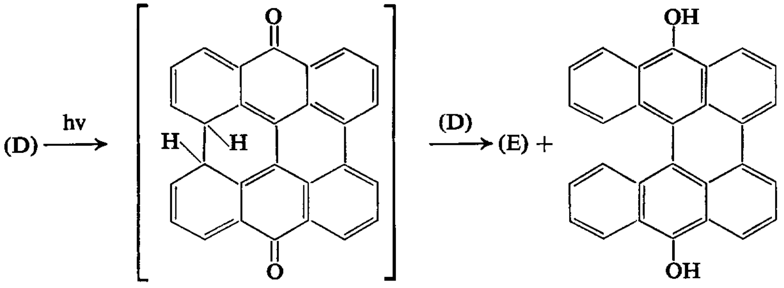
Brockmann und Mitarbeiter[42] fanden die photochemische Dehydrierung des chinoiden Dianthrons (26C) bzw. des Helianthrons (26D) zu Mesonaphthodianthron (26E), wobei Ringbildung unter Abspaltung von 4 bzw. 2 Wasserstoffatomen eintritt. Die Reaktion verläuft schnell und fast quantitativ. Unter aeroben Bedingungen wird der abgespaltene Wasserstoff zu H_2O_2 gebunden. Bei anaeroben Bedingungen verläuft die Reaktion ebenfalls, es tritt eine intermolekulare Dehydrierung ein.

Die Reaktionsgeschwindigkeit wurde als konzentrationsunabhängig gefunden, so daß man ein unbeständiges Ringschlußzwischenprodukt (F) annehmen muß, welches dann durch ein zweites Helianthronmolekül zum Naphthodianthron dehydriert wird.



(C) (E) (D)

(26)



(F)

(27)

Aus der Erniedrigung des polarographischen Grenzstromes in Abhängigkeit von der Bestrahlungsdauer wurde die Geschwindigkeitskonstante k für die Photodehydrierung nach der Beziehung $k = 2{,}3/t \log i_0/i_t$ bestimmt, wobei i_0 die Stufenhöhe vor der Bestrahlung und i_t nach der Bestrahlungszeit t bedeuten. Auch hierbei war k von der Konzentration unabhängig, wie es Brockmann[42] bereits feststellte.

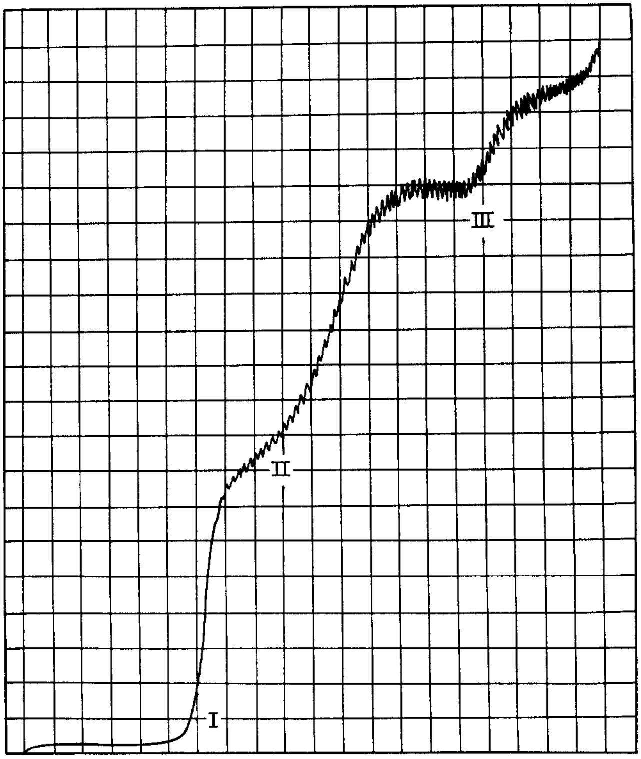
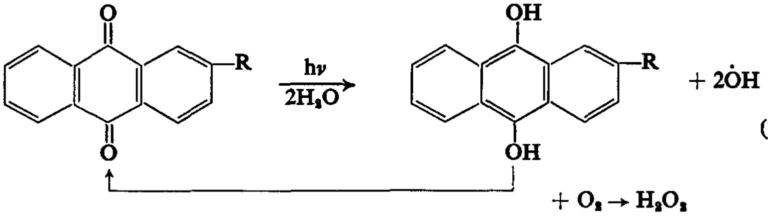


ABB. 15.—Anthrachinon-2-sulfonsäure als photodynamischer Sensibilisator $6 \cdot 10^{-4}$ M Anthrachinon-2-sulfonsäure, 0,41 M Glycerin, Isotonalpuffer ohne Glukose, belichtet. Kurve ab 0,0 V, NCE, 100 mV/Absz., Empf. 1:50 A. Vgl. [45]. Stufen: I Chinon, II H_2O_2; III Glycerinaldehyd.

Am Cytostatikum Bayer E 39, dem 2,5-Bis-(äthylenimino)-3,6-bis(n-propoxy)benzochinon-(1,4), ist die photolytische Reaktion[43] in alkalischer Lösung durch oszillopolarographische- und Gleichspannungsregistrierung, neben absorptionsspektroskopischen Messungen, verfolgt worden.

Die Photolyse wirkt hierbei im Sinne einer beschleunigten Hydrolyse, wobei ein Teil der Ausgangssubstanz zum Hydrochinon reduziert wurde. Beide Äthyleniminoringe werden geöffnet, so daß im wesentlichen die gleichen Zwischen- und Endprodukte entstehen, wie bei den hydrolytischen Reaktionen.[25]

Eingehender wurde die Photoreduktion und Reoxydation von Anthrachinonsulfonsäuren im Hinblick auf folgenden photodynamisch aktiven Brutto-Kreisprozeß (28) studiert Die daraus hervorgehenden Produkte $\dot{O}H$ und H_2O_2 wirken cytostatisch (Abb. 15).



(28)

Bei methylsubstituierten Benzochinonen konnte eine Beziehung zwischen Quantenausbeute der Photoreaktion und Halbstufenpotential aufgefunden werden, die ein Kardinalproblem der Photo-Polarographie seiner Lösung näher bringen hilft.[44] Dabei konnte erneut gezeigt werden, daß die Tropfelektrode direkt in der Bestrahlungsküvette vorteilhaft für Quantenausbeute-Bestimmungen einzusetzen ist.

Summary—A review of the polarography of quinonoid compounds is presented.

Résumé—On présente une revue sur la polarographie des composés quinoniques.

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POLAROGRAPHY OF PROTEINS AND ITS ANALYTICAL ASPECTS

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Summary—A review of the polarography of proteins and its analytical aspects is presented.

INTRODUCTION

THE position, shape and height of the observed polarographic waves of proteins depends on the composition of the electrolysed solution, to which a certain amount of protein has been added. Depending on the composition of the solution, two different kinds of polarographic protein wave can be distinguished.[1,2] In both cases the waves obtained correspond to the evolution of hydrogen at the surface of the dropping mercury electrode, at a decreased hydrogen overvoltage brought about by the catalytically active groups of proteins; the hydrogen ions are supplied to the electrode process by acidic components of the supporting electrolyte.

In buffered solutions, preferably between pH 6 and 10, even at very high dilutions, proteins show distinct polarographic waves at potentials closely preceding those from the electrolytic reduction of alkali metal cations (Fig. 1).[3–5] This led to naming this type of protein wave a *praenatrium* wave. If, in the buffer solution used, the concentration of the acid component is kept constant, the height of the praenatrium wave is limited merely by the concentration of protein present in solution.[3] Thus, in special cases, certain individual proteins can be determined on the basis of a calibration curve obtained with the protein concerned.[6] However, because waves of a similar nature are also caused by some other organic compounds,[7–9] which similarly cause the catalytic evolution of hydrogen at a decreased overvoltage, this kind of protein wave is not, in general, suitable for a reliable determination of proteins.

A more specific polarographic effect with proteins is observed, if, in addition to the buffer components, the supporting electrolyte contains cobalt or nickel salts.[10] The most convenient composition of such solutions suitable for polarographic investigation of proteins proved to be $0{\cdot}1M$ ammonium chloride in $0{\cdot}1M$ ammonia solution containing $10^{-3}M$ cobalt(II) or $10^{-3}M$ hexamminecobalt(III) chloride. After the limiting diffusion current, corresponding to the reduction of cobalt(II) ions in the presence of various proteins, has been reached, a characteristic double wave appears. The height of this wave is also related to the concentration of protein added to the solution (Fig. 2).

NATURE OF POLAROGRAPHIC WAVES OF PROTEINS IN BUFFERED SOLUTIONS OF COBALT SALTS

As mentioned above, even this second kind of polarographic wave of proteins results from the catalytic reduction of hydrogen ions supplied to the electrode by acidic components of the buffered solution. In contrast to the praenatrium wave, the catalytic reduction of hydrogen ions in the presence of cobalt ions is shifted by

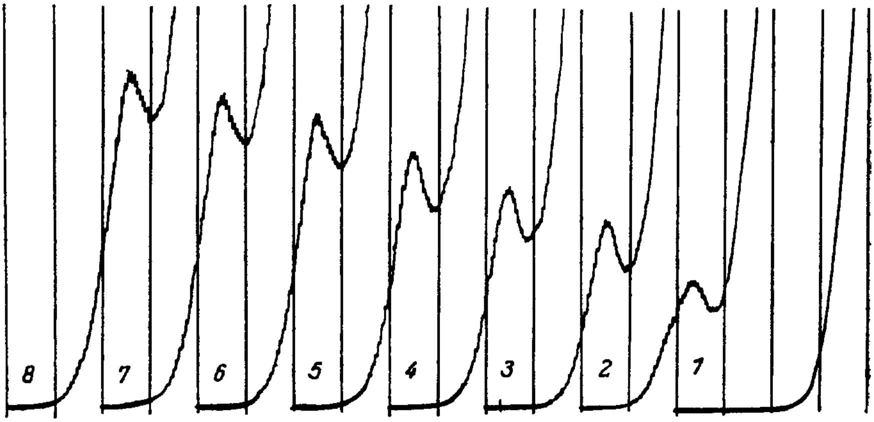

FIG. 1.—The dependence of the height of the praenatrium wave on concentration of egg-white:—

Curve 1: Borate-carbonate buffer of pH 10.

Curves 2-8: To 10 ml of this buffer, 0·1-ml portions of egg-white, diluted ten times with physiological solution of sodium chloride, were added.

The curves start from −1·4 V; full-scale sensitivity is 250 μA.

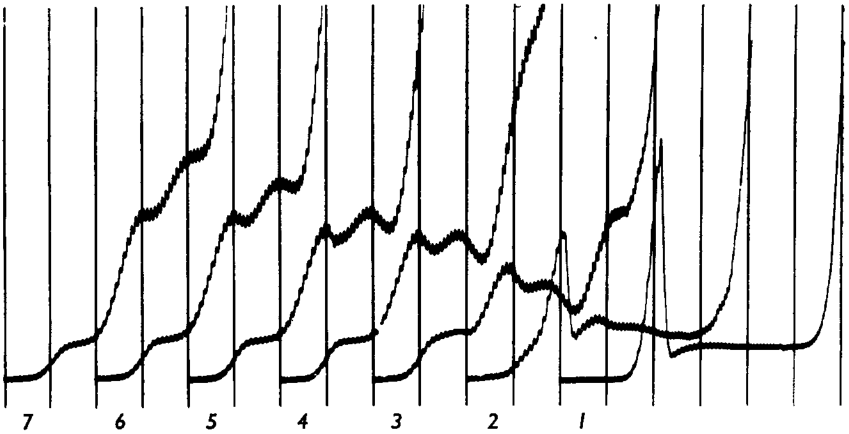

FIG. 2.—The dependence of the height of the protein double wave on the concentration of *serum* albumin (the supporting electrolyte is $0{\cdot}1 M\, NH_4Cl$, $0{\cdot}1 M\, NH_3$, $0{\cdot}001 M\, CoCl_2$).

Curves 1–7: 0, 4, 8, 20, 40 and 80 mg% of *serum* albumin.

The curves start from −0·8 V; full-scale sensitivity is 75 μA.

about 400 mV towards positive potentials and the corresponding protein wave shows a characteristic two-humped shape, which coalesces into a single wave with a rounded maximum in excess of ammonia (Fig. 3).

Although the mechanism of the electrode process concerned has not yet been explained in detail, there is no doubt that it is a complex of cobalt(II) ions with protein molecules which plays a decisive role in this peculiar polarographic effect. If cobalt(II) ions are blocked with strong complexing agents, the protein double-wave disappears completely.[11,12] A further necessary condition is the presence of sulphydryl or disulphidic groups in the protein molecule.[1,10,13] Proteins not containing these groups are polarographically inactive, and among the natural amino acids only cystine and cysteine show waves of a similar nature in buffered cobalt solutions

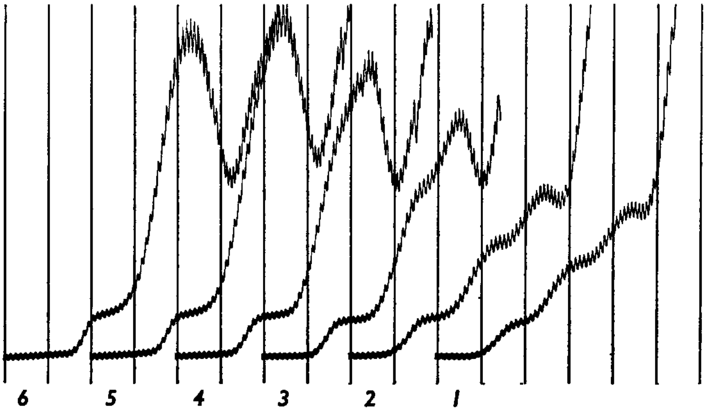

FIG. 3.—The dependence of the height of the protein double wave on the concentration of ammonia (concentration of *serum* albumin is 0·02%; supporting electrolyte is 0·1M NH_4Cl, 0·001M $Co(NH_3)_6Cl_3$ with varying concentrations of ammonia: full-scale sensitivity 75 μA):—

Curve 1: no NH_3,	Curve 4: 0·25M NH_3,
Curve 2: 0·01M NH_3,	Curve 5: 0·5M NH_3,
Curve 3: 0·1M NH_3,	Curve 6: 0·75M NH_3.

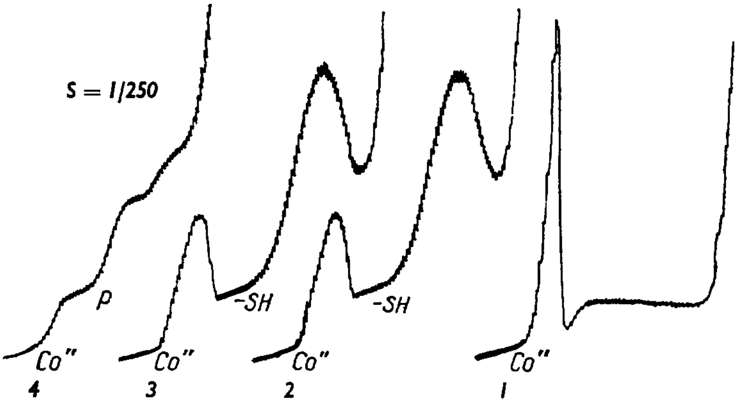

FIG. 4.—Polarographic effects of protein, cystine and cysteine in buffered cobalt(II) solution (full-scale sensitivity 50 μA):—

Curve 1: 0·0016M $CoCl_2$, 0·1M NH_4Cl, 0·1M NH_3 alone;
Curve 2: solution as 1 but containing $2 \times 10^{-5}M$ cysteine;
Curve 3: solution as 1 but containing $10^{-5}M$ cystine;
Curve 4: solution as 1 but containing 100-times diluted blood *serum*.

(Fig. 4).[13,14] Recent preliminary experiments have shown that the introduction of sulphydryl groups into the molecule of polarographically inactive gelatin gives rise to catalytic double-waves with the same features as those from natural proteins containing cystine or cysteine nuclei.[15]

Cobalt complexes with cysteine through the ionised sulphydryl groups;[16] therefore it is to be expected that, after the electrodeposition of the metallic cobalt from the complex, the ionised sulphydryl groups take up protons from the acid component of the solution. These protons, supplied to the electrode process through the sulphydryl groups, are discharged at a decreased hydrogen overvoltage.

To explain the latter fact, it is assumed that the co-ordination bond to the sulphur anion remains preserved even after the deposition of cobalt. This bond, which has the character of a chemisorption bond, can then facilitate the proton reduction caused by the adsorbed sulphydryl groups. Thus, the corresponding limiting current of the catalytic wave depends on the amount of sulphydryl groups adsorbed on the electrode surface and is controlled by the recombination rate of these groups. Their enhanced catalytic activity is obviously connected with their foregoing participation in the co-ordination bond with cobalt(II) ions in the solution. If cobalt deposited at the surface of a steady mercury drop electrode is accumulated by electrolysis and EDTA is then added to the electrolysed solution to bind cobalt(II) ions into a firm complex, no catalytic effect of cysteine or proteins appears.[12] Here the mere contact of sulphydryl groups with metallic cobalt is catalytically ineffective. This also explains the fact that in the presence of hexamminecobalt(III) ions cystine or cysteine show a weak catalytic effect which is more than 100-times smaller than that observed with cobalt(II) ions.[17,18] The stability of the hexamminecobalt(III) ions evidently hinders the formation of a complex with these amino acids in solution. Such complexes cannot be formed until the reduction of the hexamminecobalt(III) ions to the unstable hexamminecobalt(II) ions has commenced at the electrode surface. Under these conditions only a small amount of the complex is formed, which then accounts for the weak catalytic effect.

In the case of proteins which show almost the same catalytic effect in the presence of hexamminecobalt(III) ions as with the cobalt(II) ions, the formation of a complex with the freshly reduced hexamminecobalt(III) ions on the electrode surface obviously proceeds more easily than in the case of cysteine.[2] This is probably because of the considerable adsorption of proteins in the electrode interphase, where the accumulation of protein molecules might facilitate a rapid formation of the complex with bivalent cobalt ions produced by the electrode process.

A common characteristic feature of all these catalytic waves is the variation of their heights with the concentration of proteins as well as of cystine or cysteine.[10,13] The increase in height is not linear with respect to the concentration concerned, but tends to a limit which depends on the nature of the substance examined. In the case of proteins, the height of the double wave at its maximum value is roughly proportional to their cystine contents. This is illustrated by the following series: pepsin $<$ bovine albumin $<$ chymotrypsin $<$ insulin $<$ trypsin, in which the maximum height of the double wave increases with increasing content of cystine in the individual proteins.[19]

A chemical modification of the disulphidic or sulphydryl groups in the protein molecule is followed by the disappearance of the catalytic wave. This was found after treating insulin with performic acid which oxidises its disulphidic groups to sulphonic groups or after the carboxymethylation of the reduced disulphidic groups of insulin with iodoacetate.[20] *S*-sulphonation of the disulphidic groups in insulin with sulphite, however, does not lead to the loss of polarographic activity, because the foregoing electroreduction of the *S*-sulpho bonds supplies the sulphydryl groups just as in the electroreduction of the disulphidic groups.[20]

A similar behaviour is observed with simple sulphydryl and disulphidic compounds. Thus, cysteine rapidly loses its catalytic activity in the presence of iodoacetate, whereas that of cystine under the same conditions remains uninfluenced.[14]

Similarly, as with insulin the *S*-sulphonation of cystine brings about its original catalytic activity.[20] In addition to cysteine, catalytic waves are also obtained with cysteamine,[21] and thioglycolic[13] and thiopropionic[22] acids as well as with their disulphidic forms. The waves appear at potentials at which the second part of the protein double waves takes place. They have a typical shape, mostly with a rounded maximum and are readily observed at very low concentrations (down to $10^{-7}M$) of the compounds mentioned above.

The magnitude of the catalytic effect, which is different for the individual sulphydryl compounds, seems to be related both to the nature of the other functional groups taking part in the co-ordination bond and to their position on the carbon chain with respect to the sulphydryl group. Thus, a decreasing catalytic effect was observed in the following series:[13,21,23] thioglycolic acid, cysteine, cysteamine > β-thiopropionic acid. This series suggests that the formation of five-membered chelates brings about favourable conditions for giving rise to the highest catalytic currents, probably as a result of the high stability of these chelates. The steric conditions of the sulphydryl groups can also be of importance, *e.g.*, erythrophenylcysteine gives a greater catalytic effect than the threo-epimer.[24]

The nature of the bonding and structure of the complexes of proteins with cobalt are not fully understood, although there is no doubt about their existence; it follows, at least, from the analogous polarographic effects due to proteins and to their free cystine or cysteine nuclei. In view of the complicated structure of the protein molecule, it is not very surprising that the shape of the polarographic wave of protein differs somewhat from that of cystine or cysteine. Previous attempts to explain the two-humped shape of the protein wave as being due to the catalytic activity of some other amino acids in the protein molecule[25–27] or to the globular and linear structure of the polypeptides[28] did not provide sufficient evidence. It seems more likely that this peculiar shape results from the adsorption of the protein molecules at the electrode surface where they promote, in the adsorbed state presumably, the evolution of hydrogen from the sulphydryl groups. This might account for a partial shift of the catalytic protein wave towards positive potentials, so that the primary electrode process could then take place in two steps.

APPLICATIONS OF THE POLAROGRAPHIC PROTEIN TEST IN BUFFERED COBALT SOLUTIONS

The height and the shape of the polarographic double-wave of proteins varies more or less with the concentration of all the individual components of the buffered cobalt solutions.

Role of the cobalt ion

At a suitable concentration ratio of ammonium ions and ammonia, providing the electrolyte solution with an adequate buffer capacity in respect of the electrolytic uptake of the ammonium ions, the height of the protein double wave increases with the increasing concentration of the cobalt(II) or hexamminecobalt(III) ions in the form of a parabola-like curve (Fig. 5).[29,30] The height of the wave appears to be proportional to a power of cobalt concentration with an exponent which is somewhat less than one and varies within close limits for individual proteins. In solutions containing hexamminecobalt(III) ions the protein wave is usually slightly higher than in solutions of cobalt(II) ions at the same concentration.[31]

Role of the buffer components

When ammonium ions, functioning as proton donors, are in excess the height of the double wave is limited both by the concentrations of the cobalt ions and of the protein. However, it becomes controlled by the rate diffusion of the ammonium ions towards the electrode as soon as the concentration of ammonium ions in the bulk falls below the limit required for the wave to reach maximum height at the given concentration of cobalt salts and protein.[10,31] Thus, below this limit a decrease in the height of the protein double wave with decreasing concentration of ammonium ions was observed.[10,31]

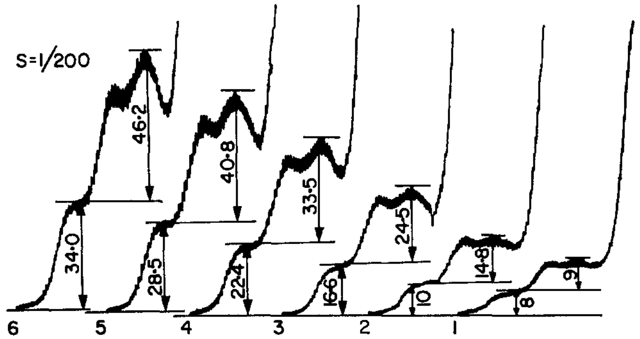

FIG. 5.—The dependence of the height of the protein double wave on the concentration of cobalt(II) ions. The supporting electrolyte consists of 0·1M NH_4Cl, 0·1M NH_3 and varying amounts of $CoCl_2$:—

Curve 1: 0·0005N, Curve 2: 0·001N,
Curve 3: 0·002N, Curve 4: 0·003N,
Curve 5: 0·004N, Curve 6: 0·005N.

The concentration of the human *serum* is 0·17%; full-scale sensitivity is 40 μA.

In addition to supplying protons to the catalytic electrode process, the ammonium ions, together with ammonia, control the pH of the solution. Any change in their concentration ratio brings about a shift in the dissociation equilibria of the acidic and basic groups in the protein molecules which, in turn, affects the degree of complex formation with cobalt as well as the extent of their adsorption on the electrode surface. The coalescence of the protein double wave into a single wave and a considerable increase in the height of the latter in excess of ammonia[10] appears to be the result of the effects considered. It is important to know that similar polarographic effects are observed when in an ammonia buffer of pH about 9 or 10, the ammonium ions are replaced with glycine[32] or with some other amino compounds.

The polarographic protein test, from the qualitative point of view, is common for all types of protein with cystine or cysteine nuclei. Thus, its application to quantitative analysis is mainly limited to samples containing either a single type of protein or a protein mixture possessing a constant composition.

Effect of denaturation of proteins

Another characteristic behaviour of proteins has to be considered when carrying out the polarographic test, *i.e.*, the effect of structural changes in the protein under investigation. The mildest changes of this kind are induced by denaturation of the proteins. These changes consist in the stretching of polypeptide chains after the break down of certain intramolecular bonds responsible for the original structure of the native protein molecules. This internal rearrangement in the protein molecule is accompanied by the liberation of a part of the disulphidic or sulphydryl groups which was masked inside the native molecule. This process which has been shown to occur by other methods[33] can also be clearly demonstrated by the changes in the polarographic protein wave.

For example, if the *serum* proteins are dissolved in a slightly alkaline solution (0·2*M* potassium hydroxide) a distinct increase of the protein double wave with time is observed (Fig. 6).[34] After reaching the maximum, the height of the wave begins to decrease. A similar effect takes place if native *serum* proteins are exposed to ultraviolet radiation.[35,36] This increase in the height of the wave, especially of its second hump, indicates that during the denaturation process the disulphidic or sulphydryl groups together with the other ligands become much more readily available for complex formation with cobalt than in the native proteins. The subsequent decay of the height of the wave corresponds to a slow coagulation of proteins because of a decrease in their solubility after the denaturation. However, this behaviour, which is typical of the *serum albumin*, is not common to other proteins. With γ-globulin, for example, only a slow decay of its double wave is shown.[37]

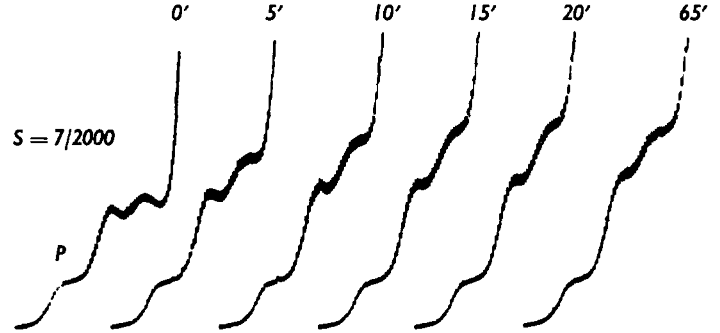

FIG. 6.—Alkaline denaturation of proteins in *serum*: dependence of the height of the double wave on the denaturation time. 0·5 Ml of *serum*, 0·5 ml of water and 0·25 ml of 1*M* KOH were mixed. After the given time intervals, 0·1 ml of the sample was diluted with 20 ml of cobalt(II) solution and polarographed (full-scale sensitivity: 40 μA).

Denaturation test

The alkaline denaturation of *serum* proteins proved to be of practical use in detecting more or less pronounced differences between normal and certain pathological *sera*. The primary objective was a diagnostic test for cancer.[38]

On direct comparison of the polarograms of the native and carcinomatic *sera* in buffered cobalt solutions only a slight difference was observed: the carcinomatic *sera* showed somewhat lower waves. However, when the *sera* were treated with dilute alkali hydroxide before electrolysis, the wave from normal *serum* always showed a larger increase than the wave due to carcinomatic *serum* (Fig. 7). In this way the difference between the two *sera* could clearly be distinguished.

Digestion test

A similar difference is found if the *sera* are treated with pepsin in dilute solutions of hydrochloric acid.[38,39] The higher protein waves in the normal *sera*, in comparison with carcinomatic *sera*, indicate a higher content of polarographically active groups liberated through denaturation or peptic cleavage; accordingly, in the hydrolysates of carcinomatic *sera*, less cystine was always found than in the hydrolysates of normal *sera*. The ratio of the cystine content in the *sera* examined was practically the same as the ratio of the heights of the protein waves.

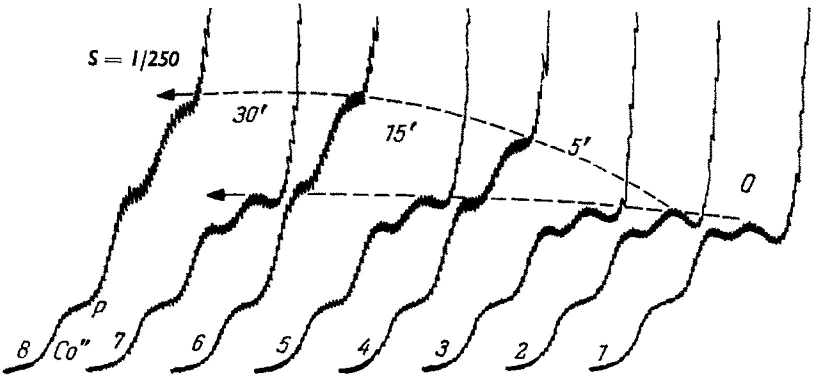

Fig. 7.—The course of the alkaline denaturation of normal and carcinomatic serum:—
Curves 1, 3, 5 and 7: normal *serum*,
Curves 2, 4, 6 and 8: carcinomatic *serum*.
0·75 Ml of 0·1*M* KOH and 0·5 ml of serum are mixed and after the given time intervals 0·05 ml of the solution is diluted with 10 ml of buffered cobalt(II) solution (full-scale sensitivity: 50 μA).

In the course of the examination of different pathological and normal *sera* it was soon ascertained that these polarographic tests are not specific for cancer, because other disorders, especially acute inflammations, open tuberculosis and febrile diseases in general, showed a similar deviation in the height of the protein wave.[39] Nevertheless, the experience concerning the polarographic behaviour of proteins exposed to denaturation or to the action of different proteolytic enzymes has provided further possibilities for the investigation of individual protein fractions after their separation from biological fluids or for estimating the proteolytic action of different enzymes present in this fluid under normal and pathological conditions.

Electrophoretic fractions

In order to obtain information about the distribution and polarographic properties of the individual protein components in blood *sera*, paper electrophoresis was used.[40,41] After electrophoretic separation on Whatman paper No. 1 at pH 8·6 the paper was dried and cut into four strips with separated fractions of albumins and α-, β- and γ-globulins. These strips were then eluated separately in physiological sodium chloride solution and the polarographic wave was recorded for each sample under standard conditions (Fig. 8). In this way certain shifts in the distribution of albumins, α-, β- and γ-globulin, which in some cases are characteristic for different pathological states, can be ascertained. This mode of procedure has shown that the decrease in the total height of the double waves observed with pathological blood *sera* is mainly due to the decrease in the albumin content. In contrast to malignant and febrile diseases, an increase in the content of the β- and γ-globulin fractions and a simultaneous decrease in the α-globulin fraction was ascertained in the case of severe hepatitis; in contrast, acute inflammations are accompanied by an increase in the α-globulin fraction with a simultaneous decrease of albumins.

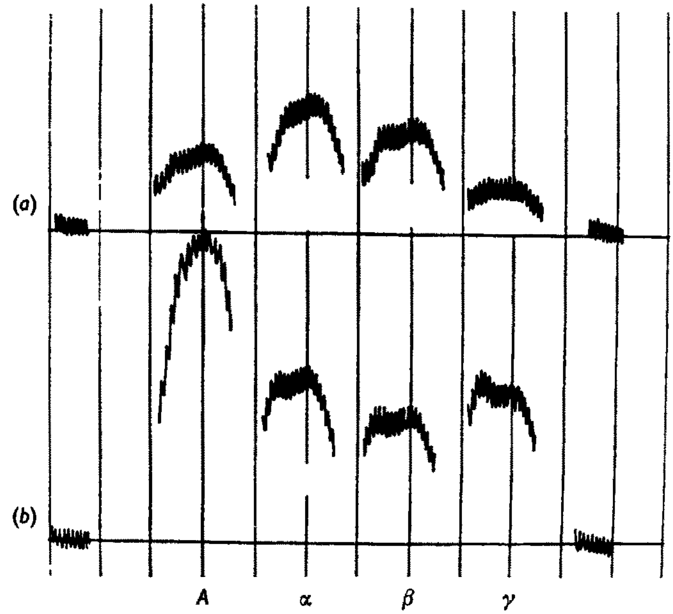

FIG. 8.—Electrophoretic-polarographic record of the proteins in blood serum: (a) native proteins, (b) denaturated proteins. Albumin is diluted three times with respect to the other protein components.

If the paper strips with separated protein fractions are eluated in dilute alkaline hydroxide, the individual effect of denaturation on these fractions can be distinguished (Fig. 8). When working with normal *sera* the largest increase in the height of the protein double wave is shown in the albumin and α-globulin fraction. If the same procedure is applied to pathological *sera*, the increase in the height of the respective protein waves takes place to a smaller extent. This fact leads to the conclusion that in pathological states the protein molecules in these fractions undergo some qualitative changes, which consist probably in a decrease of the content of the polarographically active sulphur groups.

The denaturation effects were also examined polarographically on spinal fluids.[40,41] Whilst pathological *sera* give protein waves which are generally lower than those of the normal *sera*, the pathological spinal fluids are characterised by an increase in the height of the corresponding protein wave. Moreover, pathological spinal fluids (*e.g.*, tubercular or basilar meningitis) when treated with dilute alkali hydroxide show a greater increase in the height of the protein wave than the normal, whereas with *serum* proteins opposite denaturation effects are observed. This different behaviour of blood *sera* and spinal fluids in the normal and pathological states is mainly due to albumins, which evidently have different natures and properties in the two body liquids.

Miscellaneous biological materials

Other analytical applications of the polarographic protein test cover a very broad field and cannot be discussed here. They involve the estimation of proteins in urine, transudates, exudates, milk, stomach and duodenal juice, sweat, salivas, tears, plant extracts, *etc.*[42]

The protein test was found useful in controlling the purity of the virus of tobacco mosaic. This virus in the pure state shows only the first part of the double wave (Fig. 9).[43] However, the non-virus protein present as impurities, exhibits the whole double wave, the second hump of which disappears if the virus is first purified. In this way protein impurities in amounts as low as 0·2% can be ascertained.

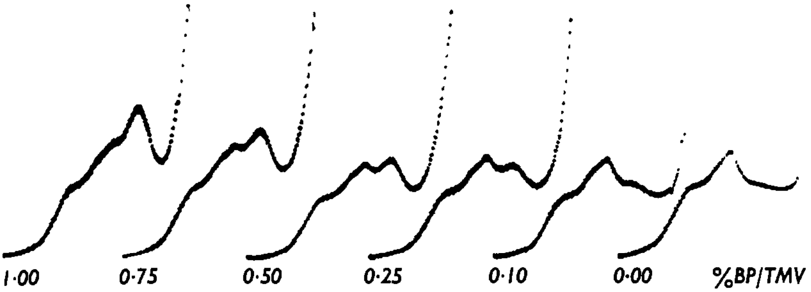

Fig. 9.—Polarographic analysis of a mixture containing 5·2 mg/ml of purified tobacco mosaic virus protein and various concentrations of non-virus protein (BP). The supporting electrolyte is 0·001M $Co(NH_3)_6Cl_3$, 0·1M NH_4Cl, 0·1M NH_3; temperature: 0°; full-scale sensitivity: 25 μA.

Effect of proteolytic enzymes

Another type of application was directed towards the estimation of the activity of different proteolytic enzymes. It is known that the products of proteolytic cleavage also exhibit catalytic waves, which can attain larger heights than those of the original protein. Thus, the proteolytic effect can be followed polarographically either in the presence of the original protein or, preferably, after precipitation with sulphosalicylic acid, when the protein degradation products are soluble. The polarographic examination of the respective filtrates enables one to obtain the catalytic waves from the proteolytic products only. The increase of these waves with time is then directly related to the proteolytic activity of the enzyme concerned. The first investigations of this kind were carried out on albumin proteolysed with pepsin in the pH range of about 2–3, where pepsin reaches its optimum activity.[44]

The fact that various proteolytic systems are active at different pH regions enabled a distinction to be made between the three proteolytic systems present in the blood *sera*.[45] Normal *sera* were acidified to certain pH values and incubated at body temperature for 24 hr. After precipitation of the *serum* proteins with sulphosalicylic acid, the polarographic examination of the filtrates revealed catalytic waves corresponding to the degradation products in samples where pH values were maintained in the following regions: 2–3, 3–4·2, 5·5–7·0. The proteolytic cleavage of *serum* proteins in the first and second region is because of the presence of pepsin and kathepsin, respectively. The nature of the third "enzyme" was not identified.

This finding has been applied to the polarographic comparison of the proteolytic activity of pepsin (Fig. 10) and kathepsin in *sera* and in spinal fluids under normal and different pathological states.[41,46] With patients suffering from pernicious anaemia (Fig. 10), stomach ulcers or cancer, a decreased proteolytic activity of pepsin from the decreased content of pepsinogen in *serum* was observed. An increased proteolytic activity of the kathepsin system was found with patients suffering from infectious hepatitis.

In spinal fluids only the proteolytic activity of the kathepsin system was detected, whilst the presence of pepsinogen in the normal spinal fluids was not observed.[41] The penetration of this enzyme into spinal fluids from blood is connected with certain pathophysiological conditions.

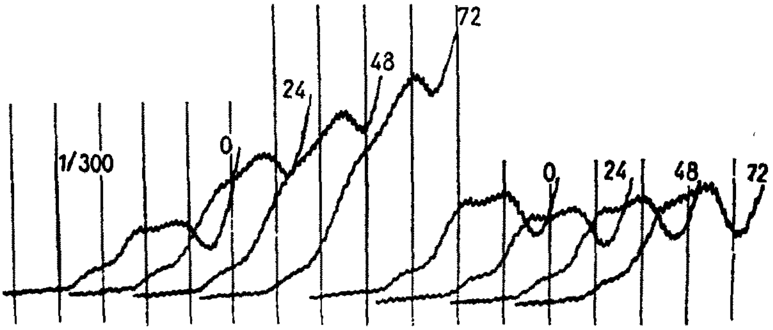

FIG. 10.—Polarographic determination of pepsinogen in normal blood *serum* (left) and in the *serum* of a patient suffering from pernicious anaemia (right). The *serum* was analysed after the given time intervals (hr) of incubation (37°) in an acidic medium (full-scale sensitivity: 90 μA).

Filtrate test

It has already been mentioned that the decomposition products of proteins, soluble in sulphosalicylic acid, can be estimated polarographically in the respective filtrates after precipitation of the original proteins. The polarographic examination of sulphosalicylic filtrates has been applied to blood *sera* in order to determine some degradation products of the *serum* proteins which may be present, and differences in their contents between normal and pathological *sera*.[1,2,38] Distinct differences have, in fact, been found; a higher content of these products was observed in those pathological *sera* which show a decrease in the total height of the protein double wave in comparison with normal *sera* after alkali denaturation or partial peptic cleavage. This proves that the increased protein wave in filtrates is also characteristic for the *sera* of patients suffering from cancer, tuberculosis, inflammation and febrile diseases.

The filtrate test was found advantageous for clinical purposes because it is more reproducible and the differences between normal and pathological *sera* are more pronounced than with the former test. It was originally assumed that the *serum* filtrate waves were caused only by the degradation products of *serum* proteins. This view was mainly supported by the fact that an arbitrary increase of these waves can be induced by treating normal or pathological *sera* with pepsin. Electrophoretic analysis of the proteinic substances concerned revealed, however, the presence of at least three protein fractions[47] in sulphosalicylic filtrates which noticeably contribute to the rise of the filtrate waves.[48] These compounds contain a sugar component and thus have the character of mucoproteins or glykoproteins.[49] Great attention was paid to the mucoprotein known as *serum mucoid* or *orosomucoid*, present in higher concentration than the other filtrate proteins, all of which are increased in a similar manner to those pathological cases where the filtrates waves are increased. The isolation of this mucoprotein was accomplished by salting out with ammonium sulphate[50] or alternatively by alcoholic fractionation[51] of the blood *plasma*. It contains about 40% of sugar, its isoelectric point is on the acid side (pI $\approx$ 2) and it has a molecular weight of about 44,000. The *orosomucoid* appears in the α_1-globulin fraction and corresponds to the acid α_1-glycoprotein. In accord with the low cystine content (0·5 %) it shows relatively low polarographic protein double waves as compared with those of the rest of the proteinic substances, present in the filtrates.[48]

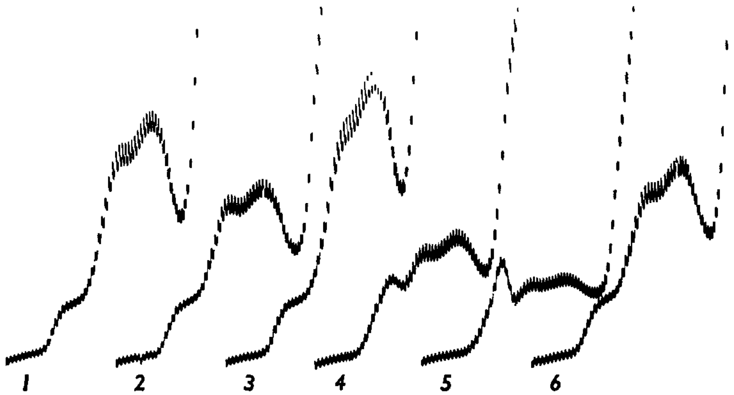

FIG. 11.—Filtrate protein waves of different *sera* (full-scale sensitivity: 50 μA):—
Curve 1: *Status febrilis*, Curve 2: *Ca hepatis*,
Curve 3: *Ca ventriculi*, Curve 4: normal *serum*,
Curve 5: *Cirrhosis hepatis*, Curve 6: *Thrombophlebitis acuta*.

The polarographic effect of all these substances can be considerably enhanced by adding an excess of ammonia to the buffered cobalt solution. This solution also has the advantage that the differences between normal and pathological *sera* are more clearly distinguished (Fig. 11).

Procedure for diagnostic filtrate test

In applying the polarographic filtrate test for diagnostical purposes the following mode of procedure proved to be the most suitable. Add 0·4 ml of fresh blood *serum* to 1 ml of 0·1M potassium hydroxide solution and allow to stand for 45 min. Precipitate the proteins at room temperature by the addition of 1 ml of 20% sulphosalicylic acid. After 10 min filter the precipitate through a hard filter paper and add 0·5 ml of clean filtrate to 5 ml of buffered hexamminecobalt(III) solution ($10^{-3}M$ in 0·1M ammonium chloride, 1M ammonia). Compare the increase in the height of the wave of the pathological filtrate with the height of the wave from the normal filtrate. Because the latter is subject to slight fluctuation it is best to take the average of the wave heights of several samples of normal *sera*. Any increase in the filtrate wave over the normal limit indicates the need for a careful clinical examination of the patient.

Disregarding the non-specificity of the filtrate test, the main interest in clinical practice is directed towards its application for the diagnosis of cancer. The extensive statistical material available shows that the height of the filtrate wave increases appreciably during the progress of the malignant disease. In early stages the filtrate test is very often inconclusive in that the respective height of the wave overlaps with the upper limit of that of normal *sera*. A surgical or successful therapeutic intervention is followed by a decrease in the filtrate wave, which returns to its normal limit, provided that the attack of the organism by metastases has not commenced. The start of recidivism is always accompanied by a new increase of the filtrate wave. Thus a repetition of the test at regular intervals provides a useful indication of the effectiveness of a cure.

The course of various non-carcinomatic diseases can be followed during the therapeutic treatment in a similar manner. In contrast to inflammations, tuberculosis, pneumonia, nephritis, ulcers, festering or necrotic processes, a decrease of the filtrate wave under the normal limit takes place with patients suffering from infectious hepatitis or cirrhosis of the liver (*cf.* Curve 5, Fig. 11). In this respect the filtrate test is specific for liver disorders, especially where liver parenchyma is severely damaged.[52] The decrease in the heights of the filtrate waves below the normal limit in liver disorders appears to be related to a deficiency of glycoproteins caused by damage to the liver parenchyma where glykoproteins are assumed to be formed.

Some of the pathological protein effects shown by *sera* can also be observed with urine. However, this biological fluid is less suitable for polarographic examination in clinical practice because the quantitative changes in the composition of urine can fluctuate over very wide limits. In spite of this, the heights of the filtrate wave obtained both with *serum* and urine, in those pathological cases where the filtrate wave is increased, were found to be roughly parallel.[53] A considerable increase of the filtrate wave in urine was observed with patients suffering from burns. The increase in the height of the filtrate wave in this case is clearly correlated with the degree and extent of the burnt tissue.

CONCLUSIONS

In conclusion, it has to be mentioned that the literature dealing with the investigations in the field of polarography of proteins, and especially with the clinical applications, has become very extensive. Therefore, only the essential features of the problem have been outlined here in order to give the reader necessary information about the theoretical and practical aspects of the subject.

Résumé—On présente une revue sur la polarographie des protéines et ses aspects analytiques.

Zusammenfassung—Es wird eine Übersicht über die Polarographie von Proteinen und deren analytische Aspekte gegeben.

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POLAROGRAPHY IN POLYMER SCIENCE

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Summary—A review of polarography in polymer science is presented.

INTRODUCTION

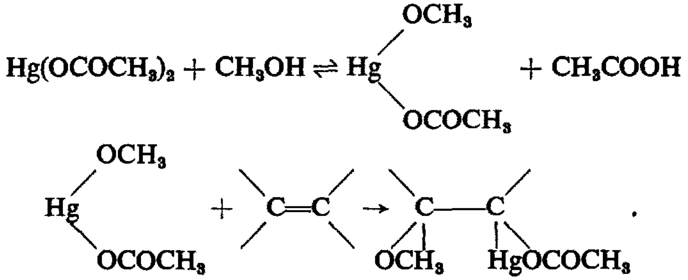
POLAROGRAPHIC techniques are useful for determination of monomers, impurities in monomers, catalysts and end groups in polymers. It is important to be able to compare the number of end groups in a polymer with the number expected from the mechanisms of polymer reactions and to determine impurities, which may greatly affect the degree of polymerisation and the properties of the polymer formed.

Applications of polarography in polymer science will be discussed, with emphasis on the contribution of the present authors. Hence, the present review is complementary to other views or books[1] which discuss the problem from a more general point of view.

ANALYSIS OF MONOMERS

Styrene, α-methylstyrene and β-methylstyrene contain conjugated double bonds which give a single reduction-wave useful for quantitative methods. Similarly, acrylonitrile and allyl methacrylate can be determined polarographically. Because vinyl esters, such as vinyl acetate and vinyl butyrate, are not reduced directly, it is necessary to determine the acetaldehyde produced by saponification of the vinyl ester. This may be carried out in a solution containing tetramethylammonium hydroxide as a supporting electrolyte. Linear dependence between the height of the acetaldehyde wave and vinyl acetate concentration has been found.[2]

In another method use is made of addition compounds formed by unsaturated organic compounds and a mercuric salt. The mixed solution of mercury(II) acetate and methanol, described by the following equations, is especially useful:



Two waves are observed on the polarogram of vinyl acetate, containing mercury(II) acetate, methanol and sodium nitrate as a supporting salt; the first wave (at about +0·35 V) corresponds to the reduction of mercury and the second wave (at about −0·35 V) to the reduction of the mercury addition compound of vinyl acetate. The height of the mercury wave is inversely proportional to the concentration of vinyl acetate, and the height of the more negative wave of the mercury addition compound of vinyl acetate is directly proportional to the concentration of vinyl acetate. The wave of the addition compound is not influenced by the presence of acetic acid, acetaldehyde and crotonaldehyde, which occur in technical vinyl acetate. Also, the same method can be applied to the determination of styrene, vinyl butyrate and allyl alcohol.[3]

ANALYSIS OF IMPURITIES IN MONOMERS

Small quantities of impurities present in monomer can act as inhibitors or chain transfer agents in the polymerisation process. They affect the polymerisation reaction, reduce the degree of polymerisation and impart some active groups to the polymer produced. For example, as impurities in technical vinyl acetate, acetic acid, acetaldehyde, crotonaldehyde, acetone, monovinyl acetylene and divinyl acetylene are present. Among these impurities, acetic acid and acetone hardly show any influence on the polymerisation reaction. On the other hand, acetaldehyde reduces the degree of polymerisation by a chain transfer reaction, and introduces a carbonyl group into the polyvinyl alcohol formed. The presence of crotonaldehyde reduces both the rate of polymerisation and the degree of polymerisation. Monovinyl acetylene and divinyl acetylene greatly retard the polymerisation reaction, even in very small amounts.[4] Some examples to the polarographic determination of these impurities are now discussed.

Crotonaldehyde

The determination of crotonaldehyde in the presence of other aldehydes present in vinyl acetate is difficult when other methods are used, but it can be easily carried out polarographically by diluting the sample in a methanol solution. Of the waves of crotonaldehyde at various pH (Table I), the waves in the acidic region are most suitable for analytical application.[5]

TABLE I.—EFFECT OF pH ON THE POLAROGRAM OF CROTONALDEHYDE

pH	$E_{1/2}$, *V vs. S.C.E.*	i_d, μA	Buffer solution
1·90	−0·98	0·724	Sörensen
3·12	−1·06	0·685	McIlvaine
4·19	−1·11	0·633	
5·09	−1·19	0·508	
7·85	−1·42	0·453	
9·88	−1·48	0·108	Sörensen

CH_3OH, 50%; crotonaldehyde,0· 418 mM; Temp.: 25°; $m^{2/3} t^{1/6} = 0{\cdot}785\ mg^{2/3}.sec^{-1/2}$.

Divinyl acetylene

Divinyl acetylene gives reduction waves in 75% dioxan.[6] Dimethylformamide, in which vinyl acetate is easily soluble, with a tetralkylammonium salt as a supporting salt is also suitable. In 100% dimethylformamide, divinyl acetylene yields waves at −1·74 V and −2·22 V. In a 25% dimethylformamide −75% vinyl acetate system, the second wave mentioned above is obscured, but the first wave is well-defined and can be used for the quantitative determination of divinyl acetylene in technical vinyl acetate.[7]

ANALYSIS OF CATALYSTS AND ITS APPLICATION

In 50% ethanol containing 0·50*M* tetrabutylammonium iodide, 2,2′-azo-bis-isobutyronitrile shows a wave proportional to concentration with a half-wave potential of −1·34 V *vs.* S.C.E. The rate of decomposition of this compound can be followed both in the absence and presence of *p*-chlorobenzenesulphinic acid.[8]

Waves of benzoyl peroxide can be applied to studies of the mechanisms of redox catalysts.[9] Generally, the determination of reducing agent in the presence of oxidising agent and *vice versa*, is difficult. Polarographic analysis of such mixtures is possible if a kinetic current, *e.g.*, in the case of the reaction between iron(II) and hydrogen peroxide, does not appear.

Polarographic curves obtained with a sample of a redox catalyst containing benzoin, benzoyl peroxide and iron(II) enabled us to carry out a simultaneous determination of all components. The results obtained indicate the formation of radicals by the following reactions:

$$\mathrm{POOP} + \mathrm{Fe}^{2+} \rightarrow \mathrm{PO}\cdot + \mathrm{PO}^{-} + \mathrm{Fe}^{3+}$$

$$2\mathrm{Fe}^{3+} + \mathrm{BzH}_2 \rightarrow 2\mathrm{Fe}^{2+} + \mathrm{Bz} + 2\mathrm{H}^{+}.$$

where POOP is benzoyl peroxide, Bz is benzil, PO· is a radical and PO^{-} an ion.

The reaction between diphenylamine and benzoyl peroxide is also a redox system and proceeds as follows:

$$(\mathrm{C_6H_5})_2\mathrm{NH} + (\mathrm{C_6H_5COO})_2 \rightarrow (\mathrm{C_6H_5})_2\mathrm{N}\cdot + \mathrm{C_6H_5COO}\cdot + \mathrm{C_6H_5COOH}.$$

To verify the above mechanism, the presence of tetraphenylhydrazine has been proved through its reaction with nitric oxide to give *N*-nitrosodiphenylamine, which can be determined polarographically:

$$(\mathrm{C_6H_5})_2\mathrm{NN}(\mathrm{C_6H_5})_2 \rightleftharpoons 2(\mathrm{C_6H_5})_2\mathrm{N}\cdot$$

$$(\mathrm{C_6H_5})_2\mathrm{N}\cdot + \cdot\mathrm{NO} \rightarrow (\mathrm{C_6H_5})_2\mathrm{N{:}NO}.$$

APPLICATION TO STUDIES OF CHEMICAL STRUCTURE OF POLYMERS

Carbonyl group in polyvinyl alcohol

Although the carbonyl groups in polyvinyl alcohol have been determined by their reaction with 2,4-dinitrophenylhydrazine,[10] spectrophotometrically and by a chemical method,[11] no definite conclusions have been reached. We have developed a method for the micro quantitative determination of carbonyl groups in polyvinyl alcohol by polarography based on the reaction of nitrophenylhydrazine with the carbonyl groups. Because polyvinyl alcohol is water-soluble and the polarographic reduction-wave of the nitro groups of the dinitrophenylhydrazones formed is very high, the sensitivity of the method developed is high. The suggested method of determination of the functional groupings is one of the few suggested for analysis of high polymer compounds.

In order to compare the polarographic behaviour of nitro groups bound to a high polymer with that of nitro groups of low-molecular compounds, the wave-heights of polyvinyl alcohol hydrazone before and after hydrolysis were compared. The wave of the unhydrolysed polyvinyl alcoholhydrazone was recorded at pH 5–6, and that of the wave of the hydrolysate at pH 0·8 (Table II). A preliminary experiment had shown that the wave-height of *p*-nitrophenylhydrazine alone was not changed in the acid range. On the other hand, in the present experiment (Table II), the wave-height of polyvinyl alcohol hydrazone after hydrolysis was twice that before hydrolysis. The wave-height of nitro groups, which are bound to a high polymer, is hence lower than that of the nitro groups in the low molecular compounds. This may be caused by either the difference in the diffusion coefficient or the lowering of the number of nitro groups accessible to reduction. Hence, because it would be difficult to calibrate and evaluate the waves for high polymeric material, it is recommended that the fragment bearing the group to be determined is separated from the polymer before the polarographic determination.

Table II.—Polarographic measurements of waves of polyvinyl alcohol hydrazone before and after hydrolysis

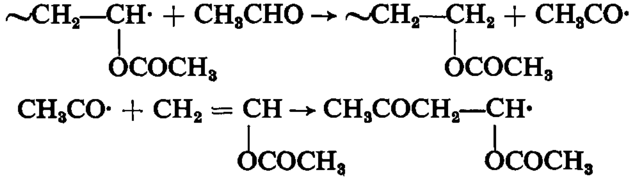
Polyvinyl alcohol, *g. l^{-1}*	pH	i_d, *μA*
8·74	5·4	0·386
5·83	5·4	0·257
2·88	5·4	0·126
8·74	0·8	0·643
5·83	0·8	0·428
2·88	0·8	0·208

Temp. = 25°C; $m^{2/3}.t^{1/6}$ = 0·94 $mg^{2/3}$. $sec^{-1/2}$

The recommended procedure for the determination of the carbonyl groups in polyvinyl alcohol follows:

To 100 ml of a 5% aqueous solution of polyvinyl alcohol, adjusted to pH 5–6 by addition of a Walpole buffer solution, add 0·2 g of *p*-nitrophenylhydrazine and allow the mixture to stand at 30° for 2 days. Precipitate polyvinyl alcohol (PVA) from the aqueous solution by adding an excess of methanol, wash with methanol in a Soxhlet extractor for 1 day, then dry. Dissolve the polyvinyl alcohol and *p*-nitrophenylhydrazone in 1*M* hydrochloric acid to make a 1% solution, and hydrolyse at 30° for 2 hr. Dilute the hydrolysed solution with Sörensen buffer solution (pH 1·2) to twice the volume and determine the free *p*-nitrophenylhydrazine polarographically.

When vinyl acetate is polymerised, acetaldehyde is considered to act as a chain transfer agent. Vinyl acetate was polymerised in the presence of acetaldehyde and the amount of carbonyl groups in the resulting polyvinyl alcohol was determined (Table III). The mole % content of carbonyl groups in the polyvinyl alcohol obtained is markedly increased when the vinyl acetate is polymerised in the presence of acetaldehyde. The chain transfer reaction of acetaldehyde can, therefore, be formulated as follows:



$$\sim CH_2-\underset{OCOCH_3}{\underset{|}{CH\cdot}} + CH_3CHO \rightarrow \sim CH_2-\underset{OCOCH_3}{\underset{|}{CH_2}} + CH_3CO\cdot$$

$$CH_3CO\cdot + CH_2=\underset{OCOCH_3}{\underset{|}{CH}} \rightarrow CH_3COCH_2-\underset{OCOCH_3}{\underset{|}{CH\cdot}}$$

Double bond in polyvinyl acetate

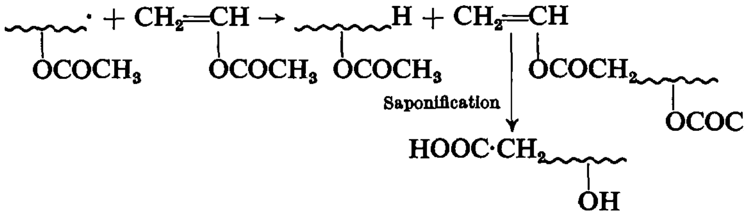
From investigations[12–15] of the branching of polyvinyl acetate it can be deduced that polyvinyl acetate molecules are branched because of the chain transfer reactions between a polymer radical and either a monomer (I), or a polymer molecule (II) in

TABLE III.—EFFECT OF ACETALDEHYDE ON THE NUMBER OF CARBONYL GROUPS IN POLYVINYL ALCOHOL

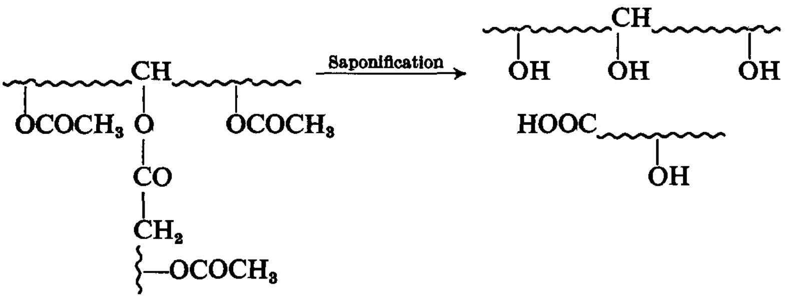
CH_3CHO, %	Polymerisation time, *min*	Conversion, %	P_{A_0}*	P_A*	Carbonyl group	
					mole %	*per polymer molecule*
0	120	27·0	4050	2590	0·027	0·7
0·25	200	28·0	1850	1590	0·072	1·1
0·50	200	28·0	1140	1130	0·105	1·2
1·00	200	27·0	620	630	0·177	1·1

Polymerisation conditions: purified vinyl acetate containing 0·015% of acetaldehyde; polymerisation temperature, 56·5°; bulk polymerisation with 0·1% of benzoyl peroxide catalyst.
* Degree of polymerisation.

the polymerisation reaction. The methyl group of the acetyl group in polyvinyl alcohol appears to be the principal site of the transfer



(I)

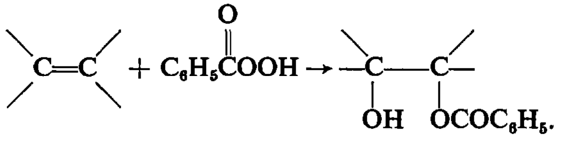


(II)

If this mechanism is correct, it follows that polyvinyl acetate obtained from monomer transfer reaction must include a double bond, and polyvinyl acetate obtained from the monomer and polymer transfer reactions must possess a carboxyl group.

Wheeler[14] determined the number of double bonds in polyvinyl acetate by the iodine monochloride method. The numerical average of the degrees of polymerisation was estimated by determination of the double bond end groups. The correlation between these values and intrinsic viscosities was in good agreement with osmotic and viscosity measurements.

We found that double bonds in polyvinyl alcohol can be determined polarographically[16] by measurement of the residual perbenzoic acid after the reaction between double bond and perbenzoic acid:[17]



Polarographic curves of perbenzoic acid in a mixture of acetic acid, benzene and water (75: 10: 15, v/v) with 0·25M ammonium nitrate as a supporting electrolyte, showed a good reduction-wave at about 0 V. Its wave-height was found to be proportional to the concentration for concentrations of perbenzoic acid lower than $2 \times 10^{-4}M$. The reactions between polyvinyl acetate and perbenzoic acid were carried out in benzene solution, and the solution allowed to stand at room temperature in the dark for 2 days. After the end of the reaction, the residual perbenzoic acid was measured polarographically. By this procedure, the content of double bonds in polyvinyl alcohol prepared under various polymerisation conditions was determined (Table IV).

TABLE IV.—CONTENT OF DOUBLE BONDS IN POLYVINYL ALCOHOL PREPARED UNDER VARIOUS CONDITIONS

Catalyst	Catalyst concentration, %	Conversion, %	P_{Ac}	Double bond, *mole* %
AZN*	0·005	10	5620	0·025
AZN*	0·005	40	7420	0·02
AZN*	0·005	52	9120	0·015
AZN*	0·002	13·5	6160	0·025
BPO†	0·01	31	8120	0·021

Bulk polymerisation, 60°
* AZN = 2,2′-azo-bis-isobutyronitrile
† BPO = benzoyl peroxide

Under the usual condition of polymerisation (bulk polymerisation at about 60°), radical chain transfer to monomer is predominant. Therefore, polyvinyl acetate should have a double bond as the end group. By kinetic analysis, the relationship between conversion and double bond content (DB) is given by

$$\frac{(DB)}{aX} = -Cm\left(\frac{1}{X} - 1\right)\ln(1 - X)$$

where a is the initial monomer, X the percentage conversion and Cm the chain transfer constant of monomer. From the results in Table IV, Cm was calculated to be $2{\cdot}5 \times 10^{-4}$. This value is in good agreement with that estimated from the determination of the carboxyl group in polyvinyl alcohol. From these results it may be concluded that the acetyl group in polyvinyl acetate is the principal site of branching.

Carboxyl group in polyvinyl alcohol

If the chain transfer occurs at the methyl group of the acetyl group in polyvinyl acetate, polyvinyl alcohol obtained by saponification of polyvinyl acetate should have a carboxyl group as end group. The concentration of carboxyl groups in polyvinyl alcohol could be determined by electroconductivity titration.[18,19] In an alternative polarographic method the determination of carboxyl groups is carried out by treating polyvinyl alcohol with calcium acetate. Calcium bound on the polyvinyl alcohol is then determined polarographically by use of 4–6M aqueous ammonia containing zinc-EDTA complex as supporting electrolyte. The carboxyl groups in polyvinyl alcohol formed by bulk and solution polymerisations were measured by this method (Tables V and VI).

According to the kinetic analysis, the relationship between conversion and carboxyl group content (—COOH) is given by

$$\frac{(\mathrm{COOH})}{aX} = Cm + Cp\left(\frac{1}{X}\ln\frac{1}{1-X} - 1\right)$$

where a is the initial concentration, X is the percentage conversion, Cm is the chain transfer constant of monomer and Cp is the chain transfer constant of polymer. The

TABLE V.—POLYMERISATION CONDITIONS OF VINYL ACETATE AND DEGREE OF POLYMERISATION OF POLYVINYL ACETATE AND POLYVINYL ALCOHOL OBTAINED

Polymerisation method	Catalyst	Catalyst concentration, %	Polymerisation temperature, °C	Conversion, %	P_{Ac}	P_A
Bulk	AZN*	0·005	60	12	6310	4320
Bulk	AZN*	0·005	60	52	9120	4295
Bulk	AZN*	0·005	60	90	24550	3170
Bulk	BPO†	0·06	60	93	16600	3055
CH_3OH 30% solution	BPO†	0·05	60	51	—	1400
CH_3OH 30% solution	BPO†	0·04	60	790	—	1530

* AZN — 2,2′-azo-bis-isobutyronitrile

† BPO = benzoyl peroxide

TABLE VI.—CARBOXYL GROUP CONTENT OF POLYVINYL ALCOHOL

$\bar{P}_A$	COOH content, *mole %*	—COOH, *per polymer molecule*
4320	0·028	1·21
4295	0·031	1·33
3170	0·046	1·45
3055	0·055	1·68
1400	0·033	0·46
1530	0·066	1·01

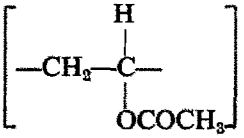
constants Cm and Cp, calculated by using the above relation, were $Cm = 2{\cdot}6 \times 10^{-4}$ and $Cp = 1{\cdot}4 \times 10^{-4}$ (at 60°).

1,2-*Glycol grouping in polyvinyl alcohol*

The 1,2-glycol grouping in polyvinyl alcohol can be determined polarographically[20] by measurement of the residual periodate ion after the reaction between polyvinyl alcohol and periodate (Table VII).

An Arrhenius plot of log Δ against 1/T, where Δ is the 1,2-glycol molar fraction, gave $\Delta = 0{\cdot}12 \exp(-1270/RT)$. This is in agreement with the value observed by Flory.

The cross-linking reaction of polyvinyl acetate was carried out in methanol solution with benzoyl peroxide as a source of radicals. The cross-linking from the abstraction of the tertiary hydrogen atom in the polymer unit



$$\left[-CH_2-\overset{H}{\underset{OCOCH_3}{C}}- \right]$$

was found by the determination of 1,2-glycol and the viscosity measurement.

Table VII.—Polymerisation conditions of vinyl alcohol and 1,2-glycol content of polyvinyl alcohol

Polymerisation type	Bulk	20% CH_3OH solution	Bulk	15% CH_3OH solution	5% CH_3OH solution	15% CH_3OH solution
Polymerisation temperature, °*C*	60	60	50	45	45	30
Catalyst	AZN*	AZN*	AZN*	AZN*	BPO† Benzoin $FeCl_3$	AZN* ClSA‡
Concentration of catalyst, %	0·005	0·02	0·1	0·16	BPO† 0·2 Benzoin 0·18	AZN* 0·15 ClSA‡ 0·16
Conversion, %	90	50	20	61	35	54
Polymerisation degree of polyvinyl alcohol	3170	1690	4850	2770	2380	3350
1,2-Glycol content, *mole* %	1·87	1·86	1·79	1·66	1·74	1·51

* AZN = 2,2′-azo-bis-isobutyronitrile.
† BPO = benzoyl peroxide
‡ ClSA = *p*-chlorobenzenesulphinic acid

CONCLUSION

As has been described above, the polarograph is an effective instrument for studies in the field of polymer science. It is expected that it can be applied to other problems than those reported in this review.

Zusammenfassung—Es wird eine Übersicht über die Polarographie auf dem Gebiet der Polymeren gegeben.

Résumé—On présente une revue sur la polarographie dans la science des polymères.

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APPLICATION OF POLAROGRAPHY TO CO-ORDINATION CHEMISTRY

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Summary—A review of the application of polarography to co-ordination chemistry is presented.

INTRODUCTION

POLAROGRAPHY of co-ordination compounds reflects to a certain extent the general trend which has been encountered with co-ordination chemistry in the past decades: after a relative stagnation in the period up to the second World War an unusually fruitful period, which started in the fifties, followed. Conditions for this vigorous development obtained much earlier, but a stimulus was necessary. This came from the intensive atomic-energy research during and subsequent to the second World War. Equally important was the recognition of the role of co-ordination compounds as catalysts of industrially important chemical processes; this led to an increased support of research in the corresponding fields. From the point of view of the research itself the progress was made possible by both the purposeful application of physical theories (especially quantum mechanics) to classical inorganic chemistry, and by the development of new preparatory techniques and use of modern physico-chemical methods. Techniques of measurement are used in modern co-ordination chemistry to describe the individual compounds and their properties as completely and systematically as possible with experimental parameters from which it is possible to verify and improve theoretical relationships. The data obtained by various physico-chemical methods can be divided into two groups: static and dynamic. The static ones, which are obtained by measuring spectra of all kinds, magnetic susceptibility, electric dipoles, refraction, *etc.*, are in general available to a much larger extent than the dynamic quantities, which express the reactivity and kinetic properties of the substances. Polarography, although it is in principle a dynamic method, was generally used, up to the forties, to yield static data, *e.g.*, complex formation constants and the number of ligands in some simple substitution labile complexes, and also served in most cases as an analytical method. The following of kinetic parameters was limited to relatively slow homogeneous reactions (with half-lives of the order of min to hr) where polarography served again as an analytical method for determining the time-variable concentration of some electroactive reaction component. Only in the late forties, with the discovery of kinetic currents by Brdička and Wiesner (for review* see [1,2]) and later with the elaboration of the exact theory of transport processes,[2,3] was it possible to exploit fully the dynamic character of the polarographic method for quantitative determination of kinetic parameters, both of electrode processes and rapid chemical

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* Because of the large number of original papers only review papers and monographs, where the citations of the original papers can be found, are referred to in the *Introduction* to this paper.

reactions occurring in the neighbourhood of the electrode. Thus, polarography in its present state represents one of the few methods which provides data in both groups and has changed from being predominantly an analytical method to a physico-chemical method suitable for solving problems of general chemistry. This feature is much appreciated by co-ordination chemists, who need still more quantitative experimental data to solve the increasing number of problems. Thus, in the past decade an increasing attention has been paid to the application of polarography to co-ordination chemistry and the results obtained have been recently reviewed by Vlček.[4]

NATURE AND SCOPE OF THE METHOD

The polarographic activity of the substances studied is dependent on their ability to undergo oxidation-reduction changes at the electrode in the attainable potential range. In the case of co-ordination chemistry this requirement is nearly always fulfilled because the compounds usually contain metals, and very often transition metals which can exist in several oxidation states. Moreover, the oxidation reduction changes are not limited to the central atoms; a number of ligands can be reduced or oxidised at the electrode. Thus, polarographic activity of co-ordination compounds is common.

A further typical feature of polarography is, as already mentioned, that it is a dynamic method in contrast to static electrochemical methods. The dynamic character of polarography is based on the fact that by impressing a certain potential to the electrode all equilibria existing in the solution are perturbed at the electrode and several processes start which tend to re-establish the disturbed equilibria. The nature and rate of these processes, both electrochemical and chemical, influence the shape and position of the polarographic current-voltage curves. Thus, as soon as the substance examined appears to be electroactive, *i.e.*, can be reduced or oxidised at the electrode, there is a possibility of obtaining from the corresponding polarographic curves information about the nature of and the mechanism and rate of processes within the examined system, under given conditions.

PROCESSES WHICH CAN BE FOLLOWED BY POLAROGRAPHY

Reactions which can be followed from polarographic curves can be divided into three following three groups:

(1) electrode reactions;
(2) chemical reactions occurring close to the electrode surface and caused by perturbation of the chemical equilibria of the system by the electrode reaction;
(3) homogeneous chemical reactions occurring in the bulk of the solution which are not influenced by the electrode reaction.

The fourth process, which accompanies all polarographic processes, is diffusion and for polarography it is characteristic that at least two of the mentioned processes proceed at the same time, *e.g.*, the electrode reaction and diffusion, or electrode reaction, diffusion and a stationary state between the diffusion and a chemical reaction occurring in a thin layer at the electrode surface. Thus, when following the polarographic curve the current corresponding to different potentials might be controlled alternately by all of the mentioned processes. From the kinetic point of view polarography is the oldest of the so-called competition methods[5] for following rapid reactions. The competitive processes occurring in polarography may yield static data (*e.g.*, concentration determined from the maximum diffusion flux of the electroactive substance) or dynamic data (*e.g.*, rate constants of chemical reactions from kinetic currents). Therefore, a detailed analysis of the polarographic curves and their relationships enable us to obtain a number of data of both static and dynamic nature.

In the following sections these processes will be discussed in more detail and which kind of information in the field of co-ordination chemistry can be obtained in the individual cases will be shown.

Electrode Reaction

The electrode reaction is a fundamental polarographic process. During this reaction one form of the redox couple is consumed and the other one generated so that at the electrode the concentration distribution and equilibria undergo a disturbance, which induces further processes. The most simple case is that in which one of the forms present in the solution exchanges electrons with the electrode and is thus converted into the other. In general, an opposing reaction is possible as well so that the electrode reaction can be expressed as

$$\mathrm{Ox} + \mathrm{ne} \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} \mathrm{Red} \qquad (1)$$

The rate constants of the electrode process, k_e and k_{-e}, are usually considered to be exponentially dependent on potential

$$k_e = k_e{}^\circ \exp\left[-\frac{\alpha nF(E - E^\circ)}{RT}\right] \text{ and } k_{-e} = k_e{}^\circ \exp\left[\frac{(1-\alpha)nF(E - E^\circ)}{RT}\right]$$

where $k_e{}^\circ$ is the standard rate constant. Any redox system may be characterised by the standard redox potential, E°, which is a thermodynamic quantity determining the oxidation-reduction power of the system, and by the standard rate constant $k_e{}^\circ$ to which both rate constants k_e and k_{-e} are equal at the standard potential:

$$E = E^\circ;\ k_e = k_{-e} = k_e{}^\circ \qquad (2)$$

The rate constant $k_e{}^\circ$ is a kinetic quantity which determines the shape and position of the wave with respect to the standard potential. The general equation of a polarographic wave corresponding to the reduction of the oxidised form of the redox system is given by the expression

$$(\bar{\imath}_d - \bar{\imath})/\bar{\imath} = \exp[nF(E - E^\circ)/RT] + (1{\cdot}14/k_e{}^\circ)\sqrt{D/t_1}\exp[\alpha nF(E - E^\circ)/RT] \quad (3)$$

Now two limiting cases can be distinguished according to the value of the rate constant $k_e{}^\circ$. If $k_e{}^\circ$ is sufficiently high so that the expression $k_e{}^\circ\sqrt{t_1/D} \gg 1$, the second right-hand side term in equation (3) can be neglected and the Heyrovský-Ilkovič equation is obtained,

$$(\bar{\imath}d - \bar{\imath})/\bar{\imath} = \exp[nF(E - E^\circ)/RT] \qquad (4)$$

which expresses the shape of the polarographic curve corresponding to a reversible electrode process. In this case the half-wave potential differs from the standard redox potential E° of a true redox-system (both forms in the solution) only by the term $(RT/nF)\ln\sqrt{D_{Ox}/D_{Red}}$ which is, in most cases, negligible.

If, on the other hand, the value of the rate constant $k_e{}^\circ$ is lower than about

2×10^{-2} cm.sec^{-1} (dimension of the heterogeneous rate constant) the second right-hand term of the above equation is no longer negligible and the half-wave potential is measureably shifted to a more negative value and the wave is less steep. Processes in which $E^\circ - E_{1/2} > 150$ mV are called totally irreversible and the shape of the polarographic curve is expressed by the relation

$$E = E^\circ + (RT/\alpha nF) \ln 0{\cdot}87\, k_e^\circ t_1^{1/2} D^{-1/2} + (RT/\alpha nF) \ln [(\bar{i} - i)/i] \qquad (5)$$

Both from the reversible and irreversible processes some data important in co-ordination chemistry can be obtained.

Reversible systems

Strictly speaking, the simple reversible processes of co-ordination compounds are limited to substitution inert complexes, which are not in mobile equilibrium with their ligands. Because the reversible processes are governed only by the thermodynamic requirements of the Nernst equation, no kinetic data can be obtained from the shape and position of the corresponding polarographic waves.

From the reversibility of the electrode reaction of a complex particle some qualitative conclusions can be drawn as regards the structure of the oxidised and reduced form. A reversible process can be expected for substitution inert complexes in which the oxidised and reduced forms possess identical atomic configuration and differ only by one electron in a vacant stable orbital in the oxidised form. Some examples of complexes fulfilling these conditions are given in Table I.

TABLE I.—EXAMPLES OF REVERSIBLE ELECTRODE PROCESSES OF COMPLEX IONS

Reaction	Electron structure of form	
	oxidised	reduced
$[Cr(CN)_6]^{3-} + e = [Cr(CN)_6]^{4-}$	$d^1d^1d^1[D^2SP^3]$	$d^2d^1d^1[D^2SP^3]$
$[Fe(CN)_6]^{3-} + e = [Fe(CN)_6]^{4-}$	$d^2d^2d^1[D^2SP^3]$	$d^2d^2d^2[D^2SP^3]$
$[RuO_4] + e = [RuO_4]^-$	d^0D^4	d^1D^4
$[NbCl_6]^- + e = [NbCl_6]^{2-}$	$d^0d^0d^0[D^2SP^3]$	$d^1d^0d^0[D^2SP^3]$

Substitution labile complexes can also be reduced reversibly and in these cases the substitution equilibria are usually very mobile and proceed much more rapidly than the diffusion process. The most simple case of such a behaviour is that in which a single complex with the ligand X is in mobile and reversible equilibrium with the metal ion, which is reversibly reduced to the metal:

$$\begin{tikzcd} MX_n \arrow[r, shift left] & M^{z+} + nX \arrow[l, shift left] \arrow[d, Leftrightarrow] \\ & M \end{tikzcd} \qquad (I)$$

(Here, and in the following, single arrows → denote a chemical reaction, and double arrows ⇒ and ⇔ an irreversible and reversible electrode reaction, respectively; *n* is the number of ligands and *z* the charge of the species; in complex particles, for the sake of simplicity, no charge is indicated.) Because both the chemical and electrode reaction are rapid and reversible a reversible diffusion-controlled wave is obtained of the same height and shape as with free metal ions but the half-wave potential is shifted towards the more negative values. From this shift the stability constant of the complex and the number of ligands, *i.e.*, the composition of the complex can be easily computed. As an example, the classical case of reduction of the biplumbite ion, $HPbO_2^-$, in strongly alkaline solution can be quoted[6,7] from a great number of other cases in which the complexity constants and composition of the complexes were determined (see, for example,[8–19]).

If the reduced form, instead of metal, is a metal ion in a lower oxidation state forming a complex with a different number of ligands X than the oxidised form, a similar shift of the half-wave potential with the ligand concentration is observed. From this shift, however, only the difference in the ligand number of the two forms and the ratio of the corresponding stability constants can be evaluated.

Similarly, if the rapid chemical equilibrium or the overall electrode process is combined with the uptake of protons, which is the case, for example, if the complexing agent is an acid or if reduction of organic ligands occurs, then the number of protons involved can be evaluated from the shift of the half-wave potential with pH.

Frequently, more complicated systems are encountered in which a stepwise complex formation occurs; this implies that several complexes can exist in the solution. In general, these systems also can be analysed polarographically. Thus, for systems of the type

$$\underbrace{M^{z+} \xleftrightarrow{k_1} MX \xleftrightarrow{k_2} MX_2 \xleftrightarrow{k_3} \ldots\ldots\ldots\ldots \xleftrightarrow{k_n} MX_n}_{\displaystyle \Updownarrow \atop \displaystyle M} \qquad \text{(II)}$$

the graphical method by De Ford and Hume[20] has been applied successfully several times[21–27] for calculating the stepwise and overall stability constants of the individual complexes and the composition of the highest complex. If the reduced form is a set of complexes of the metal in a lower oxidation state then, for the determination of one set of the stepwise stability constants, the other one must be known independently. In all these cases, in which the electrode reaction is reversible, it cannot be decided which of the complexes present in the solution reacts directly with the electrode.

In some cases the same information can be obtained from other static methods, *e.g.*, potentiometry or spectrophotometry, but often even then polarography can be preferred because it is very easy to handle and yields highly reproducible results. The same applies also to determination of the standard redox potential of reversible systems. This quantity can be obtained potentiometrically, but in cases in which one of the forms of a redox system is unstable or cannot be prepared polarography is very convenient.

As an example of the use of standard redox potentials for drawing conclusions about the structural parameters of co-ordination compounds, the method for determination of the composition of molecular orbitals in certain compounds will be mentioned. This method is based on the fact that substitution of the co-ordinated ligand causes a shift of the half-wave potential of the complex, similar to substitution of the free ligand but to a lesser extent. From this lowering of the effects, the nature of the highest occupied orbital and localisation of the corresponding electron in the reduced form can be estimated. Some substitution inert complexes, like dibenzene-chromium, react with the electrode as a whole and the orbital from which the electron is removed during the oxidation can be regarded as a molecular orbital, ϕ, formed by linear combination of atomic orbitals of the individual components

$$\phi = C_1\psi_1 + C_2\psi_2 \tag{6}$$

where ψ_1 is the eigenfunction of the central atom and ψ_2 that of the ligand, and c_1, c_2 are the mixing coefficients. Now for the electron affinity, ε, of the oxidised form one can write

$$\varepsilon = -\int \phi^* H \phi d\varepsilon \tag{7}$$

where H is the one-electron Hamiltonian. The electron affinity is related to the standard redox potential of the system by the relation

$$nFE^\circ = \varepsilon + T\Delta S^\circ + K \tag{8}$$

When following the behaviour of a series of related compounds formed, for example, by a suitable substitution of the ligand, it can be assumed that the entropy term and the constant K in (8) will not change, so that for two members of the series it follows that

$$nF(E_1^\circ - E_2^\circ) = \varepsilon_1 - \varepsilon_2 \tag{9}$$

Hence, it is seen that the standard potential and thus also the polarographic half-wave potential of the reversible system is a function of the molecular orbital and therefore must have properties of both atomic orbitals. From the shift of the half-wave potential with substitution the mixing coefficients can be estimated. In the case of dibenzenechromium it was found[28] that in the highest occupied orbital of the complex a 10–15% electron transfer occurs between the central atom and the aromatic rings, the prevailing portion of the electrons being localised at the chromium atom.

Irreversible processes

If the electrode process is irreversible the scope of obtainable information is broadened, because in this case the rate of the electrode reaction can be measured with high accuracy from the relation

$$k_c^\circ = 1{\cdot}14\, D^{\frac{1}{2}}\, t_1^{-\frac{1}{2}} \exp\,[\alpha nF(E_{\frac{1}{2}} - E^\circ)/RT] \tag{10}$$

which follows from the equation of the totally irreversible process. Moreover, as will be seen later, in systems analogous to II, the species reacting directly with the electrode can be determined, provided that the electrode process is irreversible.

The study of electron-transfer reactions by measuring the rate of the electrode process has several advantages against the study of homogeneous electron-transfer reactions in solutions. Firstly, in the electrode reaction the substance examined always reacts with the same partner, *i.e.*, with the electrode, the properties of which can easily be held constant. Further, an electrode, the potential of which changes gradually, represents a redox agent of just the necessary redox strength so that the reaction with various compounds is always performed under thermodynamically or kinetically identical conditions.

The irreversibility of the electrode process is caused by the slowness of the overall electron exchange between the electrode and the depolarising particle. The elementary act of the electron transfer proper is, however, governed by the Franck-Condon principle according to which this process proceeds quicker than the vibration of atoms in the depolariser. Hence, it follows that it takes place without any energy exchange with the neighbourhood, *i.e.*, adiabatically, and that the process must have practically zero activation energy. For this reason the slowness of the overall process must consist in a slow preformation of the particle to an energy state in which it can react with the electrode. The activation energy of this preformation can be determined directly from polarographic data[29,30] and depends on several factors, the most important of which are connected with the electronic structure of the depolarising particles. The study of the relations between the rate of the electrode reaction and the structure of the depolariser, even if it is still at the beginning, belongs to one of the most interesting fields of application of polarography in co-ordination chemistry. Thus, in a series of structurally related complexes there exists a direct proportionality between the activation energy of the electrode process and the frequency of the first absorption band.[31] From this it follows that the activation energy of the electrode reaction, within the given series of complexes, is the smaller the lower is the excitation energy of the complex particle; in other words, the preformation activation energy is proportional to the difference between the ground state and excited state of the complex. The transition state in which the complex particle is able to undergo an activation-energy-free electron transfer need not be a spectroscopic excitation state because the transition state is formed, at least partially, under the influence of the strong electric field of the electrode. As regards the particle itself, the ligand field strength plays an important role, which explains the effect of a hetero-ligand facilitating the electrode reaction.

TABLE II.—COMPARISON OF ELECTRODE AND SUBSTITUTION REACTIONS OF SOME COMPLEXES WITH DIFFERENT CONFIGURATION OF THE OXIDISED AND REDUCED FORMS

Reaction	Electrode reaction	Electron structure of form		Substitution inert–labile
		oxidised	reduced	
$[Cr(CNS)_6]^{3-} + e$ $= [Cr(CNS)_5 . aq]^{3-} + CNS^-$	slow	$d^1d^1d^1[D^2SP^3]$	$d^1d^1d^1d^1[DSP^3D]$	i–i
$[Fe(Ox)_3]^{3-} + e$ $= [Fe(Ox)_2 . aq_2]^{2-} + Ox^{2-}$	rapid	$d^1d^1d^1d^1d^1[SP^3D^2]$	$d^2d^1d^1d^1d^1[SP^3D^2]$	l–l
$[CrCl_2 . aq_4]^+ + e + 2H_2O$ $= [Cr . aq_6]^{2+} + 2 Cl^-$	slow	$d^1d^1d^1[D^2SP^3]$	$d^1d^1d^1d^1[DSP^3D]$	i–i
$[Cu(NH_3)_4]^{2+} + e$ $= [Cu(NH_3)_2]^+ + 2NH_3$	rapid	$d^2d^2d^2d^2d^1[SP^2D]$	$d^2d^2d^2d^2d^2[SP]$	l–l

Another parallel exists between the rate of the electrode reaction and that of the substitution reactions in complexes. This parallel is qualitatively shown in Table II, which represents some redox systems with different configuration of the components. It is seen that when the electrode reaction is rapid the complex is substitution labile, whereas the substitution inert complexes yield slow electrode reactions. This phenomenon is explained by the assumption that a substitution reaction proceeding by the S_N2 mechanism can be rapid only if in the complex a vacant orbital is available to accept the electron pair from the ligand.[32] If it is not, a rearrangement in the electron configuration must take place, the activation energy of which is governed by the same factors as in the electrode reaction.[31] These are, of course, rather simplified concepts and for a quantitative evaluation of all the observed phenomena in this field more experimental material is still needed.

Useful data can be obtained from a study of irreversible electrode reactions of substitution labile complexes which are in rapid equilibrium with the ligands. Thus, in system in which only one of the set of complexes undergoes an irreversible electrode reaction, scheme (III), the composition of this particular complex MX_k and the rate

$$\begin{tikzcd} M^{z+} \arrow[r, leftrightarrow, "k_1"] & MX \arrow[r, leftrightarrow, "K_2"] & MX_2 \ldots\ldots \arrow[r, leftrightarrow, "k_k"] & MX_k \ldots\ldots \arrow[r, leftrightarrow, "k_n"] \arrow[d, Rightarrow] & MX_n \\ & & & \text{products} & \end{tikzcd} \qquad \text{(III)}$$

constant of the electrode reaction can be determined.[33–36] Under suitable conditions also the stepwise stability constants and ion-pair formation constants can be determined from the irreversible polarographic waves. Thus, for example, it was found that the complex cations $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5NO_3]^{2+}$ in a sulphate medium react with the electrode in the form of ion-pairs with the sulphate anion and from polarographic data the equilibrium constants of the ion-pair formation were determined.[4,37]

Chemical Reactions at the Electrode Surface

The second type of reaction which can be followed polarographically is a chemical reaction which proceeds in a thin layer at the electrode surface. These reactions occur if one or both forms of the redox system form chemical equilibria which are disturbed by the electrode reaction, or, if the product of the electrode reaction is unstable in the given medium and reacts chemically either itself or with some components of the medium. These reactions are generally of great inportance for following, quantitatively, rapid reactions of co-ordination compounds, for tracing unstable intermediates and for determining the mechanism of reactions of co-ordination compounds.

According to their situation with respect to the electrode reaction these reactions can be divided into three groups:

(*a*) reactions preceding the electrode process;
(*b*) reactions parallel to the electrode process;
(*c*) reactions following the electrode process.

Accordingly, reactions of group (*a*) concern the depolariser whereas those of groups (*b*) and (*c*) concern product of the electrode reaction. In some more complicated cases in a given system, several of these reactions can proceed at the same time. The application of polarography for following rapid chemical reactions of groups (*a*)–(*c*) in co-ordination chemistry has been reviewed several times[1–4,36,38] and so only the basic principles together with some representative examples will now be given.

Reactions preceding electrode process

The most simple case of the first group can be represented by the following scheme

$$I \underset{k_2}{\overset{k_1}{\rightleftarrows}} A \xRightarrow{\text{el}} B \qquad K = \frac{k_1}{k_2} \ll 1 \qquad \text{(IV)}$$

i.e., an electroinactive species I is in equilibrium with the electroactive substance A which undergoes the electrode reaction yielding the product B. The equilibrium is shifted to the inactive form I. The electrode reaction plays here the role of a factor which disturbs the equilibrium $I \rightleftarrows A$ and thus causes a chemical reaction at the electrode surface, which tends to re-establish the disturbed equilibrium. If the conditions are such that the rate of the reaction is sufficiently rapid to proceed during the time of electrolysis, *i.e.*, in work with the mercury dropping electrode during the drop-time, and is at the same time slower than the diffusion of the substance I to the electrode, then a polarographic wave is obtained the height of which is governed by the rate of the chemical reaction. Therefore, the limiting current is denoted as kinetic, and is lower than would correspond to the maximum diffusion flux of the substance I and higher than corresponds to the diffusion of the equilibrium concentration of the substance A. From the relative height of the kinetic wave the rate constants k_1 and k_2 of the chemical reaction can easily be computed providing the equilibrium constant K is known. The range of the rate constants which can be evaluated in this way is from about 10^2 to 10^{11} $1.mole^{-1}.sec^{-1}$.

From the kinetic waves the rate constants can be calculated for different rapid reactions of co-ordination compounds, like complex formation and dissociation, monomerisation and dimerisation, recombination of weak acids as ligands, *etc.*

As an example, let us consider scheme (V), which has the following properties:

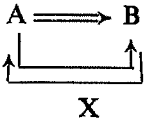
$$M \longleftrightarrow MX \longleftrightarrow MX_2 \ldots\ldots \underset{\substack{\Updownarrow \\ \text{products}}}{MX_q} \ldots\ldots MX_{p-1} \underset{k_2}{\overset{k_1}{\rightleftarrows}} MX_p \ldots\ldots MX_n \qquad \text{(V)}$$

In the set of complexes $M \ldots\ldots MX_n$ all equilibria are perfectly mobile except for that between the complex MX_{p-1} and MX_p which is established with a limited rate. The complexes $MX_p \ldots\ldots MX_n$ are electroinactive and the set $M \ldots\ldots MX_n$ may be regarded as electroactive for the case that the electrode reaction is reversible. There are, in principle, two ways of obtaining information about the system, *viz.*, from the corresponding dependences of the relative height of the kinetic limiting-current,[35,39–42] or from the half-wave potential of the kinetic wave.[35,36,40,43] From the former analysis the rate constant k_2 (and/or k_1) may be evaluated.[40–42] Both ways may serve for the determination of the composition of the highest complex (n) and of the complex by the dissociation of which the electroactive species is formed (p). From the half-wave potential of the kinetic wave the complexity constants[40,41,44] may be evaluated as in the case of all equilibria being perfectly mobile, and, in addition, providing the electrode reaction is irreversible, the composition of the complex reacting with the electrode (2) and the corresponding rate constant of the electrode reaction (k_e°) may be determined.

In this way the rate constants of a number of complex reactions have been determined and the mechanism of several reductions and oxidations of complexes were elucidated, *e.g.*, in the case of nitrilotriacetic acid and cyanide complexes of cadmium,[39–41] ethylenediamine complexes of cobalt,[42] EDTA complexes of manganese and lead,[45,46] *etc.*

Reactions parallel to electrode process

The second class of chemical reactions taking place in a thin layer at the electrode are those which can be represented by the following scheme:

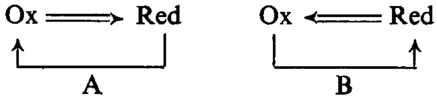


(VI)

The substance A is reduced or oxidised at the electrode with the formation of the product B and this reacts with some component X of the medium yielding again the original substance A. This cyclic regeneration of the depolariser, A, causes a polarographic current which exceeds the current corresponding to the simple electrode reaction of A to B and which is the higher the greater is the rate of reaction between B and X. These currents are called catalytic because the depolariser A is steadily being regenerated. From the relative height of the catalytic limiting current the rate constant of the reaction between B and X can be evaluated.[1,47] Numerous systems have been found, which react according to the mentioned scheme (VI) and in which the rate constants of the redox processes have been obtained from a study of catalytic currents. As examples the following oxidation reactions may be quoted:

Fe(II) + H_2O_2,[48] Fe(II)-triethanolamine + H_2O_2,[49]
Fe(II)-triethanolamine + NH_2OH,[50] Ti(III)-oxalate + ClO_3^-,[51]
Ti(III)-oxalate + NH_2OH,[52] U(III) + NO_3^-.[53]

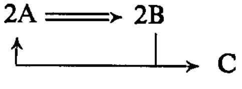
This kind of reaction is also suitable for studying the role of co-ordination compounds as homogeneous catalysts of chemical redox reactions. Let us consider as an example two substances A and B which do not react together under normal conditions. Now if one can find a redox system such that the substance A catalyses the electrode reaction in one direction and substance B in the opposite direction, *i.e.*



(VII)

then the redox system is a homogeneous catalyst of the reaction between A and B. On the basis of polarographic studies of this kind a number of catalytic systems using low valency metal complexes as catalysts have been found recently.[54–56] Thus, chloroform is not reduced by sodium borohydride but a small substoichiometric addition of $[Co(dipy)_3]^{2+}$ causes a vigorous reaction in which the whole amount of chloroform is reduced. The overall reaction mechanism is obvious: Co(II) in the dipyridyl complex is reduced by $NaBH_4$ to Co(I) which is able to reduce the chloroform with the formation of Co(II). A similar catalytic action was found with chromium(I) tris-dipyridyl, vanadium(I) tris-dipyridyl, cobaltocene, pentacyanocobalt(II) and its reduced solutions.[55,56]

A partial cyclic regeneration of the depolariser is represented by the case of dismutation of the product of the electrode reaction which can be visualised by the scheme



(VIII)

The scheme (VIII) operates in the reduction of uranyl ion, which is reduced to the quinquevalent state undergoing a disproportionation (dismutation) to quadrivalent species and sexivalent again. From the increase of the corresponding wave the rate constant of the dismutation can be evaluated.[57–60]

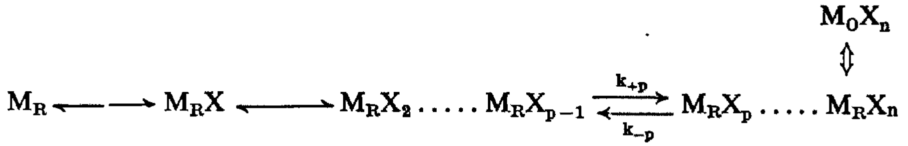
Reactions consecutive to electrode process

To the group of chemical reactions following the electrode process belong those reactions in which the product of the electrode process is inactivated:

$$A \rightleftarrows B \underset{k+}{\overset{k-}{\rightleftarrows}} I \qquad \text{(IX)}$$

i.e., the substance A reacts at the electrode to form a substance B, which undergoes a chemical reaction giving rise to an electroinactive product I. It is obvious that the polarographic wave can be influenced by the reaction $B \rightleftarrows I$ only if the electrode process is reversible or irreversible with only a small overvoltage.[61] The inactivation reaction does not influence the limiting current nor the shape of the polarographic wave but causes a shift of the half-wave potential from which the rate constant of the reaction $B \rightarrow C$ can be computed.

A more general case of the type (X) is often encountered



$$M_R \longleftrightarrow M_RX \longleftrightarrow M_RX_2 \ldots\ldots M_RX_{p-1} \underset{k_{-p}}{\overset{k_{+p}}{\rightleftarrows}} M_RX_p \ldots\ldots \begin{array}{c} M_OX_n \\ \updownarrow \\ M_RX_n \end{array} \quad (X)$$

with reduction of a substitution inert complex M_OX_n, the reduced form of which is substitution labile and the complex M_RX_p undergoes an inactivation reaction leading to inactive complexes $M_R \ldots\ldots M_RX_{p-1}$. From the dependence of the shift of the half-wave potential on the ligand concentration the composition of the complex (p) undergoing the inactivation reaction can be determined. An example of such behaviour is the reduction of tris-ethylenediaminecobalt(III) ion.[42]

In many cases several of the chemical reactions occurring at the electrode surface are combined with one or more electrode reaction steps leading to a great variety of possible reaction schemes.[4] In these more complicated cases it is sometimes impossible to determine the exact values of the corresponding rate constants. However, it is nearly always possible to deduce from the polarographic behaviour of the system the mechanism of the reactions which the system can undergo, and this is most valuable information which can hardly be obtained by any other method.

Homogeneous Reactions

The third type of reaction which can be followed polarographically is a homogeneous reaction in solution, with half-life times of the order of min to hr. These reactions have nothing to do with the electrode reaction and polarography serves here only as a suitable analytical method. Therefore, in general, polarography is not a specific method for following these reactions, but even so it can be recommended for several reasons, among which the most important are: the possibility of following the concentration changes of several components of the system at the same time, high accuracy of the direct record, very easy evaluation of the results because the measured quantity (the limiting diffusion current) is directly proportional to the concentration of the followed substance, the possibility of following the systems in media of extreme acidities (*e.g.*, up to concentrated sulphuric acid) and the high activity of components of the systems under investigation.

In conclusion it should be emphasised that the reaction schemes mentioned in the preceding columns form only a minor part of reaction mechanisms of coordination compounds which can be solved polarographically (for more detail see reference 4). Also, by enumerating the main types of reaction which can be followed by this method, it was not possible to exhaust all the possibilities of the method for solving problems of co-ordination chemistry; each system has its specific features which can be used for obtaining a certain kind of information and many of which could not be mentioned in this review. On the other hand, there are also certain limitations to the applicability of polarography in co-ordination chemistry. One of the most serious ones is the necessity to work in the presence of an excess of indifferent electrolyte which excludes work in non-polar solvents in which the salts serving as indifferent electrolytes are insoluble. This difficulty might be sometimes overcome by using mixed solvents. In some cases also, polarography is the method of choice because, in principle, the same information can be obtained by other methods, and in these instances one must resolve which method is the most suitable. In general, it would be wrong to use polarography in cases where other methods are more convenient. The aim of the present review is to indicate by some illustrative general examples that there are many areas of co-ordination chemistry where polarography is more suitable than any other method and can yield a large amount of information.

Zusammenfassung—Es wird eine Übersicht über die Anwendung der Polarographie in der Koordinationschemie gegeben.

Résumé—On présente une revue sur l'application de la polarographie à la chimie des composés de coordination.

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POLAROGRAPHIE DES POLYANIONS*

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Résumé—On présente une revue sur la polarographie des polyanions.

PROPRIETES GENERALES

QUOIQUE relativement peu nombreux, les travaux sur la polarographie des polyanions ont souvent abouti à des conclusions contradictoires, que l'on doit sans doute attribuer à la complication des mécanismes, mais aussi à la méconnaissance des propriétés de ces composés. Aussi, une revue rapide de celles-ci nous semble indispensable pour les composés ayant fait l'objet de recherches polarographiques.[1]

Formation et constitution

Isopolyanions. L'acidification des sels de polyacides faibles donne en principe un sel acide, ou l'acide faible lui-même:

$$PO_4^{3-} + H^+ \rightarrow PO_4H^{2-}.$$

Cependant, de nombreux systèmes ne se comportent pas aussi simplement; ainsi, l'acidification modérée des tungstates et molybdates conduit aux paratungstates (ou molybdates) renfermant plusieurs atomes W ou Mo

$$6WO_4^{2-} + 7H^+ \rightarrow HW_6O_{21}^{5-} + 3H_2O$$
$$7MoO_4^{2-} + 8H^+ \rightarrow Mo_7O_{24}^{6-} + 4H_2O$$

les ions simples $HW(Mo)O_4^-$ ne se manifestant que transitoirement ou dans des conditions très spéciales.

Une acidification plus poussée conduit à d'autres polyanions; on a pu mettre en évidence $H_3W_6O_{21}^{3-}$ dans la série tungstique, alors que chez les molybdates les espèces semblent en plus grand nombre, ce qui complique leur étude, car leurs domaines d'existence se chevauchent (ce qui se traduit, entre autres, par l'absence de points d'équivalence nets lors du titrage potentiométrique du sel neutre par un acide fort).

L'addition d'unegrande quantité d'acide pourra conduire à l'acide correspondant sous forme condensée (tel $H_2Mo_4O_{13}$, et non H_2MoO_4), ou précipitée (cas des tungstates). Pour un excès suffisant, on peut former des cations simples (tel VO_2^+ pour les vanadates) ou condensés comme celui (vraisemblablement $HMo_2O_6^+$) rencontré dans le "réactif molybdique", et également des complexes comme la "chlorhydrine molybdique" $Mo(OH)_4Cl_2$, qui existe en milieu HCl concentré.

En ce qui concerne leur structure, ces polyanions s'édifient par condensation des

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* NOTATIONS—Les potentiels $E_{\frac{1}{2}}$ sont donnés par rapport à l'électrode à calomel saturée, en ne figurant pas leur signe lorsqu'ils sont négatifs. Nous désignerons par *c* la concentration de l'espèce réductible, *h* la hauteur des paliers, et *n*, exprimé en Faradays, la hauteur de chaque vague particulière.

radicaux acides simples attendus, avec élimination d'eau, conduisant à des liaisons du type W—O—W. Les rayons ioniques de W^{6+}, Mo^{6+}, Nb^{5+}, sont suffisants pour qu'ils adoptent la coordinence octaédrique (type WO_6), l'union se faisant par mise en commun d'atomes O, donc de sommets ou arêtes; le rayon plus faible de V^{5+} permet seulement une coordinence de 5 (bipyramide triangulaire ou pyramide carrée).

Enfin, les atomes coordinés eux mêmes se disposent assez simplement les uns par rapport aux autres: chez les hexaniobates, par exemple, les Nb, au centre d'octaèdres NbO_6, se placent eux-mêmes suivant les sommets d'un octaèdre.

Hétéropolyanions. Au lieu de se faire, comme précédemment, entre radicaux de même nature, la condensation peut s'effectuer en présence d'un ion étranger: tout en s'unissant, les radicaux se groupent autour de "l'atome central" correspondant à cet ion pour donner un hétéropolyanion, que l'on dénomme par le rapport du nombre de radicaux à l'atome central

$$PO_4H^{2-} + 12WO_4^{2-} + 23H^+ \rightarrow [PO_4(WO_3)_{12}]^{3-} + 12H_2O.$$

(Anion phospho-12-tungstique)

Les composés de la série 12 constituent une classe très caractéristique et homogène, où l'on peut remplacer W par Mo (et dans une certaine mesure par des éléments voisins), et faire varier la nature de l'atome central (As, Si, Ge, B); cependant, les éléments de nombre d'oxydation supérieur à 5 (Te^{6+}, I^{7+}) ne donnent que des séries 6. Les séries 9, qui n'existent qu'avec P^{5+} et As^{5+}, ont un comportement voisin de celui des séries 12; la cryoscopie et les rayons X montrent qu'on doit leur attribuer une formule double, soit:

$$[(PO_4)_2(WO_3)_{18}]^{6-}.$$

La condensation peut aussi s'effectuer en présence d'un composé possédant plusieurs groupes OH: diacide (oxalique) acide-alcool (tartrique), polyalcool (mannite), polyphénol (pyrocatéchine). Contrairement à ce qu'on fait parfois, nous ne pensons pas qu'on puisse ranger ces composés parmi les hétéropolyanions, dont la définition reste, au moins au sens primitif, assez étroite. Le rapport des constituants y est peu élevé, si bien qu'aucun ne joue le rôle de groupe central, d'autant plus que les rapports peuvent s'inverser par exemple chez las molybdomalates, où l'on connait les 2 séries Mo:(acide malique) = 2:1 et 1:2.

Beaucoup d'entre eux sont d'une stabilité comparable ou supérieure à celle des iso et hétéropolyanions véritables; aussi, avant d'adopter les conclusions sur le comportement polarographique de ces derniers dans des tampons tels que ceux au citrate, convient-il de se demander dans quelle mesure ils ne s'y trouvent pas décomposés.

Cas des métatungstates. En se plaçant dans des conditions un peu différentes de celles où l'on obtient les isopolytungstates ordinaires, on a préparé des sels du type $4WO_3M_2O$, dénommés "métatungstates". Ils sont très voisins des dérivés phospho(silico)-12-tungstiques, auxquels les études de structure ont attribué des constitutions du type $[P(W_3O_{10})_4]^{3-}$ à tel point qu'on peut obtenir avec ceux-ci des cristaux mixtes; l'acide correspondant, loin de présenter les caractères de l'acide tungstique ordinaire (en particulier insolubilité), se rapproche des 12-hétéropolyacides. Pour tenir compte de cette analogie, COPAUX proposa de tripler la formule, et d'ajouter $1H_2O$ de constitution, soit: $[H_2(W_3O_{10})_4]^{6-}$.

On remarquera, qu'en ne tenant pas compte de l'eau de constitution, cette formule est double de celle de $H_3W_6O_{21}{}^{3-}$ envisagé précédemment, et dénommé "ion ψ métatungstique"; on admettait que le passage de l'un à l'autre ne pouvait avoir lieu facilement, mais des recherches en cours permettent de penser que la transformation ψ méta → méta est possible dans certaines conditions, quoique lente.

Propriétés des polyanions

Action des acides. Pour les isopolyanions, cette action a déja été envisagée (Voir *Isopolyanions*).

Les hétéropolyacides classiques sont forts; en présence d'un acide fort, ils sont extractibles à l'éther en donnant une couche liquide très dense, renfermant sans doute des composés oxonium.

Alors que les composés tungstiques sont très résistants à l'action des acides forts, ceux de Mo le sont beaucoup moins, surtout l'acide phospho-12-molybdique: la décomposition conduit à PO_4H_3 et au dérivé molybdique simple, en l'occurence le cation:

$$[PO_4(MoO_3)_{12}]^{3-} + 9H^+ \rightleftharpoons PO_4H_3 + 6HMo_2O_6{}^+.$$

Par déplacement d'équilibre, la concentration en H^+ restant constante, la dilution favorise cette dégradation, d'ailleurs réversible, au moins dans le cas de P et Ge. Ainsi, à une acidité de 0,3*M*, 13% d'acide germanomolybdique sont dégradés pour $c = 0{,}1/12$ et 70% pour $c = 0{,}01/12$, à cette dernière concentration, la dégradation est totale à une acidité 0,6*M*. Les acides silico -12 et phospho-9-molybdiques sont beaucoup plus résistants, et de plus, la vitesse de dégradation est plus faible (quelques jours sont nécessaires pour atteindre la valeur finale); néanmoins aux acidités plus fortes que 2*M*, la dégradation est rapide aux faibles valeurs de *c*. Ces faits ne semblent pas avoir été pris suffisamment en considération dans les études polarographiques.

Action des bases. Les isopolyanions, traités par les ions OH^-, redonnent les ions simples de départ par un processus inverse de celui de leur formation, si bien qu'aux pH > 7 ou 8, ils n'existent plus (cependant, les poly-niobates et tantalates cristallisent même en milieux très alcalins, l'acide précipitant dès que l'alcalinité diminue). Les 2 réactions opposées donnent lieu à des équilibres réversibles et rapides pour les molybdates; chez les tungstates et vanadates, ils sont parfois très lents dans le sens de l'alcalinisation.

La dégradation des hétéropolyanions sous l'action des ions OH^- est encore plus facile: celle des phospho-molybdates (et tungstates) apparait vers pH 1,5–2

$$[PO_4(WO_3)_{12}]^{3-} + \text{ions } OH^- \rightarrow [PO_6(WO_3)_{11}]^{7-} + \text{ions tungstiques}$$

en donnant des ions de la série 11, et des isopolyanions se trouvant, bien entendu, dans l'état ionique qu'ils doivent adopter au pH où a lieu la réaction. Il s'ensuit que les triacides correspondants, dans leurs courbes de titrages potentiométrique et conductimétrique, ne donnent des points d'équivalence que pour la formation de l'ion 11, soit 7 équivalents de base au lieu de 3, ce qui a longtemps intrigué les chimistes sur ces "acidités" anormales.

Les autres hétéropolyanions se dégradent à des pH plus élevés (3,5–4,5 suivant les cas), soit en séries 11, soit directement en constituants, sans passage par une série intermédiaire (silicomolybdates).

On notera un comportement voisin pour les séries 9, qui se dégradent en séries 8½ $[(PO_5)_2(WO_3)_{17}]^{10-}$ vers pH 4.

Enfin, les séries 11 et 8½ se dégradent à leur tour en constituants de départ, à des pH > 4,5–7 suivant les cas, les composés de W étant plus résistants que ceux de Mo.

Certains de ces processus sont réversibles, l'acidification des constituants redonnant les hétéropolyanions, mais ce n'est pas toujours le cas: l'acidification des mélanges phosphate-tungstate, quelles que soient leurs proportions ne conduit jamais aux composés des séries 9 (ou 8½), la série 9 prenant naissance dans des conditions très particulières (concentrations élevées, température élevée, grand excès de PO_4H_3).

Cas d'isomérie. Lors de la préparation des acides silico-12, boro-12-tungstiques, on obtient 2 isomères dont l'un est toujours plus abondant que l'autre, sans qu'on connaisse exactement les conditions réglant leurs proportions; la découverte de l'isomérie chez les phospho 9 tungstates est plus récente; les propriétés des 2 formes sont extrêmement voisines.

De telles isoméries furent plus difficiles à mettre en évidence chez les composés molybdiques, où la transformation de la forme instable en l'autre doit être plus rapide les équilibres étant plus mobiles. Le ler cas a été découvert par STRICKLAND chez les silicomolybdates: aussitôt sa formation à partir des constituants (silice et molybdate en milieu acide), l'acide silicomolybdique n'est pas sous sa forme habituelle (dite α) mais sous une forme β plus absorbante dans le visible, et qui, en milieu aqueux, se transforme assez rapidement, et complètement en forme α. Plus récemment SKERLAK[2] a pu montrer que dans un mélange eau-alcool à 50% cette transformation était stoppée, et utilisant ces observations, nous avons pu préparer β pur et cristallisé, par précipitation avec ClO_4H concentré. Nous avons d'ailleurs pu constater que l'isomère β de STRICKLAND dès sa formation, renfermait une proportion notable de α.

Dans le cas des polytungstates, nous avons mentionné les relations méta-ψ métatungstates qui ne constituent pas exactement une isomérie puisque la condensation en W n'est pas la même. Par contre, on a pu constater, que les propriétés des solutions de paratungstates, récemment préparées par acidification de WO_4^{2-}, se modifiaient avec le temps, une certaine proportion manifestant une réactivité beaucoup plus faible, en particulier avec les ions OH^-, et H_2O_2, ce qui a conduit à considérer qu'il existait 2 ions $HW_6O_{21}^{5-}$ dénommés A et B. Le ler, plus réactif, existe dans les solutions récemment acidifiées, le 2ème dans les solutions préparées à partir de paratungstate de sodium solide; les 2 catégories de solutions tendent, avec le temps vers le même état d'équilibre (environ 50% des 2 formes).

Les produits de réduction. Les plus caractéristiques résultent de la substitution, dans la structure des polyanions, de certains atomes par des atomes de valence inférieure; elle se traduit par l'apparition de colorations intenses.

On peut les obtenir par mélange, dans des conditions de pH déterminées, des 2 états de valence.[3] On a pu ainsi mettre en évidence, chez les polymolybdates, 3 séries dérivant du type hexamolybdique, par substitution de 2,3 et 4 Mo^{6+} sur les 6 par Mo^{5+}.

Degré de substitution	2	3	4
pH optimum de formation	1,2	3	4
Couleur	bleu	brun-rouge	brun-jaune

Chez les polyvanadates, les dérivés sont encore plus nombreux et l'on a pu mettre en évidence 6 séries résultant de la substitution progressive de V^{4+} à V^{5+} dans la structure de l'ion décavanadique $V_{10}O_{28}^{6-}$; elles se forment toutes entre pH 4 et 6,5; en milieu légèrement alcalin n'existe qu'une seule série

$$\left[\begin{matrix}V_2^{5+} \\ V_4^{4+}\end{matrix} O_{15} H\right]^{3-}$$

probablement à type hypovanadique.

Cependant, le meilleur mode de préparation, pour le but qui nous préoccupe, semble la réduction électrolytique, car ses conditions sont celles qui se rapprochent le plus de celles de la polarographie. Dans tous les cas où elle a été effectuée, nous en ferons état lors de l'étude polarographique.

REDUCTION DES ISOPOLYANIONS

Les vanadates[4]

Dénombrement des vagues. On a relevé 4 types de vagues, mais elles n'apparaissent pas simultanément dans tout l'intervalle de pH (Fig. 1)

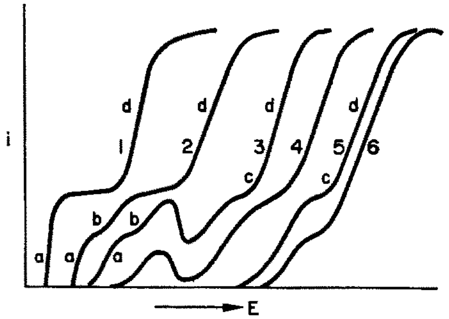

FIG. 1

—A pH < 3, on observe les vagues *a* et *d* (courbe 1); dans cette région, on rejoint la zône acide, où V est à l'état de cation VO_2^+ et non d'anion et dont le comportement, assez simple, a été bien étudié par ailleurs.

—A pH > 3, *a* commence à se scinder en 2 vagues *a* et *b* (courbe 2), cette dernière n'apparaissant pas en présence de KCl concentré, ou si $c < 0{,}5 \,.\, 10^{-3}$.

—A pH > 5, *b* en fonction de *E*, atteint un maximum, et retombe ensuite à un minimum; elle est alors suivie de l'apparition de *c* (courbe 3).

—Le maximum (comme le minimum) de $a + b$ décroit lorsque le pH augmente (courbe 4), si bien qu'à pH > 9, seules *c* et *d* subsistent (courbe 5).

Dans tous ces milieux, et à pH < 10, la somme $a + b + c$ est constante, et correspond au passage $V^{5+} \rightarrow V^{4+}$.

On a trouvé pour *a*, entre pH 5 et 8, et pour $c \sim 10^{-3}$:

$$E_{1/2} = 0{,}148\,\text{pH} - 0{,}937$$

$$\text{et pour } c\text{: } E_{1/2} = 0{,}120\,\text{pH} - 0{,}080$$

valable entre pH 5 et 12, ces valeurs restant les mêmes pour $c = 10^{-3}$ et $c = 0{,}1\ 10^{-3}$, mais changeant avec la force ionique.

Quant à *d* elle existe dans tous ces milieux, et est sensiblement le double de la somme précédente, ce qui correspond à:

$$V^{IV} \rightarrow V^{II}$$

$$\text{avec } E_{1/2} = 0{,}133\,\text{pH} + 0{,}64$$

valable entre pH 5 et 7,5 et pour $c \sim 10^{-3}$; au-delà de pH 8, la pente en fonction de pH devient nettement plus faible.

Nature des vagues. *c* et *d* sont des vagues de diffusion; la 1ère est utilisable en analyse entre pH 8,5 et 9,5, car elle est bien définie, et non accompagnée de *a* ou *b*; la 2ème est utilisable également, si des ions gênants se trouvent dans la région de *c*, mais elle n'est bien définie qu'en tampon borique: *a* et *b* sont des vagues d'adsorption, car le rapport $h/(\text{hauteur du réservoir})^{0,8}$ est constant, et d'autre part, *h*, pour *a*, tend à devenir constant lorsque *c* croit; enfin la gélatine les déprime et la saturation en camphre supprime *b* et réduit *a* à 60% de sa valeur.

Elles sont dues à l'adsorption d'anions fortement chargés* à *E* plus positif que le *O* électrocapillaire (c'est à dire $E < 0,5$ en vertu des conventions faites) ceux-ci se désorbent au-delà de 0,5 V, et le courant décroît mais *E* continuant à croître, la réduction par diffusion a lieu, d'où l'apparition de *c*. A pH < 5, $E_{1/2}$ de *c* se trouve dans la région plus positive que 0,5 V, et l'on passe du processus d'adsorption à celui de diffusion sans changement apparent, si bien que *c* n'est pas discernable de *a* ou *b*.[5]

L'action des substances adsorbables s'explique aisément, tel le camphre, qui déforme la courbe électrocapillaire entre −0,1 et −1,2 V. Quant à KCl, il la déforme aux E plus négatifs que −0,2 (où il se trouve alors plus adsorbé que V), ce qui explique qu'il inhibe *b* sans toucher à *a* puisque leurs $E_{1/2}$ sont situés de part et d'autre de cette valeur.

La dualité de *a* et *b* s'expliquerait par la formation d'une couche d'un produit de réduction insoluble qui dès qu'elle serait devenue suffisante (ce qui aurait lieu aux alentours de $c = 0,5\ 10^{-3}$) interdirait la pénétration des espèces à l'électrode; on rend compte ainsi du fait que *a* subsiste seule au-dessous de cette concentration et que son palier tende vers une limite au-dessus. Au-delà de −0,2 V, cette couche se détruirait et le courant d'adsorption atteint sa plénitude donnant *b*.

Comportement en milieu alcalin. A pH > 10, *d* s'accroit aux dépens de *c* (courbe 6) qui finit par disparaître à pH > 12,5, ce qu'on explique par une transformation progressive des ions pyro HVO_4^{2-} en ions ortho-vanadiques VO_4^{3-}; ces derniers, en raison de leur hydratation, seraient moins réductibles, mais le phénomène aurait lieu en un seul stade $V^{5+} \rightarrow V^{2+}$, qui coïnciderait avec le stade $V^{4+} \rightarrow V^{2+}$ de l'ion pyro.

Les observations de Schmid et Reilley[6] conduisent à une interprétation un peu différente: en milieu $1M$ $NH_4Cl + 6M$ ammoniaque, ils obtiennent une seule vague jusqu'à $c \sim 0,5\ 10^{-3}$; au delà apparaissent 2 vagues, mais la 1ère ne dépend plus de *c*; la forme de leurs courbes *i–t* permet de conclure à la formation, à la surface de la goutte, d'un produit insoluble ou fortement tensio-actif (hydroxyde inférieur?). Par contre, les courbes *i–t* de la 2éme vague sont normales, la substance inhibitrice ayant été soit réduite, soit devenue non absorbable.

Les molybdates[7]

Milieux acides. Dans ces milieux, Mo^{6+} se trouve à l'état de cations ou de complexes chlorhydriques ou sulfuriques; quoique notre étude soit consacrée aux

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* On sait que ce sont des décavanadates $HV_{10}O_{28}^{5-}$ à pH 3,5, et métavanadates $V_4O_{12}^{4-}$(et non VO_3^-) à pH 5–7. Au-dessus, apparaissent des espèces moins chargées (HVO_4^{2-}).

polyanions, il est nécessaire d'y connaître son comportement. Quoi qu'un peu différents, puisque les complexes n'y sont pas les mêmes les comportements en milieux HCl et H_2SO_4 présentent les mêmes caractéristiques essentielles; nous choisirons le premier de ces milieux[8] car les vagues y sont plus distinctes. On peut mettre en évidence, au maximum, 3 vagues ($c \sim 10^{-3}$).[9]

I a un $E_{1/2}$ voisin de 0,05; son palier de départ n'est généralement pas visible en raison de l'empiètement de la vague anodique de Cl^-; sa hauteur correspond à $1e^-$, au moins pour $c \leq 10^{-3}$.

III a un $E_{1/2}$ correspondant exactement à celui obtenu lors de la réduction des solutions de Mo^{5+} (de 0,70 à 0,60 lorsqu'on passe des acidités 0,1 à $1M$)

II existe seule avec I aux alentours d'une acidité de $1M$ (au dessus de $2M$, elle se confond avec I en un processus à $3e^-$); elle correspond alors au passage en Mo^{3+}; lorsque l'acidité décroit III apparait et s'accroit aux dépens de II, leur somme restant constante (Exemple: courbe 1 Fig. 2: $c = 0{,}8\ 10^{-3}$ Milieu: $0{,}1M$ HCl).

Les recherches que nous avions faites à l'époque, complétées et révisées par celles en cours laissent penser que II est due à la réduction en Mo^{3+}. Le fait qu'elle n'atteigne pas la hauteur voulue aux faibles acidités, s'explique par une réaction du Mo^{3+} formé à l'électrode sous une forme très réactive (A), qui réagit en partie sur Mo^{6+} diffusant vers l'électrode, pour donner Mo^{5+}. Comme celui-ci n'est pas réductible au palier de II, on n'atteint pas la hauteur correspondant à $3e^-$, qu'on obtient par contre au palier de III, où la réduction de Mo^{5+} est possible.

Puisque III est presque inexistante aux alentours d'une acidité $1M$, ceci prouve que la réaction de Mo^{3+} (A) sur Mo^{6+} est suffisamment lente pour que ce dernier arrive à l'électrode sans avoir réagi avec Mo^{3+}. Par contre, si l'on effectue une electrolyse en se plaçant au palier de II, Mo^{3+} formé à l'électrode retourne à l'intérieur de la solution, où il peut réagir sur Mo^{6+}, et l'on n'obtient, en définitive, que du Mo^{5+}, comme nous l'avons constaté.

Lorsque l'acidité décroit, la réaction de Mo^{3+} sur Mo^{6+} est favorisée, puisque II diminue.

Haight[10] a opéré à de plus faibles c ($0{,}0875\ 10^{-3}$), et a pu obtenir II pratiquement seule dans $0{,}3M$ HCl; l'analyse de cette vague lui fait conclure à un mécanisme à $2e^-$, donc au passage en Mo^{4+}, et $E_{1/2}$ obeit à la relation:

$$E_{1/2} = 0{,}080 - 0{,}12 \log (H^+) - 0{,}035 \log (Cl^-).$$

Cette conclusion semble être vérifiée par l'existence de vagues catalytiques: on sait qu'en présence de certaines substances à caractére oxydant (H_2O_2 anions perchlorique, nitrique) pourtant non réductibles au potentiel où l'on opère, les vagues de réduction de Mo^{6+} (ou W^{6+}) en milieu acide sont fortement accrues. De telles "vagues catalytiques" sont dues à la réoxydation par ces substances, d'une des valences inférieures, qui régénère le stade 6 [voir par exemple[11]; pour l'action mutuelle de Mo^{6+} et W^{6+} voir[12]].

On a prétendu voir là une preuve de la formation de Mo^{4+} au long de la vague II, qui jouit de cette propriété en se basant sur le fait que les formes chimiques de Mo^{5+} et Mo^{3+} ne réduisent pas d'elles-mêmes ces anions oxydants. En réalité, le Mo^{3+} que nous pensons se former au niveau de la vague II, est vraisemblablement une forme très réactive (que nous avons dénomée "A") qui, si elle ne disparait pas par réaction secondaire (avec Mo^{6+} ou un anion oxydant) se transforme rapidement en l'une des formes chimiques usuelles (rouge, verte ou brune) de Mo^{3+} moins réactives. D'ailleurs, alors que la surtension de H^+ n'est pas affectée par la présence de Mo^{3+} chimique, elle est fortement diminuée par celui issu de la réduction de Mo^{6+} en solution.[9] De plus, des recherches en cours nous montrent qu'il se forme bien du Mo^{4+} *lors de la réduction de* Mo^{5+} au départ mais que la vague d'une solution de Mo^{5+} n'est pas altérée par la présence de l'ion ClO_4^-, malgré cette formation de Mo^{4+}.[70]

Milieu peu acide non-tamponné. Il est certain que l'ion MoO_4^{2-} n'est pas réductible, mais que les polyanions le sont. Schwing[13] a montré qu'une solution de MoO_4^{2-} acidifiée donne, pour un rapport acide/Mo $< 1,14$ une hauteur de vague proportionnelle à la quantité d'acide ajoutée; or, par ailleurs, on a pu montrer que cette zône correspondait à la formation de l'anion paramolybdique $Mo_7O_{24}^{6-}$.[14]

Grasshoff et Hahn[15] ont, de même, constaté que la réduction apparait, à pH < 5, en 2 stades peu distincts, d'à peu près même hauteur, qui à pH $< 4,5$ se réunissent en un seul. Les courbes obtenues par tous ces auteurs (milieu $0,1M$ KCl $c \sim 10^{-3}$) ont une forme très étalée probablement parce qu'elles ne sont pas obtenues en milieu tamponné si bien que les vagues sont difficiles à discerner et que seul le palier de la dernière est mesurable. Ce palier croit, lorsque le pH diminue, jusqu'à pH 3, puis décroit légèrement ensuite; en son maximum, le processus correspond à $3e^-$.

En milieu nitrique (Na_2MoO_4 10^{-3} dans $NaNO_3$ 10^{-2} acidifié par HNO_3) on a observé un comportement voisin;[16] cependant la valeur maxima apparait à pH 2,15 et se maintient constante jusqu'à 1,52; au dessous, le palier s'élève fortement, et linéairement avec le pH. Il semble que les conditions soient alors propices à la réduction catalytique des ions nitrate.

Milieu peu acide tamponné. La réduction de Mo^{6+} exigeant vraisemblablement des protons, il est plus avantageux de l'effectuer en milieu tamponné. Dans son travail précédemment cité Schwing a montré qu'en tampon acétique (pH 4,6), la hauteur est proportionnelle à la concentration *globale* en Mo. Ceci s'explique si l'on sait que les ions $Mo_7O_{24}^{6-}$ seuls réductibles, et en équilibre avec MoO_4^{2-}, se forment rapidement à partir de ces derniers; grâce à cette circonstance, et au fait que le tampon constitue une importante réserve d'ions H^+, le courant n'est plus limité que par la concentration globale en Mo.

Le comportement de Mo^{6+} dans de tels milieux semble compliqué; on y observe au maximum 3 vagues comme en milieu acide, mais elles sont souvent moins distinctes:

—un fait important concerne I; on a constaté, à pH 1,3 et jusqu'à $c \sim 0,5\ 10^{-3}$, que sa hauteur est proportionnelle à c, et correspond à $1e^-$; au-delà de 10^{-3}, la hauteur de I reste constante, fait qu'on rapprochera de celui observé pour les vanadates, mais les agents suppresseurs ont peu d'effet sur cette vague.

—A pH 1,3, la somme I + II + III est proportionnelle à c jusqu'à $c \sim 4,10^{-3}$, et correspond à $3e^-$; au-delà de $5,10^{-3}$ elle correspond à des valeurs plus faibles; le rapport III/(I + II) ne dépend pas de c, et est de l'ordre de 2/3.[17]

Lorsque le pH croit, les hauteurs relatives des vagues restent pratiquement inchangées aux alentours de $c \sim 10^{-3}$; aux c plus élevées, les phénomènes, plus compliqués, sont à l'étude. Les valeurs de $E_{1/2}$ lorsque pH croit de 1,3 à 4,6 varient de 0,32 à 0,60 (vague II) et 0,68 à 0,92 (vague III).

Les tungstates

Métatungstates en milieu acide. En milieu d'acidité insuffisante, W^{6+} correspondant aux espèces ordinaires ne peut être étudié, en raison de la précipitation d'acide tungstique; en milieu HCl $> 8M$, on observe 2 vagues correspondant aux stades successifs: $W^{6+} \rightarrow W^{5+} \rightarrow W^{3+}$, la dernière double de la première.[18] Pour l'ion métatungstique (voir *Cas des metatungstates*) $H_2(W_3O_{10})_4{}^{6-}$, stable à toute acidité, la vague $W^{6+} \rightarrow W^{5+}$, plus négative que celle du tungstate, se partage en réalité en 3 vagues très distinctes corespondant à 2, 4, $12e^-$ (pour 12W); $E_{1/2} = 0{,}26$; 0,33; 0,52 dans $8M$ HCl. 0,35; 0,47; 0,60 dans $1M$ HCl.[19] Quant à la vague équivalente à la 2ème vague du tungstate, on l'observe bien en milieu acide, mais elle décroit lorsque l'acidité diminue; dans $1M$ HCl elle correspond sensiblement à $n = 1$ (au lieu de 2) ete lle devient nulle dans $0{,}1M$ HCl.

Afin d'élucider la nature des produits formés, on a effectué des électrolyses; on remarque:

—Que contrairement à de nombreux hétéropolyanions, on peut aboutir jusqu'au stade W^{3+} ($36e^-$) sans destruction du type, car la réoxydation redonne bien l'ion métatungstique, alors que dans le cas contraire il se serait précipité de l'acide tungstique.

On a pu mettre en évidence et caractériser par leurs spectres les composés à 21,26, 31 et $36e^-$ en milieu $5{,}10^{-3}$ en W.

—Qu'en milieu plus concentré ($50 \,.\, 10^{-3}$), le produit correspondant à la 1ère vague à $2e^-$, dont l'équivalent est bien connu chez les autres hétéropolyanions, apparait, coloré en bleu intense. Cependant, il se dismute rapidement, aux faibles pH, en composé à $6e^-$, rouge, beaucoup plus résistant à l'oxydation par l'air, et métatungstate. Par contre, en milieu alcalin sa stabilité est beaucoup plus grande, il est stable même dans $1M$ NaOH, contrairement au métatungstate qui conduit à $WO_4{}^{2-}$.

De même, quoique l'existence du composé à $4e^-$ se manifeste sur les polarogrammes obtenus en milieu acide, on n'a pu le mettre en évidence par électrolyse, sa dismutation étant encore plus rapide que celle du composé à $2e^-$. Par contre, sa stabilisation en milieu alcalin est certaine, car en alcalinisant une solution électrolysée au stade $4e^-$ en milieu acide (où il est manifestement dismuté) on obtient une solution bleue, de spectre caractéristique, appartenant à ce stade.

—Qu,on n'a pu obtenir jusqu'ici de produit réduit au stade $12e^-$, quoique, celui-ci apparaisse très nettement sur les polarogrammes. La vague correspondant ne s'annule complètement que pour la formation du composé à $21e^-$. Quant à la dernière vague, elle ne s'annule complètement que pour la formation de composé à $36e^-$. Dans ces solutions fortement réduites, apparait une vague anodique vers Ov., croissant lorsque le degré de réduction augmente; une 2ème vague plus négative que la précédente (0,8 V) apparait au-delà de $24e^-$, et correspond, d'après sa hauteur à une réoxydation partielle.

Isopolytungstates en milieu peu acide. Parallèlement à ce qu'on a pu constater pour Mo, seuls les polytungstates sont réductibles, et particulièrement l'ion $H_3W_6O_{21}{}^{3-}$, Si nous introduisons du tungstate dans un tampon acétique de pH ~ 4, zône vers laquelle se forme un tel ion, le polarogramme atteint son allure finale au bout d'environ 2 heures; il comporte 2 vagues de 1 faraday chacune (pour 6W), mais qui ne sont bien distinctes qu'entre pH 2,8 (0,36 et 0,65 V) et 4,6 (0,62 et 0,80). Au-dessus, leur hauteur décroit progressivement lorsque le pH s'élève, car apparait l'ion $HW_6O_{21}{}^{5-}$

(voir *Isopolyanions*), beaucoup moins facilement réductible, ce qui nous a permis l'étude de l'équilibre correspondant. Contrairement à ce qui a lieu pour les polymolybdates, en effet, les réactions de déplacement des équilibres avec les ions H^+ ou OH^- ne sont pas rapides, si bien que même en milieu tamponné, les hauteurs sont proportionnelles aux concentrations des espèces réductibles et non au W total.

Dans la zône de pH favorable à l'obtention des vagues de $H_3W_6O_{21}^{3-}$, nous avons constaté, à peu près aux mêmes potentiels, que les métatungstates présentaient leurs vagues à 2 et $4e^-$ (pour 12W);[21] des travaux en cours montrent que les vagues plus négatives du méta apparaissent aux E plus élevés; ce n'est pas le cas pour $H_3W_6O_{21}^{3-}$ où l'on est gêné par la décharge de H_2, dont la surtension semble abaissée par cet ion, plus que par le métatungstate.

Contrairement à ce que nous pensions tout d'abord, il semble qu'à la longue l'ion $H_3W_6O_{21}^{3-}$ se transforme en méta, car les solutions vieillies de plusieurs semaines et acidifiées se comportent comme du méta.[22]

Nous avons commencé l'étude des produits de réduction sur large catode de mercure, les autres conditions étant celles de la polarographie. En se plaçant au palier de la lère vague, la réduction s'arrête après passage de 1 faraday; le polarogramme présente alors une partie anodique importante, mais inférieure à la lère vague du produit non réduit, quoique la hauteur totale soit conservée.

En se plaçant au palier de la 2ème vague, on ne s'arrête pas au passage de 2 faradays (2W réduits sur 6) sans doute parce que le produit à $2e^-$ se dismute facilement, donnant naissance à du produit moins réduit, qui continue à subir la réduction. Les vagues obtenues sont irrégulières, mais lorsqu'on atteint le stade à 4 faradays, le polarogramme présente à côté d'une partie catodique peu importante, une partie anodique composée de 2 vagues de hauteurs égales, et parfaitement distinctes. Jusqu'à environ 5 faradays, le polarogramme change peu mais un précipité apparaît dans la solution. Ces phénomènes font l'objet d'études plus poussées.

REDUCTION DES COMPLEXES

Cas de Mo

Complexes avec acides-alcools.[23] Le comportement en milieu tartrique a été étudié par Parry et Yakubik.[25] A pH 2 et avec une concentration en complexant de $0,1M$, on obtient 2 vagues à 0 22 et 0,52 la dernière double de la lère, ce qui permet de supposer les étapes:

$$Mo^6 \rightarrow Mo^5 \rightarrow Mo^3.$$

Le 2ème palier diminue légèrement lorsque E croît, mais le maximum obtenu n'est pas du type ordinaire, car la gélatine abaisse la hauteur du palier en accentuant la décroissance du courant, et le camphre saturé le supprime. Ceci laisse supposer qu'il doit y avoir adsorption pour que la réduction ait lieu, l'accroissement de E provoquant une faible désorption, si bien que tous les ions parvenant à l'électrode ne sont plus adsorbés et réduits. Néanmoins, l'influence de la température et de la hauteur du réservoir montrent que l'adsorption elle-même est contrôlée par la diffusion.

A pH > 2, $E_{1/2}$ croît, la 2ème vague est abaissée considérablement et devient mal déffnie, si bien qu'elle est à peine discernable à pH > 4; en milieu neutre, il n'y a plus de réduction.

Pour le dosage, on se placera entre pH 1,5 et 2,3; il est possible même en présence de 250 fois la quantité de W; les ions Cr^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+} n'interfèrent pas. Le Fe^{3+} se réduit nettement avant; il n'est donc pas gênant s'il ne se trouve pas en excès 20 fois supérieur, sinon on en réduira la majeure partie par SO_2; Cu^{2+} ne gêne pas jusqu'à un excès 10 fois supérieur; par contre, V donne 3 vagues dont la dernière perturbe le dosage.

—Meites[26] a étudié le milieu citrate de sodium $1M$ à pH 7; on obtient une vague bien formée ($E_{1/2} = 0,927$) correspondant à un processus à $2e^-$, comme l'auteur le vérifie par coulométrie et titrage ampérométrique par V^{++}: c'est la première fois que la valence 4 est mise en évidence de façon aussi nette.

W ne donne rien, ce qui permet le dosage de Mo en présence de celui-ci.

La vague présente un léger maximum, qui disparait si le citrate est seulement $0,1M$, mais W peut alors gêner s'il est en forte quantité; enfin, le rapport h/c décroit lorsque c augmente ce qu'on attribue à une polymérisation croissante des composés formés.

c, 10^{-3} moles/l.	0,025	0,264	2,5
Rapport	8,45	8,1	6,5

—Ces milieux ont été appliqués au dosage de Mo dans divers échantillons, en particulier aciers.[27] Après attaque oxydante, on ajoute du bisulfite pour faire passer Cr, V, Mn, à l'état de cations, puis de l'acide citrique; la solution qui doit être environ $0,1M$ en H_2SO_4, et $0,5M$ en acide citrique (ou tartrique) est passée sur échangeur d'ion préalablement rincé à $0,5M$, acide citrique, qui retient les cations gênants. Les polarogrammes présentent 2 vagues (0,07 et 0,43), la 2ème double de l'autre: utiliser la 1ère si $c > 0,1.\ 10^{-4}$, sinon la 2ème, mais celle-ci est influencée par W, (le courant limite continue à croître avec E au lieu de rester parallèle au courant résiduel); la proportionnalité $i - c$ a lieu entre $0,1\ 10^{-3}$ et $5\ 10^{-3}$; les ions ClO_4^- et NO_3^- donnent des vagues catalytiques.

Pour les dosages dans les roches et minerais,[28] après attaque par $Na_2O_2 + NaOH$, on dose en milieu citrate ou tartrate ajusté à pH 6; on trouve peu d'interférences. On observe 2 vagues; l'auteur attribue la 1ère (0,3 V) à une substance gênante, ou à un 1er stade de réduction. C'est sans doute cette dernière interprétation qui est correcte, mais dans ce cas, les observations ne concorderaient pas, en milieu citrique, avec celles de Meites.

Ce point est élucidé par le travail plus récent de Grasshoff et Hahn,[15] qui opèrent généralement à $c \sim 10^{-3}$, mais ont fait varier le pH dans d'assez larges limites. Entre pH 6 et 8, on observe bien la vague signalée par Meites mais qui, au-delà de pH 6 décroit lorsque le pH augmente (à pH > 8, elle a complètement disparu).

Cette vague (dénommée III) décroit également à pH < 6 au profit de 2 autres. (I et II), si bien que vers pH 4 elle a entièrement disparu, alors que I et II ont atteint leur hauteur définitive, qu'elles conserveront aux pH < 4 sauf II, qui présente un faible minimum entre pH 2,5 et 4; on a vérifié, entre pH 1,8 et 2,4, que I et II étaient bien contrôlées par la diffusion.

Les auteurs ont représenté les variations de $E_{1/2}$ avec le pH (à teneur constante en citrate), et les variations avec la concentration en citrate (à pH constant); I ne dépend pas de cette dernière, tandis que pour II, $E_{1/2}$ varie linéairement avec le log. de cette concentration.[31]

On a fait des essais de réduction d'une solution $10 \cdot 10^{-3}$ à potentiel contrôlé, pH 2, acide citrique $0{,}1M$ en présence de KCl, à 0,3 et 0,7 V (potentiels des paliers de I et II). Les polarogrammes des solutions en cours de réduction montrent que I et II décroissent parallèlement même si l'on se place seulement au palier de I. Dans les 2 cas, on aboutit au stade 4 (coulométrie); les solutions brun-jaune ou brun rouge ont des spectres qui diffèrent nettement dans les 2 cas.

Enfin, l'emploi d'un milieu citrique a été envisagé pour le dosage de Mo dans les aciers, selon un mode opératoire peu différent de ceux déja indiqués:[29] attaque de l'échantillon par HCl en présence de $KClO_3$, précipitation de $Fe(OH)_3$ par NaOH en présence de Na_2SO_4 (l'adsorption de celui-ci sur le précipité permettant d'éviter celle du molybdate); une partie du filtrat est neutralisée à la phtaléine, et on lui ajoute une solution d'acide citrique. Polarographier ensuite; opérant sur Og5 environ, on peut effectuer plus de 20 dosages en 8 heures.[30]

Composés avec les complexons. Faisant suite à d'autres travaux,[32] le comportement de Mo^6 en présence d'acide éthylène-diamine-tétracétique (E.D.T.A.) a été étudié par Pecsok et Sawyer.[33] En solution $0{,}52 \cdot 10^{-3}$ en Mo et $4 \cdot 10^{-3}$ en E.D.T.A. on observe, de pH 2,5 à 4,5, 2 vagues (réversibles d'après les auteurs) de h décroissante lorsque le pH augmente, mais la lère décroît plus rapidement que la 2ème, si bien qu'elle a disparu à pH $> 4{,}5$, alors que la 2 ème disparait à pH > 7. L'accroissement de concentration en E.D.T.A. augmente les vagues, preuve du peu de stabilité des complexes (des essais préparatifs montrent que le complexe obtenu vers pH 4,5 contient 2 Mo par E.D.T.A.)

A pH 2,5, les 2 vagues ont des $E_{1/2}$ de 0,33 et 0,58; la pente $E_{1/2} = f(pH)$ indique l'intervention de $2H^+$ par Mo à pH $< 4{,}5$ et $\frac{1}{2}H^+$ à pH $> 4{,}5$ (la preuve n'a pas été faite que la réduction conduise au stade Mo^V).

Ces résultats montrent que le dosage de Mo nécessite des conditions bien déterminées en ce qui concerne le pH, la concentration de l'E.D.T.A., et la force ionique; si elles sont respectées, le courant est proportionnel à centre $0{,}02 \cdot 10^{-3}$ et $1{,}3 \cdot 10^{-3}$.

Des méthodes de dosage en milieu E.D.T.A. ont été mises au point: l'effet de Ca^{2+} (qui lui aussi est complexé par l'E.D.T.A.) a été étudié.[34] Sinyakova et Glinkina,[35] étudiant divers complexons, trouvent que l'E.D.T.A. donne les meilleurs résultats. Pb, Zn, V et W n'interfèrent pas, alors que Fe^{3+} et Cu^{2+} font décroître *h*; Habrcetl[36] trouve également que Cu^{2+} gêne le dosage dans les aciers. Cependant, Pressler[37] pense que Bi et Cu peuvent être dosés en même temps que Mo dans les minerais: on attaque par HNO_3, évapore à sec et reprend par HCl pour éliminer SiO_2; ajouter ensuite de l'ammoniaque pour précipiter Fe et Al, et porter à pH 5 dans un milieu tampon acétique—E.D.T.A.

—L'étude en milieu nitriloacétique a été effectuée par Manning, Ball et Menis, surtout en polarographie dérivée.[38]

Alors qu'à pH 4 on observe 2 vagues mal définies, en concordance avec des observations antérieures,[35] de pH 2 à 3,5 apparaissent 4 vagues bien définies (0,22; 0,33; 0,47; 0,63); leurs hauteurs respectives varient avec le pH, par contre, $E_{1/2}$ varie peu.

Les hauteurs et $E_{1/2}$ ne varient pas avec la concentration en réactif lorsque celle-ci varie de 0,015 à 0,25 (du moins à pH 3, où l'on a effectué la majeure partie des essais), pourvu qu'elle soit en fort excès (plus de 100 fois) par rapport à Mo.

Quoique leur étude soit faite dans un but analytique, leurs observations sont intéressantes: la réduction coulométrique au ler ou 2ème paliers donne quantitativement Mo^{5+}, ce qui prouve que les 2 premières vagues sont dues à la réduction $Mo^{6+} \rightarrow Mo^{5+}$ de 2 espèces Mo^{6+} en équilibre mobile; Mo^{5+} ainsi formé se réduit à un $E_{1/2}$ correspondant à la 4ème vague, qui représente donc le processus de réduction $Mo^{5+} \rightarrow Mo^{3+}$. La coulométrie montre également que Mo^{6+} est réduit en Mo^{4+} au 3e palier; cependant la spectrophotométrie et la polarographie montrent qu'on est alors en présence de $Mo^{5+} + Mo^{3+}$, preuve d'une dismutation complète du Mo^{4+} ainsi formé. Au 4ème palier, la réduction de Mo^{5+} en Mo^{3+} ne se fait pas avec un rendement en courant de 100%; par contre, la réduction directe de Mo^{6+} est quantitative. Les 2 espèces de Mo^{3+} obtenues en partant de Mo^{5+} ou Mo^{6+} ont des caractéristiques différentes la 1ère ne présente ni maximum d'absorption ni vague anodique, la 2ème possède une vague anodique mal définie (0,33) et s'oxyde rapidement à l'air.

L'application analytique consiste dans le dosage de Mo dans les oxydes mixtes Th-U renfermant environ 3% de U et moins de 1% de Mo, car la vague de U (0,23) est bien séparée de la dernière vague de Mo. Les interférences sont constituées par Cr^{6+}, Cu^{2+}, Sn^{4+}, Ni^{2+}, mais 100 μg de ces ions (et 500 μg de Fe^{3+}) peuvent être tolérés en présence de 70 μg de Mo.

Cas des autres éléments

Vanadium. Il offre peu de particularités intéressantes. V^{5+} en milieu oxalique a été étudié par Lingane et Meites;[39] à pH 4,6 et 7,6 les polarogrammes ont une allure voisine de ceux obtenus en l'absence d'oxalate; d'ailleurs, en ce qui concerne pH 7,6 l'oxalovanadate est vraisemblablement scindé en ses constituants.[40]

En milieu E.D.T.A., acide ou faiblement basique, on observe 2 vagues correspondant aux étapes $V^{5+} \rightarrow V^{4+} \rightarrow V^{2+}$; la lère présente un minimum explicable de façon analogue à celui des vanadates (voir *Les vanadates*); à pH $> 9,5$, on observe une seule vague $V^{5+} \rightarrow V^{2+}$ ($\sim$1,22 V à pH 9,55).[41]

Tungstene. Dans les précédentes conditions, W ne donne pas de vague, car ses complexes sont trop stables,[48] mais an accroissant l'acidité, ou choisissant d'autres milieux, on obtient des vagues de W, mais précédées de celles de Mo.

C'est ainsi qu'en milieu oxalique 0,2*M*, en présence de gélatine à 0,005% et pH 0,5–1 on obtient une vague réversible à $1e^-$ ($E_{1/2} = 0,62$, ne dépendant pas de la concentration en oxalate entre 0,05 et 0,5), et proportionnelle à c entre $1,2 . 10^{-3}$ et $16 . 10^{-3}$. Les ions Ni^{2+}, Mn^{2+}, Cr^{3+}, Cu^{2+} ne gênent pas (le dernier est précipité), mais NO_3^- (vague catalytique) et V doivent être absents.

Fe^{3+} et Mo^{6+} peuvent être déterminés dans la même solution: Mo^{6+} précéde W en donnant 2 vagues; la lère est amoindrie par la présence de W, mais la somme des 2 reste constante. Sušic[44] constate également la présence de vagues en milieu oxalique, avec $E_{1/2}$ variant de 0,8 à 0,6 lorsque la concentration d'acide oxalique varie de 0,01 (pH 3) à 0,4 (pH 0,75). La hauteur croit avec la concentration d'acide oxalique, mais est bien inférieure à ce que pourrait donner un processus à $1e^-$. La proportionalité courant—c (testée en milieu 0,1) n'a pas lieu à $c < 2,5 . 10^{-3}$.

Niobium. Les polyniobates ne sont stables qu'en milieu alcalin, mais n'y donnent aucun polarogramme; comme l'acide précipite dès que l'alcalinité diminue, les études doivent alors être effectuées en milieu fortement acide[45,46], mais les composés présents ne rentrent pas dans la catégorie des polyanions), ou en présence de complexants.[46,47] —En milieu E.D.T.A. les études ne peuvent être faites qu'entre pH 2,5 (au-dessous, l'acide E.D.T.A. précipite) et 6 (au-dessus, le complexe se détruit avec précipitation d'acide niobique).

On obtient 2 vagues ($E_{1/2}$ = 0,609 et 1,05 à pH 3,05 en milieu E.D.T.A. 0,1M); la 1ère est réversible à pH $<$ 3,2 comme le montrent sa pente et la polarographie à vague carrée; elle correspond au passage: $Nb^{5+} \rightarrow Nb^{4+}$; on peut l'utiliser au dosage de concentrations allant de 5 à 500 mg/l. ou (à l'aide de la vague carrée) de 0,1 à 5 mg/l.

La 2ème vague est le mieux visible vers pH 5, quoique gênée par celle de H_2; elle correspond au passage $Nb^{4+} \rightarrow Nb^{3+}$, car la réduction électrolytique à 1,5 V donne une solution brun-orange de Nb^{3+}.

—Le milieu citrique semble le plus favorable à la polarographie de Nb^{5+}, mais des solutions de stabilité convenable ne peuvent être obtenues qu'à partir de Nb métallique. On n'obtient alors qu'une seule vague ayant mêmes caractères que la 1ère vague dans l'E.D.T.A., utilisable dans les mêmes zônes de concentration en Nb, mais dans un intervalle bien plus grand d'acidité (pH 6 à SO_4H_2 2M, avec une concentration en acide citrique de 0,4 à 2M); $E_{1/2}$ varie de 0,75 (pH 0) à 1,13 (pH 4).

Aux fins analytiques on recommande une solution 2M à pH 1; Mn, Ni, W, Cr, Fe n'interferent pas, mais Sb, Ti, et de fortes quantités de Mo gênent.

—En ce qui concerne les milieux oxalique et tartrique, les résultats sont moins nets, et divergent avec les auteurs, ce qu'on doit peut-être expliquer par le mode de mise en solution de l'acide niobique. Ainsi, en milieu tartrique, Ferrett et Milner[46] donnent une vague vers 1,00 V à pH 1,5 (par rapport à une anode de mercure dans la solution), tandis qu' Elson[47] trouve 1,93–2 V à pH 4,7–7. De même, les premiers ne trouvent rien en milieu oxalique, ainsi que pour Ta en milieu tartrique, alors qu'Elson donne respectivement 1,52–1,53 de pH 1,2 à 5,5 et 1,56–1,58 à pH 2,8 ou 5.[69]

Vagues catalytiques

Rappelons (voir *Milieux acides*) qu'elles ont conduit à envisager l'existence de la valence 4 chez Mo et W. En raison de leur pouvoir complexant, l'addition d'acide oxalique ou acides—alcool doit tendre à les diminuer.

D'après l'importance de cet effet, suivant la concentration d'acide oxalique on en a déduit, pour W (l'oxydant étant H_2O_2) la nature et la constante d'équilibre des composés oxalo-tungstiques.[49] On remarquera que ce n'est pas la méthode la plus directe qu'on puisse utiliser, et que, d'autre part, dans le calcul de la constante d'équilibre, on a supposé les composés tungstiques non complexés, à l'état de WO_4H_2, alors qu'ils sont manifestement polytungstiques (voir *Isopolyanions*).

De plus, le stade de valence inférieur étant responsable de l'amplification des vagues, il semble logique que ce soit la formation de complexes à partir de celui-ci (plutôt que du stade 6) qui influe sur l'effet observé; Zahnov et Robinson en ont déduit la composition et les constantes des complexes correspondants avec les acides tartrique et citrique.[50]

En ce qui concerne l'acide oxalique, les mêmes auteurs constatent que les phénomènes se compliquent par la réduction catalysée de l'acide oxalique lui-même; aussi ont-ils étudié le comportement des solutions molybdiques-oxaliques en l'absence de toute autre substance réductible, et pensent prouver cette réduction. En réalité, dans les conditions où ils se sont placés (concentrations 0,8 . 10^{-3} en Mo^{6+}, 0,1 en HCl) la réduction de Mo^{6+} en l'absence d'oxalate se fait au stade 3, mais en 3 vagues (Fig. 2

courbe 1). En présence d'oxalate, elle n'a plus lieu qu'en 2 vagues, parce que le mécanisme n'est pas le même (Fig. 2 courbe 2), mais la hauteur totale reste inchangée, même en présence d'une concentration en acide oxalique aussi forte que 0,2*M*, preuve que celui-ci n'est pas réduit; les auteurs s'étant placés en *A* au palier de la 2*e* vague, on observe bien une croissance de celle-ci, mais la dernière en est diminuée d'autant.

RÉDUCTION DES HÉTÉROPOLYANIONS

Composés tungstiques

Les premières recherches ont été effectuées par Souchay, en vue de préciser, par analyse, les équilibres entre les divers hétéropolyanions, ou entre ceux-ci et les isopolyanions (voir ci-dessous); cependant, les fortes c utilisées à cet effet compliquent l'étude, lorsqu'on désire interpréter le mécanisme de réduction (faible pente des courbes, forte influence de l'électrolyte étranger), quoique les phénomènes restent les mêmes; nous ferons état des recherches plus récentes.

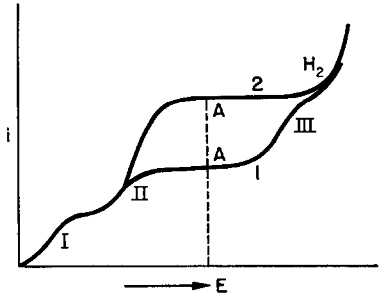

FIG. 2

Composés de la série 12. Pour l'acide phosphotungstique, à pH 1 et $c = 0{,}01$ (en W), Kennedy a observé 3 vagues contrôlées par la diffusion ($E_{1/2} = 0{,}218$; 0,448; 0,695), les 2 premières, bien distinctes, sont égales, la 3ème, égale à la somme des 2 autres, est suivie de très près par la décharge de H^+.[51]

Par électrolyse à potentiel contrôlé (0,30 V) l'auteur trouve que la 1ère correspond à $n = 2$; s'il en est ainsi, l'électrolyse au niveau de la 2ème (0,56 V) devrait consommer 4 faradays, alors qu'il n'en trouve que 2,2–2,5.

Nous avons refait des essais analogues sur l'acide silicotungstique, parce qu'il présente une stabilité supérieure à celle du précédent en milieu peu acide, mais nous avons vérifié qu'à pH $< 1{,}5$ le comportement était le même ($c = 1 \,.\, 10^{-3}$ à $8 \,.\, 10^{-3}$). Nous avons constaté que pour les 2 premières, $E_{1/2}$ ne varie pas avec le pH et qu'à pH suffisamment élevé (~4) une 4ème vague apparait alors égale à environ 6 fois la première; les $E_{1/2}$ sont alors: 0,24; 0,48; 0,90; 1,03.

La comparaison avec les vagues des métatungstates (voir *Métatungstates en milieu acide*) et le titrage des composés réduits montrent que les 2 premières vagues correspondent chacune à $n = 1$, d'où $n = 2$ pour la 3ème et 6 pour la 4ème.

Le polarogramme de la solution bleu-intense réduite au stade $1e^-$ montre un déplacement parallèle aux ordonnées; la 1ère vague est devenue entièrement anodique, mais elle a diminué de 40 à 25 % suivant le milieu (0,5*M* HCl ou tampon acétique pH ~ 4).

Celui de la solution gris-bleu réduite au stade $2e^-$ montre également une translation, les 2 premières vagues sont devenues anodiques; la 1ère est encore plus diminuée que précédemment, tandis que la 2ème n'a décru que de 10%.

Ces faits laissent supposer une certaine réversibilité, probablement compliquée par des phénoménes d'électrode; ceci est confirmé par les résultats de Kennedy, qui, en portant E en fonction de log $i/(i_D - i)$ obtient une pente de 67–70 mV pour les 2 premières vagues, et 35 mV our la 3ème.

En effectuant la réduction au palier de la 3ème vague, les phénomènes ne sont pas aussi simples que précédemment; comme le constatait Kennedy, la réduction se poursuit au-delà de 4 faradays. Tant que ce stade n'est pas atteint, on remarque que la 3ème vague n'est pas entamée, et qu'elle reste catodique; par contre, il apparait une vague supplémentaire, vers 0 V (milieu 0,5 HCl) ou bien les 2 vagues anodiques s'accroissent (tampon acétique). Au-delà de 4 faradays, la 3ème vague passe progressivement dans la région anodique; sa partie catodique disparait vers 10 faradays.

La basicité des hétéropolyacides a souvent été remise en question[52]; on a pensé la déterminer en mesurant la hauteur de la vague de H^+ dans leur solution. Cette méthode doit être accueillie avec prudence, car la vague de H^+ étant précédée de celles des produits de réduction, c'est la basicité de ceux-ci qu'on risque de mesurer; de plus, on sait qu'ils catalysent la décharge de H_2. D'ailleurs les résultats obtenus varient avec la nature du sel de fond; la potentiométrie a résolu cette question d'une façon plus sûre.[1]

La remarquable insolubilité des sels d'hétéropolyacides et de bases organiques a permis l'emploi de ceux-ci pour le titrage ampérométrique de nombreux alcaloïdes, colorants, et dérivés analogues.[53]

Autres composés. En tampon de pH suffisamment élevé (>5 pour le dérivé de Si, >2 pour le dérivé de P) apparaissent les dérivés des séries 11 (voir *Action des bases*) caractérisés par la disparition des 2 premières vagues précédemment décrites, ce qui a permis d'étudier le passage de la série 12 à la série 11:[58]

$$\text{ions } 12 + \text{ions } OH^- \rightarrow \text{ions } 11 + \text{tungstates.}$$

Inversement, les ions 11 ne sont pas stables en milieu acide, et régénèrent les ions 12, suivant une réaction du type:

$$\text{ions } 11 + \text{ions } H^+ \rightarrow \text{ions } 12 + SiO_2$$

sans le cas des silicotungstates.

Cette dernière réaction a lieu lentement, et dans une zône de pH plus basse que la précédente; par contre, elle a lieu rapidement, et dans la même zône, si l'on ajoute WO_4Na_2 ou du paratungstate A (voir *Cas d'isomérie*); cette plus grande facilité s'explique par le fait qu'on passe directement de l'ion 11 à l'ion 12 en fixant un groupe tungstique supplémentaire, ce qui exige un remaniement moins profond. Par contre, l'ion paratungstate B, moins réactif, n'accroit pas cette facilité de passage, ce qui a permis[20] d'étudier l'équilibre ion para $A \rightleftharpoons$ ion para B, puis l'équilibre de ceux-ci avec WO_4^{2-}. Il suffit d'introduire un certain volume de solution qu'on étudie dans une solution de silico-11-tungstate vers pH 3,5, où la transformation en silico-12 est possible en présence de WO_4^{2-} ou para A, mais non en leur absence et de mesurer, à 0,4 V la hauteur de palier du silico 12, proportionnelle à la teneur en ions WO_4^{2-} et para A.

De la même façon, la disparition de la vague des dérivés de la série 11 a permis de suivre la dégradation de ceux-ci dans un domaine de pH plus élevés (~7–8), en leurs constituants.

—Le polarogramme de la série 9 a été obtenu par Kennedy, qui obtient une seule vague à 0,6 V; ce résultat est en désaccord avec les observations antérieures de Souchay, qui obtenait des courbes rappelant celles de la série 12, mais avec des $E_{1/2}$ moins élevés, car il est bien connu que les composés 9 sont plus réductibles que les autres. Reprenant actuellement ces travaux, nous constatons que la vague à 0,6 V est bien précédée d'une double vague plus positive même que celle de la série 12, si au milieu utilise par Kennedy (0,1N H_2SO_4) on ajoute une quantité suffisante d'un autre électrolyte (0,5M NaCl).

Composés molybdiques

Généralités. Les études effectuées concernent presqu' exclusivement les séries 12, l'atome central étant P Si, ou Ge[54]—Comme nous l'avons fait remarquer (voir *Propriétés Genérales*) les milieux utilisés sont souvent tels que ce n'est pas l'ion, mais ses produits de dégradation, ou de réaction avec les constituants du tampon, dont on observe le polarogramme.

Ainsi, Boltz, de Vries et Mellon,[24] en tampon acétique obtiennent pour l'acide phosphomolybdique à pH 4,6 une vague proportionnelle à c (0,57 V) mais dont h dépend de la concentration en KCl ajouté, et à pH 3,5, 2 vagues (0,6 et 0,9 V) proportionnelles à c, mais mal définies. Il semble bien qu'à ces pH on ne soit plus en présence de la série 12, mais de la série 11; ce fait a d'ailleurs été utilisé par Souchay[20,55] pour étudier les équilibres entre ces 2 séries, ainsi qu'avec la série phospho-2½-molybdique.[56]

Citons de même les recherches de El Shamy, Issa et Barakat, où un grand nombre de milieux choisis sont soit très acides, soit trop peu acides, ou complexants.[57]

De plus, on a pu constater par d'autres méthodes, que la réduction de ces composés, en bleus réduits, a lieu, au moins au début, par stades de $2e^-$, $4e^-$; *etc*... (pour 12 Mo) et que la réduction totale a lieu par passage à l'état Mo^{3+}, soit $36e^-$. Il semble que, malgré leur importance théorique, les premiers soient souvent passés inaperçus en polarographie, d'autant plus qu'ils ont lieu à des E très positifs où le mercure réduit la solution; c'est pourquoi il faut avoir recours à l'électrode de platine tournante pour les étudier. (voir ci-dessous).

Réduction sur électrode de mercure. Les acides silico- et germano-molybdiques ont été étudiés par Hahn et Grasshoff.[59] Les essais effectués en tampon citrique donnent, pour le premier (pH ~ 2,5) 3 vagues, dont celle du milieu seulement (0,35 V) est attribuable à l'anion silicomolybdique, car les 2 autres s'accroissent par addition de molybdate. Il faut donc penser que dans un tel milieu, l'hétéropolyanion est partiellement décomposé, la présence de citrate favorisant, évidemment, cette décomposition; des constatations analogues ont été faites pour le dérivé de Ge (pH ~ 3,6) qui présente 5 vagues.

Par contre, l'affinité de ces composés pour les solvants oxygénés (voir éther en (voir *Action des acides*) explique que l'addition de méthyl-éthyl-cétone les stabilise, si bien que, dans le cas du dérivé de Ge par exemple, on n'observe plus que 2 vagues (0,29 et 0,55 V) non altérées par addition de molybdate. Pour ce dernier anion, en particulier, les auteurs ont étudié les meilleures ciconstances de formation (action de la température, du pH, du temps) ainsi que la proportionnalité entre h et c; l'emploi de l'oscillopolarographie, dans des buts analytiques, est envisagé.

Le cas de l'acide phosphomolybdique a été traité par les mêmes auteurs;[60] les concentrations sont voisines des précédentes, cependant la 2ème vague est moins nette (mais la 1ère est proportionnelle à c pour des concentrations en P comprises entre 3 et 30 μg par cm^3), et la stabilité moins grande, ainsi qu'on le savait; l'influence des divers facteurs (pH, excès de molybdate, temps, électrolytes étrangers, température) a été étudiée soigneusement.

Indépendamment des inconvénients dûs à l'emploi du mercure, le nombre de faradays intervenant dans les processus de réduction est mal précisé; enfin, dans le cas des ions silicomolybdiques, aucune comparaison n'a été faite entre les isomères de Strickland.

En ce qui concerne une telle isomérie, la question a été envisagée par Kemula et Rosolowski,[61] qui supposent l'existence de 3 formes: α et β à rapport Mo/Si = 8, inerte polarographiquement, et γ, à rapport Mo/Si = 12, qui se forme à chaud seulement, réduite en tampon formique, et seulement en présence de butanol. Les auteurs assimilent leurs formes β et γ respectivement aux formes β et α de Strickland.

Les essais sur électrode de platine que nous décrirons ci-dessous confirment l'existence des 2 formes α et β de Strickland, (à l'exclusion de toute autre), donnant lieu à des polarogrammes bien caractéristiques.

Applications analytiques. Les propriétés que possédent ces anions, d'être facilement réductibles et de donner avec les bases azotées des sels très peu solubles, ont été fréquemment utilisées en analyse; pour s'en tenir à la polarographie, signalons:

—Le dosage de la silice ou des silicates faciles à solubiliser (par exemple SiO_2 dans MgO ou $MgCO_3$) en milieu $1M$ en NH_4NO_3 + $0,2M$ en HNO_3 (P et As s'éliminent dans ce milieu à l'état de sels NH_4^+ des hétéropolyanions correspondants insolubles).[62]

Ce procédé a été adapté pour le dosage de Si dans les alliages d'aluminium:[63] attaquer 50 mg d'alliage par NaOH concentrée, (dans une capsule de platine), réacidifier par $1M$ HCl jusqu'à pH $\sim$ 1,5, puis ajouter 5 cm^3 de réactif molybdique (préparé à partir de 10 g Na_2MoO_4 2 H_2O, 72 cm^3 $1M$ HCl et complété à 1l.), et réajuster le plus exactement possible à pH 1,6; laisser une nuit, puis ajuster à 100 cm^3. Ensuite, prélever 5 cm^3 de cette solution qu'on complète à 25 cm^3 par une solution support (306 cm^3 de tampon citrique selon Sorensen + 77 cm^3 $1M$ HCl + 40 cm^3 méthyl-éthyl-cétone, compléter à 1 l.); polarographier entre 0,3 et 0,6 V. Etalonner avec des teneurs connues en silicate; l'emploi de l'oscillographie est envisagé.

—Le dosage, par différence, des phosphates (milieux biologiques en particulier;[64] la prise d'essai, contenant 1 à 2,5 . 10^{-4} g de P est introduite dans une fiole de 50 cm^3; ajouter 2 cm^3 de HNO_3 (obtenu en ajoutant 100 cm^3 d'eau à 120 cm^3 de HNO_3 concentré) et 30 cm de solution de NH_4NO_3 à 400 g/l., chauffer à 35° et ajouter 1 cm^3 de paramolybdate d'ammonium à 31 g/l.; laisser 15 min le précipité se former et compléter à 50 cm^3 par la solution de NH_4NO_3. Au bout de quelques heures, polarographier; on étalonnera en portant la décroissance de la vague en fonction de la teneur en P.

—Les titrages ampérométriques per précipitation: par example pour P, on utilise une solution d'oxine et paramolybdate d'ammonium dans HCl; on introduit à la microburette le phosphate à titrer, et le point final est déterminé ampérométriquement;

cependant, en ce point, 7% du Mo utilisé demeure en solution, si bien qu'un étalonnage est nécessaire.[65]

Cette méthode a été perfectionnée par Hahn et Wagenknecht pour le dosage de P, Si, Ge, As:[66] après transformation en hétéropolyanion, on se place en tampon glycocolle à pH 2–2,5, et précipite par des quantités croissantes de nitron, en solution titrée, jusqu'à disparition de la 1ère vague; un excès de molybdate ne perturbe pas le dosage.

Ainsi, pour le dosage de Si dans un alliage d'aluminium, l'attaque et la préparation de la solution pour polarographier sont voisines de celles indiquées précédemment. Introduire 10 cm³ de prise d'essai dans 40 cm³ de tampon au glycocolle à pH 2,5, désaérer, et titrer par une solution de nitron 0,0025*M* en se placant à 0,05 V. On peut ainsi doser 0,22–0,50% de Si sur une prise de 50–100 mg à ±2% près.

Réduction sur électrode de platine.[67] Nous avons choisi l'acide silicomolybdique, parce qu'il est plus stable que les autres, et présente un cas d'isomérie bien établi.

Le polarogramme de la forme α stable, à $c = 10^{-3}$ en Mo, et dans 0,5*M* HCl présente 3 vagues égales de $n = 2$ (+0,27; +0,13; 0,03 V), suivies de la décharge de H_2 (vers 0,25 V); elles ne seraient pas visibles à l'électrode à gouttes. La présence de molybdates ou Mo^{5+} n'est pas gênante, car ils ne sont pas polarographiables à l'électrode de platine.

En opérant sur l'isomère β instable, obtenu suivant la méthode de Skerlak (2), le polarogramme a même forme, mais les $E_{1/2}$ sont nettement différents (+0,33; +0,24; 0,18); cette différence a permis de montrer que l'isomère β préparé selon Strickland[68] renfermait une proportion notable de α; lorsqu'on laisse évoluer les solutions de ces 2 échantillons, on aboutit au polarogramme de α seul.

La figure 3 montre les polarogrammes d'un échantillon de β, selon Skerlak (*a*) et d'un échantillon de α (*d*); (*b*) représente un échantillon de β suivant Strickland (en réalité mélange de $\alpha + \beta$); (*c*) est un échantillon de Strickland évolué (donc enrichi en α) qui, au bout d'un temps suffisamment long donnerait (*d*).

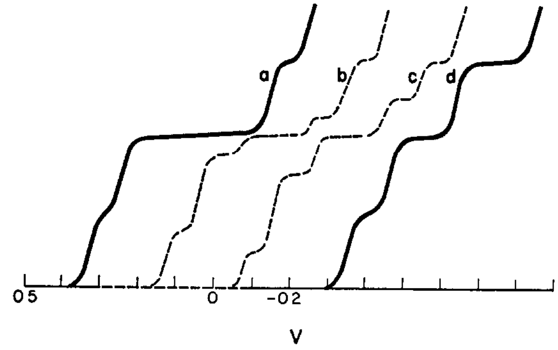

FIG. 3.—Transformation Acide $\beta(-\alpha) \rightarrow$ Acide α(*d*) (*b*) et (*c*) Acide β partiellement tranformé.

Les produits de réduction, bleu intense, des 2 isomères, ont été préparés par réduction électrolytique, et la spectrophotométrie met bien en évidence, en milieu HCl, les degrés de réduction à 2 et $4e^-$.

Leurs polarogrammes se déduisent par simple translation parallèle à l'axe des ordonnées; par exemple, pour $4e^-$, les 2 premières vagues sont devenues entièrement anodiques; les $E_{1/2}$ restent inchangés, ce qui prouve la parfaite réversibilité du système, et leurs valeurs sont identiques à celles mesurées statiquement à l'électrode de platine, ce qui suppose un équilibre rapide.

Quoiqu'apparaissant sur les polarogrammes, le composé à $6e^-$ ne peut être obtenu en milieu acide, où il se décompose, mais seulement au-dessus de pH 4: son polarogramme montre, comme on devait s'y attendre, 3 vagues anodiques en tampon acide.

Nous avons dit que l'interprétation des polarogrammes sur l'électrode de mercure pouvait être rendue difficile en raison de l'attaque du métal. Les dérivés réduits à $4e^-$ n'ayant pas cet inconvénient, nous avons pensé qu'une comparaison de leurs polarogrammes avec les 2 sortes d'électrodes serait fructueuse; la Fig 4 montre les résultats à pH 4,6:

—dans une 1ère zône (+0,4–0 V), seul le platine permet d'obtenir la vague d'oxydation $n = 2 \rightarrow n = 0$ (zône A)

—dans une 2ème zône (B) allant de 0 à 0,6 V et où l'on observe les vagues anodique $n = 4 \rightarrow n = 2$ et catodique $n = 4 \rightarrow n = 6$, les courbes obtenues avec les 2 électrodes se superposent, si les sensibilités sont convenablement ajustées.

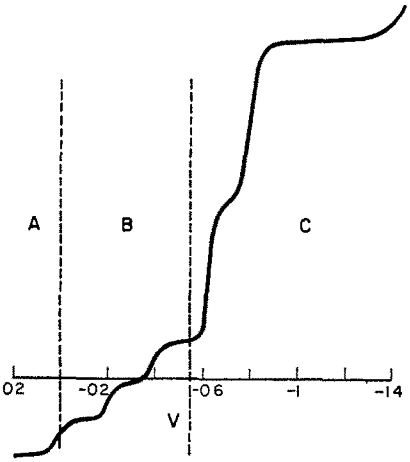

FIG. 4.—Polarographie de l'acide α n = 4
A—Pt electrode,
B—Pt et Hg electrodes,
C—Hg electrode.

—Au-delà de 0,6 V (cette limite est ramenée vers 0,3 V en milieu acide) le platine devient inutilisable à cause de la décharge de H^+, et seul le mercure convient. On obtient 2 vagues dont la signification est actuellement à l'étude: la dernière correspondrait à une réduction totale en Mo^{3+} accompagnée d'une dégradation, et celle qui la précéde, à des étapes plus réduites de l'hétéropolyanion.

En milieu plus acide (pH < 2,5) ces courbes sont décalées vers la gauche, et les 3 premières vagues se retrouvent dans la zône *A*; seules apparaissent, sur électrode de mercure, les 2 dernières, conformément aux observations des autres Auteurs.

Les autres cas d'isomérie chez les composés molybdiques sont plus difficiles à mettre en évidence que pour le dérivé de Si car l'un des isomères est encore plus instable, mais en agissant sur les conditions opératoires (température, addition de solvant) la polarographie nous permet de le mettre en évidence.

De telles études sont particulièrement intéressantes, car elle montrent que les produits de réduction de l'isomère instable peuvent au contraire être stables, et que l'ordre de stabilité peut même s'inverser.

CONCLUSION

La présente étude montre que de nombreux points restent à éclaircir dans le comportement polarographique des polyanions, mais que nous disposons d'une technique efficace pour l'étude de cette importante classe de composés, et de leurs produits de réduction.

Zusammenfassung—Es wird eine Übersicht über die Polarographie von Polyanionen gegeben.

Summary—A review of the polarography of polyanions is presented.

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[53] Ogawa (*J. Electrochem. Soc. Japan*, 1957, **25**, 613; 1958, **26**, 406) dose ainsi, par l'acide silicotungstique 3,95 à 0,05 mgr de bleu de methylène ou 5,77 à 0,08 mgr de violet de méthyle pour 10 cm^3 de solution en milieu HCl 2*M* et E = 0,70 V. Il dose également, dans les mêmes conditions 8 à 0,2 mg de chrysoïdine (SO_4H_2 4*N*) et 8 à 0,7 mg de safranine (SO_4H_2 8*N*); ces 2 dernières substances présentent elles-mêmes une vague de réduction, si bien qu'à. E = 0,60 V, on obtient une courbe en V.

Zyka (*Pharmazie*, 1955, **10**, 170) et Souckova et Zyka (*Cs. Farmacie* 1955, **4**, 181, 227) dosent 10–20 cm^3 de solution 0,01 de quinine, narcotine, atropine, procaïne, cinchonine, cocaïne, codeïne, amidopyrine, en milieu HCl 0,1–0,6*M*, par l'acidé silicotungstique 0,01*M*; E = 0,65. On peut utiliser dans des conditions voisines, et à E = 0,4, l'acide phosphostungstique pour doser les 3 derniers, ainsi que l'antipyrine, strychnine, papavérine. Ogawa (*J. Electrochem. Soc. Japan*, 1956, **24**, 476, 521; 1957, **25**, 377) opère sensiblement de la même façon; il se place généralement à E = 0,7–0,8 V; la réaction ent rapide, si bien qu'un dosage ne dure pas plus de 40 min, et la précision est de ±2% pour des concentrations de 40 à 4 mg dans 10 cm^3. L'application en a été faite à: codéine, dionine, caféine, amidopyrine, cinchonine (milieu HCl 1*M*), papavérine, dionine, vératrine (milieu neutre, NO_3K 0,42*M*). Le même auteur (*J. Chem. Soc. Japan*, 1956, **77**, 535, 537, 540) dose en milieu HCl > 0,5*M*: cocaïne, atropine, brucine, papavérine, antipyrine, vératrine en milieu HCl > 1*M* strychnine, quinine. Enfin Yoshino, Seno et Sugihara (*J. Pharm. Soc. Japan*, 1960, **80**, 1484) ont donné une méthode de dosage de l'yohimbine en milieu HCl > 0,5*M*; E = 0,4.

[54] On pouvait se demander si l'existence des titani- et zirconi-molybdates était possible. Lorsque nous avons envisagé ce problême [Souchay et Tchakirian, *Ann. Chim.* (*France*), 1946, **1**, 249] la question était controversée, et nous avions conclu à leur inexistence. Plus tard, ces composés, ainsi que leur comportement polarographique, ont été décrits (Liberti, Giombini et Cervone, *Ricerca sci.*, 1955, **25**, 883). En suivant le mode opératoire indiqué, et partant de $TiF_6(HN_4)_2$ et $Zr\ F_6(NH_4)_2$ soigneusement purifiés, nous n'avons pu obtenir ces composés.

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[70] Au moment de la correction des épreuves, nous avons connaissance d'un travail de Wittick et Rechnitz (*Analyt. Chem.*, 1965, **37**, 816) où les auteurs interprètent les diverses vagues par la réduction de 2 espèces différentes de Mo^{6+}.

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INORGANIC POLAROGRAPHY IN ORGANIC SOLVENTS

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Summary—A review of inorganic polarography in organic solvents is presented.

INTRODUCTION

INVESTIGATION in non-aqueous media is today one of the most attractive themes in polarography. During the last decade, this area has been energetically developed by many authors in spite of the difficulties in experimental techniques and of the lack of both theories and basic electrochemical data in the field concerned. Among the non-aqueous solvents studied, the organic solvents have varied considerably in their characteristics. Because the latter solvents are relatively easy to handle experimentally, many important experimental and theoretical investigations have been carried out in them. Inorganic polarography in organic solvents is suited not only for the analysis of such inorganic substances as are precipitated or hydrolysed in aqueous solution, but also for the theoretical study of non-aqueous electrolyte solutions. It has also been a necessary preliminary investigation for establishing the experimental bases for organic electrochemical studies in non-aqueous media; the solvents, supporting electrolytes, reference electrodes, *etc.*, are usually examined and fixed, using relatively simple inorganic compounds as electroactive species.

The present review covers the articles on inorganic polarography in organic solvents published in recent years together with some related electrochemical papers. Previously published reviews[27,28,34c,44,66,71,82b,88a,94] will be helpful in obtaining complete coverage of the field. It seems, on the whole, that the organic solvents used in non-aqueous polarography are generally, increasingly, limited to a few favoured solvents, such as acetonitrile and *N,N*-dimethylformamide, although the efforts to discover new solvents are still continuing. The variety of supporting electrolytes developed in the pioneering studies also seems to be decreasing in number to some conventional salts, *e.g.*, lithium perchlorate, tetraethylammonium perchlorate and tetrabutylammonium iodide, which are now commercially available in sufficiently high purity. As far as instrumentation is concerned, recent developments on automatic iR-drop compensators[1–3,48,49,68,73] will be increasingly more effective in making non-aqueous polarographic potential measurements easier and more accurate.

SUMMARY OF PUBLISHED LITERATURE

Tables I to V summarise the literature of the last several years on the organic solvents, supporting electrolytes and inorganic substances investigated.

It is evident from the tables that organic nitrogen compounds have been preferentially used as solvents. The electron donative nitrogen in these compounds results in a high dielectric constant and in a high solvation energy for binding to metallic ions. Such properties enable an electrolyte to dissolve and to dissociate sufficiently for

TABLE I.—INORGANIC POLAROGRAPHY IN ORGANIC NITROGEN-CONTAINING SOLVENTS

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Ethylenediamine	mp 11·0, bp 117·0, ε 12·9, μ 1·90, η 1·725, d 0·891	34a 79a,d, 79e,f, 80	Ag, Mg, Ba, Ca, Sr, Zn, Ti, Fe, Pb, Au, Cd, Nb, Tl, Zr, Cu, Li, Na, Cs, Rb, NH_4, K, O_2	Et_4NNO_3 $NaNO_3$ LiCl	Cell design; validity of Ilkovič eqn.; effect of coexistent anions; maximum suppression
		75	Ag, Hg, Tl, Pb, Cu, H, Cd, Zn, Cs, K, Na, Li, O_2	LiCl $NaNO_3$ Bu_4NI	Review on electrochemistry in ethylenediamine; effects of ion-pair formation and solvation; reference electrode design
Morpholine	bp 128·9, ε 7·33, d 1·002 (20°)	35, 79a	Pb, Cd, Ni, Ba, K, Na, Li, Zn, Cr, Bi, Ca, Ti, Rb	Bu_4NI	Maximum suppression
Pyridine	mp −41·8, bp 115·6, ε 12·3, μ 2·20, η 0·945 (20°), d 0·9728	13	Tl, Pb, Zn, Al	LiCl $LiNO_3$ Bu_4NI	Cell design; reference electrode design; controlled potential electrolysis also used
		84	H_2SO_4, $HPyrNO_3$	$LiClO_4$	Constant potential electrolysis also used
Formamide	mp 2·6, bp 210·5, ε 109·5, μ 3·37, η 3·302, d 1·1292	7	Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd	$NaClO_4$ Et_4NClO_4	—
N-Methylformamide (NMF)	ε 182·4, μ 3·8, η 1·65	37	Tl, Cd, Pb	KNO_3	Formamide, NMF, DMF, water and mixtures of pairs of these, were used; effects of solvent composition
N,*N*-Dimethylformamide (DMF)	mp −61, bp 153·0, ε 36·7, η 0·796, d 0·9445	31, 59	—	—	Fundamental investigations
		6	Li, Na, K, Rb, Cs, Ba, Sr, Ca, Co, Cu, Ni, Zn	Bu_4NI $NaClO_4$	
N-Methylacetamide (NMA)	mp 29·5, bp 206, ε 165·5 (40°) η 3·019 (40°) d 0·942 (40°)	83a	Cd, Pb, O_2	Et_4NBr	Preconditioning of mercury pool electrode; maximum suppression
		50	Tl, Cu, O_2	Et_4NClO_4	Maximum suppression

TABLE I (*cont.*)

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
N,*N*-Dimethylacetamide (DMA)	mp −20, bp 165·5, ε 37·8, μ 3·79, η 0·92, d 0·943 (20°)	65	Tl, Pb, Cd, Zn	$NaClO_4$	Reference electrode design; maximum suppression
Acetonitrile (AN)	mp −45·7, bp 81·6, ε 37·5, μ 3·37, η 0·345, d 0·7768	92a	H, K	Me_4NBr	Effect of water content
		52a	Li, Na, K, Rb, NH_4, Ca, Sr, Ba	Bu_4NI Et_4NBr $NaClO_4$ Et_4NClO_4	—
		52b	Ag, Cu, Mn, Ni, Eu, Yb, Sm, Co, Fe, Cr, Be, Mg, Al, Y, La, Pr, Nd, Gd, Zn, Hg, Cl, Br, I		Controlled potential electrolysis and voltammetry with rotated Pt electrode also used
		70a	Li, K, Na, Ca, Sr, Ba, Al, Mn, Cr, Fe, Co, Zn, H, Cu, Tl, Cd, Pb, Sn, Ag, Hg,	Bu_4NClO_4	Reference electrode design
		70b	I_2, Me_4NI_3, NaI	$LiClO_4$	Rotated Pt electrode; effect of heterocyclic amines
		14	$HClO_4$, HBr, HCl, H_2SO_4, O_2	Et_4NClO_4 $NaClO_4$ KSCN	Effect of acidity
		54	Th	Et_4NClO_4	—
		91	H, ClO_4	$NaClO_4$	Pt electrode; electrolytic preparation of $HClO_4$ in AN
		5a,b	—	$LiClO_4$	Applicable voltage range at Pt electrode
		61	—	—	Various $AgNO_3$/Ag reference electrodes
		67c	Ni	Et_4NClO_4	Chloro-complex formation
		55	$TiCl_4$, TiI_4	Et_4NClO_4 Et_4NCl Et_4NBr Et_4NI Et_4NSCN	Effect of anions; controlled potential electrolysis and conductivity measurements also done

TABLE I (*cont.*)

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Isobutyronitrile (IBN)	mp −71·5 bp 103·9, ε 20·4 (24°), μ 3·6, d 0·773 (20°)	16	Li, Na, Mg, Co, Ni, Cu, Ag, K, Rb, Cs, Tl, I, O_2	Et_4NClO_4 Bu_4NI $NaClO_4$	Maximum suppression
Propionitrile	mp −91·9, bp 97·1, ε 27·2, d 0·783 (21°)	60a,b	Li, Na, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ag	Et_4NClO_4	Effect of nitrile solvents; data in acetonitrile compared
Acrylonitrile	mp −82, bp 77·3, ε 38, d 0·806 (20°)				
Benzonitrile	mp −13, bp 190·7, ε 25·2, η 1·24, d 1·010 (15°)				
Phenylacetonitrile	mp −23·8, bp 234, ε 18·7, d 1·015 (18°)				
Nitromethane	mp −28·5, bp 101·3, ε 35·7, μ 3·17, η 0·684 (15°), d 1·1312	93	Fe, I_2	Me_4NCl $LiClO_4$ $NaClO_4$	Chronopotentiometry with Pt electrode

mp = melting point, °C; bp = boiling point, °C; ε = dielectric constant; μ = dipole moment; η = viscosity, cp; d = density, g.cm^{-3}; Me = methyl; Et = ethyl; Bu = butyl; AcO = acetate. Physical constants are referred to 25°C unless otherwise stated. Ionic charges have been omitted.

TABLE II.—INORGANIC POLAROGRAPHY IN ORGANIC OXY- AND HYDROXY-TYPE SOLVENTS

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Acetone	mp −95·4, bp 56·2, ε 20·7, μ 2·72, η 0·337 (15°), d 0·7851	15	O_2, Na, K, Rb, Mg, Cd, Cu, Ag, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, I, H	Et_4NClO_4	Effect of water content
Acetic anhydride	mp −73·1, bp 140·0, ε 20·7, μ 2·8, η 0·971 (15°) d 1·0691 (30°)	62	—	$NaClO_4$	Chronopotentiometry with Pt electrode; fundamental
		79a, 80	Tl, Pb, Sn, Ti	—	—

TABLE II (*cont.*)

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Methanol	mp −97·5, bp 64·5, ε 32·6, μ 1·66, η 0·545, d 0·7868	23	Ti, Zr	LiCl	Water-methanol mixture was also used.
		43	S	NaAcO NH$_4$AcO HAcO	Effect of Ag, Cd, Cu, Hg, Pb, Zn
Ethanol	mp −114·5, bp 78·3, ε 24·3, μ 1·68, η 1·078, d 0·7851	92b	H, K	Me$_4$NCl	Effect of water content
		18	Pr	LiClO$_4$ LiCl LiBr	Effect of anions
Formic acid	mp 8·3, bp 100·7, ε 58·5 (16°), μ 1·19 (22°), η 1·966, d 1·2133	69a,b	Bi, Sb, Pb, Sn, Cd, Tl, Zn, In, Ni	HCOONa HCOOH KCl etc.	Reference electrode design
Acetic acid	mp 16·6, bp 117·7, ε 6·2 (20°), μ 0·83, η 1·314 (15°) d 1·0437	12a,b	Tl, Cd, Cu, U, Pd	LiCl NaAcO NH$_4$AcO H$_2$SO$_4$	Reference electrode design; maximum suppression

For abbreviations see footnotes to Table I.

TABLE III.—INORGANIC POLAROGRAPHY IN MISCELLANEOUS ORGANIC SOLVENTS

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Dimethyl-sulphoxide (DMSO)	mp 18·4, bp 189·0, ε 46·7, μ 3·9, η 1·96, d 1·096	34d, 36, 79c, 80	Li, NH$_4$, K, Na, Rb, Cs, Sr, Ba, Mg, Ca, Sb, Zr, Hf, Ti, Nb, Si, Pb, Tl, Cd	Et$_4$NNO$_3$ Et$_4$NClO$_4$	Cell design
		79b	Rb, Cs, K, Et$_4$N, Pr$_4$N, Cetyl-pyridinium	Bu$_4$NI	Reference ion
		34e, 81	Cr	Et$_4$NClO$_4$	Complex formation; reversibility; maximum suppression
		20a,b	Al, Be	Et$_4$NClO$_4$	Acetylacetone was added
		21	SO$_2$, HCl, CO$_2$ H$_2$S, POCl$_3$, C$_6$H$_5$POCl$_2$	—	—

TABLE III (*cont.*)

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
		22a	NO_3	Et_4NClO_4	—
		53	H_2SO_4, HCl, $NaHSO_4$, Et_4NHSO_4 Co, Ni, Na, O_2	$NaClO_4$ Et_4NClO_4	Fundamental; rotated Pt and rotated Hg pool electrodes also used
Phenylphosphoroxychloride	—	34f	Mn, Cd, K, Ti, Al, Fe	—	—
		20c, 22b	HCl	—	—

For abbreviations see footnotes to Table I.

TABLE IV.—INORGANIC POLAROGRAPHY IN ORGANIC MIXED SOLVENTS

Solvent system	References	Depolarisers studied	Notes
Benzene-methanol	57	Co, Cu, Fe, Pb, Mn, Ni, Zn	Detn. of metal driers
Acetonitrile-water	87	Ag, Cu, Tl	Effect of solvent composition on limiting current intensity and half-wave potential
	88b	Tl, Cd	
	88c	Tl, Rb	
Acetone-water	64b	H	
Dioxan-water	82a	Tl, Cd	
Methanol-water	64a	H	
	82a	Tl, Cd	
	38	O_2	Detn. of O_2
Ethanol-water	64b	H	Effect of solvent composition
	82a	Tl, Cd	
	11a,b	U	—
Isopropanol-water	82a	Tl, Cd	Effect of solvent composition
Butanol-water	64b	H	
Glycerine-water	33	Cd, Zn	Effect of medium viscosity
Chloroform-methyl cellosolve-water	29, 30	Bi, Sb, Cu, Tl, Pb, In	Polarography preceded by extraction
Benzene-pyridine-methanol-water	46, 47	S	Detn. of free sulphur; a.c. polarography

For abbreviations see footnotes to Table I.

TABLE V.—INORGANIC POLAROGRAPHY IN LIQUID AMMONIA AND LIQUID SULPHUR DIOXIDE

Solvent	Physical constants	References	Depolarisers studied	Supporting electrolytes	Notes
Ammonia	mp −77·7, bp 33·4, ε 22 (−33°), μ 1·44, η 0·65	39	NH_4	$NaClO_4$	At −77°C; rotated Pt electrode used
		76	Tl, Pb, Cu, Cd, Zn	NH_4I	At 25°C, 10 atm; apparatus for high pressure polarography
$LiClO_4$-ammoniate	Liquid at 25°C and even higher temperatures; composition depends on temperature.	42	Pb, Cd, Zn	—	Oscillographic polarography also used
		19	Zn	—	—
NH_4NO_3-ammoniate		63	Cd, Tl, Pb, Cu, Zn, Sb, Sn, IO_3, IO_4, CN, S, MnO_4, H_2O_2	—	Oscillographic polarography also used
NaI-ammoniate		83b	Pb	—	Many kinds of ammoniates reviewed
Sulphur dioxide	mp −72·7, bp −10·2, ε 12·4 (22°), η 0·429, d 1·46 (−10°)	24	KCl, KBr, KI, NH_4SCN	—	Fundamental; vacuum line apparatus and cell design; Pt electrode also used

Benzoyl chloride (34b) and phosphorus oxychloride (79a) have been examined but seemed rather too reactive for polarographic use.
For abbreviations see footnotes to Table I.

polarographic purposes. Similar conditions can be assumed in the case of the sulphur in dimethylsulphoxide, which is another very promising solvent for polarography.

It is also evident from the tables that many kinds of element give polarographic waves in organic solvents (most conspicuous are the alkali, alkaline earth and lanthanide metal ions) whose polarography in aqueous media has been unsatisfactory.

Liquid ammonia and liquid sulphur dioxide must be classified as inorganic solvents; however, because the factors in their use are almost the same as those for organic solvents, they are listed in Table V. Recent investigations in some ammoniates are attractive.

POLAROGRAPHY IN A SPECIFIED SOLVENT

When the investigation is limited to a specific solvent, the experimentally observed phenomena should not be *essentially* different from those in water, although the actual electrochemical behaviour may be markedly different. The low dielectric constant of most organic solvents compared with water and their different chemical properties are important influences. Many metal ions, which form stable complexes in aqueous media, are so strongly solvated in some organic solvents as to preclude other types of complex formation, *e.g.*, in ethylenediamine,[75] in some formamides,[37] in acetonitrile,[52b,55,70a,86,87] in formic acid[69b] and in dimethylsulphoxide.[34e,53,81] Ion-pair formation[74,75] and complex formation[18,34e,55,67c,79e] between depolariser and supporting ions are enhanced in media of low dielectric constant. On the other hand, a trace of water, which is often present in organic solvents because of the difficulty of complete dehydration, sometimes significantly affects both half-wave potential and diffusion-current constant; in some combinations of solvent and solute ion, a trace of water in the solvent preferentially solvates the ion, *e.g.*, polarographic studies on hydrogen,[14,64a,b,70a,92a,b] manganese, cobalt and nickel,[15,16,17,52b,70a] and conductometric studies on calcium and chloride.[78] The factors mentioned may appreciably influence electrostatic attraction effects and chemical equilibria in the electrolyte solution, which influence the experimental techniques and the theoretical arguments necessary for polarography in organic solvents.

Reference electrode and potential measurement

Establishment of a satisfactory reference electrode has been one of the most difficult and important problems for experimental polarography in organic solvents. A polarographic reference electrode should be reproducible and constant in potential, as well as reversible and of sufficient capacity to maintain a relatively constant potential in spite of the equilibrium shift resulting from the reaction caused by the polarographic electrolysis current. Calomel and silver-silver halide electrodes familiar in aqueous media are often ineffective in many organic solvents; the solubilities of calomel and the silver halides are enhanced by complex formation;[31,70a] calomel may also undergo disproportionation. In addition, reaction rates may be small in such media and the total electrode process may become appreciably irreversible.

Many reference electrodes, whose applicability in individual solvents has been confirmed experimentally, have been investigated. Several of such reference electrodes are listed in Table VI. Many of the reference electrodes developed for

TABLE VI.—POLAROGRAPHIC REFERENCE ELECTRODES IN ORGANIC SOLVENTS

Solvent	Solution	Metal	References
Ethylenediamine	LiCl (sat. or 0·25*M*), $ZnCl_2$ (sat.)	Zn (sat. aaa.), Zn*	75
Pyridine	$AgNO_3$ (1*M*)	Ag	13
N,N-Dimethyl-acetamide	$NaClO_4$ (sat.)	Hg	65
Acetonitrile	Me_3EtNCl (sat.), AgCl (sat.)	Ag	70a
	$AgNO_3$ (0·1 or 0·01*M*)	Ag	61†
	$AgNO_3$ (0·1 or 0·01*M*), $LiClO_4$ (0·1 or 0·5*M*) or Et_4NClO_4 (0·1*M*)	Ag	
	$AgClO_4$ (0·1*M*), $NaClO_4$ (0·5*M*)	Ag	
Formic acid	Quinhydrone (0·005*M*), HCOONa (0·25*M*)	Pt	69a
Acetic acid	LiCl (sat.), Hg_2Cl_2 (sat.)	Hg	12a

* Saturated, two-phase zinc amalgam.

† Various types of $AgNO_3$/Ag reference electrode used for polarography and potentiometry in acetonitrile.

potentiometric studies in non-aqueous solution[4,8,25a,b,26,40] may be helpful for designing electrodes for non-aqueous polarography.

In the attempt to avoid the difficulties and uncertainties involved in the use of a reference electrode in non-aqueous solution, the aqueous calomel electrode has been used as a reference in many non-aqueous investigations. However, in this case, another uncertainty due to the liquid junction potential is introduced into the potential measurements. Because the behaviour of the liquid junction potential between aqueous and non-aqueous solutions is generally unknown, much care is necessary both for stabilising the junction potential and for avoiding contamination of the solvent by the water.[12a,34a,52a,65,79a] Obviously, a liquid junction potential is also involved even if a reference electrode in the same non-aqueous solvent is used, but this situation is essentially the same as in the case of the contact of two aqueous solutions.[70a]

The recently developed automatic iR-drop compensators[1–3,48,49,68,73] seem to have made it possible to use reference electrodes of smaller capacity, which may be more easily devised, because these compensators use a three-electrode system with scarcely any current flowing through the reference electrode. It should be noted, however, that these devices may not be able completely to compensate the iR-drop occurring in a medium of very high resistance, *e.g.*, 10 kilohm-cm specific resistance or greater,[77] which may be encountered during polarography in organic solvents.

Half-wave potential

Electrolytic reduction of mercury-soluble metals is fundamental as well as common in inorganic polarography. When such a polarographic reaction proceeds reversibly in aqueous medium, the half-wave potential of the system is expressed by the following equation, which assumes that the activity of the mercury in the dilute amalgam is unity,

$$E_{1/2} = E + \frac{\mathrm{RT}}{n\mathrm{F}} \ln \frac{i}{i_d - i} = E_a{}^0 + \frac{\mathrm{RT}}{n\mathrm{F}} \ln \frac{f_i/\sqrt{D_i}}{f_a/\sqrt{D_a}} \qquad (1)^*$$

There are no reasons that prevent this familiar equation from serving for polarography in a non-aqueous medium, provided that the process is still polarographically reversible and that $E_a{}^0$, f_i and D_i are defined with respect to the solvated ion in the given solvent. Consequently, other theoretical treatments derived from equation (1) should all be valid.[70a,81] In these cases, all potential values of the indicating electrode are referred not only to the reference electrode used (including the liquid junction potential) but to the solvent involved.

Because the interionic attraction is large in solvents of low dielectric constant, the influence of supporting electrolyte on polarographic waves must be significant. Even if complex formation is not involved, the anions of the supporting electrolyte, assuming a cationic depolariser, may associate with both the supporting and the depolarising cations. This problem in respect of the reversible amalgam-forming process has been treated[74,75] in a manner analogous to that for complex formation in aqueous polarography. The activity of the depolarising metal ion, M^{n+}, which is also being solvated in a given solvent and forming the potential-determining redox

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* In this review, the symbols employed in equations have usual meanings, unless otherwise noted.

couple with the metal amalgam, was stoichiometrically calculated by assuming the step-wise ion-pair association equilibria

$$\{M^{n+}, jX^-\}^{(n-j)+} + X^- \rightleftharpoons \{M^{n+}, (j+1)X^-\}^{(n-j-1)+}, \qquad j = 0, 1, 2, \ldots \tag{2a}$$

where the activity of the supporting anion, X^-, is expressed in terms of the degree of association of uni-univalent supporting electrolyte in the solvent. When the dielectric constant of the solvent is sufficiently low and the concentration of supporting electrolyte is sufficiently high, both the supporting electrolyte and the depolarising ion are present predominantly as the final associated forms, which may be neutral species. Then, the final expression derived for the half-wave potential can be written as

$$E_{1/2} = E_a{}^0 + \frac{RT}{nF}\ln\frac{f_{MX_j}/\sqrt{D_{MX_j}}}{f_a/\sqrt{D_a}} - \frac{RT}{nF}\ln\frac{K_j(C_{SX})^{j/2}}{(K_{SX})^{j/2}}, \qquad j = n \tag{2b}$$

where K_j and K_{SX} are the association constants of the depolarizing ion and the supporting electrolyte, respectively.

In a specific solvent containing a specific supporting electrolyte, the half-wave potential becomes more negative with increasing magnitude of K_j and with increasing concentration of the supporting electrolyte, C_{SX}. The appearance of equation (2b) is quite similar to that of the equation for complex formation in aqueous solution, as might be expected on the basis of its derivation, and reduces to equation (1) on introducing the condition of no ion-pair formation for the depolarising ion, *i.e.*, $j = 0$. Whether ion-pair or complex formation would predominate may depend upon the relative co-ordinating ability of the solvent molecules compared to that of the supporting anion.

In organic solvents, the reversibility of an electrode process is sometimes preserved by the formation of a stable complex;[81] however, it usually decreases. The existing theoretical treatments of irreversible process can also be employed in non-aqueous studies under the same conditions as described for the case of a reversible process. Rate constants and activation energies have been evaluated for some pure and mixed solvents.[82b,94]

Limiting diffusion current

The validity of the Ilkovič equation has often been examined and verified for many organic solvents,[12b,34a]

$$I_d = KnC_iD_i^{1/2}m^{2/3}t^{1/6} \tag{3}$$

In solvents of low dielectric constant, interionic attraction may appreciably alter the ionic diffusion coefficients as compared to those in water. In conductivity studies, conductivity in non-aqueous solvents is treated in terms of the theory for concentrated solutions.[26] This principle may be introduced into the tracer-diffusion theory,[72] which treats the diffusion of an ion in trace amount coexisting with a large amount of indifferent ions. Then, the following expression can be derived for the polarographic diffusion coefficient:[88a]

$$D_i = {}^0D_i\left[1 - \frac{z_i{}^2e^2}{3\varepsilon kT}\cdot\frac{\kappa}{1+\kappa a}\cdot\{1-\sqrt{d(u_i)}\}\right] \equiv {}^0D_i[1-\Delta] \tag{4}$$

where ${}^0D_i$ denotes the diffusion coefficient of the ionic species at infinite dilution,

z_i the ionic valency, **e** the electronic charge, **k** the Boltzmann constant, and $\kappa/(1 + \kappa a)$ is the familiar factor for interionic attraction effect. The term $d(u_i)$, which is composed of the valencies and mobilities of all the ions concerned, is very complicated in its general form, and a useful expression can be obtained only for a solution containing three ionic species, two of which originate from the supporting electrolyte. In addition, if all of the ionic valencies and mobilities are equal in absolute value, the term $d(u_i)$ becomes a constant of 0·5.

The effect of the concentation of supporting electrolyte on the diffusion coefficient can be estimated by equation (4) through the calculation of the $\kappa/(1 + \kappa a)$ value.[87] Equation (4) involves only the relaxation effect of the supporting ions on the diffusing ion, and is coincident, in appearance, with the equation left after deleting the electrophoresis term from the ionic conductivity equation under the similar restriction as to ionic species. Only at infinite dilution does the relationship

$$^{0}D_i = \frac{\mathbf{R}T^0\lambda_i}{|z_i|\,\mathbf{F}^2} \tag{5}$$

become valid.

However, the above treatments are apparently not satisfactory when any appreciable ion-pair or complex formation equilibrium exists in the solution.

COMPARISON OF POLAROGRAPHIC DATA OBTAINED IN DIFFERENT SOLVENTS

If a series of polarographic studies are made under the condition that only the solvents are different, the discrepancy between the data obtained is considered to be primarily due to the variation of such factors in the solvents as dielectric constant, viscosity and chemical reactivity. When the depolariser and the supporting electrolyte are also changed, their properties may also affect the results obtained. Many investigators have been interested in comparing the results obtained in different solvents; this is frequently one of the principal objectives in studying non-aqueous polarography. In fact, the discussion on preferential solvation or complex formation by solvent molecules described in the previous section is tacitly based upon comparison of behaviour in different solvents. For example, the polarographic behaviour of inorganic substances has been purposely compared in formamides (and their mixtures),[37] in nitriles,[60a,b] in organic solvents[9] and in aqueous organic solvent mixtures of various composition,[33,37,64a,b,82a,92a,b,] where the effects of the above-mentioned factors are discussed. It is relatively easy to get reasonably comparable current values in different media; unfortunately, this is not the case in respect to potential, which must be specified with respect to a universal reference potential.

Determination of comparable potential values in different solvents

There is no general agreement as to a reference electrode, whose potential (*vs.* solution) is constant (*i.e.*, the same) in all solvents. Potential values in different solvents, measured against a specified reference electrode, *e.g.*, aqueous S.C.E., include a variety of junction potentials between each solvent and the reference electrode, so that the potential values actually cannot be reasonably compared. The liquid junction potential between aqueous and non-aqueous solutions may at times exceed 0·15 V. However, some extra-thermodynamic methods have been suggested for estimating or cancelling the liquid junction potential.

Analogous to the Pleskov treatment for comparing standard electrode potentials in different solvents, the half-wave potential for reversible processes involving rubidium or potassium ion has been assumed in the past to be constant in different solvents,[17,79b,92c] strictly speaking, at zero ionic strength. This first approximate conception is supported by the facts that (a) these ions are almost chemically inactive and (b) both their relatively large size and minimum charge cause such small solvation energies in any solvent that the influence of the solvation change on their half-wave potentials may not be significant. On this basis, the use of caesium or some quaternary ammonium ion has also been suggested.[79b] By measuring the half-wave potentials of such a reference ion in different solvents against a specified reference electrode, the difference between any two junction potentials, if they are stable and reproducible, can be estimated as the potential difference between the corresponding half-wave potentials. Otherwise, by adding the reference ion to the test solution and measuring the potential difference between the coexistent waves, one can get a half-wave potential for the species of interest referred to the half-wave potential or, if converted, to the standard potential of the reference ion. In this case, neither the potential value of the reference electrode nor the reproducibility of the junction potentials causes any problem, provided only that they are stable.

Pleskov's pioneering work was subsequently corrected for the changes in solvation energy of the rubidium reference ion.[85] The difference of the solvation energies in two solvents is related to the difference of the corresponding standard potentials:

$$(E_{\mathrm{M}}{}^0)_2 - (E_{\mathrm{M}}{}^0)_1 = \frac{(\Delta G_i)_2 - (\Delta G_i)_1}{z_i\mathrm{F}} \tag{6}$$

where the ionic solvation energies are obtained by dividing the solvation energies of the salt by the Born-Latimer semi-empirical method. It was concluded that the standard potentials of rubidium in some organic solvents differ by 0·05 to 0·11 V from that in water. This correction approach was introduced into the determination of the half-wave potential of thallous ion in acetonitrile-water mixtures.[88c]

All of the above treatments, however, refer to rather ideal conditions and are only approximately valid for real solutions, *e.g.*, reference ion co-ordinated with solvent molecules or other solute ions. Microscopic factors such as the structure of the solvent and the dielectric constant in the vicinity of the ion, which must appreciably influence the solvation states and the standard potentials in real solution,[25c,32] are not considered. Consequently, recent studies on the utility of some organometallic compounds as reference substances seem more realistic and promising, because, in those compounds, the metal atom, which forms a potential-determining redox system, is protected from solvent molecules by the organic residues and its charge transfer in the electrode process is minimum, with the expectation that the solvation energy and its variation in different solvents should be sufficiently small to maintain the constancy of the standard potential and of the half-wave potential as well. For example, ferrocene and cobaltocene have been recommended as reference substances in comparing standard potentials in different solvents,[51] and the use of 4,7-dimethyl-1,10-phenanthroline-ferric perchlorate as a reference permitted measurement of the junction potentials between aqueous and non-aqueous solutions.[67a,b] The reversibility of the electrode processes for many related and analogous organometallic compounds in organic solvents has been shown.[10,41,58,89,90]

Comparison of half-wave potentials

For a reversible amalgam-forming process, the standard amalgam electrode potential is related to the usual standard potential as follows:

$$E_a{}^0 = E_{\mathrm{M}}{}^0 + E_s + \frac{\mathbf{RT}}{n\mathbf{F}} \ln \frac{f_{a\cdot\mathrm{sat}} \cdot C_{a\cdot\mathrm{sta}}}{a_{\mathrm{Hg\cdot sat}}} = E_{\mathrm{M}}{}^0 + A \tag{7}$$

All of the factors collected into A of equation (7) are defined independently of the electrolyte solution. When the system is transferred from solvent 1 to solvent 2, an expression for the difference in the half-wave potential can be derived by applying equation (1) and equation (7):

$$(E_{1/2})_2 - (E_{1/2})_1 = (E_{\mathrm{M}}{}^0)_2 - (E_{\mathrm{M}}{}^0)_1 + \frac{\mathbf{RT}}{n\mathbf{F}} \ln \frac{(f_i)_2}{(f_i)_1} - \frac{\mathbf{RT}}{n\mathbf{F}} \ln \frac{(D_i)_2^{1/2}}{(D_i)_1^{1/2}} \tag{8}$$

In equation (8), all of the potential values must be corrected for the junction potentials and must be referred to a common standard. If the ratios of the activity coefficients, which must be also defined with reference to a common standard, and of the diffusion coefficients are near one, the difference in the half-wave potentials simply equals that of the standard potentials. Then, introducing the Born equation

$$-\Delta G_s = \frac{\mathrm{N}z_i{}^2\mathrm{e}^2}{2r_i}\left(1 - \frac{1}{\varepsilon}\right) \tag{9}$$

into equation (6) and assuming the effective radius, r_i, to be unchanged, the following expression is obtained

$$(E_{1/2})_2 - (E_{1/2})_1 \approx (E_{\mathrm{M}}{}^0)_2 - (E_{\mathrm{M}}{}^0)_1 \approx \frac{z_i\mathrm{e}}{2r_i}\left(\frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1}\right) \tag{10}$$

which indicates a linear relationship between the half-wave potentials and the reciprocals of dielectric constants of the solvents concerned. A similar relationship derived from the difference of half-wave potentials for two coexistent waves has been studied in acetonitrile-water mixtures.[88b]

The Born treatment shows, in principle, that the solvation change caused by changing dielectric constant largely affects the half-wave potential. The effect of such solvation on half-wave potentials has been investigated,[9,82a] and the positive shifts of half-wave potential caused by reducing the dielectric constant of the solvent has been frequently described. However, the applicability of the linear relationship given by equation (10) proved to be rather limited. In such cases, the chemical properties of the depolarising ion[82a] and of the solvent,[60a,b] the steric effect of the solvent molecule[16] and the viscosity of the solvent[37] suggested in the last term of equation (8), were taken into consideration.

The quotient of the magnetic susceptibility divided by the ionic radius (χ/r) has been suggested as a factor governing the shifts of half-wave potential on changing solvents.[9] This quotient must be an essential factor in ion-pair and complex formation. Actually, a linear relationship was found between the quotients for several metal ions and their shifts in half-wave potential per unit of dielectric constant.

Recently published work on nitriles and acetone as solvent[17] includes a comprehensive table of half-wave potentials of metal ions, which have been converted on the basis of the rubidium scale mentioned.

Comparison of limiting diffusion currents

Equation (3) indicates that the influence of the medium on the diffusion-current constant is reflected only through a change in the diffusion coefficient, provided, of course, that the faradaic *n* does not change. When only the solvent is changed, the ratio of the diffusion-current constants in two different solvents can be expressed by introducing equation (4):

$$\frac{(I_d)_2}{(I_d)_1} = \frac{(D_i)_2^{1/2}}{(D_i)_1^{1/2}} = \frac{({}^0D_i)_2^{1/2}\,[1 - \Delta_2]^{1/2}}{({}^0D_i)_1^{1/2}\,[1 - \Delta_1]^{1/2}} \tag{11}$$

In the usual manner, the Stokes theory is assumed to be applicable to the diffusing ion with no effect due to ionic interactions, *i.e.*, ${}^0D_i = k(r\eta)^{-1}$. The ratio of the relaxation-correction term in equation (11) can be assumed to be very close to unity in the usual media. This leads to the familiar relationship

$$(I_d)_2(r)_2^{1/2}(\eta)_2^{1/2} = (I_d)_1(r)_1^{1/2}(\eta)_1^{1/2} = k' \tag{12}$$

Linear relationships have been observed between I_d and $\eta^{-1/2}$ (or square root of the fluidity).[9] However, other investigators, especially in dealing with mixed solvents, have reported that a variation of effective radii must be considered in connection with the solvation change,[37,64a,b,92a,b] even after the correction for their ionic interaction.[87]

It has been pointed out that the applicability of the Stokes theory is doubtful in the case of the movement of relatively small ions, where microscopic factors, such as microviscosity, microdielectric constant and alteration of solvent structure in the vicinity of the ion, should be taken into account.[56] The apparent effective radius, calculated by the Stokes theory, has been explained as resulting from the two effects of blocking and solvation.[37]

Equation (5) shows that the diffusion coefficients of ionic species at infinite dilution are proportional to the corresponding ionic conductivities, so that the ratio of the diffusion-current constants corrected for ionic interaction must coincide with that of the conductivities.[87]

ANALYTICAL ASPECTS

Inorganic polarography in organic solvents, including the use of related voltammetric methods, possesses several advantages as compared to polarography in aqueous solutions: certain compounds of some elements and organometallic compounds, which are insoluble in water, are easily soluble and determinable in organic solvents; disturbance by hydrolysis can be avoided; in some cases, a markedly increased range of potential for electrolysis can be realised. These advantages are often especially marked in some non-proton-releasing solvents.

The alkali and alkaline earth elements exhibit very good polarographic waves in many solvents (Tables I–III). Of even greater importance is the fact that well-defined waves are easily obtained for magnesium, beryllium, aluminium and many rare earth elements in non-proton-releasing solvents, such as acetonitrile,[52b] acetone[15] and dimethylsulphoxide.[34d,79c] In the last solvent, silicon compounds also give a reduction wave.[36] It must be emphasised that these reduction waves sometimes result from the reduction of the reaction product resulting from reaction of the inorganic species with the solvent or a trace of moisture, *e.g.*, in the cases of zirconium in methanol,[23] thorium in acetonitrile,[54] aluminium in pyridine[13] and magnesium and zirconium in dimethylsulphoxide.[34d,79c]

Some ions form ion-pairs or complexes in organic solvents, which are reduced at more positive potentials than their hydrated ions, *e.g.*, nickel in acetonitrile containing chloride[67c] and praseodymium in ethanol containing perchlorate, chloride or bromide;[18] this type of behaviour may obviously have useful analytical application in separating the waves of components of a mixture.

The analytical aspects of inorganic polarography in ethylenediamine, acetic anhydride and dimethylsulphoxide have been reviewed.[80]

The manner of proton (or solvated hydrogen-ion) reducion in organic solvents is quite interesting. The half-wave potential of strong acids appreciably shifts to a more negative potential on the addition of a small amount of water, which shows that the proton is preferentially solvated by water molecules. Organic solvents, such as nitriles and acetone, which are much weaker bases than water, reduce the hydrogen overpotential by more than 0·5 V at the dropping mercury electrode.[15,16,17] Several Brønsted acids, which are rather strong acids in water, exhibit their reduction waves at different potentials in acetonitrile, probably in response to their acidities.[14] On the other hand, such acids, as well as weaker Brønsted acids and some Lewis acids, are levelled in pyridine and are reduced at the same potential, which corresponds to that for the reduction of pyridinium ion.[84]

Polarography in dimethylsulphoxide has been applied to the determination of some gaseous substances.[21] Oxygen at low concentrations has been determined at low temperatures, using a methanol-water mixture as solvent.[38] The fact that the solubility of oxygen is greater in many organic solvents than in water, should facilitate its determination *via* the use of such solvents as absorbents. In general, in the determination of gaseous substances the variety of organic solvents available may be of some advantage by allowing a choice in the solvent suitable for absorbing the gaseous substance and subsequent polarography. The general increase in the solubilities of gaseous substances at decreasing temperature can be used advantageously by employing organic solvents or their aqueous mixtures of low freezing point.

A promising general aspect of the application of organic solvents to inorganic analysis is in polarographic determination preceded by extraction with organic solvents. This area has been reviewed together with other polarographic procedures.[95] Thus, a ternary mixture of chloroform-methyl cellosolve-water was used as the solvent for polarographically determining the diethyldithiocarbamate complexes of several metals extracted with chloroform.[29,30] Determination of 8-quinolinol (oxine) and salicylaldoxime complexes of copper and palladium in acetic acid,[12b] and of acetylacetone complexes of aluminium[20a] and beryllium [20b] in dimethylsulphoxide was also possible following extraction.

At present, not many cases are known of the successful application of inorganic polarography in organic solvents for practical analyses and preparations. However, it has been suggested that the method may be advantageously applicable to the analysis of polymers and petroleum.[45] Two general examples of practical analysis can be cited: free sulphur in gasoline[46] and in vulcanizates[47] was successfully determined by alternating current polarography in a benzene-pyridine-methanol-water mixture, and many kinds of metal driers in oils were directly determined by ordinary polarography in 1:1 benzene-methanol mixture.[57]

A voltammetric study of the hydrogen-perchlorate system in acetonitrile suggested a method for preparing a standard solution of perchloric acid in this solvent.[91]

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Zusammenfassung—Es wird eine Übersicht über anorganische Polarographie in organischen Lösungsmitteln gegeben.

Résumé—On présente une revue sur la polarographie minérale en solvants organiques.

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POLAROGRAPHY OF ORGANIC COMPOUNDS IN APROTIC SOLVENTS

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Summary—A review of the polarography of organic compounds in aprotic solvents is presented.

INTRODUCTION

STUDIES of the polarographic behaviour of organic compounds in aprotic solvents have been numerous in the past decade. The majority of the work had been carried out in dimethylformamide, acetonitrile and dimethyl sulphoxide; pyridine,[1] liquid sulphur dioxide,[2,3] methylacetamide,[4] tetramethylurea[5] and nitromethane[6] have been examined briefly and seem, with the exception of nitromethane, to offer no advantage. Nitromethane is relatively unaffected by *N*-chloro-compounds, which chlorinate many other common solvents, and has been used successfully in studies of these compounds.

The three commonest solvents allow electron additions to be observed with many compounds, without accompanying complications due to protonation, and give more insight into the mechanism of the electrode process. This property leads to stepwise reductions of various functional groups with the formation of stable anion radicals, and in many systems, which are irreversible in solvents containing water or alcohols, become reversible under aprotic conditions.

These solvents in oxidations at solid electrodes, offer a wider potential range for the study of anodic reactions than aqueous media. In aqueous media the range is limited to +1·0 V, whereas in acetonitrile the range is +2·0 V (*vs.* Ag^+).

Additional advantages for these solvents are their synergistic effect on the reduction of halogen compounds, better solvent properties than aqueous systems and inertness towards easily hydrolysed compounds.

This review will stress the investigations in which the results were either not possible, or were better than those obtained in solvents containing water or alcohols.

HYDROCARBONS

The first work[7] dealt with the reduction of aromatic hydrocarbons in dimethylformamide and acetonitrile and it was found that it was possible to form anion radicals from stilbene, anthracene and *p*-anisylfluorene

$$\textit{1st wave}\quad C_6H_5CH{=}CHC_6H_5 + e \rightleftarrows C_6H_5\bar{C}H\dot{C}HC_6H_5$$

$$\textit{2nd wave}\quad C_6H_5\bar{C}H{-}\dot{C}HC_6H_5 + e \rightarrow C_6H_5\bar{C}H\bar{C}HC_6H_5$$

Studies of this type were extended to naphthalene, phenanthrene, biphenyl, terphenyls, phenylacetylenes[8] and more complex aromatic hydrocarbons.[9–15] For a number of these examples only the first step was observed; the second reduction occurred at potentials beyond the usable range of the supporting electrolyte. Similar two-step reductions have been observed for anthracene and non-alternant hydrocarbons, in dioxan containing 4% water, but not for stilbene, which showed only a two-electron step under these conditions.[16] Behaviour resembling that in solvents containing water can be obtained by adding proton donors, such as water,[7] phenol[12] and benzoic acid,[7] to the aprotic solvent; the last two are better proton donors than water.

The nature of the one-electron reduction step in aprotic solvents has been confirmed by large-scale electrolysis,[7] electron spin resonance studies[17] and a.c. polarography.[10] The last of these has demonstrated that the first wave of stilbene in dimethylformamide is completely diffusion controlled and reversible. The polarographic results for these compounds parallel results obtained by the addition of alkali metals to aromatic hydrocarbons and other compounds. They suggest the possibility of a rapid method for determining those compounds that will form anion radicals. The half-wave potentials obtained have been found to correlate with molecular orbital calculations.[18]

QUINONES

Quinones in these solvents are reduced first to the semiquinone anion and then to the dianon[15,19–21]

$$\text{1st wave} \quad Q + e \rightleftarrows Q^-$$

$$\text{2nd wave} \quad Q^- + e \rightleftarrows Q^=$$

The hydroquinones are not oxidised at the dropping mercury electrode, probably because of low ionisation; the dianion, if preformed with base, gives two anodic waves at the same potentials as those observed for the reduction of the quinone.[22]

The reduction of the semiquinone is not reversible at potentials more negative than approximately −1·4 V *vs.* S.C.E and is shifted to more positive potentials by lithium ions. This phenomenon is ascribed to ion association and varies with the structure of the quinone.[23]

The formation of the semiquinone anion has been demonstrated for anthraquinone by electron spin resonance studies,[17] and that of the dianion by the formation of 9,10-diethoxyanthracene in a large-scale electrolytic reduction in the presence of ethyl bromide.[19] The dianion can be seen around the dropping mercury electrode as a red colour.

Addition of water and phenol as proton donors has no effect upon the first wave, but shifts the second wave to more positive potentials. In the presence of a sufficient amount of the proton donor, the two waves merge and give a single wave approximately equal in height to the sum of the two waves obtained in anhydrous media. This behaviour can be explained by the protonation of the quinone dianion, with the potential being determined by the rate of the reaction

$$Q^= + HA \rightleftarrows QH^- + A^-.$$

Benzoic acid as a proton donor behaves differently, and increases the first wave at the expense of the second wave. Protonation of the semiquinone must occur to give an intermediate, which is reduced more readily than the semiquinone

$$Q^- + H^+ \rightarrow QH$$
$$QH + e \rightarrow QH^-$$

This behaviour parallels that observed with the anion radicals from aromatic hydrocarbons.

Hydroxyl groups, hydrogen-bonded intramolecularly, in 1-hydroxyanthraquinones are found to facilitate the reduction more in dimethylformamide than in aqueous ethanol.[24]

o-Quinones in dimethylformamide show a similar stepwise reduction to that observed with *p*-quinones.[12]

Carbon blacks, which have complex quinone structures, are reducible polarographically if present as slurries in dimethylformamide.[25] Similar studies can only be made in an aqueous medium if adequate stirring is used.[26]

CARBONYL COMPOUNDS

In the carbonyl compound series, aliphatic aldehydes only give polarographic waves in dimethylformamide[27] in the presence of tetraethylammonium salts.[28] Phenol enhances the current and shifts the half-wave potentials to more positive values, probably by forming a complex.[27] Crotonaldehyde gives one reduction wave, corresponding to a one-electron reduction.[29]

Saturated ketones in the 3-keto steroid and 20-keto steroid series are not reducible in dimethylformamide,[30] which is in contrast to their behaviour in an aqueous medium. A number of unsaturated ketones, on the other hand, give two waves.

Aromatic aldehydes and ketones form anion radicals[31] in dimethylformamide with differing stabilities. Benzophenone gives a product which is stable and reacts with carbon dioxide and ethyl bromide on a large scale

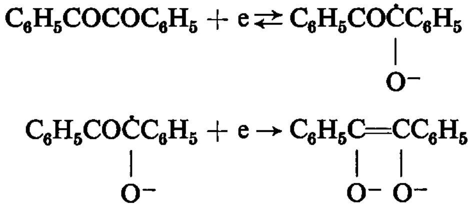
$$\textit{1st wave} \quad (C_6H_5)_2C{=}O + e \rightleftarrows (C_6H_5)_2CO^-$$
$$\textit{2nd wave} \quad (C_6H_5)_2CO^- + e \rightarrow (C_6H_5)_2\bar{C}{-}\bar{O}$$

to form benzilic acid and diphenylethylcarbinol, respectively. Electron spin resonance studies indicate that the anion radical generated from benzophenone is stable,[17] that the intermediate from acetophenone has a half-life of about twenty seconds, but that the product from benzaldehyde is much less stable.[32] In agreement with these stabilities, pinacols are obtained from large-scale electrolysis of the last two compounds.[30] Addition of phenol as a proton donor causes the first wave of benzophenone to grow at the expense of the second wave. Benzaldehyde in the presence of phenol gives a new wave, intermediate between the two original waves. Benzoic acid as proton donor generates a third wave for both benzophenone and benzaldehyde, and this wave is more positive than the original first wave; this behaviour is ascribed to the reduction of the protonated form.[12]

α,β-Unsaturated carbonyl compounds in the aromatic series give two one-electron waves,[29] and large-scale electrolytic reduction studies indicate that the intermediates from benzalacetophenone are more stable than those from benzalacetone and cinnamaldehyde.

Reduction of the diketones benzil, *p*-diacetylbenzene and *o*-dibenzoylbenzene gives two waves, *m*-dibenzoylbenzene gives one and *trans*-dibenzoylethylene three.[33]

In all cases the Kalousek technique[34] has indicated that the initial step is a reversible one involving the addition of one electron



$$C_6H_5COCOC_6H_5 + e \rightleftharpoons C_6H_5CO\dot{C}(O^-)C_6H_5$$

$$C_6H_5CO\dot{C}(O^-)C_6H_5 + e \rightarrow C_6H_5C(O^-){=}C(O^-)C_6H_5$$

Substitution of lithium chloride for tetrabutylammonium iodide in the reduction of benzil gives a reversible two-electron reduction wave. These mechanisms have been verified by electron spin resonance spectroscopy.[35]

NITRILES AND OTHER ACID DERIVATIVES

In the aromatic acid series, nitriles have been found to yield a one-electron reduction wave in dimethylformamide.[36] Electron spin resonance studies are in agreement with a mechanism such as

$$C_6H_5CN + e \rightleftharpoons C_6H_5CN^-.$$

A similar reduction is observed for pyromellitonitrile (1,2,4,5-tetracyanobenzene) in acetonitrile[37] and occurs at approximately the same point as that for pyromellitic anhydride.[38] Tetracyanoethane and tetracyanopropane in dimethylformamide give reduction waves, and electron spin resonance studies indicate that the tetracyanoethylene radical anion is formed as a product.[39]

Studies with α,β-unsaturated acid derivatives have been numerous, and stepwise reductions are reported for tetracyanoethylene,[39] 7,7,8,8-tetracyanoquinodimethan,[40] dicyanomethylene-2,2,4,4-tetramethylcyclobutanone, bis-dicyanomethylene-2,2,4,4,-tetramethylcyclobutane,[41] diethyl azodicarboxylate,[42] substituted acrylonitriles and ethyl acrylates.[43] The addition of phenol and benzoic acid to the last class gives behaviours which vary with the substituents.[44]

NITRO AND NITROSO COMPOUNDS

Anion radicals are formed in the reduction of aliphatic[45] and aromatic[46] nitro compounds in acetonitrile[46] and dimethylformamide.[47]

$$(CH_3)_3CNO_2 + e \rightarrow (CH_3)_3CNO_2^-.$$

In an aqueous or alcoholic medium a similar behaviour is observed for nitrobenzene in the presence of inhibitors such as camphor[48] and triphenylphosphine.[49] Nitrodurene at pH 12 is reported to give a one-electron wave while nitrobenzene gives only an inflection.[50]

The first wave for the reduction of an aromatic nitro compound is reversible, and is followed by an irreversible second wave, corresponding to a reduction to phenylhydroxylamine. Addition of benzoic acid to nitrobenzene in dimethylformamide causes the first wave to increase to a height equal to the sum of the original waves.[47] Water, when added, shifts the second wave to more positive potentials,[51] and alkali metal salts shift the first wave to more positive potentials.[51]

The formation of the anion radical has been verified by electron spin resonance studies for both the aliphatic[45] and aromatic[46] series. The aliphatic radical was found to be unstable. The reversibility observed for the reduction of aromatic nitro compounds in these solvents allows meaningful correlation of half-wave potentials for *m*- and *p*-substituted nitrobenzenes with various substituent constants.[52]

Nitrosobenzene in dimethylformamide gives two waves and forms an unstable anion radical; the instability of the intermediate makes the first wave slightly irreversible.[53] Addition of benzoic acid causes the formation of a new more positive reduction wave, and this is ascribed to the formation of a complex with benzoic acid.[47]

HETEROCYCLIC COMPOUNDS

In the heterocyclic series, pyridinium salts are reduced in the same way in both acetonitrile and water, but the intermediate radical dimerises much more slowly in acetonitrile.[54]

HALOGENATED COMPOUNDS

Dimethylformamide is a useful solvent for the reduction of halogenated compounds. Reductions are observed for chlorobenzene[68,69] and *p*-chloracetanilide[70] in the presence of quaternary salts; these compounds show no observable reduction wave in an aqueous medium.

Trifluoromethyl groups attached to benzene rings are reducible in an aqueous medium only if activating groups such as sulphonyl are present,[71] but the reduction in dimethylformamide occurs even for trifluoromethylbenzene.[28] In addition, the reduction occurs in one, two or three steps, depending upon the number and type of substituents on the aryl ring, in contrast to an aqueous medium where all fluorine atoms are removed simultaneously.

The polarographic reduction of polyhalogenated hydrocarbons in acetonitrile and dimethylformamide is unique. Carbon tetrachloride and bromide are reduced through a dihalocarbene[72] in one step to the methylene compound

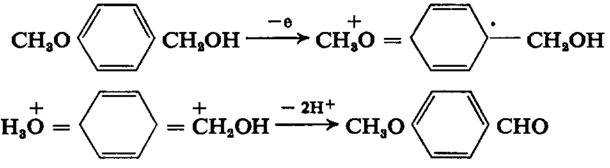
$$CCl_4 + 2e \rightarrow CCl_3^- + Cl^-$$
$$CCl_3^- \rightarrow CCl_2 + Cl^-$$
$$CCl_2 + 2e + \text{solvent} \rightarrow H_2CCl_2.$$

o-Dibromobenzene and *o*-chlorobromobenzene form benzyne as an intermediate[69] and are reduced to benzene.

The polarographic data for the reduction of *o*-bromonitrobenzene and *o*, *m* and *p*-iodonitrobenzene at a hanging mercury drop are at variance with the electron spin resonance data. Consideration of half-peak potentials indicates that the reduction of the nitro group occurs first, whereas electron spin resonance seems to show that elimination of halogen and formation of the nitrobenzene anion-radical are involved in the first step.[73]

OXIDATIONS

The use of aprotic solvents in electrolytic oxidations at solid electrodes was first applied to aryl carbinols[55] in acetonitrile



Oxidation occurs by a two-electron process to the aldehyde which, sometimes, may be further oxidised.

Extension of this work to aromatic hydrocarbons indicated that they lose two electrons and form dipositive ions which, depending on the structure, may be stable or may lose a proton to form a carbonium ion.[56] Pyridine when added as a proton acceptor shifts the waves to more negative potentials. The mechanism of oxidation has been verified by the large-scale oxidation of anthracene in the presence of pyridine and a perchlorate salt to 9,10-dihydroanthranyldipyridinium diperchlorate.

Oxidations have been carried out in dimethylsulphoxide[57] but not in dimethylformamide, because this solvent gives a high residual current.[59] Data are given for the oxidation of tropilidine,[60] aromatic hydrocarbons,[61] amines,[57,58,61,62] tetraphenylborate ion,[59] tetrakisdimethylaminoethylene[63] and sulphur compounds.[57,64,65] The oxidation potentials obtained for various aromatic hydrocarbons and amines have been correlated with various calculations.[66,67]

MISCELLANEOUS APPLICATIONS

The inertness of these solvents makes them ideal for the study of easily hydrolysed compounds. Data are reported for the reduction of the triphenylcyclopropenyl and triphenylcarbonium ions in acetonitrile[74] and trialkylchlorosilanes in dimethylsulphoxide.[75] The latter reduction is ascribed to the product from the following reaction:

$$R_3SiCl + (CH_3)_2SO \rightarrow R_3SiOS(CH_3)_2^+ + Cl^-.$$

Carbonium ions have also been studied in methanesulphonic acid.[76]

The greater solvent properties of these solvents over aqueous mixtures have been demonstrated in the determination of styrene in polystyrene,[77] the analysis of solvent extracts of coal,[78] the oxidation of 3,4-dimethoxypropenylbenzene[79] and the reduction of methylene quinones.[80]

Zusammenfassung—Es wird eine Übersicht über die Polarographie organischer Verbindungen in protonenfreien Lösungsmitteln gegeben.

Résumé—On présente une revue sur la polarographie des composés organiques en solvants aprotiques.

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POLAROGRAPHY OF OXYANIONS IN MOLTEN SALTS

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Summary—A review of the polarography of oxyanions in molten salts is presented.

INTRODUCTION

THE electrode reactions of oxyanions in molten salts are especially interesting because in many cases they are unique to high temperature systems and cannot be studied in aqueous or non-aqueous systems at room temperature. The products are often greatly influenced by solubility effects which cannot be predicted, so that it is unsafe to make generalisations or to draw analogies from behaviour in more familiar solvents.

CHROMATE ION

The first observation of the polarographic reduction of chromate ion in molten salts appears to have been that of Steinberg and Nachtrieb,[1] who reported four indistinct reduction waves at the dropping mercury electrode for potassium chromate in a molten mixture of lithium nitrate, sodium nitrate and potassium nitrate at 153°. Although no interpretation was given, an analogy was drawn to the four reduction waves reported by Lingane and Kolthoff[2] in neutral unbuffered aqueous solution. Lyalikov[3] described a reduction wave for dichromate ion in molten potassium nitrate at 360–380°. The wave-height decreased gradually with time, evidently because of the slow reduction of chromium(VI) by nitrite which was produced by thermal decomposition of the solvent. An amperometric titration of dichromate with sodium nitrite showed that the reduction reaction is rapid. The working curve of diffusion current *vs.* added chromium(VI) showed no response until a definite amount of dichromate had been added, suggesting the presence of a corresponding amount of nitrite in the solvent. Potassium chromate showed no wave at 360°, but a wave did appear at 500°. On the other hand, ammonium chromate which decomposes to give chromium(VI) oxide, gave a wave even at 250–300°.

Black and de Vries,[4] using a platinum microelectrode as cathode and a large platinum electrode as anode in lithium chloride-potassium chloride eutectic at 450°, reported a two-step reduction of chromate with waves beginning at applied potentials of about −0·25 and −0·82 V with respect to the platinum anode. The two waves were attributed to reduction of chromium(VI) to chromium(III) and chromium(II), respectively, by a comparison of the relative wave-heights. Delarue[5] considered that the reductions of potassium dichromate, potassium chromate and chromium(VI) oxide in lithium chloride–potassium chloride are all similar in producing insoluble chromium (III) oxide on the electrode surface, and that the chromate and dichromate ions are largely dissociated in the melt to give chromium(VI) oxide and oxide ion. These conclusions are, however, not substantiated by findings in our laboratory.

Ferguson[6] and Bhatia[7] both found that chromate gave a single drawn-out wave extending from about −0·9 to −1·6 V *vs.* the Pt(II)/Pt electrode, and quantitative electrolysis[6] carried out with a platinum cathode at a potential of −1·8 to −2·0 V gave an "n" value of 3·03 electrons. The black deposit on the cathode showed a chromium content of only 35·5 % as compared with 68 % calculated for chromium(III) oxide. Detailed chemical analyses of insoluble cathode films prepared by electrolysis of potassium chromate have been carried out by Ferguson,[6] Bhatia[7] and Reddy.[8] Although there appears to be some variation in the composition of the film depending upon the conditions of electrolysis, a pronounced enrichment in lithium content and of chromium(VI) content is invariably found. Little, if any, oxide ion is found to enter the bulk solution.

The film can be decomposed by leaching with water to yield chromium(III) oxide and a solution containing hydroxide, chloride, lithium, potassium and chromate ions. The mole ratio of excess lithium (beyond that equivalent to potassium and chloride in the solvent melt) to chromium(III) was found to vary from 3·86 to 5·22 in four different preparations. The simplest interpretation is that the primary cathode process is

$$CrO_4^{2-} + 3e^- \rightarrow CrO_4^{5-} \qquad (1)$$

The ion CrO_4^{5-} might be expected to lose oxide ions successively to form CrO_3^{3-}, CrO_2^{-}, and finally Cr_2O_3. It appears, however, that insolubility of a phase containing both chromium(VI) and chromium(III) tends to stabilise the more alkaline species, CrO_4^{5-} and CrO_3^{3-}.

Recent experimental work in this laboratory[9] has indicated that the voltammetry of chromate is profoundly affected by the presence of magnesium and calcium ions in the melt. A small concentration of magnesium ion, introduced in the displacement of heavy-metal impurities, caused the appearance of a double wave similar to that reported by Black and de Vries.[4] Addition of a large concentration of magnesium ion caused the second wave to disappear, so that only the early reduction wave was observed. Calcium ion caused a similar, although somewhat less pronounced shift. The cathodic reduction product was a very stable black material showing an X-ray diffraction pattern closely resembling that of a compound of formula $2Li_2O \cdot CaO \cdot Cr_2O_3$, or $Li_4Ca(CrO_3)_2$, prepared by short circuiting a galvanic cell consisting of a solution of potassium chromate in molten potassium chloride–lithium chloride, a calcium anode and an inert cathode.[10] It appears, therefore, that the double voltammetric wave reported by Black and de Vries can be traced to the contamination of the melt by calcium ion introduced by etching of the glass vessels by the moist melt used by these early investigators. We have been able to reproduce such a double wave by using a moist melt in glass containers. Further work is currently under way on the mechanism of the electroreduction of chromate in chloride melts. Although the reduction of chromate in sulphate melts has been mentioned,[18] no detailed study has been made.

NITRATE AND NITRITE ION

Although nitrate melts have been used as solvents for the polarographic study of metal ions by numerous investigators, the first detailed study of the cathodic behaviour of the solvent anion of an alkali metal nitrate melt was that of Hills and Johnson.[11]

Using a platinum microelectrode as cathode and a large platinum electrode as anode, they observed a current beginning at an applied potential of $-1{\cdot}5$ V, rising to a sharp peak, followed by a smaller steady state current (approximately 3 mA.cm^{-2}) which persisted until final reduction of the solvent at $-2{\cdot}9$ V. The post-peak steady state current was observed to have a relatively large temperature coefficient, corresponding to an activation energy of 11 kcal/mole, and suggesting a kinetically controlled process. It was proposed that a surface reaction involving the platinum cathode was involved in the mechanism, leading to a reduction of nitrate ion rather than alkali metal ions as had previously been supposed.

A more detailed study of the reduction of nitrate in a sodium nitrate–potassium nitrate eutectic melt at 250° was made by Swofford and Laitinen.[12] The fact that several metals, including gold, silver, nickel, tungsten and mercury, when substituted for platinum as a cathode led to similar peaks demonstrated that the cathodic reaction does not involve a surface attack of the metal. A solid film was observed to form, and it is the rate of dissolution of the film that determines the post-peak current. It was shown that melts of pure potassium nitrate at 350° do not show the cathodic current peak; instead, the current was observed to increase without limit at applied potentials greater than 1·35 V. Addition of 10% sodium nitrate by weight caused the appearance of a peak. Formation of nitrite ion and oxide ion were shown to correspond quantitatively to the cathode reaction

$$NO_3^- + 2e^- \rightarrow NO_2^- + O^{2-} \qquad (2)$$

Finally, it was shown that sodium oxide is sparingly soluble in sodium nitrate–potassium nitrate eutectic, and, therefore, the post-peak current must be limited by the rate of dissolution of the sodium oxide film. The final current rise at a cathode potential of $-2{\cdot}8$ V [*vs.* Ag(I)(0·07*M*)/Ag] was attributed to the deposition of alkali metal, as evidenced by the formation of a blue colouration. The alkali metal soon reacts to produce a colourless gas and oxide ion in amounts indicating nitrogen as the reduction product.

The oxidation of nitrite ion was observed several years ago by Lyalikov and Novik,[13] who reported reproducible and well-defined anodic waves at platinum electrodes in sodium nitrate–potassium nitrate melts at 260–400°. The most probable anodic reaction was considered to be

$$NO_2^- \rightarrow NO_2 + e^- \qquad (3)$$

It would be of interest to examine in more detail the reverse of reaction (2) to determine whether NO_2^- yields nitrate ion in the presence of excess oxide ion, or whether oxide ion undergoes prior oxidation to oxygen, as might be expected from the findings of Delarue.[5]

SULPHATE ION

Chovnyk[14] reported a four-step voltammetric reduction from a zinc sulphate-potassium chloride melt; the first step was interpreted[15] as the cathodic reduction of sulphate ion to give unspecified products.

Pushkareva[16] observed the formation of sulphur in carnallite melts by thermal decomposition of sulphite or thiosulphate or by reduction of sulphate by magnesium. Dissolved sulphur gave a blue colour detectable at a concentration of 0·03 weight %

sulphur, but it slowly distilled from the melt. Liu[17] found sulphite and sulphide but little or no sulphur in the cathode compartment of a lithium sulphate–potassium sulphate melt electrolysed between platinum electrodes at 625°.

Johnson and Laitinen[18] reported that a mixture of lithium, sodium and potassium sulphates at 550° gave either sulphur or a metallic sulphide, depending upon the reduction potential of the metal ions and solubility of the sulphide. The pure melt showed a residual current curve at platinium electrodes with a small wave occurring at a potential of about $-0{\cdot}6$ V *vs.* Ag(I)/Ag. The wave was unsymmetrical, showing a reasonable linear plot of $\log(i_d - i)$ *vs.* E with reciprocal slope 0·110 V as compared with $2{\cdot}303\ RT/F = 0{\cdot}163$ at 550°. Although the cathodic process was thermodynamically irreversible, it was found that an anodic hump, suggestive of the reoxidation of an insoluble product on the electrode, was obtained upon reverse polarisation. The limiting process for the cathodic wave is obscure; conceivably it could be limited by the formation of a cathodic film, or by the kinetics of a prereduction step. Chronopotentiometric experiments on small concentrations of sulphate ion in lithium chloride-potassium chloride melts[19,20] have indicated a transition time roughly equal to that expected for a diffusion-controlled two-electron reaction, but with complications. The quantity $I\tau^{\frac{1}{2}}$ was found to *increase* with increasing I, contrary to the *decrease* expected for a kinetically controlled prior chemical reaction. A complex reaction path, involving the formation of a thermally unstable primary reaction product (such as SO_3^{2-}) through a kinetically complicated pathway would be consistent with the observations. A disproportionation of the primary reaction product to form sulphate and either sulphur or sulphide would account for the increase of $I\tau^{\frac{1}{2}}$ with I. One unexplained feature of the observations was that the addition of oxide ion as calcium oxide caused a shift of reduction potential towards *less* negative values.[19,20] Conceivably this shift is due to calcium ion rather than oxide ion. In any case, it is clear that several features of the reduction mechanism should be clarified by more detailed investigations.

OTHER OXYANIONS

Senderoff *et al.*,[19] reported that several other oxyanions, including phosphates, silicates, borates and carbonates gave indications of one or more chronopotentiometric reduction waves in lithium chloride–potassium chloride eutectic at 500–900°. In view of the preliminary nature of these observations, a more detailed examination of several of these substances was undertaken in our laboratory by Woodhall.[20] Anhydrous preparations of lithium metaborate, sodium tetraborate and calcium silicate showed no definite reduction waves but only a slight increase in the residual current at 450°. It is suspected that the reported reduction of silicate was actually due to the presence of water of hydration. Borates may, however, show a true reduction, especially at higher temperatures and at higher concentrations.

Carbonate showed the beginning of a reduction process but not a fully developed wave at concentrations of $10^{-4}M$ to $0{\cdot}05M$ at a tungsten microelectrode.[20] The product was amorphous carbon, as identified by its unreactivity and its diffuse X-ray diffraction pattern which was identical with that of amorphous carbon. The cathodic formation of carbon by electrolysis of equimolar lithium carbonate–potassium carbonate at 580–600° at platinum or gold electrodes has been recently reported by Delimarskii *et al.*[21]

Metaphosphate ion yields definite voltammetric and chronopotentiometric reduction steps which are being investigated in detail.[22] Metavanadate, added as the lithium salt to potassium chloride-lithium chloride eutectic, showed two reduction waves at 450° at a platinum micro-electrode.[23] The product of the first reduction was a solid which could be reoxidised upon reverse polarisation. At higher concentrations, metavanadate did not appear stable in solution, because a light tan-coloured precipitate resembling Li_3VO_4 separated out upon the addition of more $LiVO_3$ although the wave-heights increased. The insoluble cathodic reduction product was not characterised, but to indicate the possible complexities of the process it may be pointed out that reduction of vanadium pentoxide yielded an insoluble "lithium vanadium bronze" containing both vanadium(IV) and vanadium(V).[23] The film is evidently a good electronic conductor.

In conclusion, it may be remarked that the electrochemistry of oxyanions in molten salts is a field offering unusually fruitful promise and that polarography and related electroanalytical techniques undoubtedly will play an important role in its development.

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Zusammenfassung—Es wird eine Übersicht über die Polarographie von Oxyanionen in Salzschmelzen gegeben.

Résumé—On présente une revue sur la polarographie des oxyanions dans les sels fondus.

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POLAROGRAPHIC REDUCTION OF HYDROGEN ION IN NON-AQUEOUS SOLVENTS

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Summary—The polarographic reduction of hydrogen ion, furnished by dissociation of a Brønsted acid or present in the undissociated Brønsted acid, is reviewed for the situation where a solvent other than water is involved.

INTRODUCTION

THE electrochemical reduction of hydrogen ion in aqueous solution has long been a major problem in electrochemistry, as indicated by the voluminous literature on the subject. The difficulty and complexity involved are well indicated by Frumkin's reviews of one aspect of the situation, that of hydrogen overpotential and adsorption phenomena.[18] The additional problems introduced when non-aqueous media are used, are well presented in Kolthoff's recent review[31] of polarography in inert organic solvents; the debt of the present authors to this study will be apparent to the reader. Other useful sources of data on polarography include two monographs by Charlot and collaborators.[9,10] Bockris[5] has described the rates of hydrogen evolution in a variety of solvents at a number of different electrodes.

The present review is primarily concerned with the phenomenological aspects of the polarographic reduction of hydrogen ion, furnished by the dissociation of a Brønsted acid or present in the undissociated Brønsted acid, when a solvent other than water is involved; the available literature on hydrogen ion reduction in non-aqueous media is generally not sufficiently systematic and detailed to allow more than general correlations to be made.

Because of the limited and fragmentary data available, hydrogen ion reduction in fused salt media will not be considered. Reference will be made to non-polarographic electrochemical data, where the latter illuminate the polarographic situation. The polarographic reduction of hydrogen ion in aqueous solution will be briefly reviewed to furnish a basis for comparison.

Reduction potentials

A major problem in dealing with electrochemical data in non-aqueous media is that of expressing potentials obtained in different solvents on a comparable scale; one source of the difficulty is the unknown magnitude of the liquid junction potential between test solution and reference electrode system. The interrelationship between potential scales in different solvents in terms of the Pleskov[48,49] and Strehlow[30,55] conventions is discussed by Kolthoff.[31] In the subsequent discussion, the relationships between potentials of hydrogen ion reduction in different solvents will be expressed on several bases in order better to indicate the possible factors involved.

The potential for the half-reaction in aqueous solution

$$H^+ + e \rightleftharpoons 0{\cdot}5\,H_2 \qquad (1)$$

under specified unit activity has been used to fix the potential scale for water as a solvent; the problems involved are summarised by Bates.[3] The use of this half-reaction for defining potential scales in non-aqueous media relative to aqueous media is complicated by the fact that the solvents used generally have Lewis-base characteristics appreciably different from those of water, which result in their forming with hydrogen ion more or less stable adducts, $(H \cdot solvent)^+$, as well as in a varying degree of solvation of hydrogen ion and/or its adduct. The resulting levelling effect in the case of Brønsted acids in aqueous media through the formation of the hydronium ion, H_3O^+, is well-known; analogous effects are seen in other solvents.

Calculation of the solvation energy for the hydrogen ion in various solvents in connection with the reaction of equation (1) would facilitate potential scale comparison; however, the problem is still a formidable one. Izmailov[26,27] has attempted to calculate the solution energy of hydrogen ion in a variety of solvents.

Hills[23] has discussed the use of the hydrogen electrode as a potentiometric reference electrode in non-aqueous solutions.

Hydrogen ion activity

The difficulty of expressing hydrogen ion activity and concentration in aqueous solution in a usable, operational manner from electrometric pH measurement has been considered by Bates.[3] The situation with respect to the interpretation of electrometrically measured pH numbers for non-aqueous media is far less well defined,[4] although Bates and others are beginning to explicate pH scales for aqueous-organic and organic solvents.

In the present review, hydrogen ion concentrations will generally be given in terms of the analytical concentration of the hydrogen ion source added to the test system. Admittedly, such a purely operational approach constitutes a poor way of expressing hydrogen ion activity, but any other method would result in even more confusion with respect to interpretation.

Classification of solvents

Based on proton availability, solvents may be divided into three main groups, consisting of (1) protonic, (2) aprotic and (3) non-protonic compounds.

Protonic solvents, which contain more or less readily releasable protons and thus exhibit somewhat acidic properties in aqueous media, can themselves be subdivided into three sub-groups. The hydroxylic solvents, of which water is the most familiar member, include alcohols and glycols, which usually exhibit properties similar to those of water. The protogenic solvents are considerably stronger acids than water; the protophilic solvents are considerably stronger bases than water but may exhibit acidic properties, *i.e.*, release protons, under some conditions.

Aprotic—frequently and incorrectly referred to as inert—solvents are those considered to have no acidic or basic properties. However, with the exception of pyridine and similar compounds which are actually aprotic, most other so-called inert solvents have very weak acidic or basic properties, *e.g.*, dimethylsulphoxide is a much weaker acid than water but is comparable in base strength.

Non-protonic solvents are totally devoid of hydrogen in their structure and consequently cannot act as acids in the Brønsted sense. They may, however, behave as Lewis acids or bases. Unfortunately, the scanty polarographic literature on non-protonic solvents, if fused salt media are excluded, has largely been devoted to liquid sulphur dioxide, in which the reduction of hydrogen ion has not been specifically investigated.

The autodissociation constants of some solvents are tabulated in Table I.

TABLE I.—AUTODISSOCIATION CONSTANTS*† AT 25° OF SOME SOLVENTS

Solvent	pK'_{auto}	pK_{auto}
Nitric acid	1·2	2·58
Sulphuric acid	3·1	4·37
Formic acid	6·2	7·7
Hydrofluoric acid	9·7 (0°)	11·4
Acetamide	10·5	11·9
Ethylene glycol	*ca.* 11	*ca.* 12
Water	14·0	15·7
Acetic acid	14·5	15·9
Methanol	16·7	18·3
Formamide	16·8	18·3
Dimethylsulphoxide	*ca.* 17	*ca.* 18
Ethanol	19·1	20·6
1-Propanol	19·4	20·8
Nitromethane	19·5	20·9
2-Propanol	20·8	22·3
Ammonia (liquid)	32·5 (−50°)	34·2
Hydrogen sulphide (first stage)	32·6	

* For solvent, $HA \rightleftharpoons H^+ + A^-$, $K'_{auto} = [H^+][A^-] = K_{auto}[HA]$

† The values of K'_{auto} are mostly taken from reference 10.

EFFECT OF SOLVENT CHARACTERISTICS

In addition to the effect of the chemical properties of the solvent, *e.g.*, its acid-base strength, certain of its physical properties, especially its viscosity and dielectric constant, also influence the polarographic behaviour of organic and inorganic species.

Standard and half-wave potentials

By its influence on the extent and energy of solvation of the ions involved and on the degree of ion association, the dielectric constant of the solvent plays a rather important role in determining the standard potential of an oxidation–reduction couple and, as a result, its polarographic half-wave potential, $E_{1/2}$. The change of potential with solvent is complex, because not only does $E_{1/2}$ of the species under study, *e.g.*, hydrogen ion, vary with the dielectric constant of the solvent but the standard potential of the reference couple (and hence the potential of the reference electrode) may also vary. If a system is transferred from one solvent to another, the change in $E_{1/2}$ (corrected for liquid junction potential and referred to a common standard) may be expressed as

$$(E_{1/2})_2 - (E_{1/2})_1 = (E_i{}^\circ)_2 - (E_i{}^\circ)_1 + \frac{RT}{nF}\ln\frac{(f_i)_2}{(f_i)_1} - \frac{RT}{2nF}\ln\frac{(D_i)_2}{(D_i)_1} \qquad (2)$$

where f_i is the activity coefficient of the ion concerned in the solvent indicated and D_i is its diffusion coefficient, and the other terms have their customary significance. If the ratios of the activity coefficients (referred to a common standard) and of the diffusion coefficients are close to unity, the difference in $E_{1/2}$ will equal that of the standard potentials, which is related to the difference between the solvation energies in the two solvents

$$(E_i^\circ)_2 - (E_i^\circ)_1 = \frac{(\Delta G_i)_2 - (\Delta G_i)_1}{z_i F} \tag{3}$$

where z_i is the charge on the ion and ΔG_i is its solvation energy. On estimating the solvation energy from the Born equation

$$-\Delta G_i = N z_i^2 e^2 (1 - \epsilon^{-1})/2r_i \tag{4}$$

where N is Avogadro's number, e is unit charge on the electron, ϵ is the dielectric constant of the solvent and r_i is the radius of the ion, and substituting into equation (2), one obtains

$$(E_{1/2})_2 - (E_{1/2})_1 \approx (E_i^\circ)_2 - (E_i^\circ)_1 \approx \frac{z_i e}{2r_i}\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) \tag{5}$$

Thus, a linear relationship is expected between $E_{1/2}$ and the reciprocal of the dielectric constant of the solvent concerned. This relationship must, however, be used with caution, because variation of r_i with the solvent, which probably occurs, will certainly lead to deviations from linearity.

The ideal behaviour expressed by equation (5) should be most closely approached by a large ion with a minimum charge, *e.g.*, +1. The behaviour of the larger alkali metal ions, *e.g.*, potassium(I), rubidium(I) and caesium(I), as well as that of such species as ferrocene and cobalticene, has been presumed to approximate ideality.

The standard potentials of many metal-metal ion couples have been determined with respect to the hydrogen electrode in a number of solvents (Table II). On the basis of the standard potentials of various large ion couples, the standard potential of hydrogen, referred to the aqueous hydrogen electrode, has been calculated for several solvents (Table III). Values based on E_{Na}° are obviously out of line in some solvents; these values are generally more positive than those based on the standard potentials of

TABLE II.—STANDARD POTENTIALS, E°(V), OF SOME REDOX COUPLES IN SEVERAL SOLVENTS*

Couple	Solvent							
	H_2O	HCOOH	NH_3(1)	N_2H_2	MeOH	EtOH	$HCONH_2$	CH_3CN
Li^+/Li	−3·05	−3·48		−2·20	−3·09	−3·04		−3·23
K^+/K	−2·93	−3·36		−2·02	−2·92		−2·87	−3·16
Rb^+/Rb	−2·93	−3·45		−2·01	−2·91		−2·85	−3·17
Cs^+/Cs	−2·92	−3·44						−3·16
Na^+/Na	−2·71	−3·42		−1·83	−2·73	−2·66		−2·87
Zn^{2+}/Zn	−0·76	−1·05		−0·41	−0·74	−0·64	−0·76	−0·74
Cd^{2+}/Cd	−0·46	−0·75		−0·10	−0·26	−0·38	−0·41	−0·47
Pb^{2+}/Pb	−0·13	−0·72		+0·35	−0·20	−0·15	−0·19	−0·12
H^+/H_2	0·00	0·00		0·00	0·00	0·00	0·00	0·00
Cu_2^+/Cu	+0·34	−0·14			+0·49	+0·21	+0·28	+0·28
I_2/I^-	+0·54	−0·03	+1·4		+0·36	+0·31		+0·07
Ag^+/Ag	+0·80	−0·17			+0·76	+0·75		+0·23
Br_2/Br^-	+1·07	+0·52	+1·8		+0·84	+0·78		+0·47
Cl_2/Cl^-	+1·36	+0·77	+2·0		+1·12	+1·05		+0·58

* Referred, as indicated, to the standard potential for hydrogen, E_H°, in each solvent.

the higher alkali metals. This positive difference in calculated $E_H{}^\circ$, which amounts to +0·2 V in formic acid and acetonitrile, and about +0·3 V in methanol and hydrazine, indicates that the behaviour of Na(I) deviates from ideality as expressed above and that $E_{Na}{}^\circ$ is actually more negative in these solvents than in water.

The standard potential of hydrogen in several nitriles and in acetone has been calculated by a spectrophotometric technique (Table IV).

TABLE III.—STANDARD POTENTIALS(V)* FOR HYDROGEN IN SEVERAL SOLVENTS

Solvent	E_H° (in solvent) *vs.* N.H.E. (aq.) based† on					
	K_{Na}°	E_K°	E_{Rb}°	E_{Cs}°	$E_{ferrocene}^\circ$	$E_{cobalticene}^\circ$
HCOOH	+0·71	+0·43	+0·52	+0·52		
N_2H_4	−0·88	−0·91	−0·92			
MeOH	+0·02	−0·01	−0·02		−0·01	−0·01
EtOH	−0·05					
$HCONH_2$		−0·06	−0·08		−0·15	−0·15
CH_3CN	+0·45	+0·23	+0·24	+0·24	+0·15	+0·15

* Calculated from the data in Table II for the alkali metal couples and from the data of Strehlow *et al.*[29] for the ferrocene and cobalticene couples.

† E_H° (in solvent) − E_H° (in water) = [E_H° (solvent) − E_M° (solvent)] − [E_M° (water − E_M° (water)]. Because E_H° (water) ≡ 0 and E_H° ≡ 0 in Table II, then E_H° (solvent) − E_H° (water) = E_M° (water) − E_M° (solvent)

TABLE IV.—STANDARD POTENTIAL OF HYDROGEN IN SOME NITRILES AND ACETONE*

Solvent	E_H° *vs.* N.H.E. (aq.)†, *V*
Acetonitrile	+0·30
Propionitrile	+0·26
Isobutyronitrile	+0·25
Benzonitrile	+0·29
Phenylacetonitrile	+0·26
Acetone	+0·24

* Based on spectrophotometric titration of uncharged indicator bases, B, with perchloric acid.[18]

† $(E_H^\circ)_{org} - (E_H^\circ)_{water} = (E^\circ)_{org} = 0{\cdot}059\Delta pK_{BH^+}$, where $\Delta pK_{BH^+} = (pK_{BH^+})_{org} - (pK_{BH^+})_{water}$

Acid dissociation constants

The dielectric constant of the solvent also influences the apparent dissociation constants of acids. If an acid is dissolved in two solvents of equal acid-base strength but differing dielectric constant, the difference in apparent dissociation constant of the acid in the two solvents will depend on the charge types involved and on the difference in dielectric constant.

For an acid-base couple of the type HB^+/B, *e.g.*, $NH_4{}^+/NH_3$, the electrostatic attraction between solvated H^+ and B (or H^+ and HB^+) is negligible and so the dielectric constant change has no influence. In couples of the type HA/A^-, *e.g.*, $HOAc/OAc^-$, there is attraction between H^+ and A^-, and the magnitude of pK_a will change, *i.e.*,

$$\Delta(pK_a) = k\Delta(1/\epsilon) \qquad (6)$$

where k is a constant which depends on the acid-base character of the solvents. For a couple of type HA^-/A^{2-}, *e.g.*, HCO_3^-/CO_3^{2-}, where the acid is negatively charged, the influence of the dielectric constant change will be even greater, *i.e.*,

$$\Delta(\mathrm{pK_a}) = 2\mathrm{k}\Delta(1/\epsilon) \tag{7}$$

The acid dissociation constant data listed in Table V were collected from reference 10.

Ion pair formation

Ion pairing becomes appreciable in media of low dielectric constant. Appreciable association of the background electrolyte ions results in high solution resistance and in the consequent necessity for troublesome iR-drop corrections which, in some cases, may not completely compensate for the potential drop.[51] In addition, association of the background electrolyte ions with the sample ions may lower the effective concentration of the latter and may complicate polarograms by the introduction of ion aggregates involving background anions which may be reduced at different potentials.[21] In media of very low dielectric constant, it may be difficult to find electrolytes with sufficient solubility and dissociation to serve as background electrolyte in maintaining low solution resistance.

Current magnitude

The viscosity, η, of the solvent influences the characteristics of the polarographic wave by altering the magnitude of the diffusion current through a change in diffusion coefficient. Because the diffusion current constant, I, is proportional to $D^{1/2}$, one obtains, on introducing the Stokes–Einstein equation into the Ilkovič equation,

$$(\mathrm{I_i})_2(\mathrm{r_i})_2^{1/2}(\eta)_2^{1/2} = (\mathrm{I_i})_1(\mathrm{r_i})_1^{1/2}(\eta)_1^{1/2} = \mathrm{k}' \tag{8}$$

The latter equation predicts a linear relation between I_d and $\eta^{-1/2}$ for different solvents.

HYDROGEN ION REDUCTION IN AQUEOUS MEDIA

The mechanism of electrochemical hydrogen ion reduction in aqueous solution is still a controversial subject. Reference has been made to Frumkin's review of the role of adsorption; the effect of other processes and factors has been discussed in depth, *e.g.*, Kortüm and Bockris.[37] There is still lack of general agreement as to the controlling steps even for the reduction of hydrogen ion on mercury, which has been so extensively investigated.

Many polarographic investigators tend to accept—at least implicitly—as the mechanism for hydrogen reduction on mercury the sequence of steps postulated by Heyrovský,[22] which involves a reversible discharge of hydrogen ion to atomic hydrogen

$$H^+ + e \rightleftharpoons H \tag{9}$$

which then combines with a hydrogen ion

$$H + H^+ \rightarrow H_2^+ \tag{10}$$

TABLE V.—ACID DISSOCIATION CONSTANTS, pK_a, IN VARIOUS SOLVENTS*

Acid	Solvent										
	H_2O	DMSO	HOAc	MeOH	EtOH	n-BuOH	CH_3CONH_2	$CHONH_2$	CH_3CN	DMF	Pyr.
$HClO_4$	†	†	4·85						†		3·1
H_2SO_4 (I)	†	†	7·25						7·25		
HBr			6·1–6·7	(0·8)	1·7				5·5	1·8	
HCl		†	8·6	(1·2)	2·1	3·1; 2·3			8·9	3·2	6·15
HNO_3			9·4	3·2	4·0				8·9		4·3
HPic	0·29	−1·9		3·8	4·1	4·2		(1·2)	8·9	2·9	
$Cl_2CHCOOH$	1·3			6·3	6·9	7·4		2·85–2·6			
2,4-$(NO_2)_2C_6H_3COOH$	1·43						2·9				
o-$NO_2C_6H_4COOH$	2·17			7·6	8·3		3·9	4·3			
$ClCH_2COOH$	2·87			7·8	8·5	8·5		4·5–4·7	9·8		
Salicylic (I)	3·0			7·6	8·4		3·7	4·4–4·5			
m-$NO_2C_6H_4COOH$	3·45			8·35	8·9	9·0		5·3–5·4			
2,6-$(NO_2)_2C_6H_3OH$	3·71			7·7				4·2			5·2
$(C_6H_5)_2CHCOOH$	3·94			9·4	10·1						
C_6H_5COOH	4·21	10·0		9·4	10·1	9·2	5·7	6·2–6·3	12·0	10·85	
$C_6H_5CH_2COOH$	4·3			9·5	10·2						
HOAc	4·75	11·4		9·7	10·4	9·4		6·8			
$PyrH^+$	5·22		8·35								
p-$NO_2C_6H_4OH$	7·15							8·5		11·0	
C_6H_5OH	9·99			14·0							

* The values of pK_a are taken from reference 10.

† Exhibits "strong" acid behaviour.

Reaction (10) is assumed to involve hydrogen atoms at the mercury surface and hydrogen ions in the solution with the H_2^+ ions at the surface of the electrode being rapidly discharged or reduced to molecular hydrogen

$$H_2^+ + e \rightarrow H_2 \tag{11}$$

Although the current-potential equation derived on this basis fits the experimental facts, doubt has been raised concerning the correctness of the proposed mechanism.[33]

Frumkin has suggested a mechanism, in which the slow step is the reduction of hydrogen ion to adsorbed atomic hydrogen

$$H^+ + e \rightarrow H_{ads} \tag{12}$$

This is followed by the rapid reaction

$$H_{ads} + H^+ + e \rightarrow H_2(g) \tag{13}$$

The various mechanisms advanced for the hydrogen electrode reaction have been critically reviewed by Horiuti,[24] who has also considered the relative roles of catalytic and electrochemical processes at the electrode. Breiter[8] has discussed the kinetics of hydrogen evolution and dissolution at activated platinum metals.

Kinetic waves

The situation with respect to the kinetically-controlled currents observed in the reduction of weak acids, due to the dissociation equilibria of such acids and the generally considerably easier reduction of the undissociated acid, HA, than that of the corresponding anion, A^-, is well known and has recently been ably reviewed by Brdička, Hanuš and Koutecký.[7]

Catalytic hydrogen waves

Catalytic hydrogen waves at the dropping mercury electrode have been discussed at length in the polarographic literature. In general, such waves have been assumed to be caused by the presence of an alternate path for the reduction of hydrogen ion, which has a lower activation energy than the normal process on mercury and therefore shows a lower hydrogen overpotential. The reaction path is usually assumed to be of the following type:

$$H^+ + Cat \rightleftharpoons (H{\cdot}Cat)^+ \tag{14}$$

$$(H \cdot Cat)^+ + e \rightarrow (H) + Cat \tag{15}$$

where the *Cat* species is constantly being regenerated and consequently may cause the reduction of hydrogen ion in amounts several times that of its own concentration. A typical "catalyst" of this type in aqueous solution would be pyridine with the intermediate species, which is reduced, being the pyridinium ion.[42,56]

The effect of metal ions and other organic species in producing such catalytic hydrogen waves is reviewed by Kolthoff and Lingane.[33]

It will be seen subsequently that in at least one organic solvent, pyridine, formation of a Lewis-type acid-base adduct between hydrogen ion and the solvent results in an overall reduction of the adduct rather than only of the hydrogen ion.

HYDROGEN ION REDUCTION IN PROTONIC SOLVENTS

Hydroxylic solvents

Of the hydroxylic solvents, water is the only one in which the polarographic reduction of hydrogen ion has been extensively studied.

Dissociation constants of a number of acids in several alcoholic solvents are tabulated in Table V. Overall dissociation constants for perchloric, picric and benzoic acids, and 2,4-dinitrophenol have been reported in t-butyl alcohol.[43]

Migal and Grinberg[45] determined the composition and stability of aquo complexes of hydrogen ion in an alcoholic medium by a polarographic method (presumably similar to the technique commonly used to determine the stability constants of complex species in aqueous media); the dissociation constants for the complex $[H(H_2O)_n]^+$ are reported to be 0·65, 0·68, 1·67 and 10·51 for $n = 1, 2, 3$ and 4, respectively, in ethanol, and 0·37, 0·33 and 3·41 for $n = 1$, 2 and 3, respectively, in methanol.

$E_{1/2}$ for solutions of "strong" acids (perchloric, hydrochloric) in ethanol-water solution containing tetramethylammonium chloride or lithium chloride background becomes more positive with increasing ethanol concentration; from the normal potential of the hydrogen electrode and the change in $E_{1/2}$, the overpotential for hydrogen ion reduction in ethanol (presumably at mercury) was estimated[59] as +0·1 V.

In a study of the kinetics of hydrogen evolution on liquid and solid mercury in methanol solution, Bockris and coworkers[6] found that the overpotential at a current density of 10^{-4} A. cm^{-2} decreases by about 15 mV at the freezing point of mercury. The heat of activation at the reversible potential was found to be about 1 kg. cal. mole^{-1} lower on solid than on liquid mercury.

Protogenic solvents

Because protogenic solvents are generally much weaker bases than water, hydrogen ion would consequently be expected to be much more easily reduced in such solvents than in water. Indeed, the standard potential for hydrogen is about 0·5 V more positive in acetic acid than in water (Table III). The differentiation of acids, which exhibit "strong" behaviour in water, by acid solvents (*cf.* Table V) has long been utilised in the titration of mixtures of such acids, *e.g.*, the titration of perchloric, hydrochloric and sulphuric acid mixtures in glacial acetic acid.

Acetic acid (99·5%) has been used as a solvent for the polarography of several cations;[1] at potentials more negative than −1·7 V *vs.* aqueous S.C.E., hydrogen is evolved from the solvent.

Dissociation constants of some acids in anhydrous formic acid have been calculated from potentiometric titration curves. Inorganic acids (presumably "strong" in water) remain strong in this solvent and are not differentiated as in acetic acid, while acetic, chloracetic, dichloracetic, salicylic and picric acids are so weak that they cannot be titrated.[53] The quinhydrone electrode, which has been reported to be quite stable and reversible in anhydrous formic acid, has been used as a polarographic anode in this solvent.[47] In general, the quinhydrone electrode functions as a hydrogen electrode in proton-active solvents, but not in solvents of low proton activity.

Kolthoff[31] has noted the general stabilisation of anions by hydrogen bonding, particularly in acid solvents,

$$A^- + HS \rightleftharpoons (AHS)^- \tag{16}$$

The stability of the resulting complex is greater than in water or hydroxylic solvents. The effect of such interaction on hydrogen reduction is apparent. Thus, H^+ or a Brønsted acid, HA, in an inert solvent may be stabilised by such conjugation, *e.g.*, whereas hydrochloric acid is readily volatilised from acetonitrile solution by a purging gas stream, addition of an excess of tetra-alkylammonium halide to form a conjugate ion, XHA^-, stabilises the solution.

In acid solvents, the reduction of hydrogen ion may proceed *via* protonated species produced on solute-solvent interaction, *e.g.*,

$$HA + HS \rightleftharpoons H_2A^+ + S^- \qquad (17)$$

where HA represents a weak acid added to the solvent HS. Basic solutes, *e.g.*, amines, may also form protonated species, *e.g.*,

$$B + HS \rightleftharpoons HB^+ + S^- \qquad (18)$$

which may lead to hydrogen evolution.

Protophilic solvents

The solvation energy of hydrogen ion in strongly basic solvents is much greater than in water. In such solvents, hydrogen ion would be present in the form of the Lewis acid-base adduct, *e.g.*, as NH_4^+ in liquid ammonia. This would result in a more negative standard potential for hydrogen—and, correspondingly, more negative half-wave potential—in such solvents than in water. The standard potential in hydrazine is about 0·9 V more negative than in water and in formamide about 0·1 V more negative (Table III).

Liquid ammonia has been carefully investigated as a solvent for polarography and voltammetry by Laitinen and collaborators.[38–41] $E_{1/2}$ for the reduction of ammonium ion at −36° is −1·37 V *vs.* Pb—0·1*N* $Pb(NO_3)_2$ reference electrode;[41] the reduction product was thought to be free ammonium stabilised by amalgam formation.

Hammer and Lagowski[21] reported a half-wave potential of +1·0 V *vs.* the "electron electrode" for the reduction of ammonium salts in liquid ammonia at a rotated platinum electrode at −77°. Solutions of several ammonium salts gave different slopes for the i_d *vs.* C plot in 0·1*M* solutions of the sodium salt of the corresponding anion, but the same slopes in 0·1*M* sodium perchlorate solution. This behaviour was ascribed to the formation of ion aggregates, *e.g.*, ammonium perchlorate, which are reduced simultaneously with NH_4^+. Re-use of the platinum electrodes without cleaning resulted in the appearance of a dark deposit on the electrode surface accompanied by a shift of $E_{1/2}$ to more negative potential and a split in the wave; the deposit was ascribed to the formation of finely divided platinum.

Schaap and coworkers[50] have thoroughly investigated anhydrous ethylenediamine as a solvent for electrochemical studies. Comparison of limiting conductances, Λ_0, in this solvent with those for the same salts in water reveals some significant differences. For several alkali metal salts, the ratio, $(\Lambda_0)_{en}/(\Lambda_0)_{H_2O}$, has a mean value of 0·51; for silver (I) and thallium (I) salts, which solvate more strongly with the amine solvent, the mean ratio is 0·44. The ratio for hydrochloric and nitric acids is about 0·2, which indicates that hydrogen ion is more strongly solvated in the amine solvent than in water.

From the preliminary results of Schaap,[50] the standard potential for hydrogen in ethylenediamine can be estimated to be $-0{\cdot}5$ V with respect to that in water.

Schöber and Gutmann[52] reported an $E_{1/2}$ of $-2{\cdot}05$ V *vs.* N.C.E. (aq.) for ammonium chloride in anhydrous ethylenediamine containing tetraethylammonium nitrate as background electrolyte.

Several amides have been used as polarographic solvents. Formamide and acetamide, because of their highly associated nature, are relatively poor hydrogen-bonding agents.[61] If one or both of the amide hydrogens is replaced by an alkyl group, the resulting compounds should function much more readily as hydrogen-bonding agents; this view has lead to the investigation of *N*-methylacetamide and dimethylformamide (DMF) as solvents for polarography.

$E_{1/2}$ for the reduction of strong acids in *N*-methylacetamide is $-1{\cdot}53$ V *vs.* S.C.E. (aq.); the depolarisation potentials of acetic acid and ammonium ion are reported to be $-1{\cdot}70$ and $-1{\cdot}85$ V, respectively.[28]

$E_{1/2}$ for solutions of benzoic acid in DMF containing $0{\cdot}2M$ tetrabutylammonium iodide is $-1{\cdot}58$ V *vs.* the mercury pool.[60] Given and Peover[19] report two waves for benzoic acid (*cf.* Table VI) in DMF; the diffusion current constant for the first wave was about ten times that of the second wave, which was assumed to be from reduction of the undissociated acid. No wave was found for phenol.

HYDROGEN ION REDUCTION IN APROTIC SOLVENTS

The class of non-aqueous solvents most used for polarographic studies, especially for the reduction of hydrogen ion, has been that of the aprotic solvents. While many of these solvents can be considered to be "inert" for reactions involving many organic and inorganic species, there is probably no solvent which is truly inert towards hydrogen ion. The polarographic behaviour of a "strong" acid can furnish qualitative information regarding the basic properties of a solvent; thus, the levelling effect is more pronounced the more basic the solvent is compared to water, *e.g.*, the situation in pyridine subsequently discussed.

Such a levelling effect is not observed in solvents which are much weaker bases than water, *e.g.*, nitriles and ketones, with the result that the proton of a "strong" acid is much more readily reduced in such solvents than in water. In a very weakly basic solvent, the polarographic waves of "strong" acids, which overlap in water, are separated.

Acetonitrile, in which a large number of acids have been investigated, is a strongly differentiating solvent with respect to the strength of acids dissolved in it. Acids, which are "strong" and exhibit identical polarograms in water, *e.g.*, perchloric, sulphuric, hydrochloric and nitric, give separate waves in acetonitrile (Table VI); the diffusion currents are proportional to the acid concentration.[31] $E_{1/2}$ varies from $-0{\cdot}70$ V *vs.* S.C.E. (aq.) for perchloric acid to $-2{\cdot}3$ V for acetic acid.[12,14,32] Some polyprotic acids behave as monobasic acids at the D.M.E. in exhibiting a single polarographic wave, *e.g.*, in order of increasing (negative) $E_{1/2}$: sulphuric, oxalic and phosphoric acid; diffusion-current constants seem to decrease as $E_{1/2}$ becomes more negative.[12] Controlled potential electrolysis of perchloric or acetic acid on the crest of the wave results in hydrogen evolution; perchlorates of aromatic amines give reduction waves with hydrogen evolution.[12] Addition of an excess of free base apparently has no effect. $E_{1/2}$ for dichloranilinium ion is $0{\cdot}06$ V less negative than $E_{1/2}$ for hydrochloric acid and

TABLE VI.—POLAROGRAPHIC DATA FOR THE REDUCTION OF ACIDS IN NON-AQUEOUS SOLVENTS

Solvent	Background	Electrode	Acid	Concn., m*M*	$-E_{1/2}$, *V*	Ref. elect.	I††	Ref.
Acetic anhydride*	0·1*M* $NaClO_4$	Pt	$HClO_4$		0·5†	Hg/Hg_2OAc_2		44
	0·1*M* $NaClO_4$	Pt	HBF_4		0·9†	Hg/Hg_2OAc_2		44
	0·1*M* $NaClO_4$	Pt	H_2SO_4		1·0†	Hg/Hg_2OAc_2		44
	0·1*M* $NaClO_4$	Pt	HCl		1·4†	Hg/Hg_2OAc_2		44
	0·1*M* $NaClO_4$	Pt	HOAc		1·7†	Hg/Hg_2OAc_2		44
Acetone	0·1*M* Et_4NClO_4	DME	$HClO_4$	1	0·68	SCE (aq.)	3·5	15
	0·1*M* Et_4NClO_4	DME	H_2SO_4	1	1·16	SCE (aq.)	2·7	15
			$+H_2O$	20				
Acetonitrile	Et_4NClO_4	DME	NH_4ClO_4		1·83	SCE (aq.)	3·05	32
	0·1*M* Et_4NClO_4	DME	$HClO_4$	1	0·70	SCE (aq.)	3·04	12
	0·1*M* Et_4NClO_4	DME	HBr		0·90	SCE (aq.)		12
	0·1*M* Et_4NClO_4	DME	2,5-$Cl_2C_6H_3NH_3ClO_4$	1	1·00	SCE (aq.)	2·55	12
	0·1*M* Et_4NClO_4	DME	HCl		1·06	SCE (aq.)		12
	0·1*M* Et_4NClO_4	DME	*p*-$CH_3C_6H_4SO_3H$	1	1·20	SCE (aq.)	2·47	12
	0·1*M* Et_4NClO_4	DME	H_2SO_4	1	1·20	SCE (aq.)	2·81	12
	0·1*M* Et_4NClO_4	DME	2,5-$Et_2C_6H_3NH_3ClO_4$	1	1·43	SCE (aq.)	2·51	12
	0·1*M* Et_4NClO_4	DME	$H_2C_2O_4$	1	1·55	SCE (aq.)	2·06	12
	0·1*M* Et_4NClO_4	DME	H_3PO_4	1	1·75	SCE (aq.)	1·47	12
	0·1*M* Et_4NClO_4	DME	C_6H_5COOH	1	2·1	SCE (aq.)	1·95	12
	0·1*M* Et_4NClO_4	DME	HOAc	1	2·3	SCE (aq.)		12
	0·1*M* Et_4NClO_4	DME	$HC_2O_4^-$	1	No wave	SCE (aq.)		12
	0·1*M* Et_4NClO	DME	NH_4ClO_4		1·83	SCE (aq.)		14
Ammonia (liq.)	Satd. Bu_4NI	DME	NH_4NO_3	0·3	1·37	Pb/0·1*M* $PbNO_3$, NH_3 (−36°)	2·8 ± 0·2 (i_d/C)	41
	Satd. Bu_4NI	DME	NH_4NO_3	0·3	1·06	NHE, NH_3 (−36°)		41
	0·1*M* $NaClO_4$	RPE	NH_4ClO_4	1·78	−1·0	Pt/Na° (0·001*M*), NH_3(l) (−77°) (electron electrode)		21
Dimethyl-formamide	0·2*M* n-Bu_4NI	DME	C_6H_5COOH	3	1·58	Hg pool	2·25 (i_d/C)	60
		DME	C_5H_5COOH		(I)1·27	Hg pool	1·5	19
					(II)1·7	Hg pool	0·15	19
		DME	C_6H_5OH		No wave			19

Dimethylsulphoxide	0·1*M* Et_4NClO_4	DME	H_2SO_4		1·06	SCE (aq.)		34
	0·1*M* Et_4NClO_4	DME	HCl		1·08	SCE (aq.)		34
	0·1*M* Et_4NClO_4	DME	HSO_4^-		No wave	SCE (aq.)		34
	0·1*M* Et_4NClO_4	DME	HOAc		*ca.* 2·3	SCE (aq.)		34
	0·1*M* $NaClO_4$	DME	$HClO_4$	8·9	1·06	SCE (aq.)	1·3 (t = 30°)	34
	0·1*M* $NaClO_4$	RPE	H_2SO_4		0·67 ± ·02	SCE (aq.)		34
	0·1*M* $NaClO_4$	RPE	HCl					
	0·1*M* $NaClO_4$	RPE	$HClO_4$					
		DME	HCl		1·12	SCE (aq.)		16
		DME	H_2S		1·66	SCE (aq.)		16
	0·1*M* Et_4NClO_4	DME	NH_4NO_3		2·45	SCE (aq.)		20
Ethylenediamine	Et_4NNO_3	DME	NH_4Cl		2·05	NCE (aq.)		52
Isobutyronitrile	0·05*M* Et_4NClO_4	DME	$HClO_4$	0·6	0·62 ± 0·02	SCE (aq.)		11
N-Methylacetamide		DME	H^+ (str. acid)	1	1·53	SCE (aq.)		28
		DME	HOAc		1·70‡	SCE (aq.)		28
		DME	NH_4^+		1·85‡	SCE (aq.)		28
Pyridine	0·1*M* $LiClO_4$	DME	CF_3COOH	0·07–4·3	1·30 ± 0·02**	NAgE	2·04 ± 0·10	54
	0·1*M* $LiClO_4$	DME	C_6H_5COOH	0·14–13·9	1·36 ± 0·04**	NAgE	2·23 ± 0·25	54
	0·1*M* $LiClO_4$	DME	HOAc	0·31–15·7	1·39 ± 0·03**	NAgE	2·01 ± 0·07	54
	0·1*M* $LiClO_4$	DME	2,4-$Cl_2C_6H_3OH$	0·5–2·1	1·36 ± 0·04**	NAgE	1·78 ± 0·13	54
	0·1*M* $LiClO_4$	DME	Salicylic	1·0–6·9	1·22 ± 0·04**	NAgE	1·80 ± 0·07	54
	0·1*M* $LiClO_4$	DME	H_2SO_4	0·09–9·3	1·35 ± 0·03**	NAgE	3·26 ± 0·55	54
	0·1*M* $LiClO_4$	DME	Phthalic	1·0–9·8	1·36 ± 0·01**	NAgE	3·48 ± 0·24	54
Tetrahydrofuran	0·3*M* $LiClO_4$	Pt	$HClO_4$	3	*ca.* 0·8	Ag/Ag^+		2
		Pt	$HClO_4$	6	*ca.* 0·8	Ag/Ag^+		2
		Hg	$HClO_4$	10	*ca.* 1·6	Ag/Ag^+		2

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* Also contains 0·05–0·2*M* HOAc.

† Reduction potentials from chronopotentiograms at current density of 4 mA/cm^2.

‡ These potentials were reported by the authors as depolarisation potentials

** A prewave is also found at −1·10 V *vs.* NAgE.

†† Diffusion current constant: $I = i_d/Cm^{2/3}t^{1/6}$.

0·4 V less negative than $E_{1/2}$ for diethylanilinium ion, which is a much weaker acid.[12] $E_{1/2}$ for ammonium ion is 0·8 V more negative than that for dichloranilinium ion.[14,32] No waves are observed for bisulphate and bioxalate ions.[12]

The voltammetry of the hydrogen-perchloric acid system in acetonitrile has also been studied at platinised platinum electrodes.[57]

The reduction of perchloric acid in acetonitrile has been made the basis of an analytical method for the amperometric titration of bases, *e.g.*, amines, dissolved in acetonitrile by means of a standard solution of perchloric acid in acetic acid.[31]

Addition of water, which is a much stronger base than acetonitrile, to acetonitrile solutions of a "strong" acid shifts the polarographic wave of the latter to a more negative potential.[31,58] The effect is much larger than expected from the difference in base strength and is probably caused by the hydrogen overpotential on mercury increasing with water concentration.[31]

Kolthoff and Thomas[36] report the hydrogen electrode to be suitable for the measurement of hydrogen ion activity in mixtures of sulphuric acid and tetraethylammonium bisulphate in acetonitrile.

In acetone containing $0{\cdot}1M$ tetraethylammonium perchlorate, $E_{1/2}$ is 0·48 V more positive for perchloric acid than for sulphuric acid and the diffusion current constant is about 30% greater for perchloric acid than for sulphuric acid (Table VI).[15] $E_{1/2}$ for perchloric acid shifts to a more negative potential on the addition of water.

Dimethylsulphoxide, as had been mentioned, is a much weaker acid than is water, but is comparable to water in base strength.[35] Consequently, as might be expected, perchloric, sulphuric and hydrochloric acids are "strong" in dimethylsulphoxide and furnish identical polarograms at the D.M.E. as well as at the rotating platinum electrode (R.P.E.) (Table VI); $E_{1/2}$ for these acids is about 0·4 V more positive at platinum than at mercury.[34] $E_{1/2}$ for hydrogen sulphide at the D.M.E. is about 0·6 V more negative than for the "strong" acids;[16] acetic acid[24] and ammonium ion[20] behave as weak acids in this solvent (Table VI); no wave is observed for bisulphate ion.[24]

The chronopotentiometry of several acids was investigated in acetic anhydride solutions, which were $0{\cdot}1M$ in sodium perchlorate and $0{\cdot}05$–$0{\cdot}2M$ in acetic acid.[44] Reduction (presumably chronopotentiometric quarter-wave) potentials at a platinum electrode increased, *i.e.*, became more negative, in the following order: perchloric, tetrafluoboric, sulphuric, hydrochloric and acetic acids (Table VI). Chronopotentiometry of the solvent, which, as indicated, contained acetic acid, produced hydrogen gas and acetate ions at the cathode, and hydrogen gas and acetylium ions at the anode;[44] the production of hydrogen gas at both electrodes was explained on the basis of proposed reaction intermediates.

In unbuffered 80% dioxan-water solution, $E_{1/2}$ of mineral acids varies with the dissociation constant of the acid.[46] For solutions more concentrated than $1{\cdot}5mM$ in weak acid (not specified), the polarogram exhibited three steps, which were attributed to successive reduction of the dioxan-oxonium ion, hydronium ion and the undissociated weak acid.[46]

$E_{1/2}$ for a solution of perchloric acid in tetrahydrofuran containing $0{\cdot}3M$ lithium perchlorate is reported to be 0·8 V more negative at a mercury electrode than at platinum (Table VI).[2]

Pyridine, because of its strong Lewis-base character, exhibits an apparently even more pronounced levelling effect than water. An essentially identical polarographic wave is obtained[54] for pyridine solutions of acids, whose pK_a values in aqueous solution vary from 7·9 to "very strong"; a small prewave is attributed to an impurity in the solvent, which reacts similarly to the solvent. Dibasic acids, such as sulphuric and phthalic, give a single wave, whose diffusion current constant is somewhat less than twice that found for all of the monobasic acids. Phenol (aqueous $pK_a = 9{\cdot}9$) does not give a wave; salicylic acid (aqueous $pK_a = 3{\cdot}0$ and $13{\cdot}0$) behaves like a monobasic acid. The polarographic wave was attributed to the reduction of pyridinium ion, formed in the reaction of acid with the solvent, by a one-electron attack on the pyridine ring, which results in the formation of a free radical, $pyrH^\circ$, which dimerises to a tetrahydrobipyridyl.

The latter mechanism is apparently not affected by the addition of water, up to about 10% by volume; at water concentrations above 50%, the reduction seems to proceed by the catalytic hydrogen evolution process observed in aqueous acid solutions containing traces of pyridine.[17]

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Zusammenfassung—Die polarographische Reduktion von Wasserstoffionen, gebildet durch Dissoziation einer Brønstedsäure oder gegenwärtig in der nicht dissoziierten Brønstedsäure wird erörtert für Systeme, in welchen ein organisches Lösungsmittel anstelle von Wasser vorliegt.

Résumé—On passe en revue la réduction polarographique de l'ion hydrogène, fourni par la dissociation d'un acide de Brønsted ou présent dans l'acide de Bronsted non dissocié, lorsqu'on met en jeu un solvant autre que l'eau.

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DIE BEDEUTUNG DER ADSORPTION IN DER POLAROGRAPHIE

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Zusammenfassung—In der vorliegenden Arbeit werden die wichtigsten Phänomene diskutiert, die als Folge der Adsorption an der Phasengrenze Metall/Elektrolytlösung bei polarographischen Untersuchungen in Erscheinung treten.

EINLEITUNG

IN der neueren polarographischen Literatur, vor allem bei der Beschreibung der Phänomene bei organischen Depolarisatoren, begegnet man häufig der Bemerkung, die Stromspannungskurven weisen auf "Komplikationen durch Adsorption" hin, ohne daß hierüber näheres ausgeführt wird. Man kann hieraus zweierlei entnehmen: einerseits hat sich offenbar die (wohlbegründete) Vermutung, daß die Adsorption in der Polarographie (wie überhaupt bei Elektrodenvorgängen) eine weitverbreitete und folgenreiche Erscheinung ist, durchgesetzt; zum anderen mag die Vielfalt der hierauf beruhenden Phänomene von einer eingehenderen Beschäftigung mit dieser Problematik zurückschrecken lassen. Es erscheint uns daher nützlich, die wesentlichen Gesichtspunkte dieser Vorgänge im Zusammenhang darzustellen, die theoretischen Aspekte zu umreissen und—vor allem anhand eigener Untersuchungen—zu veranschaulichen.

Es würde den Rahmen einer Zeitschriften-Abhandlung sprengen, wollte man die historische Entwicklung zu diesem Thema darstellen oder gar die hierauf bezügliche Literatur halbwegs vollständig berücksichtigen. (Vor allem in den letzten Jahren ist die Zahl der Arbeiten stark angewachsen, mag zur Zeit schon über 1000 betragen und vergrößert sich täglich.) Es kann hier auf einige Zusammenfassungen aus den letzten Jahren verwiesen werden,* wenngleich Auswahl und Berücksichtigung der Literatur-vielleicht mit Ausnahme von ref. 168—nicht immer befriedigt. Andere Arbeiten befassen sich mit Teilproblemen, so etwa die ausführlichen Übersichten über die katalytische Wasserstoffentwicklung[156] bzw. den Adsorptionseinfluß auf die Wasserstoffüberspannung allgemein.[59] (Auf Einflüsse der Adsorption bei Vorgängen an festem Elektrodenmaterial, z.B. bei der Elektrokristallisation[43,118] oder der Wasserstoffentwicklung[44,45,61] kann hier nur beiläufig hingewiesen werden. Diese Erscheinungen, die große Ähnlichkeiten mit denjenigen am Quecksilber zeigen, jedoch auch charakteristische Unterschiede auf Grund der Eigentümlichkeiten der Oberfläche fester Stoffe, sind vor allem von praktischer Bedeutung bei Fragen der Korrosion bzw. des Korrosionsschutzes, des Beizens und der galvanischen Überzüge.)

Es soll jedoch einleitend darauf hingewiesen werden, daß die ersten Ansätze zu den wesentlichen auf Adsorption beruhenden Erscheinungen in der Polarographie

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* vergl. ref. 18, 25, 37, 55, 58, 62, 168, 173, 178, 180.

auf Heyrovský und seine Schule zurückgehen; so etwa die Entdeckung der "polarographischen Maxima" und ihrer Beeinflussung durch Zusatzstoffe[40] oder die Entdeckung der katalytischen Wasserstoffwellen,[77] die dann besonders von Brdička[17] näher untersucht wurden. Letzterer entdeckte auch die "Adsorptionsstufen" und entwickelte ihre Theorie.[16] Schon in einer 1934 erschienenen Schrift sah Heyrovský[78] in der Adsorption des elektroaktiven Teilchens einen Teilvorgang der Elektrodenprozesse, wenn auch damals noch nicht alle Phänomene richtig zugeordnet werden konnten. Auch die Erforschung der Inhibitorwirkung adsorbierter Zusatzstoffe verdankt ihm schon in ihren Anfängen einige bedeutende Arbeiten,[79,80] in denen u.a. bereits der Gedanke der Hemmung chemischer Reaktionen in der Grenzfläche sowie der Reduktionserleichterung von Kationen durch adsorbierte Anionen ausgesprochen wird.

Zum Problem der Inhibitorwirkung adsorbierter Zusatzstoffe seien hier nur die wichtigeren anfänglichen Arbeiten anderer Autoren genannt* sowie die eigenen Untersuchungen,[85,86] welche den Inhibitoreinfluß auf die Reduktion aromatischer Nitroverbindungen aufzeigten und die uns in der Folge zu einem gründlicheren Studium dieser Erscheinungen führten;[89,90,106–7,111–4] im wesentlichen hierauf basieren die Darstellungen in dieser Arbeit.

Welcher Art sind nun die Folgen der Adsorption für den Ablauf der Elektrodenvorgänge? Es soll hier kurz skizziert werden, daß diese Einflüsse sowohl thermodynamischer wie kinetischer Natur sein können.

Ein seinem Wesen nach thermodynamischer Effekt liegt bei den "Adsorptionsstufen"[16] vor: Ist ein reversibler Reduktionsvorgang mit einer kräftigen Adsorption des Reduktionsproduktes verbunden, so erfolgt eine thermodynamisch bedingte Reduktionserleichterung, d.h. eine Verschiebung des Reduktionspotentials zu positiveren Werten nach Maßgabe der Adsorptionsenergie; jedoch ist der Effekt der Menge (Stromstärke) nach durch die Zahl der adsorbierbaren Teilchen, mithin durch die Größe der Elektrode (und deren Zeitabhängigkeit) sowie die Adsorptionsisotherme begrenzt. Eine entsprechende Erschwerung erfolgt bei starker Adsorption der oxydierten Form (und im Falle eines Oxydationsvorgangs vice versa).

In kinetischer Hinsicht kann die Adsorption der Reaktionspartner sowie diejenige anderer Lösungsbestandteile praktisch auf jeden Teilschritt des Elektrodenvorgangs Einfluß nehmen. Da die Adsorption die Zusammensetzung der Grenzschicht und die Struktur der Doppelschicht verändert, beeinflußt sie jeden Teilschritt, der sich an der Grenzfläche selbst abspielt, also sowohl den Ladungsübergang und chemische Reaktionen an dieser Stelle wie auch die Adsorptionsvorgänge selbst. Diese Wirkungen sind Gegenstand der Ausführungen in den folgenden Abschnitten.

Es soll jedoch an dieser Stelle noch darauf hingewiesen werden, daß die Wirkung der Adsorption nicht nur auf die unmittelbar an der Phasengrenze ablaufenden Prozesse beschränkt ist, sondern durch Sekundäreffekte auch solche Vorgänge betreffen kann, die in einer gewissen Entfernung von der Phasengrenze stattfinden. Hier sind zunächst die "polarographischen Maxima" zu nennen, die auf tangentialen Bewegungen der Grenzfläche und dadurch erhöhtem konvektiven Stofftransport beruhen.[5,187] Die Adsorption von "Maximadämpfern" beseitigt die Bewegung der Grenzfläche und damit auch die Konvektion der Lösung. (Hierzu vergleiche man zusammenfassende Referate.[169,188,203]) Eine weitere Folge der Adsorption beruht

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* vergl. ref. 115, 121, 123, 129–30, 149–51, 160, 176–7, 185, 200.

darauf, daß sich der Inhomogenitätsbereich der Phasengrenze in Form des diffusen Teiles der Doppelschicht über die eigentliche Grenzschicht hinaus—zumal bei niedrigen Elektrolytkonzentrationen—mehr oder weniger weit in die Lösung erstreckt. Adsorbierte Neutralmoleküle verringern gewöhnlich die Doppelschichtkapazität, verschrieben das Nulladungspotential und ändern dadurch die Elektrodenladung und den Potentialverlauf in der Doppelschicht. Die Adsorption grenzflächenaktiver Ionen kann—infolge des durch sie verursachten Potentialsprunges an der Phasengrenze—u.U. eine Vorzeichenumkehr der Raumladung in der Doppelschicht und damit auch des örtlichen Potentials hervorrufen. In beiden Fällen erfolgt daher eine Beeinflussung derjenigen Vorgänge, die durch das örtliche Potential bzw. die Feldstärke mitbestimmt werden. Dies betrifft zunächst chemische Reaktionen, an denen Ionen beteiligt sind, sofern sie so rasch verlaufen, daß die "Reaktionsschicht" und die diffuse Doppelschicht von vergleichbarer Größe sind; die Ursache liegt vor allem in der Potentialabhängigkeit der Ionenkonzentration. Mit dieser Frage haben sich besonders Gierst und Hurwitz[66,97] sowie Matsuda[157] befaßt (vergl. auch ref. 18, 125–6). Die Feldstärke in der diffusen Doppelschicht beeinflußt den Transport von Ionen, wenn das Produkt aus Ionenladung und Potentialgradient das entgegengesetzte Vorzeichen hat wie der Konzentrationsgradient, wenn also beim Transport eine elektrostatische Abstoßung überwunden werden muß. Auf diesen sogenannten "dynamischen ψ-Effekt" hat zuerst Levich[140–1] hingewiesen (vergl. auch die oben zitierten Arbeiten von Gierst und Hurwitz).

Schließlich sei noch bemerkt, daß enge Beziehungen zur Adsorption an anderen Phasengrenzen bestehen, etwa an der Grenze Lösung/Luft[49] oder Lösung/Ionenaustauscher.[67] Verschiedentlich ist die Adsorption an Quecksilber bzw. die Wirkung als Maximadämpfer mit der "Mizellbildung"[24,161] oder der Wirkung als Korrosionsinhibitoren[63,99,14] verglichen worden; auch die heterogene Katalyse von Gasreaktionen wurde in diesem Sinne mit Elektrodenprozessen verglichen.[179] Die auf der charakteristischen Oberflächenstruktur fester Metalle beruhenden Unterschiede der Adsorption an diesen und am Quecksilber wurden oben schon erwähnt; sie können weiterhin auch dadurch bedingt sein, daß—z.B. bei aromatischen Verbindungen—bei der Adsorption eine π-Elektronen-Wechselwirkung mit Quecksilber, nicht aber etwa mit Eisen betätigt wird.[62]

ADSORPTION DER REAKTIONSPARTNER

Das charakteristische Merkmal der Adsorption (die hier gleichbedeutend mit dem Terminus "spezifische Adsorption" verstanden wird) besteht darin, daß die unmittelbare Umgebung des adsorbierten Teilchens anders ist als im Lösungsinnern, daß sie also—zumindest teilweise—nicht mehr aus Lösungsmittelmolekülen besteht. (Insofern sollen daher Ionen, die mit ihrer Solvathülle in der äußeren Helmholtzschicht angereichert werden, nicht als "adsorbiert" angesehen werden.) Ob dabei besondere Wechselwirkungen mit dem Metall stattfinden (vergl. Abschnitt 3), ist hierfür ohne Belang. Einen solchen Zustand können offenbar alle Lösungsbestandteile erreichen; bei organischen Stoffen und einer Vielzahl anorganischer Anionen liegt bekanntlich ein ausgeprägtes Bestreben zur Adsorption vor. Aber selbst bei den schwer polarisierbaren Anionen (F^-) und den kleineren Alkalikationen (Na^+, K^+) ist diese Möglichkeit gegeben,[1] wenn auch die Grenzflächenkonzentrationen in diesem Falle gering sind, sodaß die Adsorption nicht unmittelbar nachzuweisen ist. (Beim Ion Cs^+ ist sie jedoch bereits merklich.[27,56–7])

Da die Möglichkeit zur Adsorption demnach ganz allgemein vorhanden ist und da andererseits für einen Ladungsaustausch zwischen Elektrode und adsorbiertem Teilchen offenbar besonders günstige Umstände vorliegen, erscheint die Annahme vernünftig, daß dem Ladungsübergang die Adsorption des Depolarisators im allgemeinen vorausgeht,[4,41,107,134,179] wobei es keinen grundsätzlichen Unterschied macht, ob die Adsorption (die mit einer "Desolvatation" im wesentlichen identisch sein kann) dem Ladungsübergang als Gleichgewicht vorgelagert oder selbst Teil des geschwindigkeitsbestimmenden Vorgangs ist.[7] Die Frage, ob der Ladungsübergang die Adsorption des Depolarisators voraussetzt, wurde allerdings zuweilen auch verneint.[89] So wird für die Reduktion von Anionen bei recht negativen Elektrodenpotentialen, bei denen der "dynamische ψ-Effekt"[140] den Anionen den Zugang zur Elektrode verwehrt, ein "Tunneln" der Elektronen durch die Doppelschicht in Erwägung gezogen,[52] obgleich sich diese Erscheinungen auch durch die Bildung von Ionenpaaren erklären läßt (die unserer Meinung nach wahrscheinlicher ist, vergl. weiter unten).

Abgesehen von den bereits erwähnten "Adsorptionsstufen" (die thermodynamisch und—außer durch Transport und Tropfenwachstum—nicht kinetisch bedingt sind, vergl. Abschnitt 1) erhebt sich nun die Frage, wie die Kinetik der Vorgänge, im Effekt also die Stromstärke, zu formulieren ist. Hier ist zu unterscheiden nach dem geschwindigkeitsbestimmenden Grenzflächenprozess: Ladungsübergang, chemische Reaktion, Adsorptionsvorgang. Der letztere Vorgang ist bei gewöhnlichem polarographischen Arbeiten im allgemeinen nicht geschwindigkeitsbestimmend; dies kann jedoch u.U. der Fall sein, wenn ein stark adsorbierter Inhibitor dem Zutritt des Depolarisators Schwierigkeiten bereitet, vergl. hierzu Abschnitt 4. In den beiden anderen Fällen ist das Adsorptionsgleichgewicht als eingestellt anzusehen, d.h.

$$\Gamma = f(c) \tag{1}$$

(Γ = Grenzflächen-, c = Lösungskonzentration, wobei im Falle einer transportbedingten Konzentrationspolarisation für c die Konzentration in Grenzflächennähe $c_{x=0}$ zu setzen ist). Die Funktion (1) ist die Adsorptionsisotherme, vergl. Abschnitt 3. Für die Stromstärke i ist—ob es sich nun um langsamen Ladungsübergang oder langsame chemische Reaktion in der Grenzfläche handelt—die Beziehung[3,107]

$$i = zFqk\Gamma \tag{2}$$

anzusetzen (z = Zahl der übertragenen Ladungen, F = Faraday-Konstante, q = Elektrodenfläche). Die Geschwindigkeitskonstante k ist entweder diejenige des Ladungsübergangs oder der chemischen Reaktion und enthält im letzteren Falle noch die Grenzflächenkonzentration des Reaktionspartners (die ebenfalls durch eine Beziehung wie (1) darzustellen ist). Bei schwacher Adsorption, wenn eine lineare Adsorptionsisotherme

$$\Gamma = \gamma \cdot c \tag{3}$$

gültig ist (γ = Adsorptionskoeffizient), geht die Formulierung (2) in die gewöhnlich verwendete Beziehung

$$i = zFqk\gamma c \tag{4}$$

über; handelt es sich um einen geschwindigkeitsbestimmenden Ladungsübergang, so soll die Geschwindigkeitskonstante durch $\overrightarrow{k}$ bezeichnet werden und das Produkt $(\overrightarrow{k} \cdot \gamma)$ ist mit der als "Durchtritts-Geschwindigkeitskonstante" bezeichneten Größe identisch.

Ist die Adsorption jedoch stärker, sodaß keine lineare Beziehung (3) mehr gilt, dann besteht auch keine Proportionalität zwischen Strom und Konzentration nach (4) mehr; die Lage der polarographischen Kurven wird daher konzentrationsabhängig. Im Extremfall, wenn nämlich schon bei geringen Lösungskonzentrationen die maximale Grenzflächenkonzentration Γ_{max} erreicht wird, wird die Stromstärke bei vorgegebenem Potential

$$i = zFqk\Gamma_{max} \qquad (5)$$

von der Lösungskonzentration überhaupt unabhängig (solange die Konzentrationspolarisation das Erreichen von Γ_{max} nicht verhindert, d.h. solange der Strom merklich kleiner als der Diffusionsgrenzstrom ist). Ein Beispiel für solches Verhalten ist in Abb. 1 gezeigt: vom Auftreten strömungsbedingter Maxima abgesehen ist die Stromstärke unterhalb des Grenzstromes von der Lösungskonzentration unabhängig, sodaß das Halbstufenpotential mit wachsender Konzentration zu negativen Werten verschoben wird.

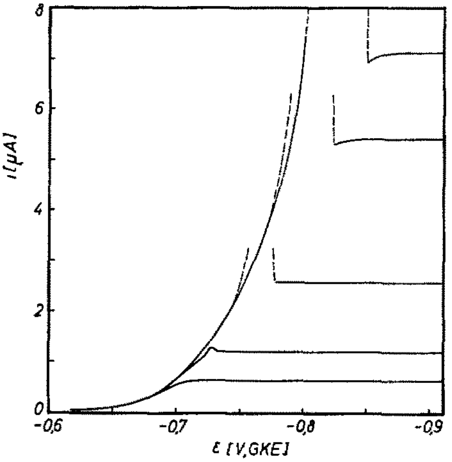

Abb. 1.—Stromspannungskurven von Methylorange (Anion der *p*-Dimethylamino-azobenzol-*p'*-sulfonsäure) bei verschiedenen Konzentrationen: 0,12; 0,24; 0,55; 1,16; 1,53 .10^{-3} Mol/1.

Ist die maximale Grenzflächenkonzentration nicht ganz erreicht (ist also der Bedeckungsgrad $\theta = \Gamma/\Gamma_{max} < 1$), so ist Gleichung (2) anzuwenden, jedoch kann Γ über einen breiten Potentialbereich nahezu konstant bleiben (vergl. Abschnitt 3). Die Stromstärke ist dann in der Weise potentialabhängig wie die Konstante k, die ihrerseits bei geschwindigkeitsbestimmendem Ladungsübergang für nicht zu kleine Werte von θ vom Bedeckungsgrad praktisch unabhängig ist, da die Umgebung für den Ladungsübergang nahezu gleich bleibt. Jedoch wurde von Frumkin[62] auch der Fall beobachtet, daß k bei Annäherung an $\theta = 1$ kleiner wird; diese Beobachtung wurde damit gedeutet, daß der Übergangskomplex mehr Platz benötigt als das adsorbierte Depolarisatorteilchen, sodaß seine Bildung bei wachsender Bedeckung und damit Verringerung des einem Molekül verfügbaren Platzes erschwert wird.

Ist der Bedeckungsgrad wesentlich von 1 verschieden, so muß seine Potentialabhängigkeit berücksichtigt werden. (Dies ist u.a. bei pH-abhängigen Halbstufenpotentialen zu beachten.[87]) Vereinfachend sei der Fall schwacher Adsorption betrachtet, für den eine lineare Isotherme (3) gültig ist. Die Potentialabhängigkeit des Adsorptionskoeffizierten γ kann (vergl. Abschnitt 3) im wesentlichen durch eine Beziehung

$$\gamma = \gamma_{\mathrm{m}} \cdot \exp\left[-\beta(\varepsilon - \varepsilon_{\mathrm{m}})^2\right] \tag{6}$$

beschrieben werden, wobei γ_{m} den Maximalwert angibt, den γ beim Potential ε_{m} erreicht. Bestimmt der Ladungsübergang die Kinetik und kann man für seine Geschwindigkeitskonstante die Beziehung (für eine Reduktion formuliert)

$$\vec{\mathrm{k}} = \vec{\mathrm{k}}_0 \cdot \exp\left[-\frac{\alpha \mathrm{zF}}{\mathrm{RT}}(\varepsilon - \varepsilon_0)\right] \tag{7}$$

ansetzen, so zeigt sich beim Einsetzen von (6) und (7) in Gleichung (4), daß die Stromstärke

$$\mathrm{i} = \mathrm{zFq}\vec{\mathrm{k}}_0\gamma_{\mathrm{m}}\mathrm{c} \cdot \exp\left[\frac{\alpha \mathrm{zF}}{\mathrm{RT}}(\varepsilon_0 - \varepsilon_{\mathrm{m}}) + \beta(\varepsilon_{\mathrm{m}} - \varepsilon_{\mathrm{i,max}})^2\right] \cdot \exp\left[-\beta(\varepsilon - \varepsilon_{\mathrm{i,max}})^2\right] \tag{8}$$

formal dieselbe Abhängigkeit vom Potential zeigt wie die Adsorption, und zwar mit einem Maximalwert bei einem Potential

$$\varepsilon_{\mathrm{i,max}} = \varepsilon_{\mathrm{m}} - \frac{\alpha \mathrm{zF}}{2\beta \mathrm{RT}} \tag{9}$$

das gegen das Potential maximaler Adsorption ε_{m} verschoben ist. Diese Verschiebung ist im allgemeinen recht beträchtlich; so werden z.B. für den Faktor β im Exponenten häufig Werte der Grössenordnung 10 V^{-2} festgestellt und daraus folgt etwa (mit $\alpha \simeq 0{,}5$, $\mathrm{z} = 1$, $\mathrm{F/RT} = 39\ \mathrm{V}^{-1}$) eine Verschiebung um 1,0 V. Aus diesem Grunde entzieht sich die Erscheinung eines hierdurch verursachten Maximums gewöhnlich der Beobachtung. Ein solcher Fall wurde etwa von Tedoradze, Ershler und Mairanovskii[192] festgestellt (vergl. auch ref. 62, 126). Auch bei der Reduktion einer Reihe anorganischer Anionen, so etwa beim PtCl_4^{2-},[54,133] bei denen der Reduktionsstrom mit negativer werdendem Potential abfällt, wird die genannte Ursache vorliegen; wegen des bei Anionen zu positiveren Werten verschobenen Potentials maximaler Adsorption muß auch das Maximum der Stromstärke bei positiveren Potentialen liegen und daher leichter zu beobachten sein als bei Neutralmolekülen.

Demgegenüber wird bei vielen anderen Anionen der Stromabfall durch einen rein elektrostatischen Effekt, den "statischen ψ-Effekt", verursacht, der von Frumkin[50] zuerst für die Reduktion des Wasserstoffions formuliert und später eingehend bei der Reduktion von Anionen untersucht wurde[47,52–4,56,60] (vergl. auch ref. 18). Er beruht in erster Linie auf der Abhängigkeit der Konzentration geladener Teilchen vom örtlichen Potential (thermodynamischer Effekt, ausgedrückt durch die Boltzmann-Funktion)

$$c_1 = c_0 \cdot \exp\left(-\frac{nF\psi_1}{RT}\right) \qquad (10)$$

(c_0 = Konzentration im Innern der Lösung, c_1 = Konzentration in der "äußeren Helmholtz-Schicht", wo das Potential ψ_1 gegenüber dem Lösungsinnern herrscht, n = Ladung des Teilchens), daneben auf der Änderung der für die Kinetik des Ladungsübergangs maßgeblichen Potentialdifferenz, sodaß in Gleichung (7) anstelle des Potentials ε die Differenz $(\varepsilon - \psi_1)$ zu setzen ist. Die Formulierung (10) bezieht sich in dieser Form zunächst auf nicht-adsorbierte Teilchen; indessen besteht kein grundsätzlicher Unterschied insofern, als es sich auch bei der Konzentration c_1 strenggenommen um eine Flächen- und nicht eine Volumenkonzentration handelt. Bei adsorbierten Teilchen, bei denen die Potentialabhängigkeit der Adsorption durch die Isotherme (3) (mit Gleichung (6)) gegeben ist, können sich Änderungen des ψ_1-Potentials (außer über die "wirksame Potentialdifferenz" $\varepsilon - \psi_1$) durch einen Einfluß auf die grenzflächennahe Lösungskonzentration $c_{x=0}$ auswirken, die in Gleichung (3) einzusetzen ist und analog zu Gleichung (10) vom ψ_1-Potential abhängen kann. Da der Potentialverlauf in der Doppelschicht und damit das ψ_1-Potential, sofern keine starke Adsorption vorliegt, wesentlich von Konzentration und Art des verwendeten Elektrolyten abhängt, ergibt sich ein Einfluß auch dieser Bedingungen auf die Geschwindigkeit.

Jedoch kann der Elektrolyt noch auf andere Weise die Geschwindigkeit solcher Elektrodenprozesse beeinflussen, an denen Ionen beteiligt sind, nämlich über die Bildung von Ionenassoziaten. Diese Erscheinung wurde in zahlreichen Arbeiten in Erwägung gezogen.* Es sind dabei zwei verschiedene Vorstellungen entwickelt worden. Im einen Falle wird angenommen, daß zwischen Elektrode und Ion ein dem letzteren entgegengesetzt geladenes Ion tritt und so den Ladungsübergang erleichtert; diese Ausbildung einer Ionenbrücke findet also unmittelbar an der Grenzfläche statt und betrifft direkt die Aktivierungsenergie des Ladungsübergangs.† Im anderen Falle wird die Bildung von Ionenpaaren, und zwar bereits im Innern der Lösung, angenommen (wobei zunächst offenbleiben mag, ob es sich dabei um rein elektrostatische Assoziate im Bjerrumschen Sinne handelt oder ob zwischen den Ionen die Solvathülle abgebaut wird). Der Verlust (bzw. die Verminderung) der Ladung bei der Assoziatbildung bewirkt eine bevorzugte Adsorption, einerseits durch die hiermit verbundene Erleichterung des Abbaus der Solvathülle, zum anderen durch Ausdehnung des Adsorptionsbereichs zu Potentialen, wo Elektrode und (nicht-assoziiertes) elektroaktives Ion gleichnamige Ladung besitzen. Die Bildung von Ionenpaaren vermag gegenüber der bloßen Vorstellung von "Ionenbrücken" auch eine plausible Erklärung für den Wiederanstieg der Reduktionsgeschwindigkeit von Anionen bei recht negativen Potentialen zu geben, der—wie bereits erwähnt—wegen des statischen ψ-Effekts zu erwarten, jedoch wegen des dynamischen ψ-Effekts

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* vergl. ref. 10, 33, 52, 56, 60, 67, 79, 81, 142, 152, 181–2, 195.

† Der Reduktionserleichterung von Metallkationen durch adsorbierte Anionen entspricht eine Erleichterung der anodischen Auflosung von Metallen ebenfalls durch adsorbierte Anionen, welche die Oberflächenatome des Metalls in einen entsprechend günstigen Polarisationszustand überführen.[120]

unmöglich sein sollte, falls ungepaarte Ionen die Doppelschicht durchqueren müßten. Eine Beteiligung von Ionenpaaren ist um so wahrscheinlicher, als ihre Bildung bekanntlich schon bei gewöhnlichen ein-einwertigen Elektrolyten durchaus merklich, bei höherwertigen Ionen aber so beträchtlich sein kann, daß die freien Ionen schon bei mäßigen Elektrolykonzentrationen in die Minderzahl geraten; besonders ausgeprägt ist dieser Effekt natürlich auch in nichtwässrigen Lösungsmitteln niedriger Dielektrizitätskonstante, wo Art und Konzentration des Elektrolyten aus diesem Grunde selbst reversible Halbstufenpotentiale beträchtlich beeinflussen.[91] Insbesondere bei der Diskussion des Elektrolyt-Einflusses auf die Geschwindigkeit des Ladungsübergangs bei mehrwertigen Ionen ist diese Erscheinung neben dem ψ-Effekt wohl oftmals zu sehr vernachlässigt worden. Daß die Assoziatbildung auch bei einwertigen Ionen angenommen werden kann, mag durch ein Beispiel eigener Untersuchungen demonstriert werden. Es handelt sich um die Reduktionsgeschwindigkeit der bei der Reduktion von Nitroverbindungen in einem reversiblen Primärakt

$$\mathrm{R{-}NO_2 + e \rightleftharpoons R{-}\overset{x}{N}O_2{}^-} \tag{11}$$

gebildeten Radikalanionen. Gestalt und Potentiallage der Stromspannungskurve werden durch das Redoxnormalpotential ${}^{N}\varepsilon$ des Vorgangs (11) und die potentialabhängige Geschwindigkeit der Weiterreduktion des Radikalanions festgelegt; dies ist durch die Beziehung

$$\frac{\mathrm{i}}{\mathrm{i_d}} = \frac{1}{1+\lambda} \cdot [1 + (3 + 4\lambda) \cdot \Psi(\eta)] \tag{12}$$

($\mathrm{i_d}$ = diffusionsbedingter Grenzstrom des 1-Elektronenvorgangs, $\lambda = \exp\,[\mathrm{F}(\varepsilon - {}^{N}\varepsilon)/\mathrm{RT}]$, $\Psi(\eta)$ = Koutecký-Funktion,[127] $\eta = \vec{k} \cdot \gamma(12\mathrm{t}/7\mathrm{D})^{1/2}/1 + \lambda)$ zu formulieren.[90,93] In Abb. 2 sind am Beispiel von *p*-Nitrochlorbenzol bei verschiedenen Elektrolytkonzentrationen beobachtete Stromspannungskurven, in Abb. 3a die hieraus mit Gleichung (12) ermittelten Werte für $\vec{k} \cdot \gamma$ wiedergegeben. (Die im Bereich um —0,7 V bei den höheren Elektrolytkonzentrationen auftretenden strömungsbedingten Maxima verhindern hier eine Berechnung: Bereich der gestrichelten Geraden in Abb. 3a.) Sowohl links wie rechts vom Knickpunkt* der Geraden im $\log(\vec{k}\gamma)/\varepsilon$—Diagramm zeigt sich eine beträchtliche Abhängigkeit der Geschwindigkeit von der Elektrolytkonzentration. Die auf das Potential ${}^{N}\varepsilon = -0{,}7$ V (GKE†) bezogenen Werte von $\vec{k} \cdot \gamma$ aus beiden Geradenzweigen weisen eine sehr gute Proportionalität mit der Elektrolytkonzentration auf (Abb. 3b; der Wert für $c_{\mathrm{Na}^+} = 1$ ist der Übersichtlichkeit halber nicht eingezeichnet; er liegt—wohl aus Gründen des verringerten Aktivitätskoeffizienten f_{Na^+}—etwas unter der Geraden). Dieser Zusammenhang läßt sich durch einen bloßen ψ-Effekt auf die Reduktion der Radikalanionen kaum quantitativ deuten, sondern ist am vernünftigsten durch die Bildung von Ionenpaaren ($\mathrm{R{-}\overset{x}{N}O_2{}^- \cdots Na^+}$) zu verstehen. Die Konzentration der letzteren ist durch das Assoziationsgleichgewicht

$$c_{\mathrm{IP}} = \mathrm{K} \cdot c_{\mathrm{RA}} \cdot c_{\mathrm{Na}^+} \tag{13}$$

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* Dieser Knickpunkt ist vermutlich dadurch bedingt, daß bei positiveren Potentialen die Sekundärreduktion in einer Umgebung adsorbierter Depolarisator-Moleküle, bei negativeren in einer solchen von Lösungsmittelmolekülen bzw. der schwächer adsorbierten Reduktionsprodukte stattfindet.

† GKE = gesättigte Kalomel-Elektrode.

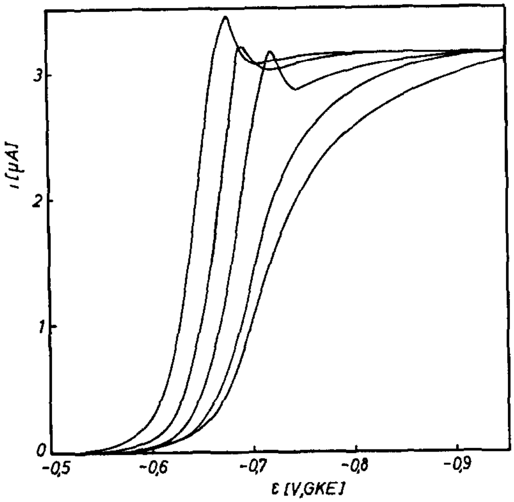

Abb. 2.—Stromspannungskurven von *p*-Nitrochlorbenzol bei verschiedenen Elektrolytkonzentrationen. Depolarisator 2 . 10^{-4} m, 30% Methanol, 0,02 n NaOH. Von links nach rechts Zusatz von 0,98 n, 0,28 n, 0,08 n, 0,02 n, 0 n NaCl.

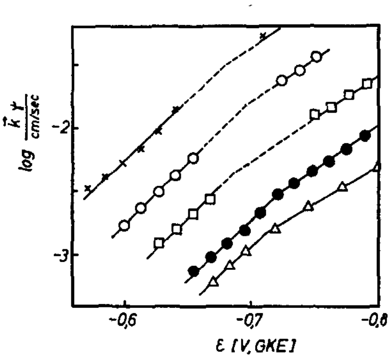

Abb. 3.—(a) Geschwindigkeitskonstante des Sekundärprozesses bei verschiedenen Elektrolytkonzentrationen, aus Abb. 2 berechnet mit Gleichung (12); c_{Na^+}: × 1,0; ○ 0,3; □ 0,1; ● 0,04; △ 0,02 Mol/l.

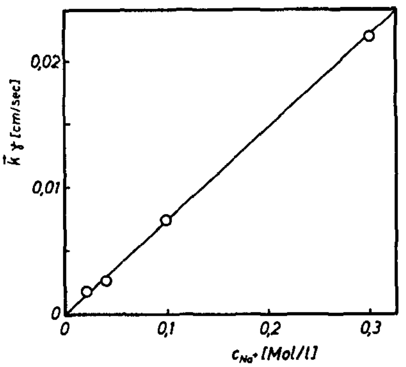

Abb. 3b.—Änderung der Geschwindigkeitskonstanten mit der Elektrolytkonzentration, aus Abb. 3a, für —0,7 V (GKE).

(IP = Ionenpaar, RA = Radikalanion, K = Assoziationskonstante) gegeben. Da sich die Formulierung von Gleichung (12) auf die (in der Lösung vorherrschenden) Radikalanionen bezieht, in Wahrheit aber die Ionenpaare den Ladungsübergang bewirken, ist das experimentell zugängliche Produkt $\vec{k} \cdot \gamma$ in der Größe η als

$$\vec{k} \cdot \gamma = \vec{k}_{IP} \cdot \gamma_{IP} \cdot K \cdot c_{Na^+} \qquad (14)$$

anzusetzen und damit—wie experimentell gemäß Abb. 3b—der Na^+-Konzentration proportional. Die Aktivität der Radikalanionen bleibt von der Ionenstärke nahezu unbeeinflußt, da sich der aktivitätserhöhende "Aussalzeffekt" und der aktivitätsmindernde elektrostatische Effekt bei steigender Ionenstärke offenbar weitgehend aufheben. Dies geht aus Tabelle I hervor, in welcher der Aktivitätskoeffizient f_N des Depolarisators aus dessen Sättigungskonzentration, das Verhältnis der Aktivitätskoeffizienten f_{RA}/f_N aus dem Halbstufenpotential der reversiblen Reaktion (11)*) mit der Beziehung

$$\varepsilon_{1/2} = {}^{N}\varepsilon - \frac{RT}{F} \cdot \ln \frac{f_{RA}}{f_N} \qquad (15)$$

(${}^{N}\varepsilon = -0{,}700$ V, GKE) ermittelt wurde.

TABELLE I.—SÄTTIGUNGSKONZENTRATION $c_{s,N}$ VON p-NITROCHLORBENZOL (BEI 4% METHANOL) UND HALBSTUFENPOTENTIAL $\varepsilon_{1/2}$ DES PRIMÄRVORGANGS (11) (BEI 30% METHANOL) SOWIE DARAUS BERECHNETE AKTIVITÄTSKOEFFIZIENTEN VON DEPOLARISATOR UND RADIKALANION BEI VERSCHIEDENEN SALZKONZENTRATIONEN

c_{Na^+} *Mol/l.*	$c_{s,N} 10^3$, *Mol/l.*	f_N	$-\varepsilon_{1/2}$, *V,GKE*	f_{RA}/f_N	f_{RA}
0,02	1,32	1,008	$0{,}699_5$	0,98	0,99
0,04	1,31	1,015	0,699	0,96	0,97
0,1	1,26	1,055	$0{,}698_5$	$0{,}94_5$	0,99
0,3	1,19	1,12	0,695	0,82	0,92
1,0	0,93	1,43	$0{,}691_5$	$0{,}71_5$	1,02

Noch augenscheinlicher ist der Einfluß der Ionenstärke im Falle der Reduktion in Gegenwart von Inhibitoren als Folge der Bildung von Ionenpaaren zu verstehen. Durch den Verdrängungseffekt des Inhibitors (vergl. hierzu Abschnitt 3) ist der Adsorptionskoeffizient γ so weit herabgesetzt, daß die Reduktion erst bei sehr viel negativeren Potentialen infolge Vergrößerung der Geschwindigkeitskonstante merklich wird.[90,107] Wie aus Abb. 4 und 5 hervorgeht, ist der Einfluß der Elektrolytkonzentration hier sogar noch größer, während ein etwaiger ψ-Effekt bedeutend kleiner als in inhibitorfreien Lösungen sein müßte. (Die Elektrodenladung ist in diesem Potentialbereich—wie aus Elektrokapillar- und Kapazitätsmessungen hervorgeht—bedeutend geringer als in Abwesenheit des Inhibitors; damit entfällt die Potentialdifferenz zu einem noch größeren Anteil auf die adsorbierte Schicht, und das ψ-Potential außerhalb derselben und seine Änderungen mit der Elektrolytkonzentration werden geringer.) Bei der Diskussion des gegenüber den inhibitorfreien Lösungen erhöhten Einflusses der Elektrolytkonzentration muß man berücksichtigen, daß neben der Zunahme der Ionenpaarbildung durch Erhöhung der Elektrolytkonzentration eine Veränderung des für γ_{IP} maßgeblichen Adsorptionsverhaltens des Inhibitors (vergl. Abschnitt 3) erfolgt: seine Aktivität, d.h. das chemische Potential μ, wird zwar erhöht, jedoch wächst gleichzeitig die Größe β [Gleichung (6)], wie sich an der Einengung des Adsorptionsbereichs zeigt. Infolgedessen findet bereits eine zunehmende "Auflockerung" der Inhibitorschicht und zunehmende Ionenpaar-Adsorption statt.

Auch wenn eine chemische Grenzflächenreaktion geschwindigkeitsbestimmend ist, kann die Beziehung (2) angeschrieben werden, und bei mäßiger Adsorption gilt

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* Ermittelt in Gegenwart eines Inhibitors, der die Weiterreduktion des Radikalanions bei diesem Potential verhindert.

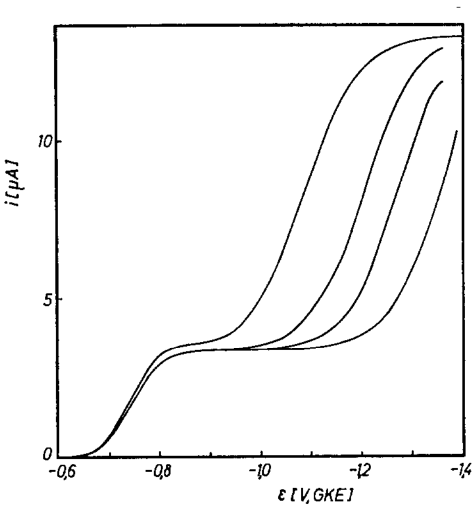


Abb. 4.—Stromspannungskurven von Nitrobenzol bei Inhibitor-Gegenwart und verschiedenen Elektrolytkonzentrationen. Depolarisator 10^{-3} m, 20% Methanol, 0,01 n NaOH, 0,15% Campher. Von links nach rechts Zusatz von 0,99 n, 0,29 n, 0,09 n, 0,02 n KCl.

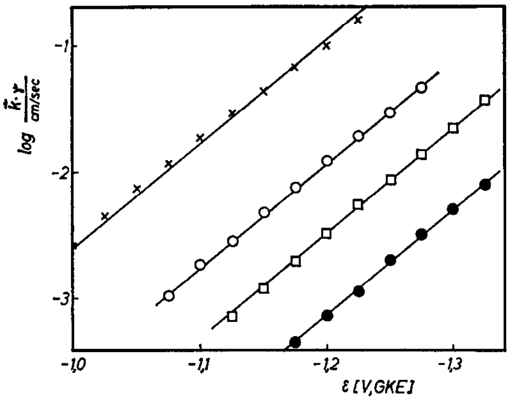


Abb. 5.—(a) Geschwindigkeitskonstante des Sekundärprozesses bei verschiedenen Elektrolytkonzentrationen, aus Abb. 4 berechnet mit Gleichung (12) ($\lambda = 0$); $c_{Na^+} + c_{K^+}$: × 1,0; ○ 0,3; □ 0,1; ● 0,03 Mol/l.

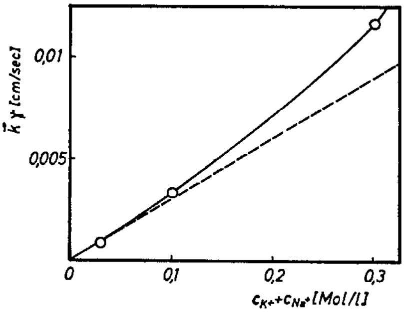


Abb. 5.—(b) Änderung der Geschwindigkeitskonstanten mit der Elektrolytkonzentration, aus Abb. 5(a), für −1,2 V (GKE).

daher Gleichung (4). Die Geschwindigkeitskonstante k enthält nun die Konzentration des Reaktionspartners. Wirkt auch dieser im adsorbierten Zustand und ist er mäßig adsorbiert, so kann auch

$$i = zFq \cdot k \cdot \gamma_1 \cdot \gamma_2 \cdot c_1 \cdot c_2 \qquad (16)$$

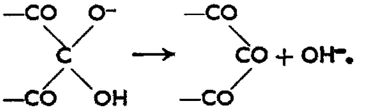
geschrieben werden. Die Konstante k zeigt nun keine derartige Potentialabhängigkeit, wie sie für den Ladungsübergang durch Gleichung (7) formuliert wurde; setzt man sie in erster Näherung potentialunabhängig an, so erhält man unter Verwendung von Gleichung (6) für γ_1 und γ_2

$$\mathrm{i} = \mathrm{zFq} \cdot \mathrm{k} \cdot \gamma_{\mathrm{m1}} \cdot \gamma_{\mathrm{m2}} \cdot \exp\left[-\frac{\beta_1\beta_2}{(\beta_1+\beta_2)^2}(\varepsilon_{\mathrm{m1}}+\varepsilon_{\mathrm{m2}})^2\right] \exp[-(\beta_1+\beta_2)(\varepsilon-\varepsilon_{\mathrm{M}})^2] \tag{17}$$

$$\varepsilon_{\mathrm{M}} = \frac{\beta_1\gamma_{\mathrm{m1}}+\beta_2\gamma_{\mathrm{m2}}}{\beta_1+\beta_2} \tag{18}$$

Allerdings kann auch in diesem Falle eine gewisse Potentialabhängigkeit der Konstante k vorliegen, da die adsorbierten Teilchen unter dem Einfluß des (mit dem Potential veränderlichen) starken elektrischen Feldes in der Grenzschicht ihre Eigenschaften ändern können, wie z.B. Grabowski und Kemula[71] zeigten.

Mit diesen Oberflächenreaktionen, die in der Polarographie organischer Verbindungen wahrscheinlich eine sehr bedeutende Rolle spielen (vor allem Protonenübergänge im Bereich niedriger pH-Werte[70,93,109]) hat sich besonders Mairanovskii[154] theoretisch und experimentell eingehender beschäftigt. Oftmals werden dabei die nach Gleichung (17) zu erwartenden Maxima in den Stromspannungskurven beobachtet. Ein Beispiel aus eigenen Arbeiten stellt die erste Reduktionsstufe von Ninhydrin (sowie ähnlicher, hydratisierbarer Di- bzw. Triketoverbindungen) in alkalischen Lösungen dar. In diesem Falle liegt der Depolarisator in Lösung vor allem in hydratisierter und dissoziierter Form vor, aus der das dehydratisierte Molekül, das allein bei den relativ positiven Potentialen dieser ersten Stufe reduzierbar ist, erst gebildet werden muß:[92]



Diese Reaktion kann sowohl als Lösungs-(Volumen-) wie als Oberflächenprozess ablaufen. Während in inhibitorfreien Lösungen beide zugleich erfolgen und sich als Folge des Oberflächenanteils ein charakteristisches Maximum ausbildet (entsprechend Gleichung (17) oder einer ähnlichen Formulierung), bleibt in Gegenwart eines Inhibitors, der die Oberflächenreaktion ausschaltet, nur die Volumenreaktion mit einem praktisch potentialunabhängigen Grenzstrom bestehen (Abb. 6).

Oberflächenreaktionen liegen vermutlich auch der Stufenvorverlagerung bei der Reduktion von Azoverbindungen in Gegenwart mäßiger Konzentrationen adsorbierter Gelatine (die als Protonenübertrager wirken könnte) zugrunde.[94,96] (Zu diesen Fragen vergl. auch ref. [107,186])

Weiterhin ist hier noch die katalytische Wasserstoffentwicklung zu erwähnen, deren Ursache darin zu sehen ist, daß die an sich wenig zur Adsorption neigenden Wasserstoffionen in Form der Kationen besonders von Stickstoffbasen in den adsorbierten Zustand überführt und leichter reduziert werden können. Geschwindigkeitsbestimmend kann sowohl der Protonenübergang auf die Stickstoffbase (im adsorbierten Zustand) wie auch der Ladungsübergang sein. Neben den bereits erwähnten ersten Untersuchungen von Brdička[17] liegen hierzu zahlreiche weitere Arbeiten vor, von denen hier nur wenige genannt werden können;[44,155,167,189] im übrigen muß auf ausführliche Übersichten[59,156] verwiesen werden.

Schließlich soll—im Zusammenhang mit der Adsorption der Reaktionspartner und als Überleitung zu den im nächsten Abschnitt zu besprechenden Inhibitionseffekten—noch die Erscheinung der "Autoinhibition" erwähnt werden. Eine solche Eigenhemmung findet in erster Linie dann statt, wenn das Produkt des Elektrodenprozesses selbst stark adsorbiert ist, sodaß es die Oberfläche blockiert, d.h. die für die Geschwindigkeit des Vorgangs maßgebliche Adsorption des Ausgangsstoffes herabsetzt. Dieser Effekt wird sowohl bei organischen wie anorganischen Stoffen beobachtet (vergl. z.B. ref. 11, 122, 190, 202, 204). Als Beispiel ist in Abb. 7a die Oxydationsstufe von Hydrazobenzol wiedergegeben,[95–6] die um so irreversibler wird, je höher die Konzentration ist, je mehr Azobenzol also gebildet wird und je dichter daher dessen Adsorptionsfilm ist. Daß es sich tatsächlich um eine Wirkung des Oxydationsproduktes handelt, läßt sich leicht dadurch zeigen, daß dieselbe Irreversibilität auch dadurch hervorgerufen wird, daß bei niedriger Hydrazobenzol-Konzentration Azobenzol zugesetzt wird (Abb. 7b).

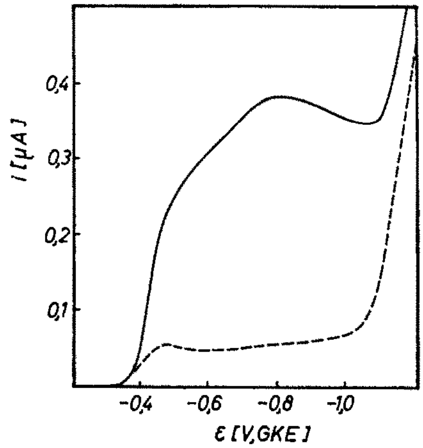


Abb. 6.—Die erste Reduktionsstufe von Ninhyrin ("Vorstufe") in alkalischer Lösung. Depolarisator 10^{-3} m, 10% Methanol, pH 10,4 (0,05 m Phenol + 0,037 m NaOH): ——— ohne Zusatz, - - - - 0,1 % Campher.

Häufig werden solche Hemmungserscheinungen auch beobachtet, wenn das Produkt der Elektrodenreaktion einen unlöslichen Niederschlag bildet, so etwa bei der Oxydation des Quecksilbers in Gegenwart von Chlorid (Bildung von Hg_2Cl_2)[194] oder anderer Anionen, mit denen es schwerlösliche Salze bildet[138] (vergl. ferner ref. 83). Diese Erscheinungen sind der "Passivierung" von Metallen infolge anodischer Deckschichten-Bildung analog.

Unter bestimmten Umständen kann auch der Ausgangsstoff selbst eine Hemmung ausüben, nämlich dann, wenn der Primärprozess reversibel verläuft und der geschwindigkeitbestimmende Schritt mit dem Produkt dieser Primärreduktion erfolgt, wie es bei den Nitroverbindungen der Fall ist (vergl. die Deutung der Knickpunkte in Abb. 3a).

ADSORPTIONSISOTHERME-ADSORPTIONSVERDRÄNGUNG

In diesem Abschnitt soll kurz dargestellt werden, welche Ursachen für die Adsorption maßgeblich sind, wie sich die Adsorption beschreiben läßt bzw. von welchen Faktoren sie im wesentlichen beeinflußt wird (potentialabhängige Adsorptionsisotherme), wie die konkurrierende Adsorption zweier Adsorbate zu formulieren ist (Adsorptionsverdrängung des Depolarisators durch Inhibitoren) und welche Folgen diese Konkurrenz-Adsorption für die Geschwindigkeit des Elektrodenvorgangs hat.

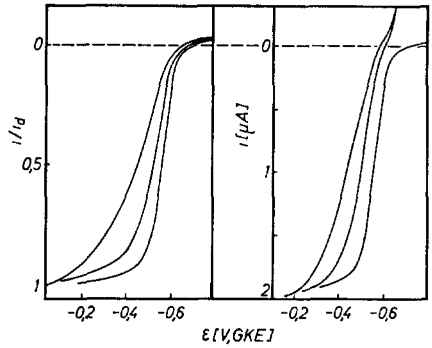


Abb. 7.—Stromspannungskurven von Hydrazobenzol (Oxydation), pH 10. (a) bei verschiedenen Konzentrationen, von links nach rechts: 1,6; 0,8; $0{,}32 \cdot 10^{-3}$ Mol/l (Stromstärke bezogen auf den Grenzstrom).
(b) Hydrazobenzol $0{,}32 \cdot 10^{-3}$ Mol/l, Zusatz von Azobenzol von links nach rechts: 1,28; 0,8; $0 \cdot 10^{-3}$ Mol/l.

Hinsichtlich der Ursachen der Adsorption sei zunächst bemerkt, daß gewisse Analogien mit der Tendenz zur Bildung von Niederschlägen bestehen, sodaß auch—unter sonst gleichen Umständen—quantitative Zusammenhänge zwischen Adsorption und Löslichkeit beobachtet werden können.[65] Die Ursachen der Adsorption (vergl. hierzu auch ref. 163) lassen sich in folgende drei Gruppen klassifizieren:

(a) Die Wechselwirkung zwischen Lösungsmittelmolekülen untereinander ist stärker als diejenige zwischen ihnen und gelösten Molekülen, sodaß letztere—besonders beim Vorliegen "lyophober" Gruppen—bestrebt sind, sich an einem Ort anzureichern, wo sie sich, zumindest teilweise, dem Lösungsmittel entziehen können. (Das Einbringen des Moleküls etwa in Wasser zerstört eine Reihe von Wasserstoff-Brückenbindungen, ohne ein Äquivalent an Hydratationsenergie zu liefern. In nichtwässrigen Lösungsmitteln ist die Adsorptionstendenz, analog zur erhöhten Löslichkeit, besonders bei organischen Stoffen meistens wesentlich geringer. Darum bereitet es oftmals Schwierigkeiten, geeignete Maximadämpfer zu finden;[74] auch fehlen häufig charaketristische Kennzeichen der Adsorption;[73] jedoch lassen sich unter geeigneten Umständen auch hier die Hemmungserscheinungen adsorbierter Inhibitoren beobachten.[110]) Wo diese Ursache der Adsorption maßgeblich ist, ist sie zweifellos auch verantwortlich für die oftmals vermutete Erscheinung,[116] daß bei mäßigen Bedeckungsgraden keine statistische Verteilung der Adsorbatmoleküle auf der Grenzfläche vorliegt, sondern zusammenhängende Bereiche vollständiger Bedekkung und "freier Oberfläche" (d.h. durch Lösungsmittelmoleküle besetzter) nebeneinander existieren.[107] Hiermit in Zusammenhang steht auch die Abhängigkeit der

Adsorptionstendenz[197] und der Inhibitorwirkung[86] polymerer Produkte vom Polymerisationsgrad.

(b) Zwischen dem Metall und den angrenzenden Lösungsmittel- bzw. adsorbierten Molekülen werden Wechselwirkungskräfte betätigt. Sie beruhen vor allem auf Wechselwirkungen zwischen den Leitungsbandelektronen des Metalls und freien Elektronenpaaren bzw.—besonders bei aromatischen Molekülen—dem π-Elektronensystem des Adsorbats.[25,31,62,101,170–1] Dieser Effekt trägt also zur Adsorptionsenergie bei, wenn die Wechselwirkung des Metalls mit dem Adsorbat größer als mit dem Lösungsmittel ist. Gelegentlich treten auch reguläre kovalente Bindungen auf, etwa mit solchen Anionen, mit denen schwerlösliche Hg-Verbindungen gebildet werden[72] und insbesondere mit Schwefelverbindungen. Hinzu treten die Wechselwirkungen der adsorbierten Teilchen untereinander (bzw. zwischen den am gleichen Ort befindlichen Lösungsmittelmolekülen untereinander). Hierbei sind natürlich auch die geometrischen Verhältnisse von Bedeutung, sodaß etwa starke Unterschiede zwischen Stereoisomeren beobachtet werden können.[117,205] Welcher der unter (a) und (b) genannten Effekte für die Adsorption in erster Linie verantwortlich ist, hängt wesentlich von der chemischen Natur des Adsorbats (und natürlich auch den Eigenschaften des Lösungsmittels) ab. So wurde z.B. festgestellt, daß bei der Adsorption von n-Decylamin (an festen Metallen) beide Effekte je etwa zur Hälfte zur Adsorptionsenergie beitragen.[15]

(c) Schließlich werden elektrostatische Wechselwirkungen betätigt, und zwar nicht nur mit Ionen sondern—über permanente und induzierte Dipole—auch mit Molekülen (also auch mit denen des Lösungsmittels). Diese Kräfte sind im wesentlichen für die Potentialabhängigkeit der Adsorption verantwortlich. Sie treten zunächst—in Umgebung des Ladungsnullpunktes—im allgemeinen hinter den unter (a) und (b) genannten Effekten zurück, sodaß durchaus gelegentlich Dipole dem in der Grenzschicht herrschenden Feld entgegengesetzt ausgerichtet sind und damit primär zu einer gewissen Schwächung der Adsorptionskraft führen. Andererseits kann die Orientierung des Moleküls auch potentialabhängig sein, so etwa bei Anilin, das gewöhnlich in "senkrechter" Lage adsorbiert wird, jedoch bei positiven Elektrodenpotentialen in eine Parallellage umorientiert wird, da die π-Elektronenwechselwirkung mit dem Metall dies begünstigt.[31,206] Als weiteres Beispiel sei die Adsorption des Ionenpaares $N(C_4H_9)_4{}^+J^-$ genannt, bei der zunächst das Anion zum Metall orientiert ist, jedoch mit negativer werdendem Potential kurz vor der Desorption eine Umorientierung erfolgt, sodaß das Kation zum Metall weist.[58]

Die Methoden zur Untersuchung der Adsorption sind recht zahlreich; ihre Literatur kann hier auch nicht annähernd vollständig berücksichtigt werden. Immerhin mag eine kurze Zusammenstellung den Überblick erleichtern. Soweit nicht Verfahren angewandt werden, mittels derer die Grenzflächenkonzentration selbst ermittelt wird, etwa durch Verwendung radioaktiver Stoffe[6,13,15,159,183,193] oder durch spektralphotometrische Messungen,[26,119] beruhen die Methoden meistens in dieser oder jener Form auf der grundlegenden thermodynamischen Beziehung

$$d\sigma = -\Gamma \cdot d\mu - Q \cdot d\varepsilon \qquad (19)$$

(σ = Grenzflächenspannung, μ = chemisches Potential = $\mu_0 + RT \cdot \ln c$, Q = Elektrodenladung, ε = Elektrodenpotential). Die gemessenen Größen sind dabei die

Grenzflächenspannung, die Elektrodenladung oder die Elektrodenkapazität ($dQ/d\varepsilon$). Klassische Verfahren sind die Elektrokapillarmessungen,[68] Kapazitätsmessungen mittels Wechselstrom[175] (vergl. auch ref. 64, 75) und die Bestimmung der Elektrodenladung aus dem "Kapazitätsstrom".[98] Für die Untersuchung der Adsorption auf Grund der Änderung der Elektrodenladung (bzw.-kapazität) sind verschiedene Abwandlungen verwendet worden,[104] so die Wechselstrompolarographie (bzw. "Tensammetrie"),[19,20,38] die "oszillographische Polarographie" mit kontrolliertem Strom[82,105] bzw. linear veränderlicher Spannung,[32,42,153] die Hochfrequenzgleichrichtung ("faradaic rectification"),[9] Messungen mit Rechteckwellen ("square-wave polarography")[8] sowie verschiedene galvanostatische oder potentiostatische Einschaltvorgänge ("Chronopotentiometrie", "Ladekurven")[2,23,46,103,128,136,146,158,166] (vergl. auch ref. 111).

Die Beschreibung der Adsorption durch rein thermodynamische Zusammenhänge ist nur im Bereich sehr schwacher ("verdünnter") Adsorption möglich, wo man Grenzflächenaktivität und. konzentration gleichsetzen kann (analog dem idealen Gas- bzw. Henryschen Gesetz usw.), sodaß man zur linearen Beziehung (3) kommt. Im allgemeinen liegt jedoch ein typisch "realer" Zustand vor, da schon bei mäßigen Bedeckungsgraden eine Konkurrenz der adsorbierten Teilchen um die besetzbare Fläche sowie Wechselwirkungen der adsorbierten Teilchen untereinander einsetzen. Die theoretische Entwicklung von Zusammenhängen beruht daher auf Modellvorstellungen, aus denen eine Reihe verschiedener "Adsorptionsisothermen" abgeleitet wurden (vergl. z.B. Parsons[172,174]). Es hat sich jedoch gezeigt, daß die Langmuir-Isotherme (von Langmuir[137] zunächst auf kinetischem Wege für die Adsorption von Gasen an Festkörpern abgeleitet), vor allem in ihrer durch Frumkin[48] modifizierten Form, in sehr zahlreichen Fällen die experimentell gefundenen Zusammenhänge befriedigend beschreibt.* Die Langmuir–Frumkin–Isotherme kann in der Form

$$c = \frac{\theta}{1-\theta} \cdot \exp\left(\frac{\Delta\mu + A \cdot \theta}{RT}\right) \tag{20}$$

geschrieben werden. Der Quotient vor dem Exponentialausdruck berücksichtigt die Begrenzung der Zahl adsorbierbarer Teilchen, indem die Grenzfläche in "Zellen" vom Ausmaß eines Teilchens eingeteilt und das chemische Potential aus der Zahl der Realisierungsmöglichkeiten statistisch hergeleitet wird. Das Glied $A \cdot \theta$ im Exponenten gibt die infolge der Adsorption veränderte Wechselwirkung der in der Grenzschicht vorhandenen Teilchen untereinander näherungsweise durch einen dem Bedeckungsgrad θ proportionalen Energieterm an. (Bei negativem A kann dieser Effekt auch durch die Bildung von Molekülassoziationen im adsorbierten Zustand beschrieben werden.[145,148,165]) $\Delta\mu$ bedeutet den Unterschied der chemischen Potentiale in Lösung und adsorbiertem Zustand unter Standardbedingungen ($c = 1$ bzw. $\theta = 1/2$; letzteres für "ideales Verhalten", d.h. bei fehlenden Wechselwirkungsänderungen). Die Energiegröße $\Delta\mu$ ist sowohl für Ionen wie für Neutralmoleküle potentialabhängig, und zwar werden die experimentellen Ergebnisse im allgemeinen gut beschrieben, wenn

$$\Delta\mu = \Delta\mu_0 + \mu' \cdot \varepsilon + \mu'' \cdot \varepsilon^2 \tag{21}$$

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* vergl. ref. 29, 30, 134–5, 139, 148, 163, 191.

angesetzt wird. Die Isotherme (20) kann daher in der potentialabhängigen Gestalt

$$c = \frac{\theta}{1-\theta}\cdot\exp\left[\frac{\Delta\mu_{m} + \mu''(\varepsilon-\varepsilon_{m})^{2} + A\cdot\theta}{RT}\right] \tag{22}$$

geschrieben werden, wobei $\varepsilon_m = -\mu'/2\mu''$, $\Delta\mu_m = \Delta\mu_0 - \mu''\varepsilon_m{}^2$. Die physikalische Deutung des Zusammenhangs (21) gab Butler:[22] das Einbringen eines Permanentdipols (oder Ions) in das elektrische Feld der Phasengrenze erfordert (bzw. liefert) eine der Feldstärke (die mit dem Potential näherungsweise linear zusammenhängt) proportionale Energie; da zusätzlich ein Dipol induzierbar ist (der proportional dem Feld wächst), liegt außerdem ein quadratisches Glied vor; gleichzeitig werden entsprechende Energiebeträge durch das Herausbringen von Lösungsmittelmolekülen aus der Phasengrenze umgesetzt. Es hängen daher die Größen μ' mit der Differenz der Dipolmomente von Adsorbat und Solvens, μ'' mit den Polarisierbarkeiten beider Moleküle zusammen. Im Prinzip dasselbe—jedoch in einem für reale Verhältnisse nützlicheren Ausdruck—bedeutet eine Formulierung von Frumkin,[48–9] die wie folgt geschrieben werden kann:

$$\mu' = N_L\cdot\left(\frac{\mu_{Lm}\Gamma_{max,Lm}}{l_{Lm}\Gamma_{max,A}} - \frac{\mu_A}{l_A}\right) \tag{23}$$

$$\mu'' = \frac{1}{2\cdot\Gamma_{max,A}}\cdot(C_{\theta=0} - C_{\theta=1}) \tag{24}$$

Darin bezeichnen die Indizes "A" bzw. "Lm" adsorbierten Stoff bzw. Lösungsmittel, μ und l sind Größe und Länge des molekularen Dipols in Feldrichtung, C sind die differentiellen Doppelschichtkapazitäten bei dem angeschriebenen Bedeckungsgrad. (N_L = Loschmidtsche Zahl.) Unter Umständen kann auch die Wechselwirkungsgröße A in Gleichung (20/22) mit dem Potential veränderlich sein.[28,30,201]

Bei einer gleichzeitigen Adsorption mehrerer Teilchensorten, wie sie im Falle der Hemmung von Elektrodenprozessen durch Inhibitoren infolge Adsorptionsverdrängung vorliegt, kommt man bei unterschiedlicher Teilchengröße mit der einfachen Langmuir–Frumkin–Isotherme nicht mehr aus. (Die Langmuir-Isotherme wird z.B. von Lorenz und Möckel[143] der Beschreibung der Adsorptionsverdrängung zugrundegelegt. Auch Gierst *et al.*[65] setzen auf Grund dieser Beziehung die Reaktionsgeschwindigkeit der "freien Oberfläche", d.h. der Konzentration "monomolekularer Löcher" und diese der Inhibitorkonzentration umgekehrt proportional an, was im allgemeinen nicht zutreffen wird.) Wir haben daher bereits in vorhergehenden Arbeiten eine Adsorptionsisotherme hergeleitet, die die unterschiedliche Molekülgröße (genauer: den unterschiedlichen Flächenbedarf verschiedenartiger Moleküle im adsorbierten Zustand) berücksichtigt.[90,113] Analoge Überlegungen führen bei einer Einstoff-Adsorption—wenn man dem unterschiedlichen Flächenbedarf von Lösungsmittel- und Adsorbatmolekül Rechnung trägt—für das chemische Potential des Adsorbats im adsorbierten Zustand zu dem Ausdruck

$$\mu_{ads} = \mu_{ads,0} - RT\cdot\ln\left[\chi_1\cdot\left(1-\theta_1+\frac{1}{\chi_1}\cdot\theta_1\right)^{(1-\chi_1)}\cdot(1-\theta_1)^{\chi_1}\cdot\theta_1^{-1}\right] \tag{25}$$

worin χ_1 das Verhältnis des Flächenbedarfs von Adsorbatmolekül (P_1, z.B. in Å²/Molekül) und Lösungsmittelmolekül (P_0) angibt:

$$\chi_1 = P_1/P_0 \tag{26}$$

Daraus folgt bei Gleichsetzen mit dem chemischen Potential in Lösung ($\mu_L = \mu_{L,0} + RT \cdot \ln c$) und unter Berücksichtigung eines Wechselwirkungsterms $A_{11}\theta_1$ analog zu Gleichung (20) die Isotherme*

$$c_1 = \frac{\theta_1 \cdot \left(1 - \theta_1 + \frac{1}{\chi_1}\theta_1\right)^{(\chi_1 - 1)}}{(1 - \theta_1)^{\chi_1} \cdot \chi_1} \cdot \exp\left[\frac{\Delta\mu_1 + A_{11}\theta_1}{RT}\right] \tag{27}$$

Zu einer gleichlautenden Beziehung kann man auch, wie kürzlich von Bockris und Swinkels[15] formuliert, kommen, wenn man für das Gleichgewicht

$$(A)_{Lös} + \chi_1(H_2O)_{ads} \rightleftharpoons (A)_{ads} + \chi_1(H_2O)_{Lös} \tag{28}$$

die thermodynamische Gleichgewichtsbeziehung auf Grund des Massenwirkungsgesetzes anschreibt.

Für die konkurrierende Adsorption zweier Stoffe ergibt sich weiterhin (vergl. hierzu unsere vorhergehenden Arbeiten[90,113])

$$c_1 = \frac{\theta_1 \cdot \left(1 - \theta_1 - \theta_2 + \frac{1}{\chi_1}\theta_1 + \frac{1}{\chi_2}\theta_2\right)^{(\chi_1 - 1)}}{(1 - \theta_1 - \theta_2)^{\chi_1} \cdot \chi_1} \cdot \exp\left[\frac{\Delta\mu_1 + A_{11}\theta_1 + A_{12}\theta_2}{RT}\right] \tag{29}$$

und—durch Index-Vertauschung—ein entsprechender Ausdruck für c_2. (A_{12} berücksichtigt die Wechselwirkung beider Adsorbate untereinander.)

Für die Diskussion der Adsorptionsverdrängung als Ursache der Inhibitorwirkung ist nun—eher als die bloß graduelle Beeinflussung bei mäßigen Bedeckungsgraden—vor allem der Fall stärkerer Hemmung infolge vorherrschender Inhibitoradsorption interessant. Bezeichnet man mit dem Index "1" den Inhibitor, mit "2" den elektroaktiven Stoff, so gilt unter diesen Umständen

$$\theta_2 \ll \theta_1 \approx 1, \qquad (1 - \theta_1 - \theta_2) \ll 1 \tag{30}$$

und durch entsprechende Vereinfachung erhält man aus Gleichung (29) (und der entsprechenden Beziehung für c_2) den Ausdruck

$$\theta_2 = \frac{c_2}{c_1{}^{\chi}} \cdot \chi \cdot \exp\left[\frac{\chi\Delta\mu_1 - \Delta\mu_2 + \chi A_{11} - A_{12}}{RT}\right] \tag{31}$$

$$\chi = \chi_2/\chi_1 = P_2/P_1 \tag{32}$$

---

* Es mag noch erwähnt werden, daß für große Moleküle, d.h. für $\chi_1 \gg 1$, diese Isotherme durch Umformung und unter Verwendung der Beziehung $\lim\limits_{n\to\infty}[1 + x/n]^n = e^x$ in die Volmersche Isotherme[196]

$$c = \text{const} \cdot \frac{\theta}{1 - \theta} \cdot \exp\left(\frac{\theta}{1 - \theta}\right)$$

(die die Adsorptionsschicht als "zweidimensionales Gas" behandelt und nach neueren Überlegungen[76,84] in etwas abgewandelter Form wieder diskutiert wird[174]), für $\chi_1 = 1$ hingegen in die Langmuir-Frumkin-F-Isotherme übergeht, sodaß sie zwischen beiden eine nicht nur formale Beziehung (wie in ref.[164]) herstellt.

Dieser Zusammenhang läßt sich anschaulicher auch aus dem Gleichgewicht

$$\chi_2(A_1)_{ads} + \chi_1(A_2)_{Lös} \rightleftharpoons \chi_2(A_1)_{Lös} + \chi_1(A_2)_{ads} \tag{33}$$

über die zugehörige Gleichgewichtskonstante

$$K = \frac{\Gamma_2^{\chi_1} \cdot c_1^{\chi_2}}{\Gamma_1^{\chi_2} \cdot c_2^{\chi_1}} \tag{34}$$

herleiten, da aus letzterer für vorherrschende Inhibitoradsorption ($\Gamma_1 \approx \Gamma_{1,max}$) und mit Gleichung (32)

$$\Gamma_2 = K' \cdot c_2 \cdot c_1^{-\chi} \tag{35}$$

hervorgeht, was ganz analog zu Gleichung (31) ist. Auch durch Formulierung kinetischer Gleichungen läßt sich dieser Zusammenhang, wie wir früher zeigten,[90] veranschaulichen.

Es sei noch bemerkt, daß der Flächenbedarf eines Moleküls des elektroaktiven Stoffes nicht unbedingt derselbe ist wie in Abwesenheit der Inhibitoradsorption, da durch sterische Verhältnisse und Wechselwirkungen eine von Inhibitor zu Inhibitor variable Orientierung des elektroaktiven Teilchens erzwungen werden kann. Anstelle von $\theta_2 = \Gamma_2/\Gamma_{2,max}$ schreibt man daher besser

$$\theta_2 = \chi \cdot \Gamma_2/\Gamma_{1,max} \tag{36}$$

Die Gleichung (31) zeigt, daß bei vorherrschender Inhibitoradsorption für den elektroaktiven Stoff eine lineare Adsorptionsisotherme nach Gleichung (3) vorliegt. Der Adsorptionskoeffizient γ_2 ergibt sich—mit Gleichung (36)—zu

$$\gamma_2 = \frac{\Gamma_{1,max}}{c_1^{\chi}} \cdot \exp\left[\frac{\chi\Delta\mu_1(\varepsilon) - \Delta\mu_2(\varepsilon) + \chi A_{11} - A_{12}}{RT}\right] \tag{37}$$

Die Abhängigkeit vom Potential, die hier nur angedeutet ist und durch Beziehungen wie (21) berücksichtigt werden muß, sowie diejenige von der Inhibitor-Lösungskonzentration kann auch in der Form

$$\ln \gamma_2 = \text{const} - \chi \ln c_1 + \frac{\chi\mu_1'' - \mu_2''}{RT} \cdot (\varepsilon - \varepsilon_M)^2 \tag{38}$$

$$\varepsilon_M = \frac{\chi\mu_1''\varepsilon_{m1} - \mu_2''\varepsilon_{m2}}{\chi\mu_1'' - \mu_2''} \tag{39}$$

geschrieben werden. Der Adsorptionskoeffizient kann demnach innerhalb des Adsorptionsbereichs des Inhibitors—für den allein diese Beziehungen wegen der Bedingung (30) gelten—ein Maximum oder ein Minimum durchlaufen; seine Potentialabhängigkeit kann auch sehr schwach sein.

Da die Geschwindigkeit des Ladungsübergangs im adsorbierten Zustand von der Inhibitor-Lösungskonzentration (immer bei vorherrschender Inhibitoradsorption) näherungsweise unabhängig ist, muß man daher auch für das der Messung unmittelbar zugängliche Produkt $\vec{k} \cdot \gamma_2$ (Gleichung (4)) eine Beziehung

$$\ln (\vec{k} \cdot \gamma_2) = f(\varepsilon) - \chi \cdot \ln c_1 \tag{40}$$

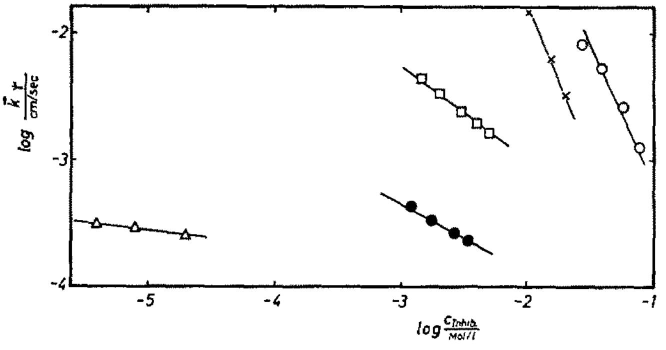


Abb. 8.—Formale Geschwindigkeitskonstante ($\vec{k}\cdot\gamma$) der Reduktion von Methylorange in Abhängigkeit von der Inhibitorkonzentration. Depolarisator 3 . 10^{-4} m, 30% Methanol, pH 12, $\varepsilon = -0{,}875$ V, GKE. Inhibitoren:
○ Benzonitril, × *p*-Tolunitril, □ Diphenylsulfoxyd, ● Triphenylphosphinoxyd, △ Tylose SL 600.

Tabelle II.—Molekularer Flächenbedarf verschiedener Inhibitoren (P_1), Exponent χ und molekularer Flächenbedarf von Methylorange (P_2) in Adsorptionsschichten dieser Inhibitoren (nach Ref. [113]).

Inhibitor	P_1, Å²/*Molekül*	χ	P_2, Å²/*Molekül*
Benzonitril	24	2,2	53
p-Tolunitril	31	2,4	74
Diphenylsulfoxyd	45	0,75	34
Triphenylphosphinoxyd	59	0,55	32
Methylzellulose ("Tylose SL600")	550	0,1	55
ohne Inhibitor	—	—	53

erwarten. Diesen Zusammenhang haben wir für verschiedene Systeme verifiziert.[90,112–3] Auch die unmittelbare Messung des Adsorptionkoeffizienten γ_2 unter vorherrschender Inhibitoradsorption gelang durch Faraday-Impedanz-Messungen an einem (auch unter diesen Umständen) reversiblen Redoxsystem[111] und entsprach den Erwartungen. Eine entsprechende Beziehung wie Gleichung (40) ist auch früher schon empirisch aufgefunden worden.[39] Die hier entwickelte Potentialabhängigkeit wurde ebenfalls beobachtet und mit Überlegungen begründet,[151] die mit der hier gegebenen Formulierung zwar nicht direkt übereinstimmen, jedoch in engem Zusammenhang stehen (vergl. auch ref. 147, 165).

Als Beispiel sind in Abb. 8 die Logarithmen von $\vec{k}\cdot\gamma_2$ für Methylorange als Depolarisator gegen diejenigen der Konzentration verschiedener Inhibitoren aufgetragen;[112] die Größe χ (Neigung der Geraden) ändert sich in entgegengesetzem Sinne wie die Größe der Inhibitormoleküle, wie dies nach Gleichung (32) zu erwarten ist. Eine genauere Untersuchung unter Zuhilfenahme von Elektrokapillarmessungen, aus denen P_1 direkt bestimmt wurde, zeigte jedoch, daß der Flächenbedarf des elektroaktiven Teilchens je nach dem umgebenden Inhibitor verschiedene Werte annehmen kann.[113] Entsprechende Ergebnisse sind in Tabelle II wiedergegeben.

In der zitierten Arbeit[113] wurde auch eine quantitative Auftrennung der mit der Adsorptionsverdrängung verbundenen Effekte durchgeführt, und zwar auf Grund der aus den Elektrokapillarmessungen weiterhin bestimmten Energiegrößen (charakterisiert durch $\Delta\mu_1$, $\Delta\mu_2$, A_{11}, A_{12} in Gleichung (37)); in diesem Zusammenhang konnte wahrscheinlich gemacht werden, daß die je nach Inhibitor verschiedene Orientierung des elektroaktiven Teilchens, wie sie in den unterschiedlichen P_2-Werten zum Ausdruck kommt (Tab. II; für *p*-Aminoazobenzol als Depolarisator treten noch wesentlich größere Unterschiede auf[113]), erheblich zur Aktivierungsenergie des Ladungsübergangs beiträgt und damit also die Geschwindigkeitskonstante $\vec{k}$ verändert wird. (Die Abhängigkeit der Adsorptionsenergie von der Orientierung[192] ist demgegenüber in der hier gewählten Darstellung in den Differenzen der A-Größen enthalten.)

Schließlich sei noch darauf hingewiesen, daß auch beim Problem der Adsorptionsverdrängung Zusammensetzung und Konzentration des Elektrolyten eine wesentliche Rolle spielen können. Der Elektrolyt beeinflußt das Adsorptionsverhalten des elektroaktiven Stoffes durch Änderung von dessen Lösungsaktivität bzw. durch Bildung von Ionenpaaren, wie schon im vorhergehenden Abschnitt besprochen; hierdurch wird besonders die Größe $\Delta\mu_2$ und ihre Potentialabhängigkeit verändert. Dieselben Einflüsse werden aber auch auf den Inhibitor ausgeübt: Veränderung seiner Lösungsaktivität (die anstelle von c_1 richtiger in Gleichung (37) eingeht) sowie der Potentialabhängigkeit von $\Delta\mu_1$, da hier—vergl. Gleichung (24)—die Kapazität der inhibitorfreien Elektrode eingeht, die erheblich vom Elektrolyten abhängen kann. Endlich kann auch beim Inhibitor—wenn es sich um Ionen handelt, z.B. bei Tetraalkylammoniumionen—Ionenassoziation erfolgen, die zu verstärkter Adsorption und damit Inhibition führt.[58,67,100] Die unter der Wirkung von Inhibitoren—wie bereits oben erwähnt—beobachteten Elektrolyteinflüsse auf die Geschwindigkeit von Elektrodenvorgängen[93,107,111] (vergl. auch Abb. 4 und 5) wird man in diesem Sinne noch weiter diskutieren müssen.

Schließlich sei darauf hingewiesen, daß Inhibitoren auch zur Reaktionslenkung benützt werden können. So konnten instabile Zwischenprodukte (Radikale) noch unter Bedingungen gefaßt und untersucht werden, bei denen sie ohne Anwendung von Inhibitoren durch Elektroden-Folgeprozesse sofort vernichtet werden.[108]

ADSORPTIONSKINETIK

In den vorhergehenden Abschnitten wurde im allgemeinen vorausgesetzt, daß das jeweilige Adsorptions-Gleichgewicht [Gleichung (1)] stets eingestellt ist. Diese Voraussetzung ist nun natürlich nicht ohne Einschränkung richtig, vielmehr sind auch hier kinetische Aspekte zu berücksichtigen. Man kann grundsätzlich zwei Fälle unterscheiden:

(a) Das Gleichgewicht zwischen der Konzentration im Lösungsinnern und der Grenzflächenkonzentration c_L/Γ ist nicht eingestellt, jedoch herrscht Gleichgewicht zwischen dem grenzflächennahen Lösungsraum und der Grenzfläche $c_{x=0}/\Gamma$. Hier handelt es sich also un eine Transporthemmung des Adsorptionsvorgangs.

(b) Das Gleichgewicht an der Phasengrenze selbst $c_{x=0}/\Gamma$ ist nicht eingestellt, d.h. es liegt eine Hemmung des Adsorptionsschrittes selbst vor. (Dabei kann zusätzlich eine Konzentrationspolarisation wie unter (a) vorliegen.)

In der klassischen Polarographie hat man es in erster Linie mit einer Hemmung nach a) zu tun, dann nämlich, wenn die Lösungskonzentration so gering ist, daß die zur Gleichgewichtseinstellung erforderliche Stoffmenge durch den Diffusionsvorgang nicht in Zeiten herangeschafft werden kann, die klein gegenüber der Tropfzeit sind. Liegt im Gleichgewicht praktisch vollständige Bedeckung vor ($\theta_{eq} \approx 1$), so ist die zur Einstellung desselben erforderliche Zeit nach Koryta[124] durch

$$t_{\theta=1} = 1{,}82 \cdot 10^6 \cdot \frac{\Gamma_{\mathrm{Imax}}^{\;2}}{D \cdot c_L{}^2} \tag{41}$$

(Γ_{max} in Mol/cm², c_L in Mol/l, D in cm²/sec) und die Zeitabhängigkeit der Bedeckung durch

$$\theta = (t/t_{\theta=1})^{1/2} \tag{42}$$

gegeben. (Diese Beziehungen stehen auch mit der Theorie der "Adsorptionsstufen" bei Reaktantenadsorption[16] in engem Zusammenhang.) Mit dem Fall, daß im Gleichgewicht die Sättigung nicht erreicht wird ($\theta_{eq} < 1$), der rechnerische Schwierigkeiten bereitet, haben sich Delahay *et al.*[34–5] beschäftigt. Der Ablauf des Adsorptionsvorgangs kann experimentell z.B. durch die zeitliche Änderung der Elektrodenkapazität verfolgt werden,[35,102] da im Innern des Potentialbereichs der Adsorption näherungsweise

$$C_\theta = (1 - \theta) \cdot C_{\theta=0} + \theta \cdot C_{\theta=1} \tag{43}$$

gilt.

Die diffusionsbedingte Adsorptionsverzögerung ist natürlich von Bedeutung bei der Inhibition: mit fortschreitender Adsorption kann auch die Hemmung durch den adsorbierten Inhibitor zeitlich zunehmen. Mit diesen Zusammenhängen haben sich besonders Autoren der tschechischen Schule befaßt,[131–2,198–9] wobei sie die Beziehung (42) und für die Geschwindigkeitskonstante des Elektrodenvorgangs als Näherung einen linearen Zusammenhang

$$(\overrightarrow{k} \cdot \gamma)_\theta = (1 - \theta) \cdot (\overrightarrow{k} \cdot \gamma)_{\theta=0} + \theta \cdot (\overrightarrow{k} \cdot \gamma)_{\theta=1} \tag{44}$$

zugrundelegten und hieraus die zeitliche Änderung der Stromstärke für den Zeitraum $0 < t < t_{\theta=1}$ berechneten. (Es wurde dabei auch berücksichtigt, daß im Zuge fortschreitender Bedeckung eine Änderung des ψ-Potentials erfolgt und auch aus diesem Grunde die Geschwindigkeit zeitabhängig ist.) Besonders anschaulich sind die Verhältnisse, wenn bei erfolgter Sättigung praktisch vollständige Hemmung vorliegt ($k_{\theta=1} \to 0$) und die Geschwindigkeit an der unbedeckten Grenzfläche sehr groß ist ($k_{\theta=0} \to \infty$); in diesem Falle weisen die Stromzeitkurven an Einzeltropfen in der Nähe von $t = t_{\theta=1}$ einen sehr scharfen Abbruch der Stromstärke auf.

Hier muß jedoch noch ein anderer Umstand Erwähnung finden. Bei der Ableitung von Gleichung (42) wird nämlich vorausgesetzt, daß die Konzentration in Grenzflächennähe bis zum Zeitpunkt $t_{\theta=1}$ klein gegenüber der Lösungskonzentration ist ($c_{x=0} \ll c_L$); andererseits folgt aus Gleichung (37), daß das Konkurrenz-Adsorptionsgleichgewicht Inhibitor/Depolarisator auch bei praktisch vollständiger Bedeckung durch den Inhibitor ($\theta \to 1$) noch recht merklich von der grenzflächennahen Konzentration des Inhibitors ($c_I = c_{x=0}$) abhängt. DerEnd wert "$k_{\theta=1}$" ist also zum Zeitpunkt $t_{\theta=1}$ noch nicht erreicht, wie es Gleichung (44) voraussetzt, sondern hierzu bedarf es erheblich längerer Zeiten. Auf diesen Umstand haben schon Gierst *et al.*[65] hingewiesen; eine genauere Berechnung dieser Verhältnisse wurde in einer eigenen

Arbeit[114] durchgeführt. Daraus folgen für die Konzentration $c_{x=0}$ die Approximationen

(a) für Zeiten kurz nach $t = t_{\theta=1}$

$$\frac{c_{x=0}}{c_L} \simeq 0{,}417 \cdot \left(\frac{t}{t_{\theta=1}} - 1\right)^{1/2} \tag{45}$$

(b) für Zeiten lange nach $t = t_{\theta=1}$

$$\frac{c_{x=0}}{c_L} \simeq 1 - 0{,}86 \cdot \left(\frac{t_{\theta=1}}{t}\right)^{1/2} \tag{46}$$

Die numerischen Werte aus beiden Beziehungen schließen näherungsweise aneinander an. Anstelle einer Vorausberechnung des zeitlichen Stromverlaufs i(t) unter Zugrundelegung von Gleichung (42) und (44) und Vergleich mit den experimentellen Kurven, wie es in den oben zitierten Arbeiten der tschechischen Autoren geschieht, kann man daher die zeitliche Änderung der Geschwindigkeitskonstante $(\vec{k} \cdot \gamma)$ aus dem experimentellen Strom–Zeit–Verlauf durch eine Beziehung[114]

$$(\vec{k} \cdot \gamma)(t) = \left(\frac{7D}{3\pi t}\right)^{1/2} \cdot \frac{\frac{i}{i_d}(t)}{1 - \int_0^1 \frac{i}{i_d}\left[t \cdot \sin^{6/7}\left(\frac{\pi}{2} \cdot \xi\right)\right] d\xi} \tag{47}$$

feststellen. Als Beispiel ist in Abb. 9 eine Stromzeitkurve und der daraus mit Gleichung (47) ermittelte Verlauf $(\vec{k} \cdot \gamma)(t)$ wiedergegeben. Beim Vergleich mit der nach Gleichung (45/6) berechneten Zeitabhängigkeit von $c_{x=0}$ ergab sich, daß auch unter diesen Bedingungen der zufolge Gleichung (37) zu erwartende Zusammenhang

$$(\vec{k} \cdot \gamma)(t) \sim c_{1,x=0}(t)^{-x} \tag{48}$$

erfüllt ist.

Während die bisherigen Erörterungen die oben als Fall (a) bezeichnete reine Transporthemmung der Adsorption betreffen, kann eine Hemmung des heterogenen Adsorptionsschrittes selbst (b) in der klassischen Arbeitsweise der Polarographie nur beobachtet werden, wenn dieser Vorgang ungewöhnlich langsam ist. Dies ist möglicherweise für die Adsorption von Campher in der Nähe seines Desorptionspotentials der Fall.[88] Liegt nicht gleichzeitig auch eine Transporthemmung vor (d.h. im allgemeinen für $c_L > 5 \cdot 10^{-4}$m), so ist der Zeitverlauf des Bedeckungsgrades durch

$$\theta = \theta_{eq} \cdot F(k_{ads}, k_{des}, t) \tag{49}$$

auszudrücken, wobei die Funktion F neben der Zeit die Geschwindigkeitskonstanten des Adsorptionsvorgangs enthält; diese Funktion wurde berechnet und tabelliert.[88] (Im Anschluß an unsere Arbeit wurde später eine ausführlichere Tabellierung durchgeführt.[199])

Außerdem kann eine Hemmung des Adsorptionsschrittes vorliegen, wenn ein adsorbierter Inhibitor dem Eindringen des elektroaktiven Stoffes in die Grenzschicht besonders starken Widerstand entgegensetzt. So wurden von Loshkarev und

Kryukova[54,129,149,151] die Hemmungserscheinungen bei der Reduktion verschiedener Metallionen durch grenzflächenaktive Stoffe gedeutet, bei denen potentialunabhängige Grenzströme wahrscheinlich machten, daß nicht der Ladungsübergang selbst geschwindigkeitsbestimmend ist. Jedoch können solche Grenzströme bei zu kleiner Konzentration des Inhibitors auch durch eine Transporthemmung des letzteren—wie weiter oben dargestellt—auftreten,[132] sodaß stets zu prüfen ist, welcher der beiden Fälle vorliegt. Sie lassen sich am besten durch Stromzeitkurven am Einzeltropfen unterscheiden, wie Abb. 10a zeigt: bei transportbedingter Verzögerung der Inhibitoradsorption erfolgt während der Tropfdauer plötzlicher Stromabfall (bei $t_{\theta=1}$; hier schematisch für den Grenzfall $(\vec{k} \cdot \gamma)_{\theta=0} \to \infty$, $(\vec{k} \cdot \gamma)_{\theta=1} = 0$ gezeichnet), bei Hemmung der Adsorption des elektroaktiven Stoffes wächst der Strom monoton ($\sim t^{2/3}$). Eine Unterscheidung ist auch leicht anhand der unterschiedlichen Abhängigkeit der mittleren Stromstärke von der Hg-Niveauhöhe möglich, wie Abb. 10b zeigt: Im ersteren Falle wächst der mittlere Strom mit steigender Niveauhöhe stark an ($\sim h^{5/3}$), im zweiten ist er davon unabhängig. Als drittes Beispiel ist ein sehr häufig beobachtetes Verhalten dargestellt, das auftritt, wenn bei Transporthemmung der Inhibitoradsorption auch nach Abschluß der Bedeckung noch eine endliche Geschwindigkeit des Elektrodenvorgangs vorliegt (also $(\vec{k} \cdot \gamma)_{\theta=1} > 0$); in diesem Falle gilt in guter Näherung $\bar{i} = a + b \cdot h^{5/3}$. In Abb. 11 sind die den drei Beispielen der Abb. 10b zugrundeliegenden polarographischen Kurven bei verschiedener Niveauhöhe wiedergegeben. Es handelt sich um die gehemmte Reduktion von Cd^{2+} unter verschiedenen Bedingungen: (a) niedrige Inhibitorkonzentration; Inhibitoradsorption-Transporthemmung mit nahezu vollständiger Hemmung für $t > t_{\theta=1}$, (b) hohe Inhibitorkonzentration; gehemmter Adsorptionsschritt des Depolarisators; (c) niedrige Inhibitorkonzentration; Inhibitoradsorption-Transporthemmung mit unvollständiger Hemmung für $t > t_{\theta=1}$.

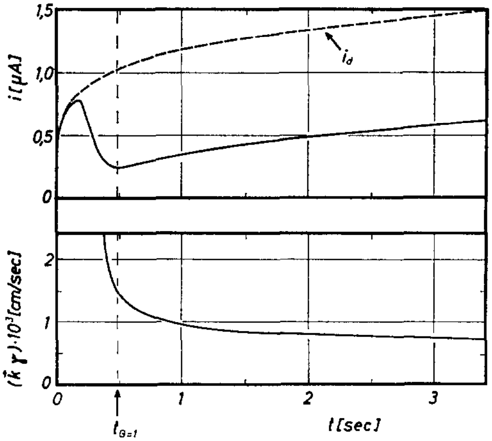
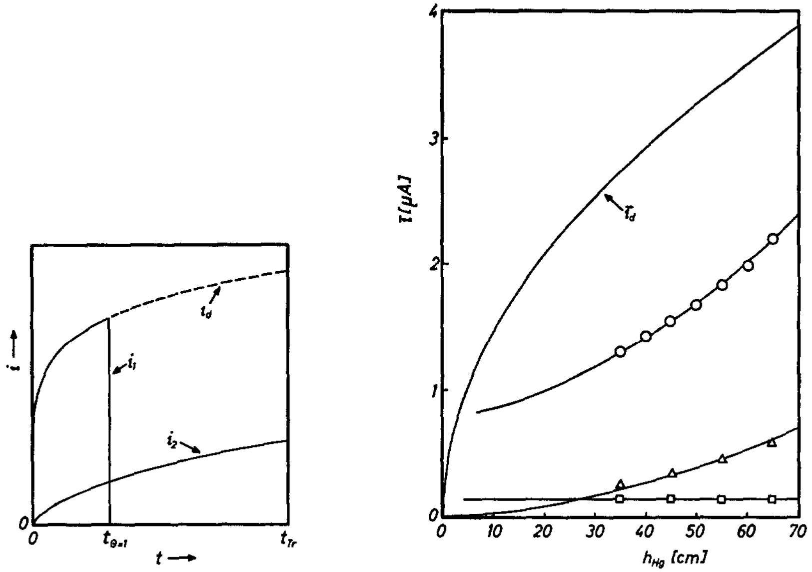


ABB. 9.—oben: Stromzeitkurve am Einzeltropfen bei zeitlich verzögerter Inhibitoradsorption. Depolarisator $3 \cdot 10^{-4}$ m Methylorange, 30% Methanol, pH 12, $\varepsilon = -0{,}92$ V, GKE, Inhibitor 0,0072% Triphenylphosphinoxyd.
unten: daraus mit Gleichung (47) berechneter zeitlicher Verlauf der formalen Geschwindigkeitskonstante $(\vec{k} \cdot \gamma)$.



(a) (b)

Abb. 10—(a) Schematische Stromzeitkurven am Einzeltropfen,
i_d: Diffusionsgrenzstrom,
i_1: bei verzögerter Inhibitoradsorption,
i_2: bei gehemmtem Adsorptionsschritt des Depolarisators.

(b) Abhängigkeit der mittleren Stromstärke von der Hg-Niveauhöhe:
$\bar{i}_d$: Diffusionsgrenzstrom,
△ (Abb. 11a): verzögerte Inhibitoradsorption, $(\vec{k}\cdot\gamma)_{\theta=1} = 0$,
□ (Abb. 11b): gehemmte Adsorption des Depolarisators,
○ (Abb. 11c): verzögerte Inhibitoradsorption, $(\vec{k}\cdot\gamma)_{\theta=1} > 0$.

Zur Untersuchung der Kinetik des Adsorptionsschrittes selbst werden im allgemeinen Wechselstromverfahren angewendet, wobei die Messungen in der Umgebung des "Desorptionspotentials" durchgeführt werden, da nur hier eine hinreichende Potentialabhängigkeit des Adsorptionsgleichgewichts vorliegt; dazu sei auf Arbeiten von Frumkin und Melik-Gaikazyan,[51,162] Delahay *et al.*,[12,184] Lorenz und Möckel[143–5] sowie Breyer und Hacobian[20–1] verwiesen. Im Falle eines reversiblen Elektrodenvorgangs kann durch Faraday–Impedanz–Messungen neben der Adsorption der elektroaktiven Teilchen auch die kinetische Konstante der Reaktion ermittelt werden; jedoch bereitet es Schwierigkeiten zu entscheiden, ob der Adsorptionsschritt oder der Ladungsübergang geschwindigkeitsbestimmend ist.[111]

Für die Kinetik des Adsorptionsvorgangs wird gewöhnlich eine ebensolche Potentialabhängigkeit der Aktivierungsenergie angenommen wie für die Adsorptionsenergie selbst [Gleichung (21)],[22,144] jedoch sind Mechanismus und Kinetik dieses Prozesses theoretisch noch nicht vollkommen ausgeleuchtet (siehe hierzu auch ref. 36).

Summary—The more significant phenomena occurring in polarography in consequence of adsorption at the interface are discussed.

Résumé—On discute des phénomènes les plus importants qui se produisent en polarographie par suite de l'adsorption à l'interface.

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CORRELATION OF POLAROGRAPHIC HALF-WAVE POTENTIALS WITH QUANTUM-CHEMICAL CHARACTERISTICS

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Summary—Data on empirical correlations of half-wave potentials with HMO characteristics is collected, and a comparison of these relationships with analogous dependences for electronic spectra and ionisation potentials is made.

SINCE the publication of the first studies[1-3] concerned with the connection between polarographic half-wave potentials and the energy of the lowest unoccupied π-molecular orbital, several dozen papers on this subject have appeared in the course of the last fifteen years. As it is not the aim of our present work to undertake a systematic treatment of all the investigations in this respect, it will be sufficient to refer to a few surveys.[4-7]

Our communication is concerned with a collection of data on empirical correlations of half-wave potentials with HMO characteristics, and with a comparison of these relationships with analogous dependences for electronic spectra and ionisation potentials. At the same time we should like to point out the most urgent open problems involved in the studies.

Let us briefly review the conditions for a justified comparison of theoretical and experimental data. The mechanism of the process under investigation should be known to an extent permitting utilisation of results measured for ascertaining a quantity characterising a quite definite reaction; moreover, it must be verified experimentally that the reaction proceeds analogously with all members of the respective series of structurally related compounds. Such experimental characteristics can be compared with their theoretical analogues. Only in this case is the studied correlation physically meaningful. Unfortunately, as far as polarographic data are concerned, the situation is most unfavourable among all experimental energy values. Apart from the special case of benzenoid hydrocarbons,[8] the mechanism of the electrode process in reduction or oxidation of conjugated compounds has not been appropriately studied from the electrochemical viewpoint. However, even in this case it is not possible to regard the mechanism of the electrode process as definitely established.[9] Consequently, it cannot be said whether the potential-determining reaction proceeds reversibly or irreversibly.

In a reversible process, in which by acceptance (loss) of one electron a stable radical-anion (radical-cation), not subject to any further changes, is formed, the half-wave potential should be proportional in the first approximation to the difference of the π-electron energy of the reduced (oxidised) form and of the depolariser. In the HMO treatment of conjugated compounds this difference is, in the case of acceptance (loss) of one electron, equal to the energy of the lowest unoccupied (highest occupied) π-molecular orbital (k_{-1} or k_1). On the other hand, in an irreversible process, in the same approximation, the corresponding theoretical value is given by the difference of the π-electron energy of the transition complex of the potential-determining process and of the depolariser. As a rule, these differences can be replaced by some quantum-chemical indices of chemical reactivity (atomic localisation energy, free valence).

It is known that in numerous cases a parallelism was found between half-wave potentials and energies of frontier orbitals. However close these correlations are, because of our insufficient knowledge of the nature of the respective electrode processes, as already mentioned, one cannot regard them as physico-chemically established, and for the time being one must consider them as mere *empirical* correlations.

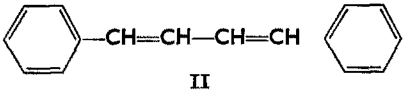
Despite these limitations we believe that it is desirable to investigate the correlations of half-wave potentials with the energies of frontier orbitals for several reasons:
(a) The polarographic method permits (at least for some systems) to determine significant, otherwise not easily obtainable values of electron affinities and ionisation potentials, although the half-wave potentials involve the change in the solvation energy accompanying the conversion of the depolariser into an ion.[10–12]
(b) Empirical relationships of this type serve as useful interpolation formulae for estimating the half-wave potential of substances so far not studied experimentally.
(c) Summarising the results obtained seems so interesting that, in our opinion, it could intensify the study of topical experimental and theoretical questions in this field.

SURVEY OF INVESTIGATED SUBSTANCES

The compounds studied can be classified into three groups: hydrocarbons, their hetero-analogues and derivatives (for illustration, the representatives of the individual groups are given in brackets in the following enumeration). The hydrocarbons are further divided into alternant and non-alternant compounds. Of alternant hydrocarbons were studied polyenes (butadiene, I), α,ω-diphenylpolyenes (1,4-diphenylbutadiene, II) and benzenoid hydrocarbons (naphthalene, III). The investigated non-alternant hydrocarbons were fluoranthenes (fluoranthene, IV, and its benzo derivatives) and azulene and its benzo derivatives (azulene, V).

$CH_2{=}CH{-}CH{=}CH_2$

I



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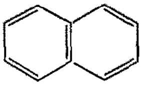

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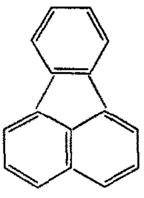

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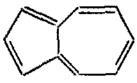
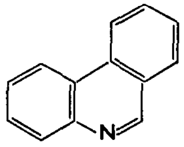


V

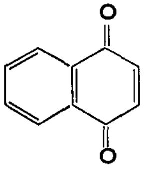
$CH_2{=}CH{-}CH{=}O$

VI



VII

R-Br	R-NH$_2$	R-OH	R-CHO	R-NO$_2$	R-CH$_2$Cl	R-COOC$_2$H$_5$	R-NCS	; R = aryl
VIII	IX	X	XI	XII	XIII	XIV	XV	



XVI

$(CH_3)_2N{-}CH{=}CH{-}CH{=}\overset{+}{N}(CH_3)_2ClO_4^-$

XVII

The studies of hetero-analogues were concerned with polyene aldehydes (acrolein, VI) and pyridine heterocycles (phenanthridine, VII). Moreover, several groups of derivatives of benzenoid hydrocarbons were investigated: bromo (VIII), amino (IX), hydroxy (X), formyl (XI), nitro (XII), chloromethyl (XIII), carbethoxy (XIV) and isothiocyanato (XV) derivatives; quinones (1,4-naphthoquinone, XVI). Polymethinium salts may be regarded as derivatives of polyene hetero-analogues (*e.g.*, XVII).

RESULTS

Table I presents the constants of the straight regression lines and the correlation coefficients of the relationships between the half-wave potentials of the cathodic (anodic) waves and the HMO energies of the lowest unoccupied (highest occupied) π-molecular orbital. The table also contains the conditions under which the half-wave potentials were determined.

The slopes of the dependences studied (a), with the exception of the regression lines 15, 17, 23 and 24, lie in the range of 2.0 – 2.7 eV/β. As will be seen later, this range also comprises the values of the slopes of some relationships between other experimental quantities and the corresponding theoretical values. Lower slopes were found for quinones (15), which are reduced reversibly, as well as for phenols (24) and amines (23), which are undoubtedly oxidised irreversibly. With the exception of the regression line 4, the correlation coefficients of all relationships are very high and are significant at the 1% probability level. It can be said that the correlations of the half-wave potentials belong to the closest among all correlations of energy quantities.

For the dependences of the excitation energies of the L$_a$ bands[36,37] and the charge-transfer bands of the π-complexes,[38] as well as of the ionisation potentials[37] on the corresponding HMO theoretical values, it has been shown that the data for polyenes and benzenoid hydrocarbons lie on approximately parallel but mutually significantly shifted straight lines; the data for α,ω-diphenylpolyenes (which have the character of transient compounds among the mentioned hydrocarbons) are located on a sigmoidal curve lying in the region between the mentioned straight lines. On the other hand, the relationships between the half-wave potentials of both the cathodic and anodic waves of α,ω-diphenylpolyenes and the energies of the frontier orbitals can be approximated by a straight line the constants of which differ only slightly

TABLE I.—CONSTANTS *a* AND *b* OF STRAIGHT REGRESSION LINES OF RELATIONSHIPS BETWEEN HALF-WAVE POTENTIAL ($E_{1/2}$) AND ENERGY OF LOWEST UNOCCUPIED (k_{-1}) OR HIGHEST OCCUPIED (k_1) π-MOLECULAR ORBITAL, AND CORRELATION COEFFICIENTS *r*

No.	Group of substances	*a*	*b*	r^{a}	n^{b}	Electrolyte	Reference electrode	Reference
						Cathodic waves $E_{1/2}(V) = a\,k_{-1}(\beta) + b$		
1	α, ω-Diphenylpolyenes^{c}	2·390	−1·081	0·997	7	0·175*N* $(C_4H_9)_4NI$, 96% dioxan	SCE	13
2		2·122	−1·163	0·996	6	0·175*N* $(C_4H_9)_4NI$, dimethylformamide	SCE	14
3	Benzenoid hydrocarbons	2·407	−0·396^{d}	0·967	14	0·1*N* $(C_4H_9)_4NI$, dimethylformamide	Hg bottom	15
4		2·542	−0·352^{d}	0·872^{e}	5	0·1*N* $(C_2H_5)_4NI$, dimethylformamide	Hg bottom	16
5		2·405	−0·420^{f}	0·965	40	0·1–0·2 *N* $(C_4H_9)_4NI$ or $(C_4H_9)_4NBr$, 2-methoxyethanol	Hg bottom	17
6		2·715	−0·787	0·962	14	0·175*N* $(C_4H_9)_4NI$, 96% dioxan	SCE	13
7	Fluoranthenes	2·682	−0·329^{f}	0·991	12	0·1–0·2 *N* $(C_4H_9)_4NI$ or $(C_4H_9)_4NBr$, 2-methoxyethanol	Hg bottom	17, 18
8	Polyene aldehydes^{g}	2·429	−0·035	0·998	5	50% dioxan, buffer, pH 0	SCE	19
9	Vinyl compounds	2·33	−0·80	0·995	9	0·05*M* $(C_4H_9)_4NI$, 75% dioxan	SCE	20
10	Pyridine heterocycles^{g}	2·127	−0·555^{d}	0·986	6	0·05*N* $(C_2H_5)_4NI$, 95% dimethylformamide	Hg bottom	21
11		2·012	−0·450^{d}	0·991	7	0·1*N* $(C_2H_5)_4NI$, dimethylformamide	Hg bottom	22
12		3·844	0·066	0·986	9	0·01*N* KOH or 0·01 *N* LiBr, ethanol-water (9:1), *cf.* ref. 24	SCE	23, 24
13	Aromatic aldehydes^{g}	2·034	−0·818	0·982	6	Britton-Robinson buffer, pH 13·0 50% ethanol	SCE	25
14	Aromatic esters of carboxylic acids^{g,h}	2·407	−0·941	0·965	13	0·175*M* $(C_4H_9)_4NI$, 75% dioxan	SCE	26
15	Quinones^{g}	1·745	−0·735	0·954	6	0·1*N* $(C_2H_5)_4NClO_4$, acetonitrile	SCE	27
16		1·576	0·450	0·973	10	Oxidation-reduction potentials, for conditions see ref. 28	—	28
17	Polymethinium salts^{g}	4·029	0·181	0·998	4	0·5*M* $Mg(ClO_4)_2$, dimethylformamide	satd. $MgCl_2$ in H_2O, Hg bottom	29

Anodic waves[i]
$E_{1/2}(V) = a\,k_1(\beta) + b$

18	α, ω-Diphenyl-polyenes	2·231	0·317	1·000	4	0·1*N* NaClO$_4$, acetonitrile	SCE	30
19	Benzenoid hydrocarbons[j]	2·041	−0·004[k]	0·993	12	0·5*N* NaClO$_4$, acetonitrile	0·1 *N* Ag$^+$/Ag, 0·5 *N* NaClO$_4$, CH$_3$CN	31
20		2·013	0·063[k]	0·999	3	0·5*N* NaClO$_4$, acetonitrile	0·1 *N* Ag$^+$/Ag, 0·5 *N* NaClO$_4$, CH$_3$CN	32
21		2·126	0·178	0·982	22	2*N* NaClO$_4$, acetonitrile	SCE	33
22	Benzenoid bromo derivatives	2·243	0·173[k]	0·986	8	0·5*N* NaClO$_4$, acetonitrile	0·1 *N* Ag$^+$/Ag, 0·5 *N* NaClO$_4$, CH$_3$CN	34
23	Benzenoid amines	1·652	−0·157[k]	0·986	11	0·5*N* NaClO$_4$, acetonitrile	0·1 *N* Ag$^+$/Ag, 0·5 *N* NaClO$_4$, CH$_3$CN	34
24	Phenols	1·512	0·093[k]	0·991	5	0·5*N* NaClO$_4$, acetonitrile	0·1 *N* Ag$^+$/Ag 0·5 *N* NaClO$_4$, CH$_3$CN	34

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[a] If not indicated otherwise, all values are significant at the 1 % probability level.

[b] Number of substances.

[c] A moderately bent sigmoidal curve is better suited than a straight line.

[d] For conversion against SCE add −0·50 (see ref. 16).

[e] At the 5 % probability level.

[f] For conversion against SCE add −0·52 (see ref. 13).

[g] Parameters: $\alpha_X = \alpha + \delta_X\beta$, $\beta_{XY} = \rho_{XY}\beta$ (the symbols have their usual meaning). 8: $\delta_O = 1$, $\rho_{CO} = 1$. 10: $\delta_N = 0{\cdot}5$. 13: $\delta_O = 2$, $\rho_{CO} = \sqrt{2}$. 14: $\delta_{=O} = 1{\cdot}8$, $\delta_{-O} = 1{\cdot}2$, $\delta_{C(O_2)} = 0{\cdot}2$, $\delta_{O(OOO)} = 0{\cdot}2$, $\rho_{O=O} = 1{\cdot}4$, $\rho_{C-O} = 1{\cdot}2$. 15: $\delta_O = 1{\cdot}3$, $\delta_{C(O)} = 0{\cdot}2$, $\rho_{CO} = \sqrt{2}$. 17: $\delta_N = 1$. 22: theoretical data were based on a perturbation treatment. 23: $\delta_N = 1$. 24: $\delta_0 = 2$.

[h] Including fluoranthene derivatives.

[i] Vibrating or rotating platinum electrode.

[j] Including fluoranthene.

[k] For conversion against SCE add 0·30 (see ref. 35).

from the constants of the straight lines for benzenoid hydrocarbons (Table I). Here it must be pointed out, however, that in the case of the cathodic waves of α,ω-diphenylpolyenes a certain tendency towards a sigmoidal course is noticeable; this is illustrated schematically in Fig. 1 (the graphical representation is given in reference 7). Finally, it is worth mentioning that the half-wave potential of the cathodic wave of butadiene[20] (Fig. 1) is in accordance with the fact that the data for α,ω-diphenylpolyenes[14] (Fig. 1) lie in the region of the data for benzenoid hydrocarbons. Let us add that there is no significant split of points in a plot of theoretical values of ionisation potentials based on the Pariser-Parr and Hückel procedure.[40] On the other hand, however, there is a significant split of points when experimental excitation energies of charge-transfer[38] bands are plotted against the HMO data. Therefore, one can conclude that some important feature of charge-transfer complexes is not included in the current treatment of these complexes. A satisfactory correlation was recently found[39] between the oxidation potentials of methyl-substituted benzenoid hydrocarbons and the energies of the highest occupied π-molecular orbital calculated from perturbation data.

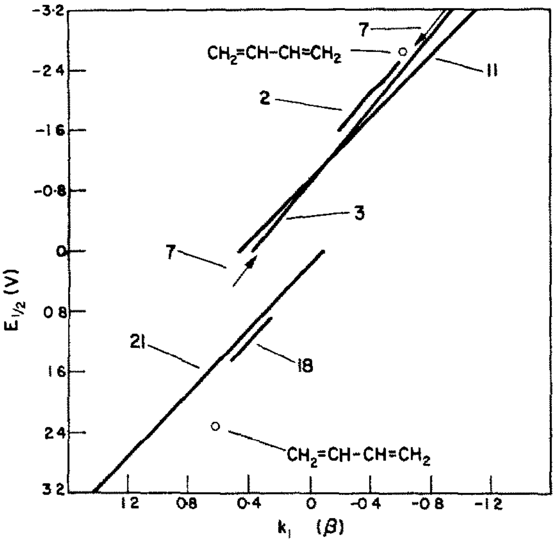

FIG. 1.—Regression lines of the relationships between the reduction or oxidation half-wave potentials of some conjugated compounds ($E_{1/2}$, all lines recalculated against SCE) and the energies of the lowest unoccupied or highest occupied π-molecular orbital (k_{-1} or k_1, respectively).

Reduction: (2) α,ω-diphenylpolyenes, (3) benzenoid hydrocarbons, (7) fluoranthenes, (11) pyridine heterocycles; for butadiene, see reference 20.

Oxidation: (18) α,ω-diphenylpolyenes, (21) benzenoid hydrocarbons; for butadiene, see reference 30.

The numbers of the regression lines are the same as in Table I.

Of interest is the circumstance that the data for non-alternant fluoranthenes satisfy very well a linear dependence,[17] practically in accordance with benzenoid hydrocarbons. The case with biphenylene polyenes is similar.[13] The value for the anodic half-wave potential of fluoranthene also falls well on the regression line for benzenoid hydrocarbons. On the other hand, however, in the case of azulene and twobenzazulenes, the HMO data do not even indicate the order of the reducibility of these compounds.[41] The SC method, however, leads to qualitatively correct results;[42] the same is true for the SCF and CI data.[43] Evidently, each method in which the non-uniform distribution of π-electrons is taken into consideration leads to an agreement with experiments.

As far as polynuclear nitro compounds,[44] isothiocyanates[45] and arylmethyl chlorides[46] are concerned, it seems that the polarographic half-wave potentials would characterise more or less the conditions in the functional group and not in the entire conjugated system.

TABLE II.—COMPARISON OF THE SLOPES OF RELATIONSHIPS ($y = ax + b$) OF EXPERIMENTAL ENERGY QUANTITIES (y) WITH THE CORRESPONDING HMO QUANTITIES (x)

Substances	y	x	a(eV/β)	Reference
Benzenoid hydrocarbons	Excitation energy of L_a band	$E(N \rightarrow V_1)$	2·38	36
	Excitation energy of charge-transfer band	k_1	3·26[a] 2·30[b]	38 38
	Ionisation potentials	k_1	3·26	37
	Cathodic half-wave potentials	k_{-1}	2·41–2.72	—
	Anodic half-wave potentials	k_1	2·04–2·13	—
Fluoranthene-like hydrocarbons	Excitation energy of first band	$E(N \rightarrow V_1)$	2·80	17
	Excitation energy of charge-transfer band	k_1	3·66[c]	17
	Cathodic half-wave potentials	k_{-1}	2·68	—
Pyridine-like heterocycles[d]	Excitation energy of L_a band	$E(N \rightarrow V_1)$	2·98	47
	Excitation energy of charge-transfer band	k_1	2·77[e]	38
	Cathodic half-wave potentials	k_{-1}	2·01 and 2·13	—

[a] Tetracyanoparaquinodimethane. [b] Phthalic anhydride. [c] Trinitrofluorenone. [d] $\delta_N = 0·5$.
[e] Tetracyanoethylene.

Table II presents a comparison of the slopes of the dependences of experimental energy values with the corresponding theoretical quantities. In the case of hydrocarbons, the slopes of the dependences of the half-wave potentials are nearer to the slopes of the dependences of the excitation energies of the first bands in the electronic spectra than to the slopes in analogous dependences for charge-transfer bands.

In conclusion it can be said that there are first of all two questions to be regarded as open. From the experimental viewpoint it is highly necessary to study the electrochemical nature of the electrode process in the case of cathodic and anodic waves of conjugated systems (mainly of hydrocarbons); from the theoretical viewpoint it is first of all indispensable to undertake a critical analysis of the differing behaviour of polyenes, α,ω-diphenylpolyenes and benzenoid hydrocarbons in correlation concerning, on the one hand, the half-wave potentials and, on the other hand, the excitation energies of the L_a bands, the charge-transfer bands and the ionisation potentials.

NOTE ADDED IN PROOF

Several studies have recently been published in which the experimental half-wave potentials were correlated with the energies of frontier π-molecular orbitals. The data (type of compound; nature of electrode process; constants a and b of regression line; correlation coefficient r; number of compounds; electrolyte; reference electrode; literature reference) are summarised below:—

(1) phenyl-substituted borazines; reduction; all data lie in the neighbourhood of the regression line for benzenoid hydrocarbons; –; 4; 0·1N $(C_4H_9)_4$ $NClO_4$ in 1,2-dimethoxyethane; sat. $AgNO_3/Ag$ in 1,2-dimethoxyethane; D. F. Shriver, D. E. Smith and P. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 5153.

(2) thiocarbonyl compounds; reduction; 1·070, –0·612; 0·944; 20; phosphate buffer (pH 7·2) in water-40% 2-propanol; SCE; A. Mehlhorn, J. Fabian and R. Mayer, *Z. Chem.*, 1965, **5**, 21; A Mehlhorn and J. Fabian, private communication.

(3) anions of β-dicarbonyl compounds; reduction; 1·16, –1·10; –; 4 (9); 0·1N KOH in 10–50% ethanol; SCE; J. Stradins, E. Gren, V. Kamper and G. Vanag, *Zhur. obshcheǐ Khim.*, 1965, **35**, 222.

(4) diphenylamine, p-phenylenediamine and benzidine derivatives; oxidation (platinum rotating electrode), 2·48, –0·46; –; 18; 0·5N $NaClO_4$ in acetonitrile; SCE; P. Smejtek and V. Dvořák, private communication.

(5) methylthio-substituted benzenes, anisoles and N,N-dimethylanilines; oxidation; 3·735, –1·346; –; 12; acetonitrile SCE; A. Zweig and J. E. Lehnsen, *J. Amer. Chem. Soc.*, 1965, **87**, 2647.

Also, a paper containing a correlation of polarographic oxidation half-wave potentials of benzenoid hydrocarbons and their derivatives with photoionisation potentials has appeared recently (W. C. Neikam, G. R. Dimeler and M. M. Desmond, *J. Electrochem. Soc.*, 1964, **111**, 1190).

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Zusammenfassung—Gesammelte Daten über empirische Wechselbeziehungen zwischen Halbwellenpotentialen und quantenchemischen Kennzahlen werden mit analogen Beziehungen zwischen Elektronenspektren und Ionisierungspotentialen verglichen.

Résumé—On a réuni des données sur les relations empiriques entre les potentiels de demi-vague et les caractéristiques de l'orbitale moléculaire occupée de niveau le plus élevé (HMO), et l'on compare ces rapports à des relations analogues entre spectres électroniques et potentiels d'ionisation.

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EFFECT OF COMPOSITION OF AQUEOUS-ORGANIC SOLVENTS ON POLAROGRAPHIC BEHAVIOUR OF ORGANIC COMPOUNDS

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Summary—A review of the effect of the composition of aqueous-organic solvents on the polarographic behaviour of organic compounds is presented.

INTRODUCTION

THE electrochemical behaviour of organic compounds differs from that of inorganic substances in a number of specific features. These specific features are largely due to:[1]

(a) the marked adsorptivity of organic depolarisers on the electrode surface, generally resulting in a considerable acceleration of the process occurring on the electrode and near the electrode, caused both by increasing depolariser concentration near the electrode surface, *e.g.*, in the case of catalytic processes, and by polarisation of the depolariser in the high electric field of the double layer (Grabowski effect);[2,3]

(b) the participation of hydrogen ions in the potential determining step;

(c) the inhibiting effect of the electrode reaction products if their surface activity is greater than that of the initial compounds (sometimes the inhibition is because of complete coverage of the surface with the adsorbed depolariser);[4,5]

(d) the formation of external hydrogen bonds or other interactions of the depolariser with the solution components.

Therefore, apart from the effects observed during the discharge of inorganic depolarisers (see, for example, Schwabe's reviews[6,7] as well as other works[8–16]) the change in the solvent composition in the case of electrode processes involving the participation of organic substances has an additional specific effect.

Before considering the effect of the composition of aqueous-organic solvents on the polarographic waves, let us discuss some quantitative relationships between $E_{1/2}$ of the reduction waves of organic substances and different factors determining the values of $E_{1/2}$.[17]

EFFECT OF pH ON $E_{1/2}$-VALUES OF QUASI-DIFFUSION WAVES IN ACIDIC AND NEUTRAL SOLUTIONS

If the $E_{1/2}$-value of a polarographic wave is a function of pH and the limiting current (i_{lim}) obeys the Ilcovič equation, the wave is of a quasi-diffusion nature, *i.e.*, its electrochemical step proper is preceded by protonation of the organic depolariser:[17,18]

$$R + DH^+ \rightleftharpoons RH^+ + D \qquad (I)$$

where DH^+ are proton donors of the solution.

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With a sufficient increase in pH of the solution the limiting current of such a quasi-diffusion wave usually decreases (provided there is no direct electron transfer to a non-protonised particle of the depolariser) and assumes a kinetic nature.

On the basis of Frumkin's slow discharge theory[19] and Brdička's theory of kinetic currents, for $E_{1/2}$ of irreversible electrode processes with preprotonation at sufficiently high pH one can write (with mean values for the drop time):[17,18]

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{nsFk_{el}{}^0 c}{\sigma i_{lim}} \tag{1}$$

and

$$E_{1/2} = \varphi_{1/2} + E_M = \frac{bb'}{b' - b}\left(\log \frac{nsFk_{el}{}'c}{\sigma_S i_{lim}} + \log \beta_0 \Gamma_\infty + 0{\cdot}43\mathbf{a}\varphi_{1/2}^2\right) \tag{2}$$

Equation (1) is valid for electrode processes with a volume preprotonation and equation (2) for a *surface* wave, provided the adsorption of an electrochemically inactive form of the depolariser obeys the Langmuir isotherm and the equilibrium state of adsorption has been established.[20]

In these equations n and n_a denote the numbers of electrons transferred during the whole process and during the potential-determining step, respectively; F—the Faraday number; c—the volume analytical concentration of the depolariser; $k_{el}{}^0$ and $k_{el}{}'$—the rate constants of the electron transfer at $E = 0$, for the volume and surface concentrations of the particles to be discharged, respectively; E_m—the potential of maximum adsorption of the depolariser in the solution (according to Frumkin[21]); β_0—the factor of Langmuir's isotherm for the non-protonised form of the depolariser at $E = E_m$; a—a constant of Frumkin's equation relating the adsorptivity on the electrode surface to the potential;[21] Γ_∞—the maximum amount of the adsorbed substance; s—the area of a dropping mercury electrode; $bb'/(b' - b)$—the slope of the logarithmic plots for the surface quasi-diffusion wave; σ and σ_s determine (at $\sigma \gg 1$) the ratios of the concentrations of R and RH^+ in the bulk of the solution and on the electrode surface, respectively:

$$\sigma = [R]/[RH^+] \qquad \text{and} \qquad \sigma_s = \Gamma_R/\Gamma_{RH^+} \tag{3}$$

where Γ is the amount of the adsorbed substance.

When the pK_A of the depolariser is much less than the pH of the solution, the value of σ may be written as:

$$\sigma = K_A/[H^+] \tag{4}$$

and the dependence of $E_{1/2}$ on pH for a volume quasi-diffusion wave is determined by means of equations (1) and (4):

$$\frac{\Delta E_{1/2}}{\Delta pH} = -\frac{RT}{\alpha n_a F} \tag{5}$$

Thus, with pH increasing by unity, $E_{1/2}$ of the quasi-diffusion irreversible volume wave should become more negative by the value of the reciprocal slope of the semi-logarithmic plot of the wave.

In the case of the wave with a surface preprotonation, with increasing pH the $E_{1/2}$-value also becomes more negative, but the dependence of $E_{1/2}$ on pH is more complicated than that given by equation (5). This is for the following reasons:[18]

(i) the change in pH affects somewhat the value of $bb'/(b' - b)$;

(ii) the pH on the electrode surface differs from that in the bulk of the solution;

(iii) pH affects both the first and the third terms in the brackets in the right-hand side of equation (2).

Thus, if the quantity $\Delta E_{1/2}/\Delta pH$ differs from that predicted from equation (5), one may expect the protonation to be partially or completely of a surface nature, *i.e.*, the particles of R adsorbed on the electrode surface will be protonised.

Holleck was the first to note[22] that the adsorption of a depolariser or of an electrode product may be responsible for the deviation in an experimental value of $\Delta E_{1/2}/\Delta pH$ from the theoretical one (see also the excellent review by Elving[23]).

At a low enough value of the pH of the solution, when the inequality $pK_A \ll pH$ is no longer valid, σ in equation (1) should be substituted by the ratio $c/[RH^+]$:[17]

$$\frac{c}{[RH^+]} = \frac{[H^+] + K_A}{[H^+]} \tag{6}$$

so that equation (1) may be written as:

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{nsFk_{el}{}^0 c}{i_{lim}} + \frac{RT}{\alpha n_a F} \ln \frac{[H^+]}{[H^+] + K_A} \tag{7}$$

It can be seen from equation (7) that with increasing hydrogen ion concentration in the solution, when $[H^+]$ becomes more than K_A, $E_{1/2}$ stops changing with pH. From the dependence of $E_{1/2}$ on pH it is possible to determine the value of pK_A of the depolariser for the waves with a volume preprotonation. An equation of the same form as equation (7) was first derived by Laviron[24] to explain the shape of the dependence of $E_{1/2}$ on the pH of the reduction waves of a number of heterocyclic compounds.

Nearly the same shape of the $E_{1/2}$–pH dependence is observed in the case of waves with a surface preprotonation. It is impossible, however, to estimate the $(K_A)_S$ value of the adsorbed depolariser directly from the shape of such a dependence. In the case of processes with a surface preprotonation, it is necessary to plot the dependence of $E_{1/2}$ on $p[H^+]_S$, *i.e.*, on the concentration of the hydrogen ions at the electrode surface[25] and to take into account the change of $bb'/(b' - b)$ with pH as well as the effect of the double layer structure on the values of $p(K_A)_S$ and $p[H^+]_S$.[25] It should also be kept in mind that when $p[H^+]_S \rightarrow p(K_A)_S$ the overall adsorptivity of the depolariser changes significantly because the greater part of it is transformed into the protonised form, the value of β_0 of this form differing sharply from that of the non-protonised form.

At $p[H^+]_S \ll p(K_A)_S$ the value of $E_{1/2}$ for the surface waves is independent of pH, and equation (2), after the substitution of $\Gamma_{sum}/\Gamma_{RH^+} \approx 1$ for σ_S[Γ_{sum} is the total amount of the adsorbed substance (R and RH^+) per unit of the electrode surface A] can be written[17] as:

$$E_{1/2} = \varphi_{1/2} + E_M = \frac{bb'}{b' - b}\left(\log \frac{nsFk_{el}'}{\kappa} + \log \beta_0 \Gamma_\infty + 0{\cdot}43a\varphi_{1/2}^2\right) \tag{8}$$

where $\kappa = i_d/c$. Thus, equation (8) is valid for $E_{1/2}$ of the waves without preprotonation, but with the adsorption of the depolariser obeying Langmuir's isotherm.

It is known that there are waves the heights of which do not change until the solutions become alkaline. In alkaline solutions their $E_{1/2}$ no longer depends on pH, but in acidic media the electrode process involves the preprotonation of the depolariser (for instance the waves of nitro compounds). In such cases a direct electron transfer to a non-protonised depolariser takes place and although the rate of this process is usually small, at a high enough pH of the solution it becomes greater than the rate of the process with preprotonation because of the slowness of this chemical reaction in alkaline solutions.

Let us consider now the effect of the solvent composition on the $E_{1/2}$ of the processes without preprotonation but with adsorption of the depolariser.

ELECTRODE PROCESSES WITHOUT PROTON TRANSFER IN POTENTIAL-DETERMINING STEP

The reduction waves of various bromothiophenes can serve as an example of such processes;[26] the $E_{1/2}$-values of these waves in aqueous-organic mixtures (as referred to the aqueous S.C.E., without a correction for the liquid-junction potential) are given in Fig. 1.

Fig. 1 shows that an increase in the organic solvent content in the solution results in the shift of the waves towards more negative potentials, this shift being the greater, the less negative is the $E_{1/2}$-value of the wave. A similar relationship was observed by Cisak[27] during the investigation of the reduction waves of various isomers of chlorocyclohexane and dibromocyclohexane in 50 and 90% ethanol; still earlier, a differing effect of ethanol addition on the waves with different $E_{1/2}$-values was noted by Levin and Fodiman[28] and Lothe and Rogers.[29]

The shift of the waves towards more negative potentials with increasing alcohol concentration Cisak[27] explains by the adsorption of alcohol on the electrode surface, resulting in the inhibition of the electron transfer. With increasing cathodic potential of the electrode the adsorption of alcohol on its surface sharply decreases, which, in Cisak's opinion, is responsible for a lesser effect of alcohol on more cathodic waves. Schwabe,[6a,7] who has studied the effect of the concentration of various organic solvents in aqueous-organic mixtures on the polarographic behaviour of hexachlorocyclohexane and some other compounds, also believes the shift of $E_{1/2}$ of the waves of the irreversibly discharging depolarisers (when no hydrogen ions participate in the potential-determining step of the process) towards more negative potentials to be caused by the inhibition of the transfer of electrons by the organic solvent particles adsorbed on the electrode.

As a rule, an increase in the organic solvent content in the aqueous-organic mixture results in a decrease in the adsorptivity of organic substances on mercury and brings about a change in the shape of the adsorption isotherm.[30] Thus, in my opinion, the effect of an organic solvent on the electrode processes of the kind under consideration (when the depolariser is adsorbed on the electrode), amounts to the displacement of the depolariser from the electrode surface [*i.e.*, to the diminution of β_0 in equation (8)] rather than to a change (at any rate, a considerable one) in the rate constant of the electron transfer k_{el}', which results in a decrease in the overall-process rate. The effect of organic solvents is the stronger, the greater is the adsorption of the depolariser on the electrode; therefore, the maximum effect of the solvent, as pointed out by Cisak,[27] is observed in the vicinity of the electrocapillary zero potential.

Formally, the shift of $E_{1/2}$ may be considered to be the result of a decrease in the activity of the depolariser from its solubility rising considerably with increasing organic solvent content.

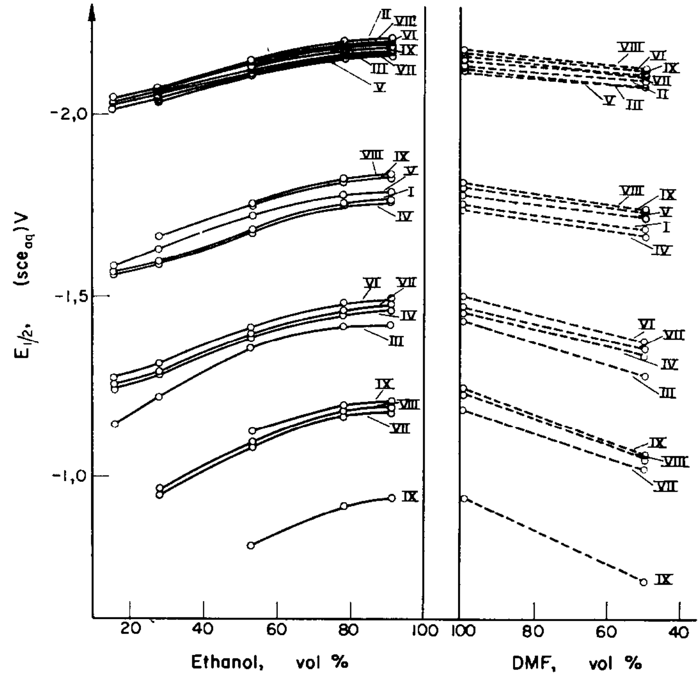

FIG. 1.—Dependence of $E_{1/2}$ of the waves of various bromothiophenes on the content in the aqueous-organic mixture of ethanol (left) and dimethylformamide (right). Roman numerals relate to derivatives with bromine-atom positions in the thiophene cycle: for monobromoderivatives I–2, II–3; for dibromoderivatives III–2,3; IV–2,5; V–3,4; VI–2,4; for tribromoderivatives VII–2,3,5; VIII–2,3,4; tetrabromoderivative IX–2,3,4,5.

It should be noted that a rigorous quantitative evaluation of the effect of the solution composition on $E_{1/2}$ [according to equations of the type of (2), (8) or others] is impossible because the change in the liquid junction potential is not known.

At low concentrations of the organic solvent, the shift of $E_{1/2}$ of the waves is the greater, the higher is the surface activity of the solvent.[7,29] However, on transition to solvents with a low water content, the $E_{1/2}$-values of the waves for the same depolariser become almost similar in different solvents (*e.g.*, the $E_{1/2}$-values of bromothiophenes in 91% ethanol and 99% dimethylformamide in Fig. 1, see also Fig. 9 in [7]). Apparently, at a very high concentration of the organic solvent, a practically complete desorption of the depolariser occurs, and the nature of the solvent has almost no effect on the $E_{1/2}$ of the waves

ELECTRODE PROCESSES WITH PREPROTONATION

An increase in the organic solvent content results in a rise of the pH of acidic solutions[6a,7] and in an increase in the dissociation constant K_A of protonated substances;[30] both these factors sharply lower the rate of the preprotonation and, consequently, lead to a shift of $E_{1/2}$ of the reduction waves in the case of processes with preprotonation towards more negative potentials [see equations (1) and (4)].

Upon addition of organic solvents to an aqueous solution, the rate of protolytic interaction between the bases and water also decreases sharply. Fig. 2 shows, as an example, the dependence of the rate constants of pyridine and 2,6-lutidine protonation under the action of water[30]

$$B + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH^+ + OH^- \qquad \text{(II)}$$

on the ethyl alcohol concentration in $0{\cdot}5M$ potassium chloride solution; the constants

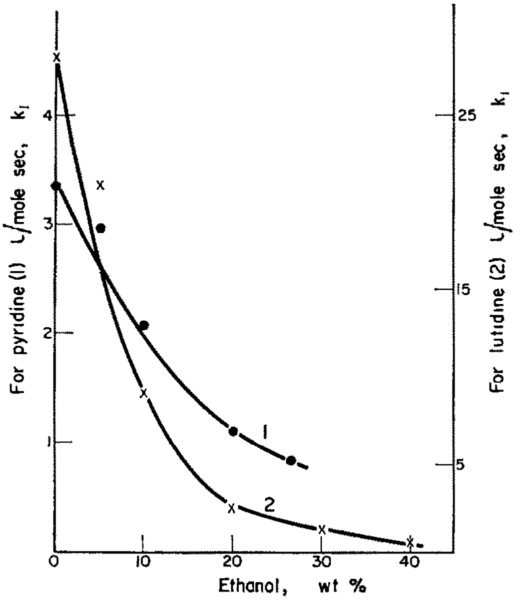

FIG. 2.—Dependence of the rate constants of pyridine (1) and 2,6-lutidine (2) protonation under the action of water on the ethyl alcohol concentration in aqueous-ethanol solutions.

were calculated from the slope of the dependence of the heights of the *bulk* catalytic hydrogen waves on the concentration of pyridine and lutidine, respectively, using the equations for the limiting catalytic currents of hydrogen in non-buffer solutions.[31] It is clear from Fig. 2 that when the ethanol concentration is increased up to 20% (by weight), the rate constant k_1 for pyridine is decreased 4 times and for 2,6-lutidine—10 times! The logarithm of the rate constant of protonation under the action of water in aqueous-ethanol solutions proved to change almost linearly with the reciprocal of the dielectric constant of the solvent (in the values of D no allowance was made for the effect of the dissolved potassium chloride on the dielectric constant).

An increase in the ethanol content results in a decrease both in the catalyst basicity (pK_A becomes lower) and in the proton-donor (water) acidity (pK_W increases). Both these factors result in a decrease in the rate constant k_1 for the reaction of the catalyst with water. According to Brönsted's relation, the change in log k_1 with an increasing ethanol content is proportional to the sum of the absolute values of the changes in pK_A

and pK_W (Fig. 3). The ratio $\Delta \log k_1/(|\Delta pK_A| + |\Delta pK_W|) \approx 1$ for the pyridine protonation is close to the sum of the values of the slopes of the Brönsted lines, expressing the relationship between $\log k_1$ and pK of the acids (proton-donors) ~0·5 [32] and between $\log k_1$ and pK_A of the catalysts ~0·58.[33] This ratio for 2,6-lutidine is equal to ~1·35 (Fig. 3).

A still greater decrease in the rate of the electrode process is observed with an increasing organic solvent content in the case of a surface preprotonation, because in addition to a decrease in the protonation rate constant, the adsorptivity of the basic (electrochemically inactive) form of the depolariser also diminishes.

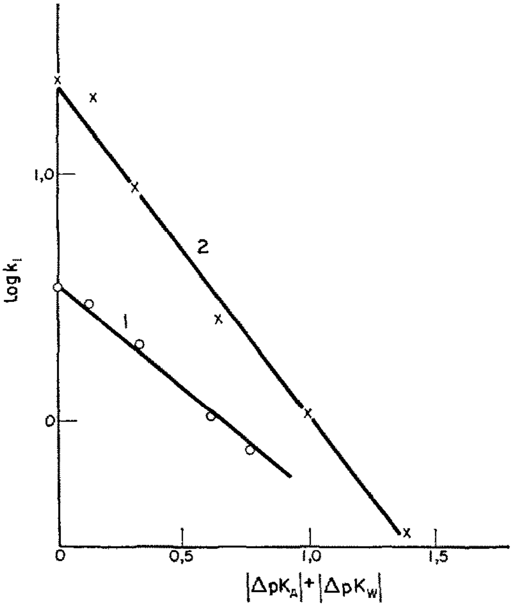

FIG. 3.—Dependence of the logarithm of the rate constants of pyridine (1) and 2,6,-lutidine (2) protonation by water on the changes of $|\Delta \rho K_A| + |\Delta \rho K_W|$ in aqueous-ethanol mixtures.

Fig. 4 shows the reduction waves of 2-acetyl-5-bromothiophene in an alkaline solution at various methanol concentrations observed by Mairanovskii and Filonova.[34] It was shown that the electrochemical breaking of the C–Br bond in this compound is preceded by the protonation (under the action of water) of the carbonyl group, the process occurring on the electrode surface with adsorbed acetylbromothiophene molecules. Therefore, the addition of methanol to the solution results in a shift of the wave towards more negative potentials and in a decrease in its limiting current (Figs. 4 and 5) both on account of the diminishment of the surface concentration of acetylbromothiophene and because of the lowering of the rate constant of its protonation.[34]

Stradinš, Reichmanis and Gavar[35] observed a decrease in the protonation rate in the case of the electrochemical reduction of 2-nitrofuran and its derivatives on the addition of ethanol to the solution. As the ethanol content increases, the four-electron reduction wave drops to the one-electron wave (the reduction to an

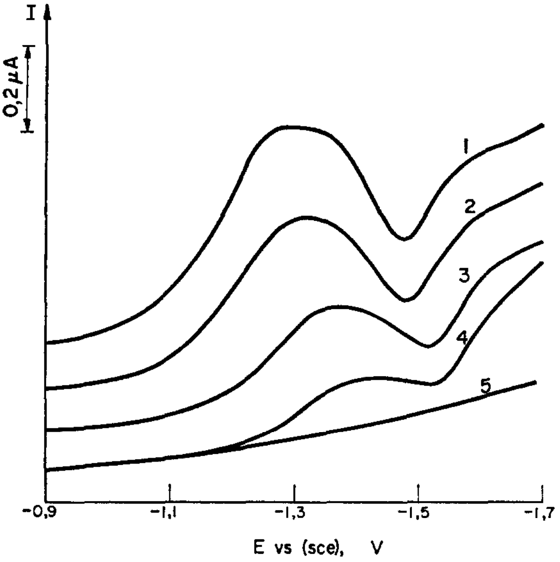

FIG. 4.—Polarograms of 0·2 mM 2-acetyl-5-bromothiophene solution with a 0·1*M* KCl + 0·1*M* KOH supporting electrolyte in aqueous-methanol mixtures. Methanol concentration (volume %): 1–1·6; 2–20; 3–40; 4–60 (at 25°; electrode: m = 0·89 mg/sec, t = 0·42 sec).

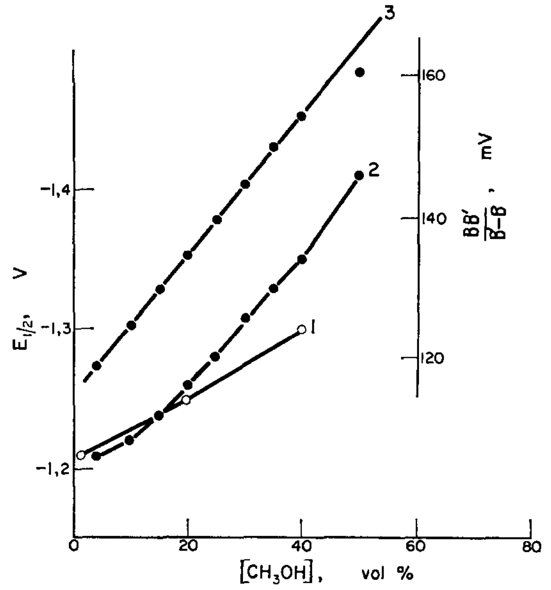

FIG. 5.—Dependence of $E_{1/2}$ (1 and 2) and of the values of the slope of the semi-logarithmic plot (3) of the first reduction wave of acetylbromothiophene in alkaline solutions on methanol concentration.

Acetylthiophene concentrations: 1–0·20 mM, 2 and 3–0·26 mM.

anion-radical), a new wave of the reduction of the non-protonised anion-radicals arising at more negative potentials. There are many examples of this phenomenon.

With increasing organic solvent content in aqueous-organic mixtures, the $E_{1/2}$-values of the waves corresponding to the electrode processes with preprotonation become more negative. Schwabe,[6a,7] however, showed for the case of the first wave of benzaldehyde that the shift of $E_{1/2}$ towards more negative potentials observed with increasing concentration of organic solvents is much greater than it should be if it were caused only by the change in pH of the solution. A greater shift than that corresponding to the apparent pH change was also observed for the wave of the reduction of *p*-dinitrobenzene in phthalate buffers where the shift is 85 mV with an apparent change in pH by unity.[36]

Schwabe supposed the additional shift of the wave to be caused by the inhibition of the electrode process by the solvent molecules adsorbed on the electrode. This conclusion is at variance with a number of observations; in particular, it was demonstrated[37] that an increase in the concentration of the isopropyl and ethyl alcohols did not reduce, but even somewhat increased the reversibility of the first waves of benzaldehyde and acetophenone in acidic media. The absence of the effect of the ethanol concentration (up to 80%) on the reversibility of the first waves of these compounds was also proved by Faraday's impedance measurements.[38] In addition, the reversible wave of benzophenone was observed in the presence of acids in the dimethylformamide media[39] and in pure pyridine,[40] and the wave of benzyl in ethanol-water mixtures and in dimethylformamide.[41]

In the case of benzaldehyde and acetophenone reduction in acidic media at small concentrations of organic solvents, the electrochemical step is close to a reversible one; it is preceded by the surface protonation of the carbonyl group.[42] The existence of preprotonation of the carbonyl group during its electrochemical reduction in acidic solutions was clearly proved by Ivcher *et al.*[43] They observed the division of the one-electron polarographic wave of cyclohexenone into two steps, the first of which, corresponding to the reduction of the protonised molecule, decreases with increasing pH, whereas the second step, corresponding to the reduction of the non-protonised cyclohexenone, increases the overall height of both waves being independent of pH and corresponding to the one-electron diffusion-controlled process.[43]

With increasing organic solvent content, the shift of $E_{1/2}$ is caused not only by the changes in pH and probably in pK_A of the protonated depolariser, but mainly by the decrease in the surface concentration of the depolariser. The appearance of the latter effect is because of an incomplete reversibility of the electrochemical step proper of the process.[37]

A decrease in the surface component of the current with increasing organic solvent content often "improves" the shape of the waves of complex processes, causing it to approach the theoretical one. Thus, in the investigation of catalytic hydrogen waves in non-buffer solutions of pyridine and its homologues the values of the current observed on the lower part of the wave are somewhat higher than the calculated ones (see Fig. 6). This increase in the current arises because a sufficient amount of adsorbed catalyst is still present at the potentials of the lower part of the wave, which sets up an appreciable surface current; with a rising cathodic potential, the catalyst adsorptivity rapidly decreases and the current becomes a purely bulk one. A decrease in the catalyst adsorptivity on addition of alcohol to the solution makes the catalytic wave of pyridine and its homologues purely bulk (space) over its whole length. Fig. 6 shows, as an example, the wave plots in log $i^{5/3}(i^{3/2}_{\text{lim}} - i^{3/2})$-E co-ordinates for the catalytic current in non-buffered solutions of 2,6-lutidine: a purely aqueous solution and an aqueous alcohol one.[30] From the figure, the semilogarithmic wave plot in these co-ordinates for an aqueous alcohol solution is a straight line with a theoretically predicted slope—$(59)^{-1}$ mV^{-1}.[31,33]

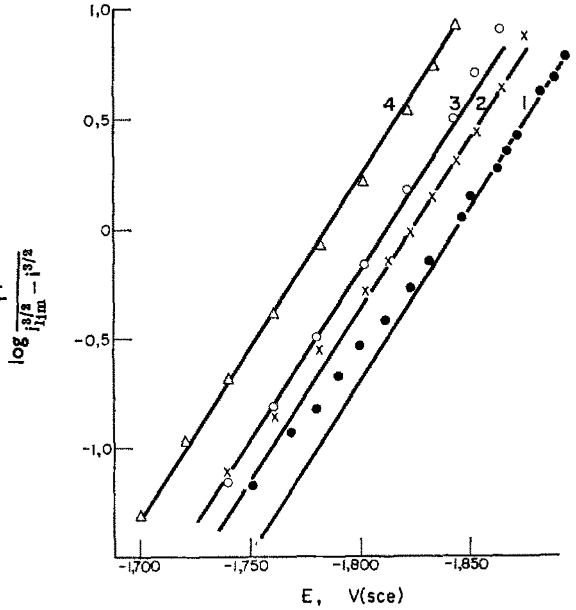

FIG. 6.—Logarithmic plots of catalytic hydrogen waves in 30 mM 2,6-lutidine solution with a 0·5*M* KCl supporting electrolyte: 1–aqueous solution, 2–10, 3–20, 4–30% (by weight) of ethanol.

If the component of the preceding reaction is but very slightly adsorbed on the electrode surface, the kinetic current observed is often of a mixed bulk-surface nature. Sometimes the adsorption of a substance on the electrode cannot reach the equilibrium state during the drop life. In this case, as shown by Levich *et al.*,[20] the quantity of adsorbed substance per unit surface increases approximately in proportion to the square root of the adsorption time. By making use of this fact and by studying the dependence of the mixed limiting kinetic current on the drop time, it is possible to estimate separately the bulk and the surface components of this current[17] as well as to determine the effect of various factors on each of these components. This method was used to study the effect of ethanol concentration on the bulk-surface kinetic current of maleic acid reduction, which is controlled by its recombination from the mono-anions in an acetate buffer solution.[17] Fig. 7 shows the dependence of the kinetic current function R on the square root of the drop time of a dropping electrode at different ethanol concentrations. From Fig. 7, at low ethanol concentrations R rises with $t^{1/2}$, which corresponds to an increase in the contribution of the surface component of the current with time. With increasing ethanol concentration the straight lines expressing the dependence of R on $t^{1/2}$ become less steep and at ethanol concentrations over 30% is almost independent of it. Because the steepness of this dependence is also determined, among other factors, by the adsorptivity of the depolariser,[17] the decrease in the steepness of the straight lines in Fig. 7 corresponds to a decrease in the adsorptivity of the mono-anions of maleic acid, hence to a smaller contribution of the surface component of the current, the latter dropping almost to zero at ethanol concentrations over 30%.

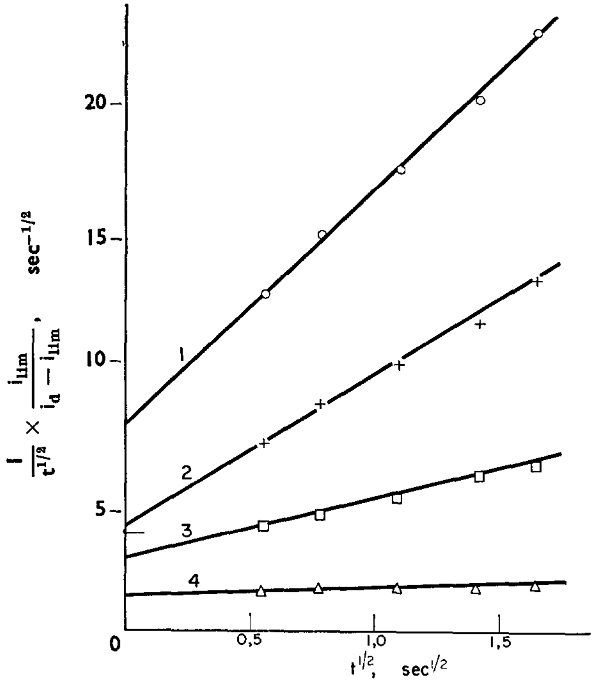

FIG. 7.—Dependence of $[i_{lim}/(i_d - i_{lim})] \times (1/t^{1/2}) = R$ on $t^{1/2}$ for the mixed bulk-surface kinetic waves of the maleic acid mono-anion recombination at 25° in an acetate buffer of pH 5·1 (without ethanol) at different ethanol concentrations (% by weight): 1–0, 2–10, 3–20, 4–30.

Afanasiev[44] observed a similar decrease in the surface component of the kinetic current on the addition of n-amyl and n-hexyl alcohols to an acetate buffer (Fig. 8). Because of the high surface activity of these alcohols, the displacement of adsorbed mono-anions and a complete suppression of the surface component occur already at $1{\cdot}8 \times 10^{-2}$% of hexyl alcohol, and at 1.4% of amyl alcohol. Polyvinyl alcohol which has a high surface activity, exerts an even stronger suppressing action (Fig. 9).[44] By the measurements of the i–t curves Afanasiev showed that the decrease of the current in the presence of the polyvinyl alcohol is caused both by the displacement of the adsorbed mono-anions of maleic acid from the surface and by the inhibition of the electrochemical reaction proper, which occurs only on the uncovered parts of the electrode surface.

It should be noted that separate determinations of the surface and of the bulk components of the current are especially convenient when the constants of the protonation rate in the bulk layer and on the electrode surface are different,[17] *i.e.*, when the

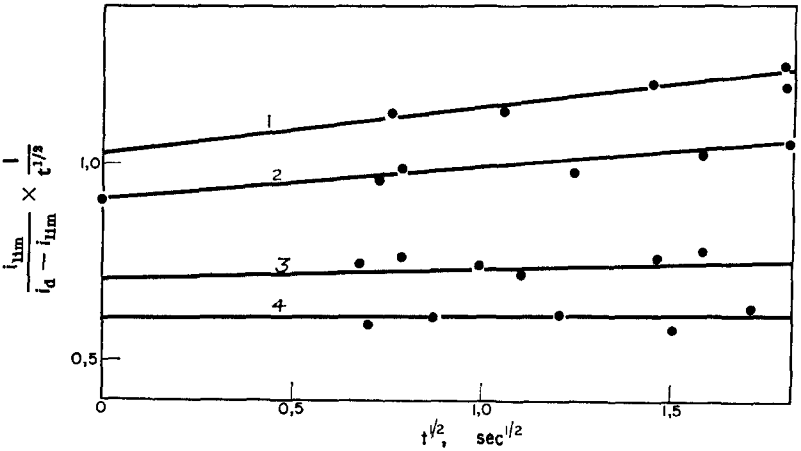

FIG. 8.—The same dependence as in Fig. 7 at pH 5·8 and different n-amyl alcohol concentrations: *1*–0, *2*–0·25, *3*–0·8, *4*–1·4% (from ref. 44).

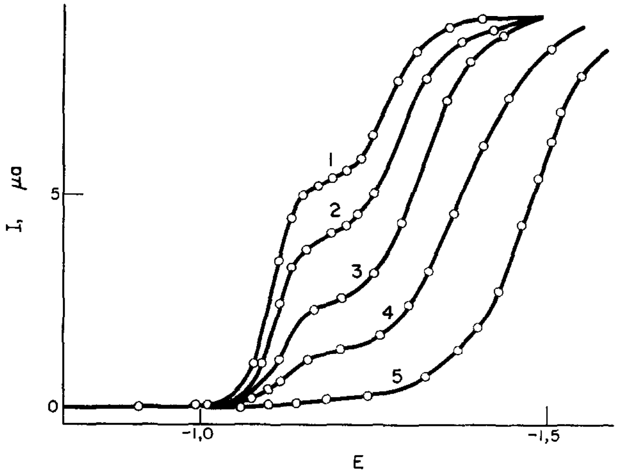

FIG. 9.—Effect of polyvinyl alcohol (PVA) additions on the maleic acid waves in an acetate buffer of pH 5·8. Concentrations of PVA: 1–0, 2–0·002, 3–0·006, 4–0·010, 5–0·018% (from ref. 44).

Grabowski effect is displayed.[2,3] The different dependences of these two components of the current on time can be used for this purpose only under the conditions when the adsorption is far from the equilibrium state. Usually, however, the adsorption equilibrium is practically established at the very beginning of the drop life, so that the density of the surface current does not depend on the drop time.

PROCESSES INVOLVING ADSORPTION OF ELECTROCHEMICAL REACTION PRODUCTS

With an increase in the size of an organic molecule, its adsorptivity on a mercury electrode increases (at not too negative potential values). Therefore, a higher adsorptivity of the reaction products compared to the adsorption of initial substances should be observed in the case of electrode processes resulting in the formation of dimers. It is most convenient to observe the effect of adsorption of the reaction products in the case of processes with the electron transfer occurring so fast that the electrochemical step can be considered to be a reversible or an almost reversible one.

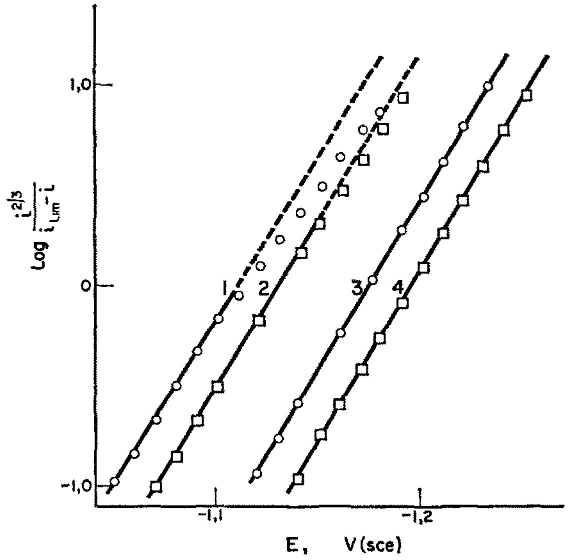

FIG. 10.—Semilogarithmic plot of the first wave of benzaldehyde (c = 1·5 mM) in an acetate buffer (0·1*M* NaAc + 0·1*M* HAc). Isopropanol concentration (% by volume) in solution and apparent pH equal to, respectively: 1–0%, 4·37; 2–12%, 4·48; 3–32%, 4·95; 4–42%, 5·09

(electrode characteristics: m = 0·91 mg/sec, t = 0·28 sec).

An electrode process with a fast electron transfer and a subsequent dimerisation of the products formed occurs in the case of the first wave on the polarograms of aromatic aldehydes and ketones in an acidic medium[17] as well as during the reduction of *N*-alkylpyridinium salts.[17] The shape of the polarographic wave for such processes, as was shown[17] on the basis of Koutecký and Hanuš's data, is described by the equation

$$E = \varepsilon_0 - \frac{RT}{F} \ln \frac{i^{2/3}}{i_{lim} - i} \tag{9}$$

where ε_0 is the characteristic potential independent of the depolariser concentration. Consequently, the wave plot in the log $i^{2/3}/(i_{lim} - i)$ — E co-ordinates should be a straight line with the reciprocal of the slope 59 mV. Fig. 10 shows the plots[37] in the above co-ordinates for the waves of benzaldehyde in solutions with different isopropanol* content. From the figure, in the absence of isopropanol (curve 1) a straight-line plot with a theoretical slope is observed only on the bottom part of the wave, *i.e.*, for

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* It is erroneously stated in reference 37 that the experiments with benzaldehyde were carried out in aqueous-ethanol solutions.

small current values. The top part of the wave is somewhat shifted towards more negative potentials, the shift being the greater, the higher is the value of the current. The shift of the top part of the benzaldehyde wave is caused by the inhibition of the electrode process by the dimeric products accumulated on the electrode surface, the surface coverage with these products and the inhibition effect increasing with a rising current.[37] The addition of isopropanol to the solution, which lowers the adsorptivity of dimeric products, makes the wave shape approach the theoretical one (Fig. 10); at an isopropanol concentration about 30%, the wave over its whole length obeys equation (9). A similar effect is also observed for the first wave on the polarograms of acetophenone.[37]

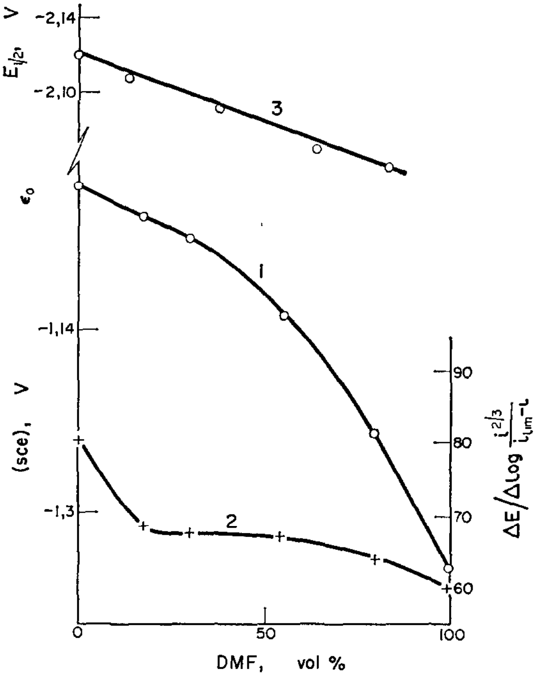

FIG. 11.—Dependence of the characteristic potential ε_0 (1) and of the reciprocal of the slope of the semilogarithmic plot (2) in E — log $i^{2/3}/(i_{lim} - i)$ co-ordinates for the waves of *N*-ethylpyridinium iodide (c = 0·64 mM) and of the $E_{1/2}$ values of the wave of the rubidium discharge (3) on the concentration of dimethylformamide with a 0·05*M* $(C_2H_5)_4NI$ supporting electrolyte.

In a polarographic reduction of *N*-ethylpyridinium iodide with a tetra-alkylammonium salt used as supporting electrolyte, the mean value of the reciprocal of the slope of the semilogarithmic wave plots drawn in accordance with equation (9) also falls with a rising organic solvent concentration (see curves 2 in Figs. 11 and 12), tending to approach the theoretical value —59 mV. In this case, as well as in the polarographic reduction of aldehydes and ketones, the organic solvent reduces the adsorptivity of a dimer, *N,N*-diethyldihydrodipyridyl, on the electrode and thus diminishes the inhibition of the electrode process.

It should be noted that the ε_0 (and $E_{1/2}$ as well) of the waves of *N*-ethylpyridinium iodide become less negative when the organic solvent content in the solution increases (curve 1 in Figs. 11 and 12), just as is the case for the reversible discharge of metal cations under the conditions when no formation of complexes occurs (see, for example, curve 3 in Figs. 11 and 12 for the wave of the rubidium ions discharge as well as the data for the wave of other ions in refs. 6, 8–14). Formally, this shift of $E_{1/2}$ can be explained by an increase in the activity of the metal ions with the decreasing dielectric constant of the solution.

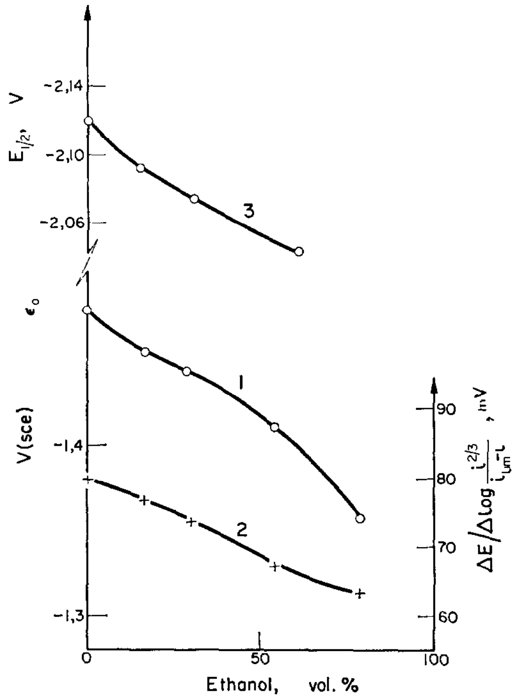

FIG. 12.—Dependence of ϵ_0 (1) and of the reciprocal of the slope of the semi-logarithmic plot (2) of the wave of *N*-ethylpyridinium iodide and of $E_{1/2}$ of the rubidium wave (3) on the concentration of ethanol in aqueous-ethanol solutions with a 0·05*M* $(C_2H_5)_4NI$ supporting electrolyte.

As has already been pointed out, in the case of the first waves of aromatic aldehydes and ketones, with increasing content of organic solvents, their ϵ_0 (and $E_{1/2}$) become more negative (Fig. 10) in spite of the fact that electrons are also transferred to the protonised positively charged particle. Such behaviour of carbonyl-containing compounds is because their discharge step is preceded by the surface protonation, whose rate falls with increasing concentration of the organic solvents both on account of a reduced activity of the hydrogen ions and because of the diminishment of the amount of the non-protonised particles adsorbed on the electrode.

It should be emphasised, in conclusion, that only in the presence of organic solvents reducing the adsorption effects is it possible to obtain purely bulk kinetic and catalytic waves the behaviour of which is accurately described by relatively simple theoretical equations. In addition, only by a polarographic analysis in organic solvents is it possible to obtain the values of the half-wave potential of organic compounds undistorted by adsorption effects, which can be used to establish correlations with the structure of these compounds. When working with organic solvents, however, it is necessary to take into account the possibility of an interaction between the depolariser and the solvent.

INTERACTION OF DEPOLARISER WITH SOLUTION COMPONENTS

It should be noted that sometimes when the composition or the nature of the solvent is changed, $E_{1/2}$ can be somewhat affected not only by the protolytic properties of the solvents, but also by the specific interaction of the depolariser with the solvent.

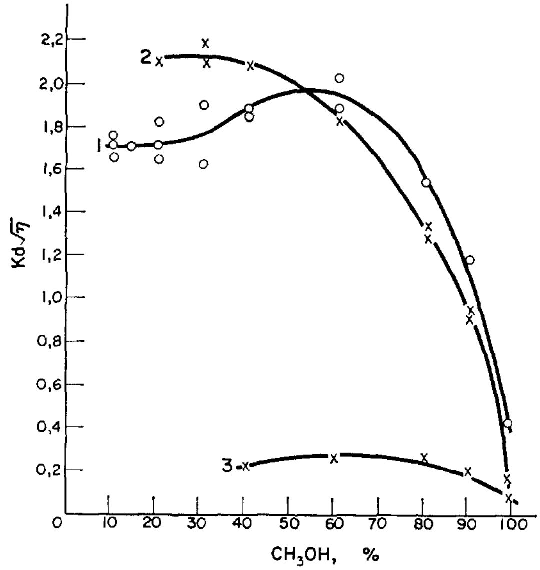

FIG. 13.—Dependence of $i_{lim}\sqrt{\eta}/cm^{2/3}t^{1/6}$ (for the equilibrium state) on methanol concentration on acidic media of the waves of:
1-benzaldehyde, 2-*p*-chlorobenzaldehyde, 3-phenylacetaldehyde (from ref. 48).

This seems to be the case when hydrogen bonds are formed between the depolariser and the solvent (see, for example, reference 45), as well as in some other instances. In particular, the specific interaction seems to take effect in the polarographic reduction of *p*-nitrochlorobenzene in non-aqueous solvents,[46] when upon the transition from methanol to acetonitrile $E_{1/2}$ of *p*-nitrochlorobenzene shifts from −0·84 V (S.C.E.) to −1·18 V, and in dimethylformamide becomes −1·41 V (with 0·1*M* sodium iodide as supporting electrolyte).

In some cases the solvent can affect the formation of the ionic pairs. Thus, a readier formation of the ionic pairs[47] with a decreasing ionic radius of the cation of the supporting electrolyte *in the series of the iodides of* $(C_2H_5)_4N^+$, Cs^+, Na^+ *shifts the* reduction waves of *p*-nitrochlorobenzene towards more positive potentials (−1·87, −1·52 and −1·41 V, respectively).

Bezuglyi and Raporta,[48] investigating the dependence of the limiting currents of the reduction waves of some aromatic aldehydes (benzaldehyde, *p*-chlorobenzaldehyde, phenylacetaldehyde) on the concentration of various alcohols in aqueous-alcohol solutions, established that in acidic media at high enough alcohol content in the solution, the product $i_{\text{lim}}\sqrt{\eta}$ (where η is the viscosity of the solution) begins to decrease (Fig. 13). A particularly strong decrease in the wave height is observed in methanol solutions, a much less pronounced one in ethanol solutions (but only in those with a low water content); the value of $i_{\text{lim}}\sqrt{\eta}$ remains almost unchanged in the solutions of isopropyl and butyl alcohols. The values of i_{lim} of the waves of the compounds investigated directly at the moment of their introduction into an acidic alcohol solution (extrapolation to zero time) corresponds to a normal diffusion current. However, the value of i_{lim} decreases fast with time, after 10–20 min reaching a constant value (see Fig. 14). Bezuglyi and Raporta[48] explain the decrease in the current with time by the formation of polarographically inactive semiacetals from aldehydes, the attainment of a constant in time current value corresponding to the establishment of the equilibrium state. The equilibrium constants of the reactions of the formation of semiacetals with methanol and ethanol at different temperatures are evaluated from the dependence of the equilibrium value of i_{lim} on methanol and ethanol concentrations.

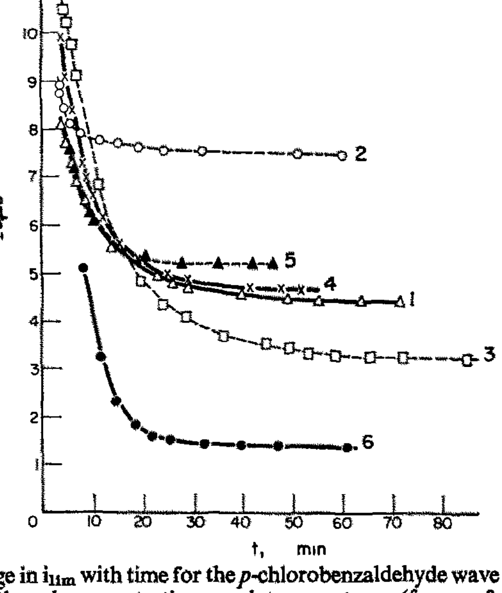

FIG. 14.—Change in i_{lim} with time for the *p*-chlorobenzaldehyde wave in acidic solutions at different methanol concentrations and temperatures (from ref. 48). 1–80%, 6°; 2–80%, 25°; 3–90%, 7°; 4–90%, 15°; 5–90%, 25°; 6–98·8%, 25°.

Résumé—On présente une revue sur l'influence de la composition des solvants organiques aqueux sur le comportement polarographique des composés organiques.

Zusammenfassung—Der Einfluss der Zusammensetzung der Mischungen von wasser mit organischen Lösungsmitteln auf das polarographische Verhalten organischer Verbindungen wird in einer Übersicht besprochen.

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POLAROGRAPHY AT HIGH PRESSURES

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Summary—A review of polarography at high pressures is presented.

INTRODUCTION

THIS contribution is concerned with perhaps the most esoteric application of polarographic methods, namely to systems and solutions at high pressures. In spite of the small number of recorded applications, I hope to justify its consideration in terms of its immediate application to electroanalytical chemistry, as well as in terms of its theoretical interest.

Pressure is not a commonly considered variable in relation to condensed phases, *i.e.*, liquids, because relatively high pressures (10^3–10^4 atm) are required to effect significant changes in their properties and this entails special equipment, more usually to be found in engineering laboratories. However, over the last few years, standard items of high-pressure equipment have become readily available. A range of high-pressure vessels, pumps, gauges, *etc.*, can be assembled without special tools or facilities; pressure can, therefore, reasonably be regarded as a normal practical variable rather than as a remote thermodynamic concept or a measure of gaseous molecular concentration.

In one important instance, resort to high-pressure techniques is a matter of necessity rather than of choice. To study solutions at temperatures above the normal boiling point of the solvent requires a closed system able to withstand increasing pressures at increasing temperatures. This is the situation in many high-temperature aqueous systems typical of hydrothermal situations, of autoclave procedures, *etc.* Although very often the pressures involved are only a few hundred atmospheres, similar apparatus and similar problems are involved and a consideration of these systems will also be included here.

Over the last few years, several reviews of high-pressure chemistry have been published[1–3] and in Hamann's book, in particular,[1] a detailed consideration of several electrochemical systems is included. A more comprehensive survey of high-pressure electrochemistry as such has, even more recently, been given by Hills and Ovenden.[4]

GENERAL CONSIDERATIONS OF PRESSURE AS A VARIABLE

The conjugate variable of pressure is volume and the effect of pressure on electrochemical systems is manifested not only in changes of total density, and therefore of concentration, but also in terms of displacement of equilibria and of changes in rate-constants, diffusion coefficients and ionic mobilities.

Equilibrium properties

The properties of equilibrium electrochemical situations may be summarised in terms of the equations*

$$\left(\frac{\partial G}{\partial P}\right)_T = V; \quad \left(\frac{\partial S}{\partial P}\right)_T = -\alpha V; \quad \left(\frac{\partial V}{\partial P}\right)_T = -\beta V \tag{1}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] = \frac{\alpha}{\beta} \tag{2}$$

For multi-component systems, *i.e.*, solutions, further partial derivatives arise:

$$\left(\frac{\partial V}{\partial m_2}\right)_{T,P,m_1} \ldots . = \bar{V}_2 \tag{3}$$

$$\left(\frac{\partial \bar{V}_2}{\partial P}\right)_T = -\bar{K}_2 \tag{4}$$

$$nF\left(\frac{\partial E}{\partial P}\right)_{T,\mu} = -\overline{\Delta V} = -\left[\sum^{p} \bar{V}_2 - \sum^{r} \bar{V}_2\right] \tag{5}$$

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_T = -\Delta\bar{V}^0 = -\left[\sum^{p} \bar{V}_2^0 - \sum^{r} \bar{V}_2^0\right] \tag{6}$$

$$2RT\left(\frac{\partial \ln \gamma_{\pm}}{\partial P}\right)_T = \bar{V}_2 - \bar{V}_2^0 \tag{7}$$

In all these equations, the subscript 2 refers to the solute. The superscript zero refers to the standard state implicit in the definition of $\gamma_{\pm}$ which, for electrolyte solutions, is infinite dilution.

The practical significance of these relationships to electrochemical systems will depend on the relative magnitudes of the various V terms and will vary from system to system. The compressibility is small (5×10^{-5} atm^{-1}) so that within the range of most accessible pressures the volume of solutions, and hence the solute concentration, will not change by more than a few per cent. From the viewpoint of polarography, the pressure-dependence of concentration is hardly a significant variable.

Activity coefficients also vary only slightly with pressure. It may be assumed that most of the change in activity coefficient can be described in terms of the corresponding variation in the macroscopic dielectric constant of the solvent which, for aqueous solutions, is well known. Owen and Brinkley[5] have tabulated experimental values of ε which fit the Tait relationship

$$\varepsilon_1/\varepsilon_P = 1 - A' \log_{10} \frac{B' + P}{B' + 1} \tag{8}$$

where A′ and B′ are characteristic quantities for each liquid. For water at 20°, values of $A' = 0{\cdot}4060$ and $B' = 2{,}925$ atm were obtained which, within the experimental precision, account for the gradual increase of ε from 81 at 1 atm to 100 at 6000 atm.

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* Symbols undefined in the text are defined at the end of the paper.

From values interpolated from this equation, Whitehouse[6] has calculated values of $\gamma_\pm$ for a (1:1) electrolyte over a range of pressures. He used the full Debye-Hückel equation and assumed a constant value of 4.3×10^{-8} cm for the distance of closest ionic approach. Some of his results are given in Table I.

TABLE I.—VALUES OF $\gamma_\pm$ AT 25° FOR A (1:1) ELECTROLYTE*

Pressure, *atm*	Molality	$\gamma_\pm$
1	0·01	0·9036
	0·05	0·8296
	0·10	0·7973
500	0·01	0·9061
	0·05	0·8343
	0·10	0·8037
1000	0·01	0·9084
	0·05	0·8392
	0·10	0·8106

* Calculated from the Debye-Hückel equation,

$$\log \gamma_\pm = - \frac{Ac^{1/2}}{1 + Ba_ic^{1/2}} + Cc - \log (1 + 0{\cdot}03604\, m).$$

The effect of pressure on the activity of completely dissociated electrolytes is thus small, but this is not the case with incompletely dissociated electrolytes. Invariably, the ionisation of neutral molecules is accompanied by electrostrictive compression of the surrounding solvent. The right-hand side of equation (6) is then positive and increasing pressure should, therefore, enhance the degree of dissociation. This is found experimentally (see Table II) and the observed variation can be semi-quantitatively described in terms of the Born equation and the variation of ε with pressure.[9]

It may, therefore, be anticipated that the ionisation of water also increases with

TABLE II.—THE EFFECT OF PRESSURE ON THE DISSOCIATION CONSTANTS OF WEAK ELECTROLYTES IN AQUEOUS SOLUTION AT 25°

	10^5K *mole kg*$^{-1}$				
	Pressure, *atm*				
Electrolyte	1	1000	2000	3000	Authors
HCO_2H	17·4	24·4	32·5	41·8	Hamann and
CH_3CO_2H	1·71	2·70	3·91	5·38	Strauss[8]
CH_3CO_2H	1·77	2·75	3·88	—	Ellis[7]
$C_2H_5CO_2H$	1·26	2·06	3·14	4·44	
NH_4OH	1·75	5·11	12·2	24·3	
CH_3NH_3OH	41·9	118	257	464	Hamann and
$(CH_3)_2NH_2OH$	58·9	162	366	752	Strauss[8]
$(CH_3)_3NH\ OH$	6·28	18·0	43·3	91·5	
H_3PO_4	710	1330	2100	—	Ellis[7]
$C_6H_5CO_2H$	5·9	9·3*	13·7*	17·7*	

* 1030, 2030 and 2780 atm, respectively.

pressure. Relative values of the dissociation constant of water have been calculated by Owen and Brinkley[5] in terms of the sum of ionic partial molar volumes for hydrogen and hydroxyl ions, which is assumed to be constant. These values are given in Table III; they have yet to be confirmed experimentally but are probably adequate for most purposes.

TABLE III.—THE CALCULATED VARIATION WITH PRESSURE OF THE DISSOCIATION CONSTANT OF WATER*

P, *bars*	K_p/K_1				
	5°C	15°C	25°C	35°C	45°C
1	1	1	1	1	1
200	$1·24_8$	1·225	1·202	1·180	$1·16_3$
400	$1·54_8$	1·490	1·435	1·384	$1·34_5$
600	$1·8_{96}$	$1·80_0$	1·703	$1·61_2$	$1·5_{45}$
800	$2·3_{17}$	$2·16_3$	2·009	$1·86_8$	$1·7_{66}$
1000	$2·8_{16}$	$2·58_5$	2·358	$2·15_4$	$2·0_{09}$

* From Owen and Brinkley.[5]

Non-equilibrium systems, irreversible processes

The rates of irreversible processes, such as diffusion, migration, charge-transfer, *etc.*, will also be pressure-dependent. Aside from changes in initial concentration, such rates will be specifically pressure-dependent if the transition or activated state of the rate-limiting step has a different density or molar volume compared with the corresponding unactivated state. In terms of the transition state theory, this is expressed as

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} \tag{9}$$

Again it may be noted that because many reactions in solution proceed through charged intermediate species, $\Delta V^{\ddagger}$ is negative and the pressure coefficient is, therefore, positive.

For diffusion and migration, a different situation obtains. The degree of electrostriction is virtually constant and the volume of the activated state reflects the consequential change in density associated with the rearrangement of solvent molecules. Additional degrees of freedom invariably imply a reduced density and hence volumes of activation for migration are normally positive. It follows that diffusion coefficients, ionic mobilities and solvent fluidities normally decrease with increasing pressure.[10–12]

The single and important exception to this generalisation concerns aqueous solutions at room temperatures. Between 0 and 60°, these translational properties are, to varying degrees, anomalously dependent on pressure. This is especially true of the mobility of the hydrogen ion and least true of the fluidity; but, in both cases, it is evident that the special structural features of water are involved.[13,14] Negative volumes of activation for translational processes are a particular feature of low-temperature aqueous solutions. They rapidly become positive at high temperatures and above 200°, water is a normal liquid, in this respect at least[15] (*cf.* Fig. 1).

APPARATUS

The general techniques of high pressure chemistry have been described elsewhere.[1,3,10,16] The design of components from steels of high tensile strength is based on well-established principles of elasticity. Most of the apparatus likely to be needed can be obtained from the increasing number of engineering companies specialising in high-pressure equipment.

A typical arrangement is shown in Fig. 2. Either oil or gas can be used as the pressurising fluid. The use of gases is simpler, cleaner but slightly more hazardous.

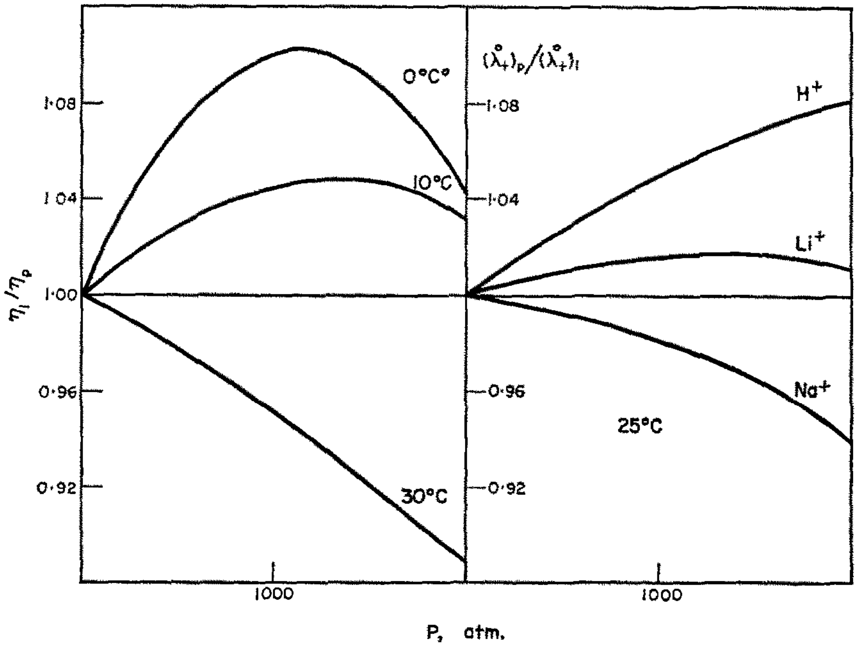

FIG. 1.—The variation with pressure of solvent viscosities and ionic mobilities for aqueous solutions.

Some compromise on the size of the pressure vessel is required and inevitably leads to the use of miniature electrochemical apparatus. Almost any rigid, glass apparatus will withstand large uniform hydrostatic pressures, but not shock treatments or even small pressure gradients. Efficient transmission of pressure is, therefore, essential and can be achieved by a number of simple devices, such as the mercury seals, pistons and flexible diaphragms shown in Fig. 3. Multiple electrical leads can readily be brought through the closure and a wide range of electrical and electromagnetic operations can be carried out in a normal pressure vessel. Specific applications of these procedures to voltammetric measurements have been made by Ewald and Lim,[17] Hayasi and Kono,[18] Mairanovskii, Gonikberg and Opekunov,[19] Payne[20] and Ellis and Hills[21] and will be described in greater detail below.

ELECTRODE POTENTIAL

The effect of pressure on reversible electrode potentials and, *inter alia*, on $E_{1/2}$ is described by equation (5) in terms of the cell reaction and of the corresponding partial molar volumes. Not many unambiguous experimental measurements have been made, *i.e.*, of cells without liquid junction, but it may be generally concluded that because $\bar{V}_2$ terms are small and often similar, $(\partial E/\partial P)_T$ is also small (1–10μV atm^{-1}).

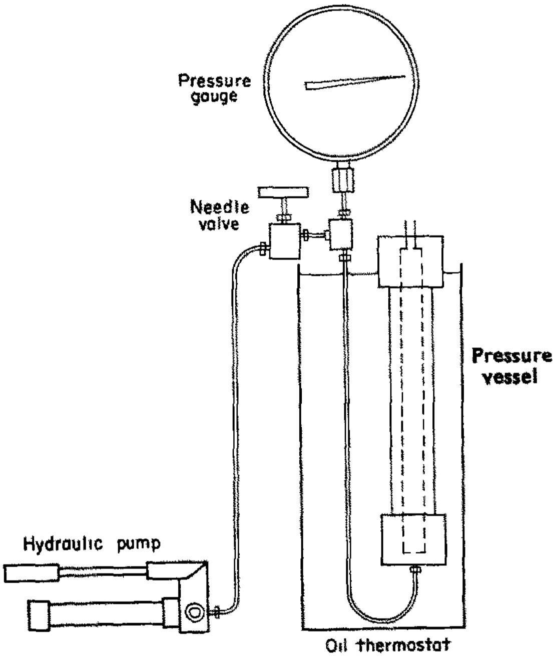

FIG. 2.—A typical high-pressure assembly for electrochemical measurements on the range 1–5000 atm.

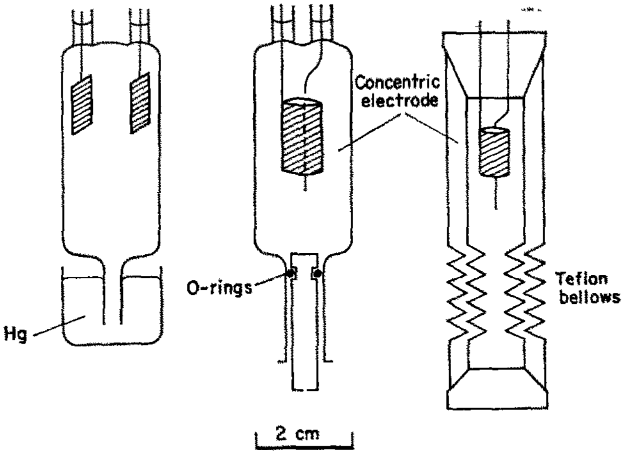

FIG. 3.—Pressure-transmission devices for electrochemical cells.

If a gaseous component is involved, then much larger values of $\Sigma \bar{V}_2$ and $(\partial E/\partial P)_T$ will be observed. MacInnes[2] studied the cell

$$\begin{array}{l} H_2, Pt/HCl\ (aq)/Hg_2Cl_2/Hg \\ (P\ atm) \end{array}$$

and the observed pressure coefficient is almost entirely determined by the molar volume of molecular hydrogen.

Direct polarographic measurements of $E_{1/2}$ have so far been neither accurate nor comprehensive enough for general conclusions to be drawn. Because dielectric constants increase with pressure, it could be argued that any overall increase in valency or ionic character in the cell reaction would be correspondingly enhanced. Thus, the reduction of multivalent ions will take place at increasingly negative potentials with respect to a reference electrode involving only singly charged ions. This appears to be confirmed experimentally.[17]

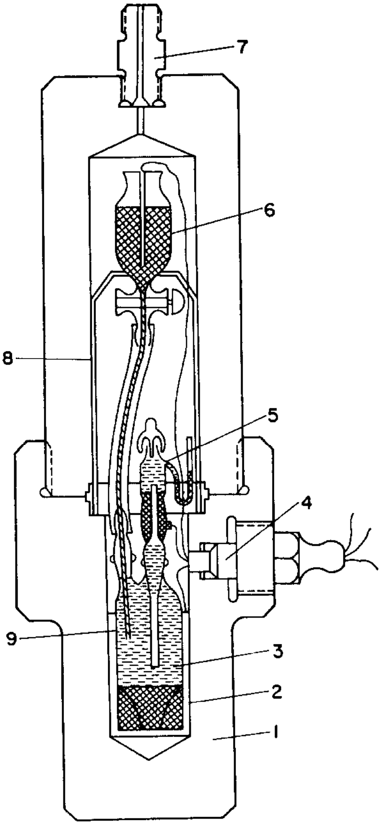

FIG. 4.—A cell for polarography with pressure (from ref. 19).

The case of irreversible electrode processes is dealt with below. An increase in pressure causes a marked fall in hydrogen overpotential which is, however, a consequence of the change with pressure of the associated rate constant.

DIFFUSION-CONTROLLED ELECTRODE PROCESSES

Dropping mercury electrode

The use of the mercury electrode at pressures of several thousand atmospheres presents no fundamental difficulties. It was first reported by Mairanovskii *et al.*[19] and their apparatus is shown in Fig. 4. The mercury reservoir and the mercury pool both transmit the pressure and normal polarograms are obtained.

They studied the reduction of thallium(I), zinc, cadmium and hydrogen ions in aqueous 0·1*M* potassium chloride and found no detectable change of limiting current with pressure at 25° for any of these species. In terms of the Heyrovský-Ilkovič equation

$$\bar{i}_L = 607\, cnm_{Hg}^{2/3}\tau^{1/6}D^{1/2} \tag{10}$$

the pressure-dependent terms are seen to be m_{Hg}, τ, c and D. The viscosity of mercury is not significantly pressure-dependent and, in any case, a timed drop-detachment device was used to regulate and maintain the drop size. Any pressure-dependence is, therefore, restricted to the product $cD^{1/2}$. However, $D \approx k_\eta \eta^{-1}$ and $c \approx k_c V$ and Bridgman[10] has shown that at room temperature the product $\eta^{1/2}V$ for water is practically constant. It follows that $cD^{1/2}$ and hence $\bar{i}_L$ will not be appreciably independent of pressure, at least up to 3000 atm.

In fact, the approximation that $D \approx k_\eta \eta^{-1}$ is not a good one, and in a later study Payne[20] detected small systematic changes of $\bar{i}_L$ with pressure for cadmium ions in potassium chloride (Fig. 5). $\bar{i}_L$ is seen to increase slightly with pressure, in keeping with the conductance isotherms of aqueous solutions at 25°. The half-wave potentials were also observed to be sensitive to pressure. The reductions of cadmium and zinc ions were found to be reversible and to follow a linear E *vs.* $\log (i/\bar{i}_L - i)$ relation of the appropriate slope.

Solid micro-electrodes

Two independent studies of platinum micro-electrodes have been made, by Ewald and Lim[17] and by Hayashi and Kono,[18] in both cases using d.c. polarisation. The agreement between the two sets of results is not good, even allowing for the fact that they relate to different reducible species. Ewald and Lim's results for 0·01*M* copper sulphate in 0·5*M* potassium chloride are shown in Fig. 6. The limiting currents are seen to be very pressure-dependent whereas those of the Japanese workers barely change at all. It is possible that the copper(II) ion is partly associated, although in this case pressure should enhance the degree of ionisation and, therefore, also the limiting current. The use of stationary electrodes and d.c. polarisation is always liable to give anomalous results and it would be interesting to use shorter polarisation times to ensure the absence of spurious conviction.

Hanging mercury drop

The hanging mercury drop electrode also functions well at high pressures. Little systematic polarography has been carried out, but its use in another type of study is described below.

INTERFACIAL EQUILIBRIA AND ELECTRODE CAPACITY

By means of relaxation methods, other properties of reversible electrode systems can be investigated. Both the exchange current and the interfacial capacity can be determined and made the basis of a total description of the equilibrium electrode interface. Up till now, only the pressure-dependence of the capacitance has been measured[23] but this isolated study has already allowed an extensive thermodynamic analysis to be made of the adsorption into the interface of solvent and of ions. This type of analysis is based on the Gibbs' adsorption equation for a charged interface, *i.e.*,

$$-d\gamma = \sum \Gamma_{\pm}\, d\mu + q\, d\varepsilon_{\pm} + \Gamma_S\, dT - \Gamma_V\, dP \tag{11}$$

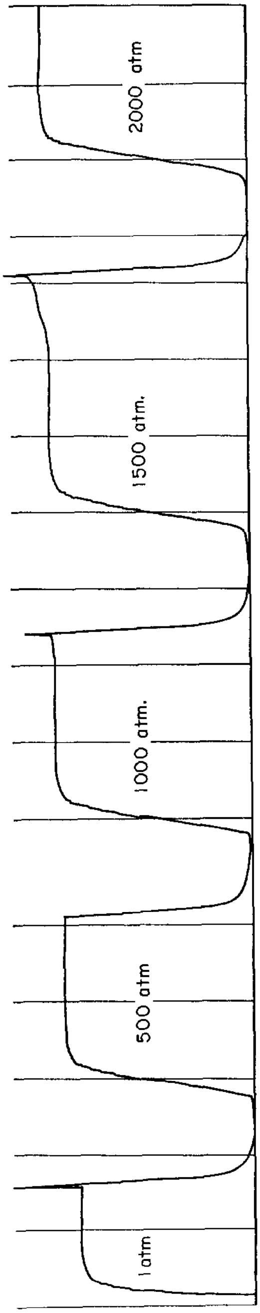

FIG. 5.—The polarographic reduction of 0·001*M* lead(II) in 0·1*M* KCl at 25°.

where $\Gamma_{\pm}$, q, Γ_S and Γ_V are the interfacial excesses of constituent ions, charge, entropy and volume, respectively. $\varepsilon_{\pm}$ is an electrical variable defined by the total cell e.m.f. and the chemical potentials of the components of the reference electrode. Thus, in the cell

$$\mathrm{Hg/solution/Hg_2Cl_2/Hg},$$

$$\varepsilon_{\pm} = \varepsilon_{-} = \mathrm{E} + \frac{\frac{1}{2}\mu_{\mathrm{Hg_2Cl_2}} - \mu_{\mathrm{Hg}}}{\mathrm{F}} \tag{12}$$

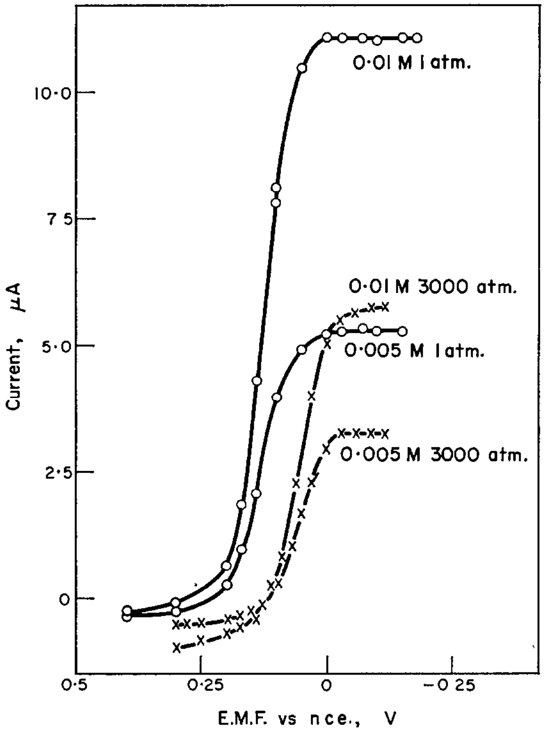

FIG. 6.—Polarograms of $CuSO_4$ in aqueous 0·5*M* KCl at 25° (from ref. 17).

The interfacial excess volume is the change in total volume when the two bulk phases, metal and solution, are brought together. It will be largely a function of the solvent and thus the pressure coefficient of interfacial tension will be a measure of extent to which the solvent is involved in the interface. So far, this coefficient has not been determined although it would not be difficult. Instead, Γ_V has been obtained by an indirect procedure based on the measurement of the pressure coefficient of electrode capacity.

After Parsons,[24] equation (11) can be expressed in terms of another variable, $\xi_{\pm}$ defined as

$$\xi_{\pm} = \gamma + \mathrm{q}\varepsilon_{\pm} \tag{13}$$

whereby

$$-\mathrm{d}\xi_{\pm} = \sum \Gamma_{\pm}\,\mathrm{d}\mu - \varepsilon_{\pm}\,\mathrm{dq} + \Gamma_S\,\mathrm{dT} - \Gamma_V\,\mathrm{dP} \tag{14}$$

Cross-differentiation of this equation at constant temperature and constant chemical potential then gives

$$\left(\frac{\partial\Gamma_V}{\partial q}\right)_{T,\mu,P} = \left(\frac{\partial\varepsilon_\pm}{\partial P}\right)_{T,\mu,q} \tag{15}$$

$\left(\frac{\partial\varepsilon_\pm}{\partial P}\right)_{T,\mu,q}$ can be related *via* equation 12 to the pressure coefficient of cell e.m.f., *i.e.*,

$$\left(\frac{\partial\varepsilon_\pm}{\partial P}\right)_{T,\mu,q} = \left(\frac{\partial E}{\partial P}\right)_{T,\mu,q} + \frac{\frac{1}{2}V_{Hg_2Cl_2} - V_{Hg}}{F} \tag{16}$$

$\left(\frac{dE}{\partial P}\right)_{T,\mu,q}$ can then be obtained from the general relation

$$\left[\frac{\partial(1/C)}{\partial P}\right] = \frac{\partial}{\partial P}\left(\frac{\partial E}{\partial q}\right) = \frac{\partial}{\partial q}\left(\frac{\partial E}{\partial P}\right) \tag{17}$$

and it follows, therefore, that by integration of the pressure coefficient of the capacitive reactance, $\left(\frac{\partial E}{\partial P}\right)$ can be obtained. Further integration of this quantity then leads to Γ_V, *i.e.*,

$$\int_0^q \int_0^q \left[\frac{\partial(1/C)}{\partial P}\right]_{T,\mu,q} dq\, dq \approx \Gamma_V + \text{constant} \tag{18}$$

The first integration constant is found from the variation with pressure of the capacity at $q = 0$. The other integration constant requires that the absolute interfacial tension be known as a function of pressure. This is not yet known and thus all the values of Γ_V obtained so far are relative to that of the system Hg/aqueous NaF (0·1*M*) at $q = 0$.

Precise measurements of capacity were made at the dropping mercury electrode using the apparatus shown in Fig. 7. The pressure was transmitted *via* the head of mercury and an inflatable plastic bag in which the mercury collected without either creating a back-pressure or an additional head-pressure through distention of the bag. Multiple leads through the top closure enabled inpedance measurements to be made on a controlled and timed dropping electrode.

The results of Payne's study are shown in Figs. 8 and 9. They illustrate the significant changes in volume accompanying the adsorption or desorption of water in the inner region of the double layer. The anodic hump, which has been the subject of a number of recent papers,[25,26] is identified not with re-orientation of the water but rather with the competing effects of increasing adsorption of water, of the outward displacement of the inner Helmholtz plane and, for specifically adsorbed ions, of the displacement of water from the inner layer. It is particularly noticeable that the steep fall in capacity (on the anodic side of the hump) caused by nitrate ions is associated with the largest volume change. The positive volume change accompanying the adsorption of ions is an important feature in a later discussion of electrode kinetics.

CHARGE-TRANSFER PROCESSES: THE HYDROGEN-ELECTRODE REACTION

Only a single study has so far been made of the pressure coefficient of a clearly identifiable electrode reaction. Kinnibrugh[27] has measured the rate of the hydrogen evolution reaction on mercury in aqueous 0·1*M* hydrochloric acid. He used a hanging mercury drop of precisely known surface area formed inside the pressure system by means of an electrically driven syringe.

At 25° and from 1 to 1500 atm hydrostatic (not hydrogen) pressures, constant Tafel slopes of 2RT/F were obtained. The transfer coefficient is, therefore, independent of pressure but the current density at constant overpotential was found to be very pressure dependent, increasing by 100% for a rise of 1000 atm pressure. The exact pressure coefficient, $(\partial \ln i/\partial P)_{T,\mu} = 1{\cdot}3 \times 10^{-4}\ \text{atm}^{-1}$ corrected for the pressure-dependence of the reference electrode potential, then corresponds, in terms of equation (9), to a volume of activation of $-3{\cdot}4$ ml. faraday^{-1}.

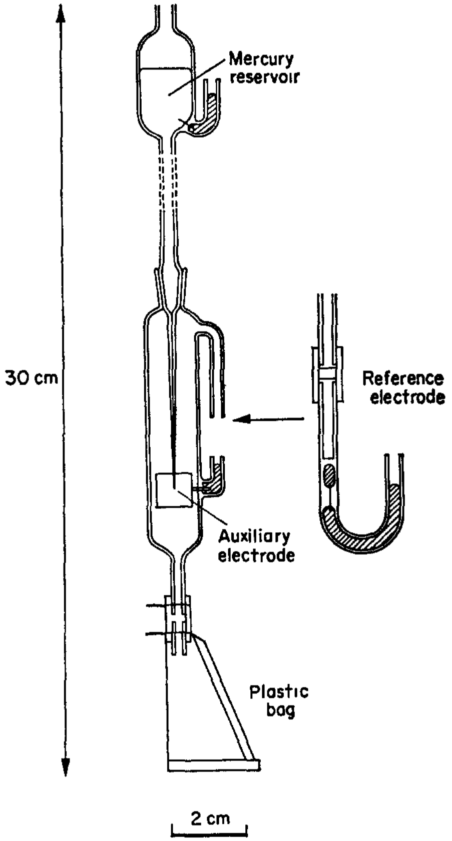

FIG. 7.—Miniature dropping mercury electrode for measurements of electrode impedance at high pressures.

This decrease in hydrogen overpotential has been noted earlier and discussed somewhat inconclusively by Hamann[28] in terms of variable pressures of dissolved hydrogen and oxygen. In Kinnibrugh's experiments, the solutions were oxygen-free but were initially saturated with hydrogen such that the working and reference electrodes were in equilibrium with the same partial pressure of dissolved hydrogen. This greatly simplified the definition of the overpotential. A further important simplification arises in this system because the observed current density is independent of the

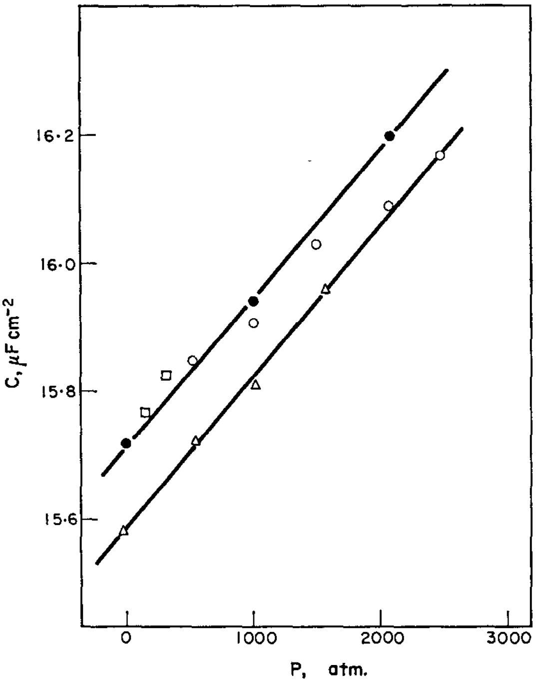

FIG. 8.—Variation with pressure of the capacity minimum in 0·1*M* NaF at 25° (from ref. 23). Results of three independent measurements (i) ●; (ii) ○ (increasing *P*); △ (decreasing *P*); (iii) □. All measurements have a common starting point at $P = 1$ atm and $C = 15{\cdot}72\,\mu$F cm^{-2}.

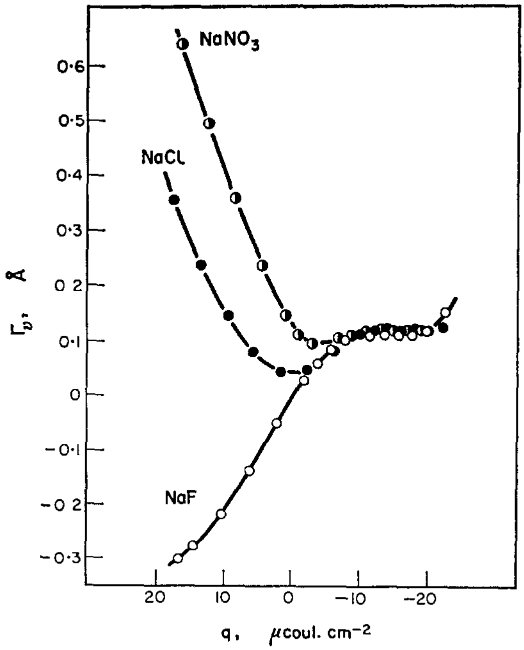

FIG. 9.—Surface excess volume as a function of charge for 0·1*M* solutions of the salts at 25° and 1 atm. Values are relative to the arbitrarily chosen zero at $q = 0$ for the NaF system.

bulk hydrogen-ion activity. This results from the relation between the ionic concentration and the potential of the diffuse double layer and it follows that the pressure-dependence of the 'initial state' of the charge-transfer reaction is not a significant factor. If, then, the rate-limiting step of the hydrogen evolution reactions is the reaction

$$H^+(aq) + e \rightarrow H \tag{I}$$

this passes through a transition state of higher density. It is not easy to see how this can be so, because the transfer of ions through the double layer and the neutralisation of charge are both normally accompanied by increases in solvent volume, which would suggest a transition state of *lower* density.

On the other hand, the second step

$$H^+(aq) + H + e \rightarrow H_2 \tag{II}$$

is much more easily correlated with the negative $\Delta V^\ddagger$, because the likely intermediate, H_2^+, is known to be a small ion and either as a transition state or a precursor from the equilibrium $H + H^+ \rightleftharpoons H_2^+$, it would be favoured by increased pressures. However, this rate-limiting step is difficult to sustain in the face of the observed Tafel slope unless there is also a constant (high) activity of adsorbed hydrogen atoms or H_2^+ ions. There is little evidence to support this further requirement and an explanation of the negative colume of activation must be sought in mechanism (I). It has been suggested[27] that the transfer of an electron through the Helmholtz layer of water is part of the rate-limiting step and one which might, therefore, give rise to further electrostriction and a volume decrement. There is little sign of this in Payne's study and the problem stands unresolved.

HIGH-TEMPERATURE HIGH-PRESSURE POLAROGRAPHY

The final application of high-pressure techniques is concerned with systems at temperatures above the normal boiling point of the solvent, where a pressure-tight vessel is required to retain the vapour. Not very high pressures are involved (*e.g.*, <100 atm) but pressure is nevertheless best seen as an independent variable.

A general review of 'hot-water' electrochemistry has been given by Ellis and Hills,[21] who describe in detail the use of the dropping mercury electrode and platinum microelectrodes in sealed aqueous systems up to 250°.

Using a blanketing pressure of argon ($\sim$100 atm), these authors made a polarographic study of aqueous solutions of cadmium, zinc, nickel and indium ions up to 250°, using the apparatus shown in Fig. 10. This apparatus is novel in its use of a looped system of two pressure vessels, one of which is the mercury reservoir. Reversible polarograms were obtained for cadmium and zinc ions (Fig. 11) and also for indium at high temperatures. The reduction of nickel became progressively more reversible, but even at 225° gave an n value of only $\sim$1.

Ellis and Hills were able to correlate the average limiting currents with the Ilkovič equation

$$\bar{i}_L = 605\, nm\rho m_{Hg}^{2/3} \tau^{1/6} D^{1/2} \tag{19}$$

where m_{Hg} is the *mass* flow of mercury. The water density term, ρ, is necessary to allow for the change with temperature of the volume concentration.

This equation may be changed to a form better suited for testing the characteristics of the dropping mercury electrode over a range of temperatures and pressures, *i.e.*, by using[29] the relationships

$$m_{Hg}\tau = 2\pi r_c\gamma/g \tag{20}$$

and

$$m_{Hg} = \pi r_c^4 dP_c/8l\eta \tag{21}$$

In these equations, r_c is the capillary radius, γ the mercury/solution interfacial tension,

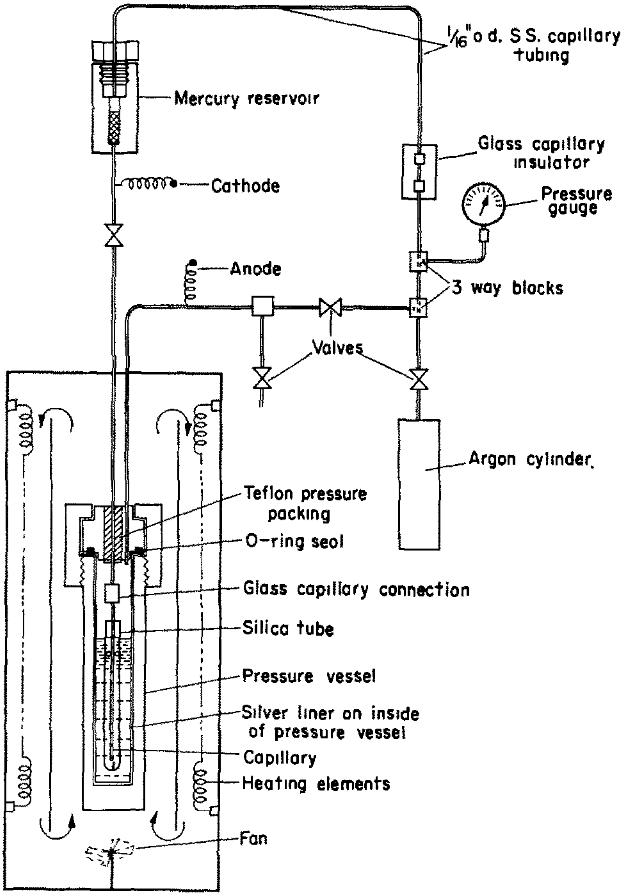

FIG. 10.—Ellis's apparatus for the polarographic analysis of hot water solutions.

g the gravitational constant, d and η the density and viscosity of mercury, respectively, l the length of the capillary, and P_c the hydrostatic pressure head of mercury (P_h) corrected for the back pressure due to interfacial tension at the surface of the growing drops. For the present purposes the mean current can be expressed by the following equation, where A is a numerical constant

$$\bar{i}_L = \frac{AnD^{1/2}m\rho r^{13/6}d^{1/2}P_c^{1/2}\gamma^{1/6}}{l^{1/2}\eta^{1/2}} \tag{22}$$

Although it is not significantly compressible, mercury changes in density from 13·55 at 20° to 13·00 at 250°. All other things being constant this would cause $\bar{i}_L$ at 250° to be about 2% less than at 20°, which is hardly within the experimental precision. It is shown below that γ changes very little in the temperature range of interest, so that this factor can also be neglected. The viscosity of mercury decreases from 1·55 at 20° to 0·995 centipoise at 250°. On this basis the diffusion current will increase by about 25% between these temperatures due to the increased flow of mercury.

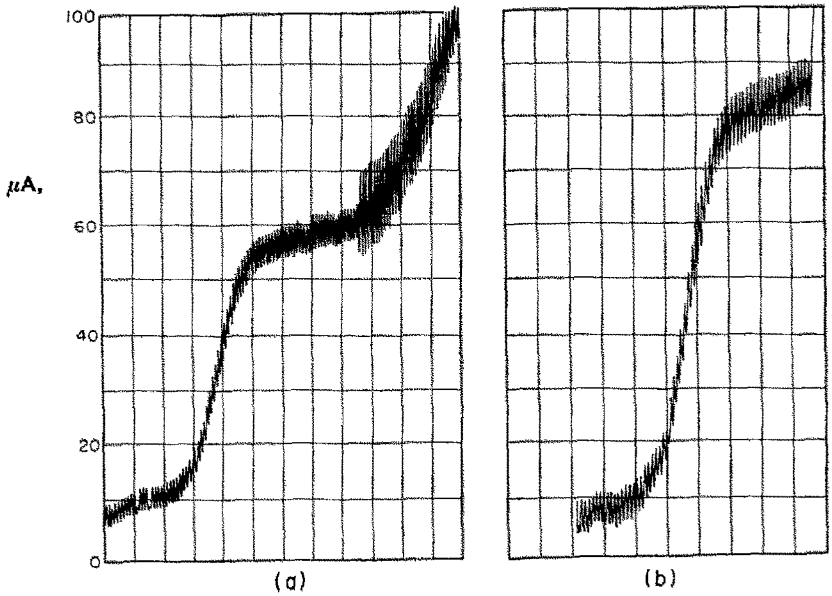

FIG. 11.—(a) The polarographic reduction of 3 × $10^{-4}M$ TlCl in 0·1M KCl at 187° the degree of damping was altered during the recording). (b) The polarographic reduction of $10^{8}M$ TlCl in 0·1M KCl at 220°.

The correction to the hydrostatic head of mercury P_h for the back pressure also varies with temperature and therefore

$$\left.\begin{aligned} P_c &= P_h - 4{\cdot}31\gamma d^{1/3}/m_{Hg}{}^{1/3}\tau^{1/3} \\ &\simeq P_h - B\gamma^{2/3}/r_c^{1/3} \end{aligned}\right\} \tag{23}$$

Equation (23) ignores minor effects caused by small changes in the density of mercury and B is approximately a constant. If, as in these experiments, r_c is 0·005 cm, the corrected pressure in terms of cm head of mercury at any temperature is

$$P_c\,(\text{cm Hg}) = P_h\,(\text{cm Hg}) - 1{\cdot}3\left(\frac{\gamma_t}{\gamma_{25}}\right)^{2/3} \tag{24}$$

From equation (22) the polarographic analysis procedure with a given capillary can be checked at each temperature and pressure for the proportionality between $\bar{i}_L$ and P_c, and between $\bar{i}_L$ and c. With satisfactory electrode behaviour, the variation with temperature of the quantity $\bar{i}_L\eta/P_c(m\rho)^2$ can be equated within a few per cent to the corresponding variation of the diffusion coefficient D for the reducible species under consideration. The variation of σ with temperature can be obtained approximately from the drop time of the electrode through the following equation (K′ is a numerical constant for each capillary)

$$\gamma = K'\tau P_c d/\eta \tag{25}$$

The results of these experiments can be evaluated in terms of the linear dependence of $\bar{i}_L$ on $P_c^{1/2}$ and also on m. Some of the evidence for the satisfactory behaviour of the dropping mercury electrode at high pressures and high temperatures is given in Tables IV and V.

TABLE IV.—CORRELATION OF $\bar{i}_d$ WITH m FOR THE REDUCTION OF THALLIUM(I) ION IN 0·1*M* AQUEOUS POTASSIUM CHLORIDE

Temperature, °*C*	20		135		170		210	
m	$\bar{i}_L$	$10^{-3}\bar{i}_L/m$	$\bar{i}_L$	$10^{-3}\bar{i}_L/m$	$\bar{i}_L$	$10^{-3}\bar{i}_L/m$	$\bar{i}_L$	$10^{-3}\bar{i}_L/m$
10^{-3}	8·0	8·0	20·5	20·5	23·8	23·8	25·7	25·7
3×10^{-4}	2·55	8·5	6·1	20·3	7·00	23·3	8·25	27·5
10^{-4}	0·80	8·0	2·05	20·5	2·41	24·1	2·68	26·8

TABLE V.—THE DEPENDENCE OF $\bar{i}_L$ ON THE CORRECTED HYDROSTATIC MERCURY PRESSURE P_c, FOR REDUCTION OF 10^{-3}*M* THALLIUM(I) ION (TlCl) IN 0·1*M* POTASSIUM CHLORIDE

Temp, °*C*	$\bar{i}_L$(μA)	P_c	$\bar{i}_L/P_c^{1/2}$	Temp, °*C*	$\bar{i}_L$(μA)	P_c	$\bar{i}_L/P_c^{1/2}$
20°	9·4	41·2	1·47	115°	21·4	36·0	3·56
	7·85	30·7	1·42		18·4	27·0	3·54
	6·85	23·1	1·43		15·1	19·2	3·45
167°	25·5	34·5	4·3	221°	28·5	32·2	5·0
	22·0	26·2	4·3		27·7	30·2	5·0
	17·5	19·0	4·0		22·5	23·3	4·7

Another interesting feature of these results was the decline with temperature of the hydrogen overpotential. Over a range of 200°, this falls by ~1 V and it would appear that at 350° and above, the hydrogen electrode reaction, even at mercury, becomes fast and reversible.

Ellis and Hills also used a stationary platinum microelectrode. Using slow d.c. polarisation, this type of electrode functioned with increasing efficiency as the temperature was raised. Satisfactory polarograms for copper(II) and lead(II) ions were obtained.

CONCLUSIONS

It is evident that polarographic analysis at high temperatures and pressures is feasible and is accompanied by no great loss of precision. *In situ* analysis of chemical reactions in pressure systems in autoclaves, *etc.*, is, therefore, possible and is likely to be useful in hydrothermal analysis and oceanographic analysis, to name two areas of current interest.

It should also be emphasised that pressure coefficients are especially indicative of changes in solvent density and solvent structure. Unlike temperature-coefficients which are invariably positive, pressure-coefficients can be negative or positive, and as such are more discriminating.

SYMBOLS NOT OTHERWISE DEFINED IN THE TEXT

a_1	distance of closest ionic approach	P	pressure (atm)
A,B,C	Debye-Hückel constants	r	reactants
c	concentration (mole $litre^{-1}$)	R	gas constant
C	interfacial capacitance	S	entropy
D	diffusion coefficient	t	temperature (°C)
E	e.m.f.	T	absolute temperature
F	faraday	U	internal energy
G	Gibbs free energy	V	volume
i	current	V	volts
$\bar{i}_L$	average limiting polarographic diffusion current	$\Delta V^‡$	activation volume
k	specific rate constant	$\bar{V}_2$	partial molar volume
k_η, k_c	proportionality constants	α	coefficient of cubical expansion
K	equilibrium constant	β	coefficient of isothermal compressibility
$\bar{K}_2$	isothermal partial molal compressibility	γ	interfacial tension
m	molality	$\gamma_\pm$	mean molal ionic activity coefficient
m_{Hg}	flow rate of mercury	ε	dielectric constant
n	number of electrons in the electrode (cell) reaction	λ	ionic conductance
p	products	τ	drop time

Zusammenfassung—Die Polarographie bei hohen Drucken wird in einer Übersicht besprochen.

Résumé—On présente une revue sur la polargraphie à hautes tensions.

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POLAROGRAPHY OF ALICYCLIC COMPOUNDS

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Summary—A review of the polarography of alicyclic compounds is presented.

INTRODUCTION

Less attention has been paid so far to the polarography of alicyclic compounds than to other types of organic compound. On the other hand, the possibilities of structural variations in this class of compound are numerous and often more diverse than in other classes. These two inversely proportional factors account for our present fragmentary understanding of structural effects operating in alicyclic compounds. Because scarcity of data prevents broader generalisations and explanations of the observed facts, the present reviewer set as his goal to summarise some relationships that can be found when published data are compared. The limited amount of available data prevented application of linear free energy or other similar relationships and the reviewer was forced to restrict himself, in most cases, to a qualitative discussion of structural effects.

The situation is further aggravated by the fact that, in several instances, only the values of half-wave potential in unbuffered solutions were available, even in cases where the half-wave potential is known to be pH dependent. Hence, it cannot be taken for granted that all the half-wave potentials compared are really comparable. The aim of this review is more to demonstrate the possibilities that application of polarography offers in this field rather than to draw conclusions.

To compare related types of electrode process the electroactive compounds were divided into three groups:

(a) Compounds bearing the electroactive group in the side-chain bound to the ring, *e.g.*, methyl cycloalkyl ketones.

(b) Compounds in which the reducible group is directly attached to the ring, *e.g.*, cyclanones or halogen derivatives, in which the halogen is bound by a reducible bond directly to the ring.

(c) Compounds in which, during polarographic reduction, a bond that is part of the ring system is cleaved or formed, *e.g.*, cyclan-1-on-2-enes and vicinal dibromides.

Each of these groups of compound can, in principle, be affected by various structural effects, such as

(1) the effect of substituents in another position on the ring;*

(2) the effect of size of ring and type;

(3) the effect of position of the electroactive grouping in the ring system, which is of particular importance in complicated ring systems, such as steroids;

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* Effects of substituents in the same side chain as the electroactive group are beyond the scope of this review.

(4) the effect of change of the electroactive group, including the effect of change or the extent of the conjugated system;

(5) the effect of some other steric effects, including the relative position of the electroactive group towards the ring system.

In the subsequent discussion, of all possible combinations those cases will be discussed for which experimental examples are known.

Substituent effects considered in this review can belong to several categories: polar effects transmitted *via* the chemical bonds, steric effects of bulky substituents in the proximity of the electroactive group, transannular effects, long-distance effects, *etc.* The other types of effect being already well recognised, it seems useful to mention briefly the latter type.

In principle, the rule that substitution in a position in the molecule distant from that of the electroactive group little affects the half-wave potential (*cf.*, for example, reference 1) has been accepted as generally valid until recently. In the special case of steroid compounds it has been shown recently (*cf.*, for example, reference 2) for homogeneous reactions that effects of substituents can be transmitted even from other rings and from distant positions. Even when such effects on the polarographic half-wave potential have not been discussed in detail by the authors of original papers, they can be deduced from the published data. Hence, polarographic reduction of a group in ring A can be affected by substituents in rings B, C and even D, and *vice versa.* Some examples of effects based on half-wave potentials published in the literature[3–12] are given here. It can be assumed that, in most cases, a difference of 0·01 V in the half-wave potential is significant. To ensure that the values are comparable, only those measured by one author are compared below. It was demonstrated (*cf.*, for example, references 3, 5 and 11) that the shifts of half-wave potential with pH are parallel for all substances compared, but the role of acid-base equilibria accompanying the electrode process[3,6] cannot be excluded, especially in the case of α,β-unsaturated ketones and of α-halogeno ketones. It is possible that in these cases the effect of proton transfer accompanying the electrode process contributes to the observed shifts of half-wave potential. Little attention has been paid so far to the form of the reduction waves, but from the published data[9,12] on αn-values it seems probable that these values for compounds studied do not differ substantially. Hence, the comparison of half-wave potentials should give sufficient information about the change of the relative free energy of the electrode process.

Compounds with benzene-like properties, such as tropylium salts, azulenes, cyclopentadienyl derivatives, ferrocenes, *etc.*, are excluded from this review, because they can nowadays be considered as a special class of compound.

ELECTROACTIVE GROUP IN SIDE CHAIN

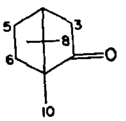
For molecules R—Z bearing the reactive centre R in the side chain of a ring Z in which the R—Z bond is not cleaved (*e.g.*, cycloalkyl alkyl ketones, compounds containing an alicyclic ring to which is attached a nitro or aldehydic group, *etc.*), neither the effect of a substituent in another position of the alicyclic ring nor the effect of the size of ring has been studied in sufficient detail. Cyclopentyl and cyclohexyl derivatives sometimes included into reaction series of aliphatic compounds represent a too restricted group to allow discussion. Hence, the few cases of effects of substitution on the steroid ring on the reduction of a C═O or C═N group in position 21 that would principally belong to this group were included in the discussion during appropriate subsequent sections.

ELECTROACTIVE GROUP ATTACHED TO RING

Molecules R—Z in which the electroactive atom or grouping R is bound to the ring Z by a bond which is broken in the course of the electrode process, belong to this group. The bond between R and Z can be single or multiple. Such a definition includes cycloalkyl halogenides, saturated cyclanones and their derivatives as well as hydroxy-2-cycloalkanones and similar compounds.

Substituent effects

Examples of substituent effects transmitted along the chemical bonds are lacking in this group of compound. Examples of the transannular effects can be found in the camphor series (I)

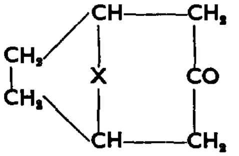


I

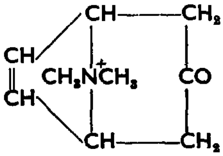
The keto group in unsubstituted camphor is not reducible in the commonly used buffer solutions before —1·9 V. Similarly, no reduction waves have been observed[13] for 5-oxocamphor. On the other hand, a reduction wave has been recorded for 6-oxocamphor at —1·67 V (pH 8), indicating a transannular interaction of the two carbonyl groups.

Also, the effect of the exchange of a methyl group in position 8 for an aldehydic group, causing a shift of the half-wave potential of the C—Br bond in 3-bromocamphor derivatives from —0·66 to —0·45 V, is unlikely to be transmitted *via* three carbon atoms. A transannular interaction between the aldehydic group and the CO—CHBr grouping can be postulated.

Similarly, the reducibility[14] of compounds II in the tropone series [where X = $^{(+)}$N-$(CH_3)_2$, $N(CH_3)$, $^{(+)}S(CH_3)$ and S] and compound III can be explained only on the basis of transannular interaction between the heteroatom* and the carbonyl group.



II



III

Sulphur derivatives are more easily reducible than the corresponding nitrogen derivatives and onium compounds easier than corresponding nor-derivatives that are reduced in the protonated form [X = $^{(+)}NH(CH_3)$]. The sulphur derivative (X = S) is unprotonised and therefore polarographically inactive.

Among the long-range effects, those operating in ketosteroids, α-hydroxyketosteroids and α-haloketosteroids can be mentioned here.

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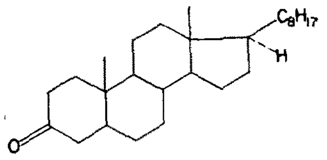
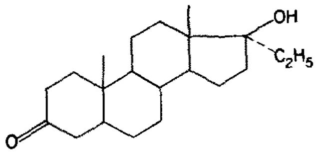
* It is understood that the introduction of a heteroatom makes the inclusion of these compounds in the present review disputable.

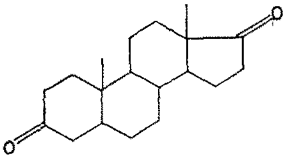
The effect of substituents in position 17 on the reduction of the carbonyl group in position 3 is demonstrated on the shifts of half-wave potential[8] of compounds IV to VII [90% ethanol, 0·05*M* $N(C_4H_9)_4Cl$]:



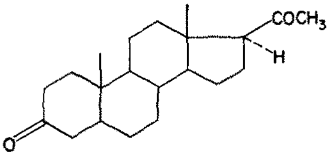
IV −2·28 V



V −2·37 V



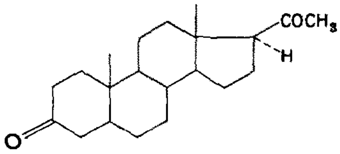
VI −2·38 V



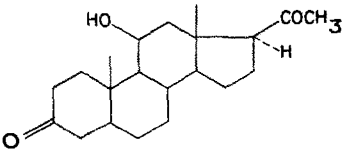
VII −2·44 V

In compounds VI and VII reduction of the carbonyl groups in positions 3 and 17 or 3 and 20, respectively, occurs at slightly different potentials, so that both waves merge and only one wave of double height is observed. The measured half-wave potential of this wave given above hence expresses not strictly only the effect of substitution.

Substituents in position 11 have much less effect on the reduction of the carbonyl in position 3 as can be seen from a comparison of the half-wave potential[8] of VIII and IX [90% ethanol, 0·05*M* $N(C_4H_9)_4Cl$]:

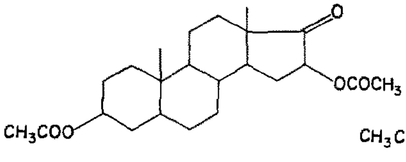


VIII −2·44 V

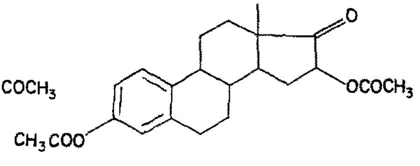


IX −2·46 V

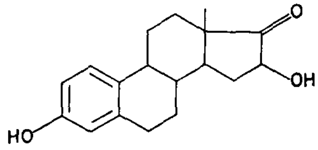
In some α-hydroxyketones the reduction of the C—O bond occurs at more positive potentials than that of the C=O group.[8] The reduction of the C—O bond in position 16 is shifted to considerably more positive values by the aromatisation of ring A (compare X and XI). Substitution of hydroxylic hydrogen for acetoxy groups results in a shift in the same direction [compare XI with XII; 90% ethanol, 0·05*M* $N(C_4H_9)_4Cl$]:



X −2·04 V

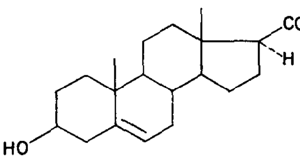


XI −1·96 V

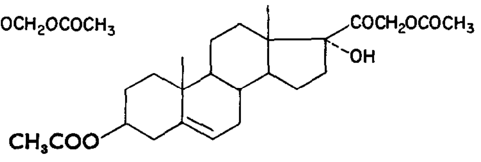


XII −2·09 V

A shift in a similar direction was observed[8] for XIII and XIV [90% ethanol, 0·05*M* $N(C_4H_9)_4$ Cl]:

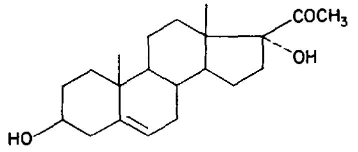


XIII −2·38 V

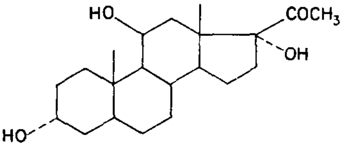


XIV −2·35 V

for steps in which the reduction waves of C=O and C—O coalesce. The effect of remote substituents is clearly seen even from a comparison of XV and XVI [90% ethanol, 0·05*M* $N(C_4H_9)_4$ Cl]:



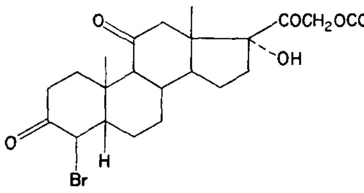
XV −2·43 V



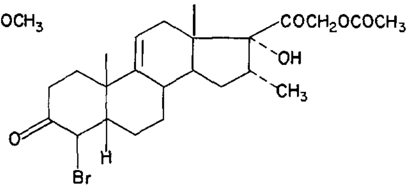
XVI −2·48 V

the reported values of half-wave potential corresponding to the combined wave.

Further data are available for half-wave potentials of α-haloketones. Thus, for 4-bromo-3-ketosteroids[9] the effects of substituents on rings C and D are demonstrated in compounds XVII and XVIII (80% ethanol, 2% lauryl sulphonate, acetate buffer pH 6·7):

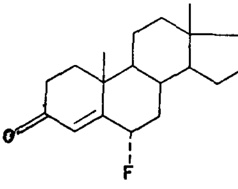


XVII −0·18 V

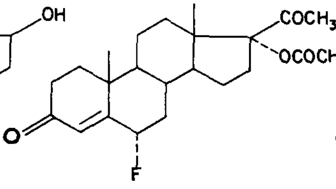


XVIII −0·28 V

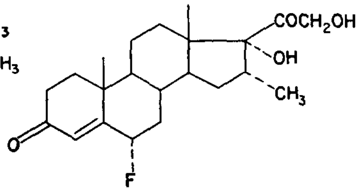
The effect of substituents in positions 16 and 17 on the reduction of compounds bearing a fluorine atom in position 6 is shown by compounds XIX to XXIV (50% ethanol, Britton–Robinson buffer pH 6·0):



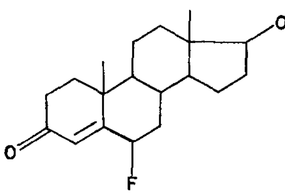
XIX −1·09 V



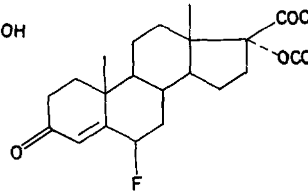
XX −1·04 V



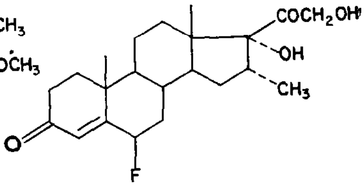
XXI −1·06 V



XXII −0·86 V

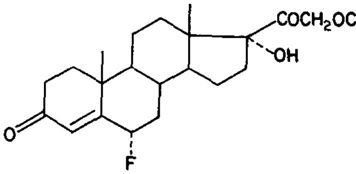


XXIII −0·89 V

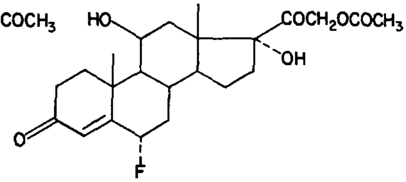


XXIV −0·82 V

This type of compound is also affected[12] by substituents in position 11 [XXV and XXVI, dimethylformamide, 0·1M $N(C_4H_9)_4I$ and 0·01M $N(C_2H_5)_4I$] (values for three waves):

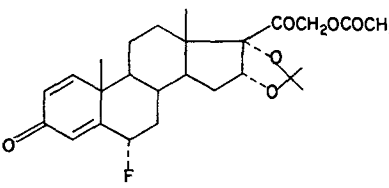


XXV −1·31 V
−1·72 V
−2·03 V

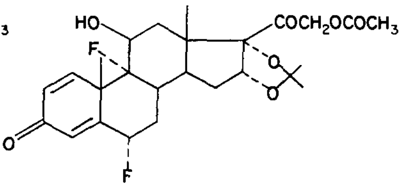


XXVI −1·28 V
−1·72 V
−2·06 V

and by substituents in positions 9 and 11 (XXVII and XXVIII in the same electrolyte):

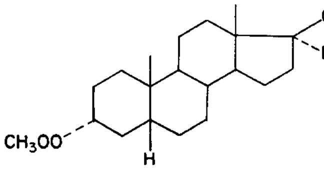


XXVII −1·16 V
−1·52 V
−1·77 V
−2·06 V

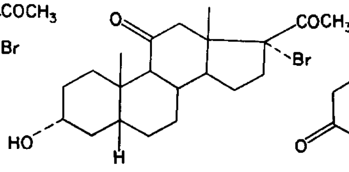


XXVIII −1·20 V
−1·43 V
−1·76 V
−2·06 V

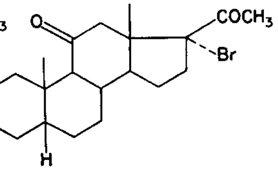
The half-wave potentials of 17-bromo derivatives are affected by substituents in positions 11 and 3 (XXIX to XXXI, 80% ethanol, 2% lauryl sulphonate, toluene sulphonic acid):



XXIX -0 09 V

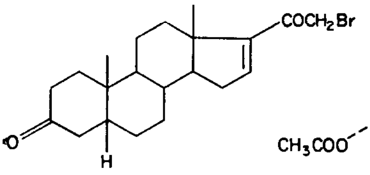


XXX 0·01 V

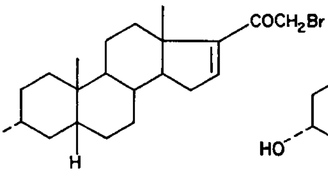


XXXI 0·06 V

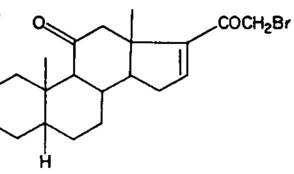
Even the reduction of bromine in position 21 is affected by substituents in positions 3 and 11 (XXXII to XXXVII, 80% ethanol, 2% lauryl sulphonate, toluene sulphonic acid):



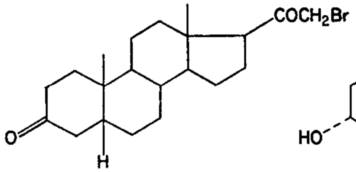
XXX -0·23 V



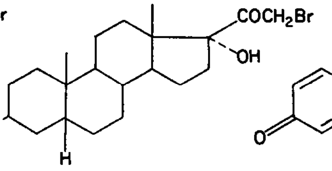
XXXIII -0·27 V



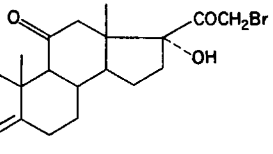
XXXIV -0·30 V



XXXV -0 24 V



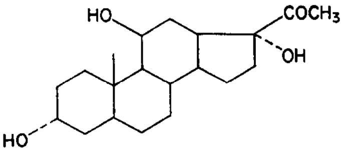
XXXVI -0·41 V



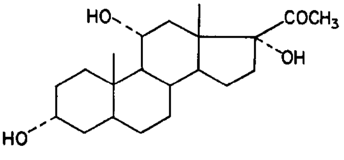
XXXVII -0·26 V

In substance XXXVI the hydroxyl group in position 17 and in XXXVII the unsaturation of ring A may also contribute to the observed shifts that is particularly marked for XXXVI.

The difference[8] between the effect of axial and equatorial hydroxyl group in position 11 on the reduction of the α-hydroxy ketone grouping in position 17, 20 [XXXVIII and XXXIX, 90% ethanol, 0·05*M* $N(C_4H_9)_4Cl$] is just at the limit of significance:



XXXVIII -2·48 V



XXXIX -2·49 V

The quoted examples allow us to make qualitative conclusions on the presence of long-range effects. A more systematic treatment, based on the study of a greater group of substituents for each combination of the electroactive group in one position and the substituent in another one, seems necessary before any further conclusions are attempted.

Size of ring and type

The half-wave potentials of compounds bearing a polarographically-active group attached to an alicyclic ring can be affected by the size of ring and conformation and for unsymmetrical systems also by the position of the electroactive group in the ring. These problems are discussed in the following paragraphs. Because of the multitude of possibilities and the variety of the little consistent data, the comparison of half-wave potentials corresponding to a given electroactive group in various positions of the steroid ring is discussed separately. For steroid compounds a sufficient number of related data was also available to allow a comparison of various electroactive groups to be made.

Effect of size of ring. When a single electroactive group is attached to an alicyclic ring (as in cycloalkyl bromides†), two types of quantitative treatment are possible.

Firstly, one can consider the ring as a special substituent attached to the electroactive group. Because the ring is directly attached and because no mesomeric interaction is to be expected, Taft polar substituent constants $\sigma_X{}^*$ and the following equation[15]

$$\Delta E_{1/2} = \rho^*_{\pi,R}\sigma_X{}^* \qquad (1)$$

can be applied. With non-cyclic substituents the value of the reaction constant $\rho^*_{\pi,R}$ can first be determined. The half-wave potentials for cyclopentyl and cyclohexyl derivatives (for which the $\sigma_X{}^*$-values are known) are next compared with the above $E_{1/2} - \sigma_X{}^*$ plot. Departures from a linear plot are explained either by steric effects or by a change in the mechanism of the electrode process. For larger rings it is possible to calculate from $\Delta E_{1/2}$ and $\rho^*_{\pi,R}$ the values of $\sigma_X{}^*$ and to discuss the magnitude of substituent constants obtained in this way.

Secondly, the half-wave potentials of a given reaction series can be correlated with either the half-wave potentials of another reaction series (compounds of the same size of ring always being compared) or the rate constants (or equilibrium constants) of a homogeneous reaction undergone by compounds of the same reaction series.

For those cases for which neither of the above quantitative treatments is possible, the effect of the size of ring can be discussed in qualitative terms. It is also possible to compare the shape of the plot of the half-wave potential as a function of the ring size.

For cycloalkyl bromides the first type of treatment involves complications. Whereas the value of the half-wave potential of cyclohexyl bromide fits well the linear dependence of the half-wave potential on the substituent constant σ^* obtained for open-chain compounds (Fig. 1), the value for cyclopentyl bromide shows deviation.

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† Another reaction series allowing this kind of treatment would be 1-piperidinomethyl-2-cycloalkanones, but for these substances the values of the half-wave potentials of the corresponding 1-piperidinoalkyl-2-alkanones of the type $C_5H_{11}N-CH_2CO-R$, where R = alkyl, are lacking.

A deviation in a similar direction has been observed for isopropyl and t-butyl bromide. It was deduced[16,17] that another mechanism can participate in the reduction of the latter two substances, different from that operating in the reduction of straight-chain bromides and cyclohexyl bromide. This deduction can also be extended to cyclopentyl bromide, where the predominance of another mechanism besides that for the cyclohexyl derivative cannot be excluded.

Because the participation of one or other mechanism for other cycloalkyl bromides is not known, all further deductions are to a high degree uncertain. Moreover, the large value of the reaction constant ($\rho^*_{\pi,\mathrm{Br}} = 4{\cdot}5$ V was accepted as the best value) makes the determination of σ^*-values from polarographic measurements too insensitive towards the substituent effects. This means that a relatively large shift of half-wave potential results in a relatively small change of the calculated value of the substituent constant $\sigma_X{}^*$.

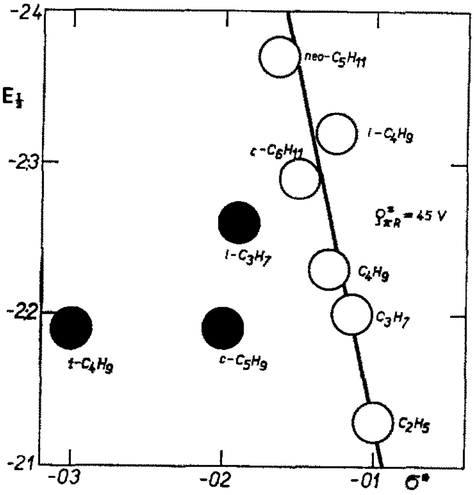


FIG. 1.—Dependence of half-wave potentials for reduction of alkyl bromides on Taft polar substituent constants $\sigma_X{}^*$ (half-wave potentials from reference 17; full points deviate).

Bringing the numerous experimental data[17–21] to the same scale and using the value $\rho^*_{\pi,\mathrm{Br}} = 4{\cdot}5$ V, the values gathered in Table I were obtained. These values are of little use in the discussion of the effect of size of ring and stereochemistry.

The other possibility, *i.e.*, the correlation of half-wave potentials with the logarithms of rate constants of reactions of cycloalkyl bromides presents another difficulty. Whereas for nucleophilic reactions of the branched-chain alkyl halides attention has been paid to the participation of a continuously changed transition state, or to various contributions of canonical structures with a positive charge on carbon to the resonance hybrid in the transition state, respectively (commonly denoted as parallel participation of various contributions of mechanisms S_N1 and S_N2), no such detailed studies are known involving the cycloalkyl bromides. For these compounds the reaction of the cycloalkyl halide with a given reagent was expected to follow either an S_N1 or S_N2 mechanism (according to the reagent used) for all the cycloalkyl halides studied.

TABLE I.—APPROXIMATE VALUES OF POLAR SUBSTITUENT CONSTANTS FOR CYCLIC SUBSTITUENTS (computed from half-wave potentials[17-21] of cycloalkyl bromides using equation $\Delta E_{1/2} = \rho^*_{\pi,R}\sigma^*_X$ and $\rho_{\pi,Br} = 4{\cdot}5$ V)

Substituent	σ^*
Cyclopropyl	−0·15
Cyclobutyl	−0·15
Cyclopentyl	−0·20*
Cyclohexyl	−0·15*
trans t-Butyl cyclohexyl	−0·17
cis t-Butyl cyclohexyl	−0·14
Cycloheptyl	−0·13
Cyclo-octyl	−0·13
Cyclononyl	−0·12
Cyclodecyl	−0·13
Cyclo-undecyl	−0·13
Cyclododecyl	−0·13
1-Bicyclo[2.2.2]octyl	−0·18
Adamantyl	−0·16
endo-Bornyl	−0·17
exo-Bornyl	−0·15

* Values given by Taft.

Little correlation has been detected for the dependence of the half-wave potentials of cycloalkyl bromides on the logarithms of rate constants of reactions for which an S_N1 mechanism was expected, such as solvolysis of methyl cycloalkyl chlorides,[22,23] of cycloalkyl *p*-toluene sulphonates[24] and of cycloalkyl chlorides.[24] The greatest deviations were observed for the cyclobutyl derivatives.

On the other hand, the half-wave potentials of cycloalkyl bromides have shown a relatively good correlation with those reaction rates to which an S_N2 mechanism was attributed, such as the exchange reaction of cycloalkyl iodides with radio-iodine[25] or reaction of cycloalkyl bromides with potassium[24,26] or lithium iodide[27] (Fig. 2).

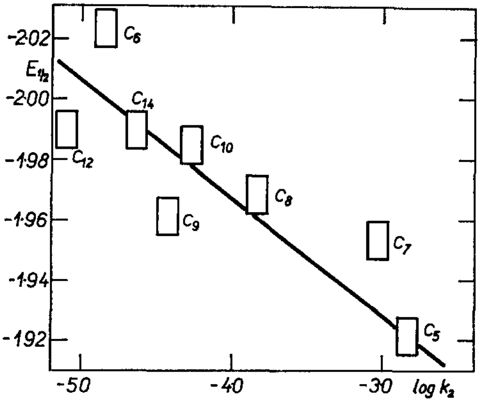


FIG. 2.—Dependence of half-wave potentials of cycloalkyl bromides on logarithms of rate constants of their reaction with potassium iodide in acetone [half-wave potentials in 99·97% dimethylformamide containing 0·1*M* $N(C_2H_5)_4Br$ from reference 18; rate constants at 60° from reference 26].

Because the participation of various mechanisms for homogeneous reactions cannot be excluded, it is not safe to deduce that all cycloalkyl bromides are reduced with an S_N 2-like mechanism. Thus, it is assumed that the contribution of the particular mechanisms differs for cyclopentyl and cyclohexyl derivatives, so that it is preferable to state that the participation of the particular mechanisms in the polarographic reduction of cycloalkyl bromides is similar to the homogeneous reactions of these compounds with iodides.

For some compounds it cannot be ruled out that a homolytic mechanism is involved.[20] On the other hand, it seems unlikely that this mechanism is predominating in the whole reaction series. Firstly, it seems improbable that at the negative potentials, where the electrical double-layer is negatively charged, the cycloalkyl bromide would be oriented towards the negatively charged surface of the electrode by the negative end of its dipole, as would be expected according to the halogen-bridge theory. Secondly, no metalorganic compounds with mercury are formed[28] during the electrolysis of alkyl halides with the exception of benzyl and allyl halides. Finally, no correlation of the half-wave potentials of cycloalkyl bromides with kinetic data involving homolytic splitting of the C—Br bond has been found.[18]

The last possibility is to correlate the half-wave potentials of cycloalkyl bromides with half-wave potentials of other alicyclic compounds using the following equation:

$$(E_{1/2})_{Br,Z^1} - (E_{1/2})_{Br,Z^2} = \rho_\pi'[(E_{1/2})_{R^2,Z^1} - (E_{1/2})_{R^2,Z^2}] \tag{2}$$

where Z^1 and Z^2 refer to two different rings, and R^2 to the other electroactive group. Satisfactory correlation has been found for half-wave potentials of cyclanones,[8] their betainyl hydrazones[29] and 1-piperidinomethyl-2-cycloalkanones[30] (Fig. 3). Among the cyclanones, cyclopropanone, and among the betainyl hydrazones the cyclopentanone derivative deviated. For 1-piperidinomethyl-2-cycloalkanones no correlation was found for the cyclo-octanone, cyclononanone and cyclodecanone derivatives, for which the shape of the waves[30] indicated a change in the mechanism of the reduction process. For cycloalkyl bromides, as well as for cyclanones, the cyclopentyl derivative is reduced at more positive potentials than the cyclohexyl derivative. On the contrary, for cyclanone betainyl hydrazones and for the Mannich bases the reverse sequence was observed, namely reduction of the cyclohexyl derivative at more positive potentials than that of the cyclopentyl derivative. For this fact, which is expressed by the different slope of curve 1 from that of curves 2 and 3, no explanation is at present known.

For 1-piperidinomethyl-2-cycloalkanones[30] the treatment using Taft equation (1) is made impossible by the fact that the half-wave potentials of a greater number of straight-chain 1-piperidino-2-alkanones have not so far been measured.

A very good correlation has been observed (Fig. 4) for the dependence of the half-wave potentials of 1-piperidinomethyl-2-cycloalkanones on the logarithms of the rate constants for the sodium borohydride reduction[30] of these compounds. This supports that a nucleophilic attack on the carbonyl group occurs in both cases. On the contrary, attempts failed to correlate the half-wave potentials with the logarithms of rate constants of eliminations of these Mannich bases. This can be taken as proof that in the elimination process not the electron density on the carbonyl

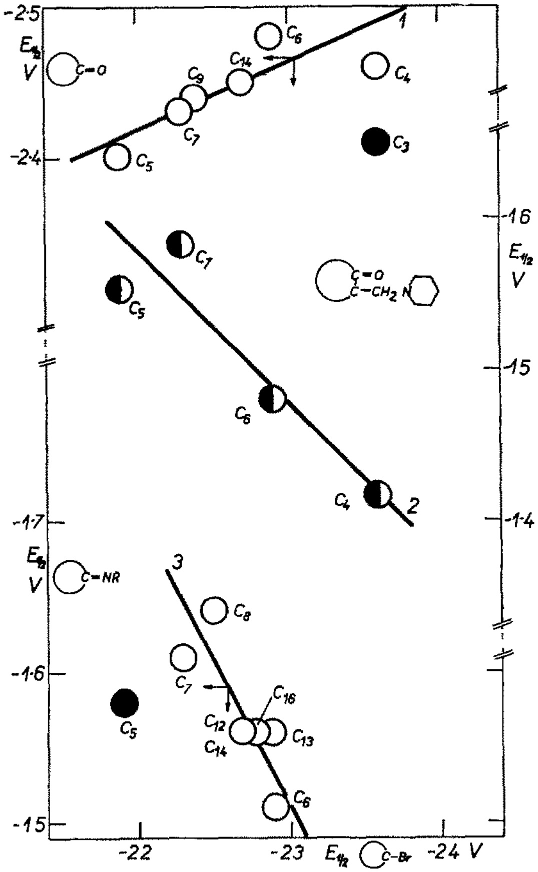


FIG. 3.—Dependence of half-wave potentials of cyclanones (1), their betainyl hydrazones (3) and of 1-piperidinomethyl-2-cycloalkanones (2) on half-wave potentials of cycloalkyl bromides [half-wave potentials of cyclanones (○) from reference 8, of 1-piperidino-2-cycloalkanones (◐) from reference 30, of betainyl hydrazones of cyclanones (○) from reference 29 and of cycloalkyl bromides from references 17 and 18; full points deviate].

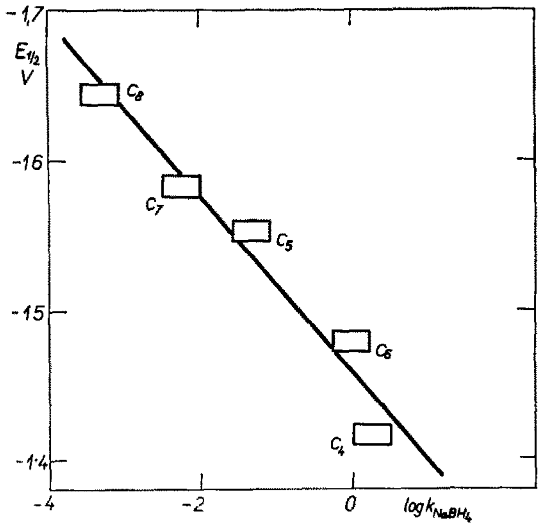


FIG. 4.—Dependence of half-wave potentials of 1-piperidinomethyl-2-cycloalkanones on logarithms of relative rate constants of the sodium borohydride reduction of cyclanones (half-wave potentials of 1-piperidinomethyl-2-cycloalkanones at pH 8 from reference 30; similarly for rate constants).

group but the proton transfer from the α-carbon to nitrogen is essential in the transition state.

The possibility of correlation of the half-wave potentials of 1-piperidinomethyl-2-cycloalkanones[30] with the half-wave potentials of cycloalkyl bromides was mentioned earlier (Fig. 3). Similarly, equation (2) can be used for the correlation of half-wave potentials of 1-piperidinomethyl-2-cycloalkanones with half-wave potentials of the betainyl hydrazones of cyclanones[29] (Fig. 5). Good correlation is observed even for cyclo-octyl and cyclononyl derivatives, showing a departure in the polarographic behaviour of Mannich bases from that observed for lower members of the series. Only for the cyclodecyl derivative is this change in reduction mechanism reflected by a deviation from linear dependence.

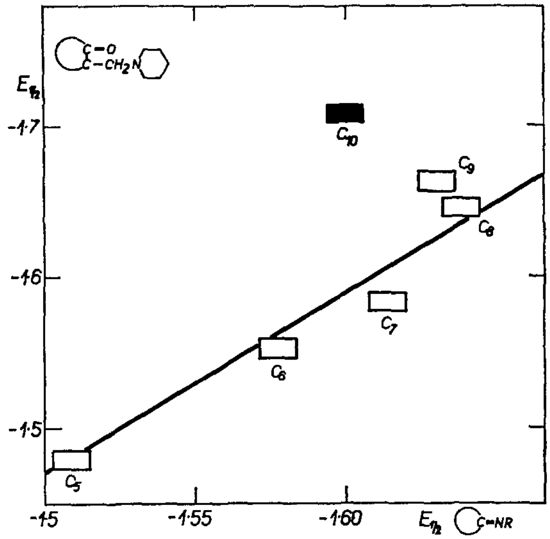


FIG. 5.—Dependence of half-wave potentials of 1-piperidinomethyl-2-cycloalkanones on half-wave potentials of cyclanone betainyl hydrazone (half-wave potentials of 1-piperidinomethyl-2-cycloalkanones at pH 8 from reference 30, those of betainyl hydrazones from reference 29).

A similar situation exists for cyclanones reduced[8] in the vicinity of $-2{\cdot}4$ V in 90% ethanol containing 0·05*M* $N(C_4H_9)_4Cl$. Correlations of their half-wave potentials with those of cycloalkyl bromides is given in Fig. 3.

For the betainyl hydrazones of cyclanones[295] the number of aliphatic compounds studied and the differences of their half-wave potentials were also too small to allow determination of the reaction constants and computation of the apparent substituent constants. The half-wave potentials have shown correlation with those of cycloalkyl bromides (Fig. 3) and Mannich bases (Fig. 5). The shift of 70 mV towards more negative values for cyclopentanone betainyl hydrazone was comparable with values[31] of 80–120 mV obtained for semicarbazones and with shifts of 20–50 mV observed[32] for imines derived from ammonia, methylamine and glycine.

For 1-methylenecyclanones the exocyclic C=C bond is probably reduced in the observed[30] reduction step. The half-wave potentials of these substances measured at pH 9 have shown a rather good correlation with those of the cyclanones and betainyl hydrazones (Fig. 6) although deviations were found for the eight and nine-membered ring. This seems to indicate that the carbonyl group in cyclanones is affected by the size of ring in a similar way to an exocyclic C=C bond.

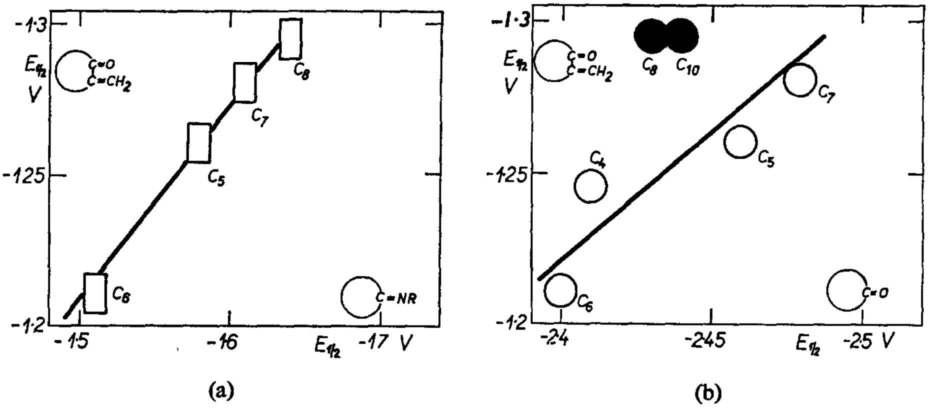
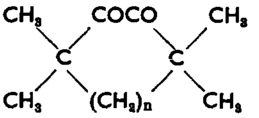


FIG. 6.—Dependence of half-wave potentials of 1-methylene-2-cycloalkanones on half-wave potentials of (a) cyclanone betainyl hydrazones and (b) cyclanones (half-wave potentials of 1-methylene-2-cycloalkanones at pH 9 from reference 30, those of betainyl hydrazones from reference 29 and of cyclanones from reference 8; full points deviate).

For cyclic diketones of the type XL, the following shifts of half-wave potential have been found[33] (in 50% isopropyl alcohol, 0·1*M* acetic acid, 0·1*M* sodium acetate):



XL

n	$E_{1/2}$ (*V*)
n = 2	−0.75
3	−1.16
4	non-reducible
14	−1.25

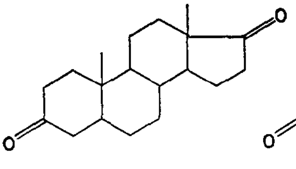
and compared with the values of aliphatic diketones:

RCOCOR		
	R = CH_3	−0.81
	C_3H_7	−0.83
	$CH(CH_3)_2$	−0.87
	$C(CH_3)_3$	−1.27

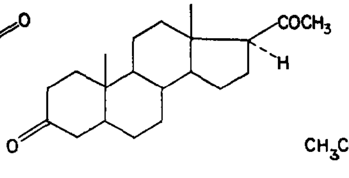
Reduction of the cyclic diketones is assumed to take place in the cis-form, the non-reducibility of 3,3,8,8-tetramethyl-1,2-cyclo-octanedione being a result of a steric hindrance of coplanarity of the COCO grouping and the effect of the α-methyl groups. For n = 2 the reduction occurs in a similar way to that in sterically unhindered aliphatic diketones; with an increasing value of n, steric effects analogous to those operating in dipivaloyl play an increasingly important role.

Position of reducible group in steroid ring. The most numerous examples of the effect of the position of the electroactive grouping on the half-wave potentials have been reported with the α-haloketosteroids.[9,10] Some examples are summarised in Tables II–IV. More extensive data would be necessary for each structure to allow some general conclusions to be made.

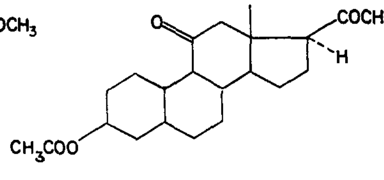
The mutual position[8] of two (XLI to XLIII) or three (XLIV and XLV) simultaneously reducible carbonyl groups also affects the resulting half-wave potential.



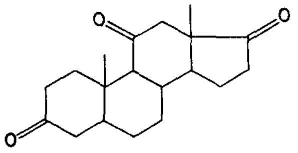
XLI -2·38 V



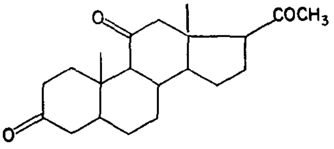
XLII -2·44 V



XLIII -2·46 V

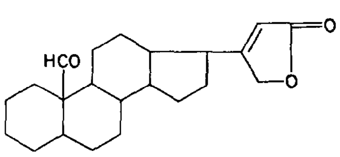


XLIV -2·37 V

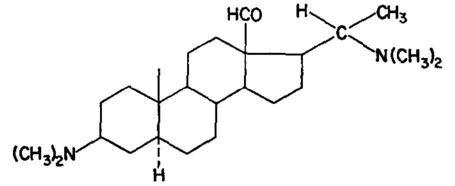


XLV -2·41 V

Furthermore, the reducibility of the aldehydic groups depends on their position in the steroid ring. Hence, substances of the type XLVI, such as cymarin or convallotoxin, are reducible[34] at −2·2 to −2·3 V, as has similarly been observed for saturated terpene aldehydes.[35] On the other hand, compounds of the holarrhimine type (XLVII) are reduced[36] in one pH-independent wave at −1·65 V. With respect to the chemical inactivity of XLVII it is assumed that even hydration of the aldehydic group is sterically hindered. The more positive reduction process was attributed[36] to reduction of the unhydrated carbonyl group.

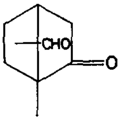


XLVI

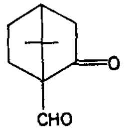


XLVII

There is also a difference between the reduction[13] of 8-oxocamphor (XLVIII) and 10-oxocamphor (XLIX) (pH 6·8)



XLVIII -1·73 V



XLIX -1·70 V

TABLE II.—COMPARISON OF HALF-WAVE POTENTIALS OF α-BROMO STEROIDS

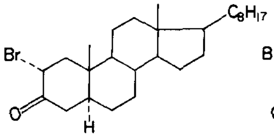
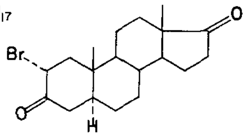
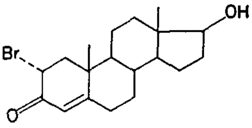
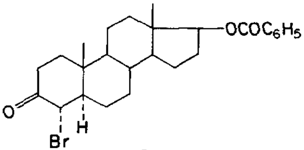
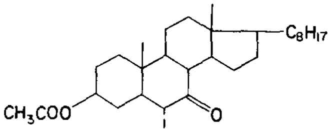
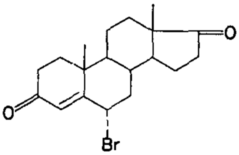
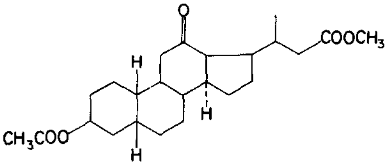
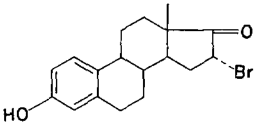
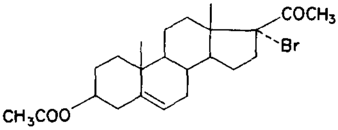
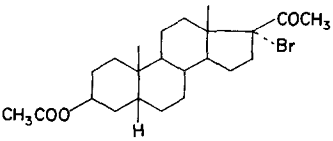
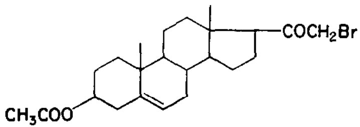
Substance, $E_{1/2}$ (*V*)			Br	CO
 -0.06 V[10]	 -0.14 V[9]	 -0.28 V[9]	2α(e)	3
 -0.04 V[9]			4α(e)	3
 Br -0.33 V[10]	 -0.05 V[10]		6α(e)	7:3
 -0.08 V[10]			11α(e)	12
 -0.16 V[10]			16α(b)	17
 -0.08 V[10]	 -0.09 V[9]		17α(p − a)	20
 -0.21 V[10]			21	20

TABLE III.—COMPARISON OF HALF-WAVE POTENTIALS OF β-BROMO STEROIDS

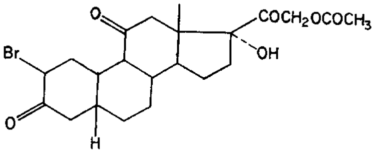
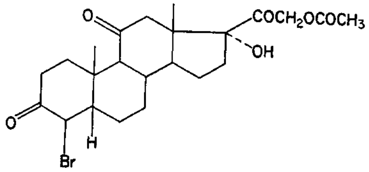
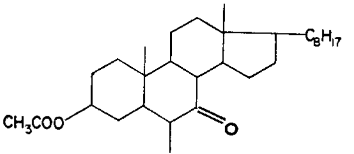
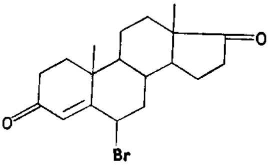
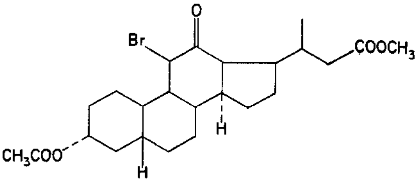
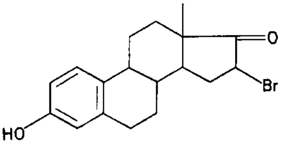
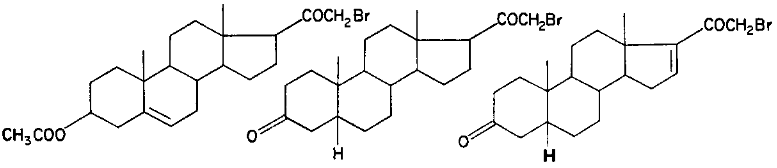
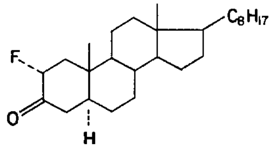
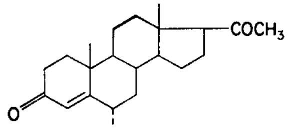
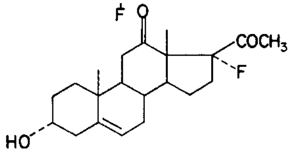
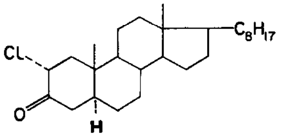
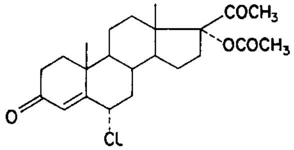
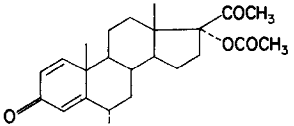
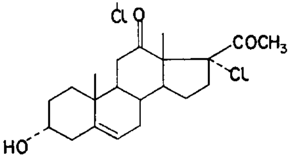
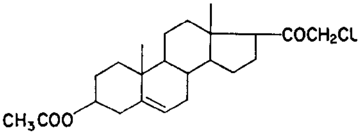
Substance, $E_{1/2}$ (*V*)	Br	CO
 -0 45 V^{9}	2β(a)	3
 -0 19 V^{9}	4β(e)	3
 -0 14 V^{10}  -0 02 V^{14}	6β(a)	7:3
 -0·07 V^{10}	11β(a)	12
 -0 28 V^{10}	16β(b)	17
 -0 21 V^{10} -0 24 V^{9} −0·23 V^{9}	21	20

TABLE IV.—COMPARISON OF HALF-WAVE POTENTIALS OF α-FLUORO AND α-CHLORO STEROIDS

Substance	$E_{1/2}$ (*V*)	Halogen	CO	Ref.
	−2·23	2α-F(e)	3	10
	−1·46*	6α-F(e)	3	10
	−2·15	17α-F(p − a)	20	10
	−0·94	2α-Cl(e)	3	10
	−0·94	6α-Cl(e)	3	11
	$-0{\cdot}96_8$	6α-Cl(e)	3	11
	−0·93	17α-Cl(p − a)	20	10
	−1·25	21	20	10

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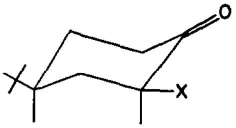
* Probably reduction of the COCH═CH system.

Comparison of halogens. In practically all cases reported so far (Table V) the half-wave potentials of α-halogenoketones are increasingly negative in the sequence: I < Br < Cl < F. This sequence would be in agreement with both a mechanism involving a nucleophilic attack as well as with the change in deformability which would explain the change in reactivity according to a bridge-mechanism. Hence, the observation of this sequence cannot be used as an argument for or against either of these possibilities.

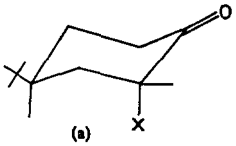
Stereochemical factors. In addition to the effect of size of ring and to the position of electroactive group in the steroid ring which both involve stereochemical factors, even when not always clearly understood, some other stereochemical factors affecting half-wave potentials will now be discussed.

Reduction of α-halogenoketones will be discussed first because the most extensive material is available for this group of compounds.

Among the simpler compounds, 2-halogeno-4-t-butylcyclohexanones were studied in some detail.[37] It is assumed that in these substances the bulky t-butyl group takes up almost exclusively an equatorial position. Moreover, it is taken for granted that cis and trans isomers are conformationally almost homogeneous, cis halogen being equatorial (e) and trans axial (a):



(e)



(a)

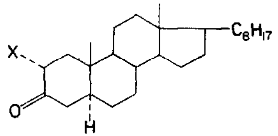
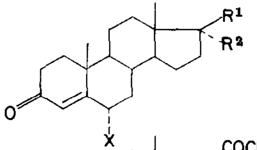
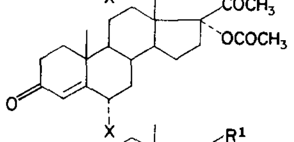
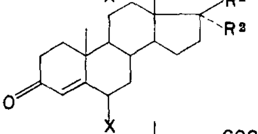
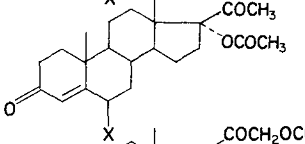
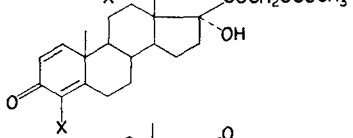
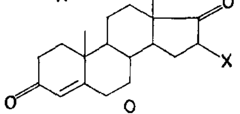
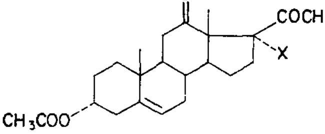
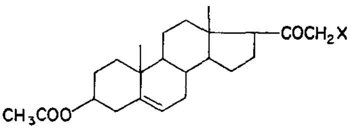
The thermodynamically more stable equatorial halogen is reduced in both pairs of 2-halogeno-4-t-butylcyclohexanones (Table VI) at more negative potentials than the axial halogen.

Similarly, in the rigid system of B and C rings of steroids the equatorial halogen is also reduced at more negative potentials than the axial halogen (Table VII). The differences in the half-wave potential of equatorial and axial halogen in α-halogenoketones varies according to the position of the halogen in the ring system and to the position of the vicinal carbonyl (Table VI and VII). The differences also depend on the nature of the halogen involved, generally increasing in the sequence: Br < Cl < F (Tables VI and VII). This sequence parallels that observed for benzene derivatives, *viz.* that the more negative the reduction the more susceptible it is to substituent effects.

The observed differences in the half-wave potential of equatorial and axial halogen were also used for a discussion of the reduction mechanism of vicinal halogenoketones. Whereas for alkyl halides nucleophilic substitution and the bridging mechanism were chiefly considered (p. 1345 and 1347), for α-halogenoketones an elimination process was also taken into consideration,[11,37] in which enolate is formed in the electrode process, followed by a subsequent chemical transformation into ketone not affecting the electrode process proper.

An important experimental finding that contributed to the proof of formation of enolate as intermediate (considered also in other reductions of carbonyl compounds[38,39]) was the comparison of the wave-shape with the results of controlled

TABLE V.—COMPARISON OF THE REDUCTION OF VARIOUS HALOGENS

Type	Substituent	X	$E_{1/2}$ (*V*)	Ref.
	2α(e)	I	−0·02 −0·26	10
		Br	−0·06	
		Cl	−0·94	
		F	−2·23	
	6α(e) R^1, $R^2 = O$	Br	−0·05	10
	$R^1 = COCH_3$ $R^2 = OH$	Cl	−1·12	
	$R^1 = COCH_3$ $R^2 = H$	F	−1·46	
	6α(e)	Cl	−0·94	11
		F	−1·04	
	6β(a) R^1, $R^2 = O$	Br	−0·02	10
	$R^1 = COCH_3$ $R^2 = OH$	Cl	−0·74	
	$R^1 = COCH_3$ $R^2 = H$	F	−1·18 −1·48	
	6β(a)	Cl	−0·7	11
		F	−0·895	
	4	Br	−1·18 −1·48*	10
		Cl	−1·19 −1·50*	
	16β(b)	Cl	−1·59 −1·72*	12
		Br	−1·23 −1·71*	
	17α(p − a)	Br	−0·08†	10
		Cl	−0·93‡	
		F	−2·15**	
	21	I	−0·22	10
		Br	−0·21	
		Cl	−1·25	

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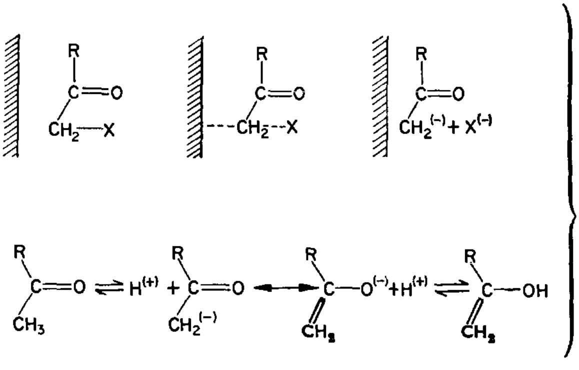
* The possibility of the reduction of the system COCH=CH was not excluded.
† Without 11-carbonyl group.
‡ With a β-hydroxy group in position 3 instead of α-acetoxy.
** With an α-hydroxy group in position 3 instead of α-acetoxy.

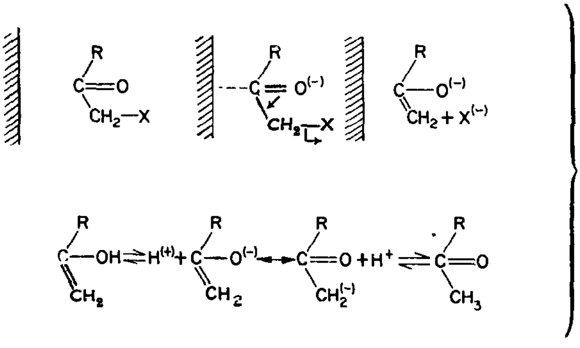
TABLE VI.—REDUCTION OF α-HALOCYCLOHEXANONES[37] IN DIMETHYLFORMAMIDE WITH 0·1*M* $N(C_4H_9)_4Br$

Substituent	cis (e)	$E_{1/2}$ (*V*) flexible	trans (a)	(e − a)
2-Chloro-4-t-Butyl	−1·57		−1·43	−0·14
2-Chloro		−1·40		
Trans-2-chloro-5-Methyl		$-1{\cdot}45_5$		
2-Fluoro-4-t-Butyl	−2·08		−1·85	−0·23
2-Fluoro		−2·00		

potential electrolysis of Δ^4-2-halogeno-3-ketosteroids.[9] For these compounds electrolysis at the limiting current of the first two-electron step yielded Δ^4-3-ketosteroid. Simultaneous generation of an equivalent amount of bromide ions was confirmed. On the other hand, on the polarographic curves of Δ^4-2-halogeno-3-ketosteroids only the wave corresponding to the reduction of the C—Br bond was observed and no wave for the corresponding Δ^4-3-ketosteroid. This occurred even in media in which the wave for Δ^4-3-ketosteroid was well developed, when a sample of the particular steroid was added to the supporting electrolyte used. This can be explained by formation at the dropping mercury electrode of an intermediate, which is subsequently transformed into the Δ^4-3-ketosteroid. The structure of the enolate is attributed to this intermediate and its formation can be interpreted principally in one of two ways: either by an attack of the electron on the carbon of the C—Br bond (I), or by an attack of the electron on the carbonyl carbon (II). In the former case it must be assumed that the carbanion resulting from the electrode process can preferably accept hydrogen on the carbonyl oxygen than on the carbon from which the halogen left.

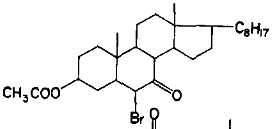
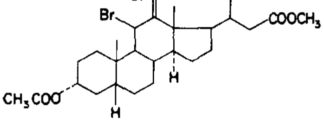
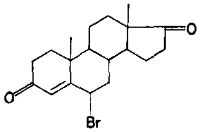
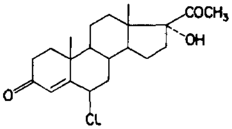
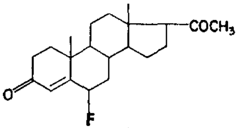
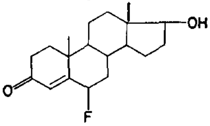
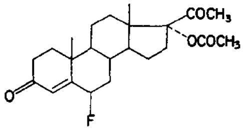
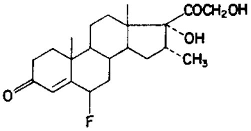
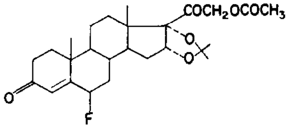
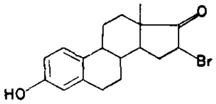


I



II

TABLE VII.—COMPARISON OF VICINAL HALOKETOSTEROIDS WITH AXIAL AND EQUATORIAL HALOGEN

Compound	$E_{1/2}$ (V)			X	CO	Ref.
	α (e)	β (a)	Δ(α − β)			
	−0·33	−0·14	−0·19	6Br	7	10
	−0·08	−0·07	−0·01	11Br	12	10
	−0·05	−0·02	−0·03	6Br	3	10
	−1·12	−0·74	−0·38	6Cl	3	10
	−1·46	−1·18	−0·28	6F	3	10
	−1·09	−0·86	−0·23	6F	3	11
	−1·04	−0·89$_5$	−0·14$_5$	6F	3	11
	−1·06	−0·82	−0·24	6F	3	11
	−1·31*	−1·18*	−0·13	6F	3	12
	α (b)	β (b)				
	−0·16	−0·28	+0·08	16Br	17	10

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* First wave.

To follow mechanism (I) the carbon atom bearing bromine would have to pass through a trigonal form. It is assumed that for vicinal halogenoketosteroids bearing the halogen on ring B or C the rigidity and the shape of the molecule prevent the attack from the rear.

Hence, mechanism (II) is preferred. Both carbons, in C—X and C=O, are expected[9] to be oriented in the electrical field of the electrode in the way depicted in Fig. 7 with the double bond of the carbonyl group parallel with the surface of the electrode. Simultaneously, the ring attains a pseudochair form. For axial halogen this deformation is only slight, whereas for equatorial halogen the carbon-bearing halogen is separated by an axial hydrogen from the surface of the electrode. To attain the most preferred configuration relative to the electrode, additional energy is necessary. This explains why equatorial bromine is reduced at more negative potentials than axial bromine (Tables VI and VII).

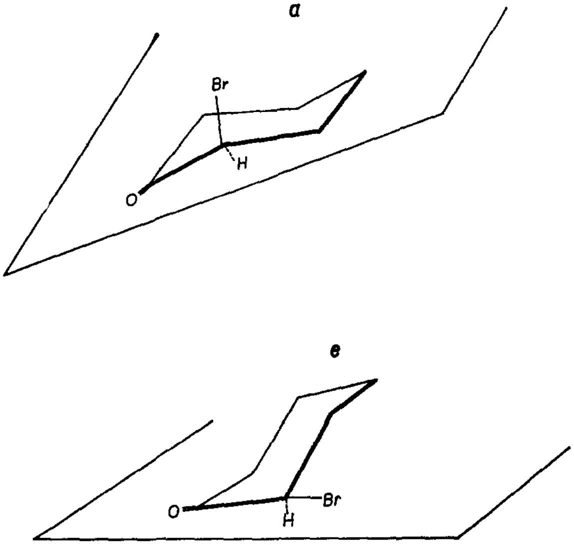
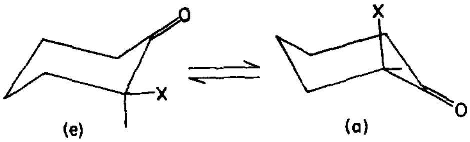


FIG. 7.—Scheme of orientation of 2-bromo-3-ketosteroids at the surface of the electrode.

For flexible molecules, *e.g.*, cyclohexyl derivatives without a t-butyl group, an equilibrium of the type (e) $\rightleftharpoons$ (a) is to be considered



If the equilibrium (e) $\rightleftharpoons$ (a) is mobile when compared with the rate of the electrode process, only one wave would be observed on the polarographic curves at potentials at which the reduction of the more positively reducible form (a) occurs.

When the rate of establishment of the equilibrium (e) $\rightleftharpoons$ (a) would be comparable (or slow) compared with the rate of the electrode process, two waves of kinetic (or diffusion) character would be observed. One of those would lie at potentials characteristic for the axial bond in (a), the other, more negative, for the equatorial bond in (e). The observation of two waves was not reported.[37] This means that either the equilibrium is rapidly established compared with the electrode process and the observed wave corresponds to the reduction of the axial bond. Alternatively, the equilibrium cannot be regarded as being established rapidly and the impossibility to distinguish two waves is because these two waves are not sufficiently separated. The difference in half-wave potentials of −0·14 V for chlorine and −0·23 V for fluorine (Table VI) would usually be sufficient for development of well-separated waves but for the high irreversibility of the measured waves ($RT/\alpha nF$ ranging from 0·12 to 0·23 V). With such drawn-out waves, separation of two waves differing by less than 0·3 or 0·4 V cannot be expected.

In the case of two merged waves the measured effective "half-wave potential" would be affected by the ratio of concentrations of both forms. Because the observed values for flexible molecules (Table VI) are nearer to the observed value for the reduction of an equatorial or an axial bond, it can be assumed that for these flexible compounds equilibrium is not rapidly established and the two waves merged. Quantitative deductions concerning the position of the equilibrium would be possible only then, when the role of the polar effect of the alkyl (t-butyl, methyl) group introduced would be quantitatively understood. So far it is impossible to distinguish (when one of the t-butyl conformers is compared with 2-halogenohexanone) which part in the observed shift is from the polar effect of the $C(CH_3)_3$ group and which part from the equilibrium involved.

It is now possible to summarise the role that polarography can play in distinguishing between epimers.

For truly rigid systems, such as the B and C rings of the steroid system, it seems possible from polarographic data to distinguish between the epimers of an α-halogenoketone, if both epimers are available and their half-wave potentials can be measured. In this respect polarography is superior to standard methods, using ultraviolet spectra or optical rotatory dispersion for axial and infrared spectra for equatorial halogen. Each of these methods determines either axial or equatorial halogen, not both as does polarography. Moreover, the above-mentioned methods depend principally on the effect exerted by halogen on the carbonyl group and not on halogen itself as in polarography.[10]

Moreover, polarography even enables a distinction to be made between the bisectional bonds as in 16 α- and 16 β-halogeno 17- oxoderivatives[10] for which spectral methods show an identical wavelength for the two isomers.

The data given in Table VII show that the regions of potentials in which α-haloketones in various positions in the steroid ring are reduced, overlap. Hence, the possibility of determination of conformation, when only one epimer is available, seems questionable, even when the available data are too limited to allow a final judgement.

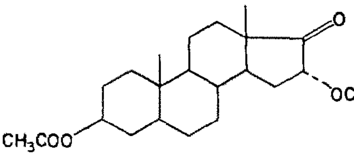
The situation is more complicated with flexible molecules. Here quantitative data about the equilibria of the two conformers can be expected only from measurements of the ratio of wave-heights for sluggishly established equilibria for which two separate waves are observed. To draw at least qualitative deductions from the position of the effective half-wave potential of the merged wave it would be necessary to possess information about other factors which affect the half-wave potential in the transition from the flexible system studied to the chosen rigid model system. For example, for rigid systems based on t-butyl cyclohexyl it would be necessary to elucidate firstly the effect of other alkyl groups, in order to separate from the observed shift for t-butyl cyclohexyl the contribution from the polar effect of the t-butyl group.

For α-dichlorocyclohexanones[40] the half-wave potentials in water-dioxan mixtures followed the sequence:

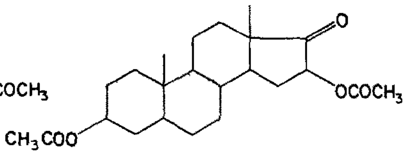
$$\begin{array}{ccc} \text{gem} < & \text{cis} < & \text{trans} \\ \text{(ae)} & \text{(aa)} \rightleftharpoons \text{(ee)} & \text{(ae).} \end{array}$$

In view of the results obtained for monohaloketones the more positive reduction of the cis-form would be better explained by predominance of (aa) than of (ee). In dimethylformamide the waves of the cis- and trans-form did not differ significantly.

The 16 α-bond reduction occurs at more positive potentials than for 16 β (similarly for 16 α-Br in Table VII) also for the C—O bond [L and LI in 90% ethanol containing[8] 0·05M $N(C_4H_9)_4$ Cl]:



L α.-199 V



LI β:-204 V

The relative positions of rings A and B are of considerable influence on the half-wave potentials (Table VIII).

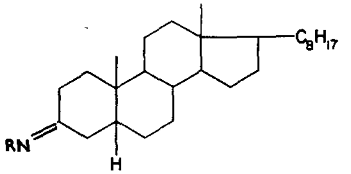
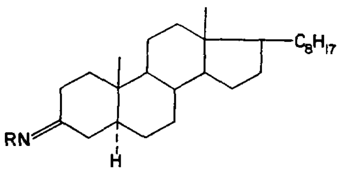
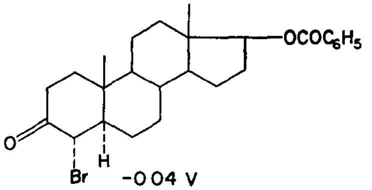
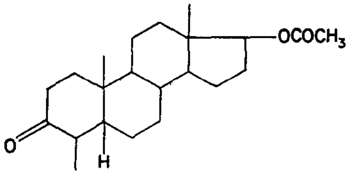
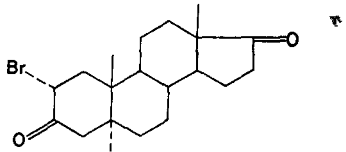
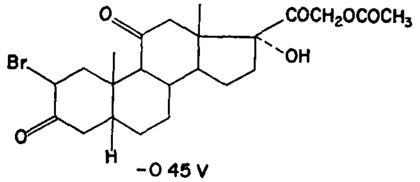
Reduction of some bridgehead bromides, such as 1-bromobicyclo[2.2.2] octane, endo-8-bromobicyclo[3.2.1] octane or 1-bromadamantane (Table IX) occurs[19–21] at potentials of about —0·2 to —0·1 V (according to the media used) more negative than the reduction of straight-chain bromides. This difference has been interpreted as a result of (a) change in mechanism or (b) steric strain. The bridgehead molecules are assumed not to be accessible to rear attack on carbon as was expected for the S_N2-like reduction mechanism predominant for straight-chain bromides (*cf.* reference 21 and p. 1345). A frontal attack on bromine[20] or an S_N1-like mechanism[21] is suggested.

The more positive reduction of the exo-norbornyl bromide than that of endo-norbornyl bromide[21] is quoted in support of the S_N1-like mechanism. Ionisation in the field of the electrode to form carbonium ions would occur more readily in exo-norbornyl bromide than in endo-norbornyl bromide because of anchimeric aid in the exo-bromide. Further confirmation of the S_N1-like reduction mechanism of the bridgehead bromides is sought in the fact that the reduction of cis-4-bromo-t-butylcyclohexane occurs at more positive potentials than that of its trans-isomer. Because of the steric conditions the rear of the carbon attached to the equatorial bromine in trans-4-t-butylcyclohexyl bromide is almost as hindered as a bridgehead bromine. Therefore, an S_N2-like mechanism cannot occur and the negative reduction wave is ascribed predominantly to the S_N1-like mechanism. The far less hindered cis-4-t-butylcyclohexyl bromide can be attacked from the rear. A predominantly

S_N2-like mechanism is in agreement with the more positive potential, which is almost in the range of reduction potentials of aliphatic bromides.[21]

The predominance of steric strain as the reason for the more negative potential of 1-bromobicyclo[2.2.2] octane was confirmed by comparison with 1-bromadamantane. Reduction of the latter occurs at potentials about 0·1 V more positive* than those of the bicyclo-octane derivative. It is assumed that in the transition state the adamantyl group would be less strained than the bicyclo-octyl group.[20]

TABLE VIII.—EFFECT OF RELATIVE POSITION OF RINGS A AND B IN STEROIDS ON HALF-WAVE POTENTIALS

Substance		Δ (*V*)	Ref.
 -134 V*	 -1·44 V*	0·10	4
 -0·04 V an=0·52‡	 -0·19 V a n=0·35‡	0·15	9
 -0·14 V an=0·54‡	 -0·45 V a n=0·27‡	0·31†	9

* R = $NHCOCH_2N(CH_3)_3Cl$.

† This value also involves contributions resulting from other changes in the molecule.

‡ The difference in values of αn is rather too great for a direct comparison of half-wave potentials.

The fact that the half-wave potential of 1-bromobicyclo[2.2.2]octane can also be (*cf.* Table IX and reference 20) in the region in which the reduction of alicyclic bromide was observed (Table IX) makes the evidence given above less conclusive. A compensation of various factors cannot be ruled out. In any case, further studies

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* Závada, Sicher and Krupička,[19] however, found a more negative value for 1-bromadamantane.

TABLE IX.—REDUCTION OF BRIDGEHEAD BROMIDES

Type	95% Dimethylformamide; 0·03*M* $N(CH_3)_4Br$[19]			Dimethylformamide; 0·01*M* $N(C_2H_5)_4Br$[21]		Dimethylformamide; 0·03*M* $N(C_2H_5)_4Br$[20]	
	Substance	$\frac{2 \cdot 3RT}{nF}$	$E_{1/2}$*(*V*) *vs.* S.C.E.	Substance	$E_{1/2}$(*V*) *vs.* S.C.E.	Substance	$E_{1/2}$(*V*) *vs.* Ag/AgBr
Aliphatic	Butyl bromide	0·254	−1·90	Butyl bromide	−2·23	Butyl bromide	−1·77
	Isopropyl bromide	0·200	−1·91	Isopropyl bromide	−2·26	Octyl bromide	−1·81
Cyclic	Cyclohexyl bromide	0·231	−1·91	trans-4-Bromo-t-cyclohexane	−2·45	—	
	Cyclodecyl bromide	0·225	−1·92	cis-4-Bromo-t-cyclohexane	−2·32	—	
Bridgehead	1-Bromobicyclo[2.2.2]-octane	0·150	−1·99	1-Bromobicyclo[2.2.2]-octane	−2·48	1-Bromobicyclo[2.2.2]-octane	−1·79
	endo-8-Bromobicyclo-[3.2.1]octane	0·187	−2·15	endo-norBornylbromide	−2·43	1-Bromobicyclo-[2.2.1]heptane	−2·17
	endo-8-Bromobicyclo-[3.2.1]oct-2-ene	0·183	−2·16	exo-norBornylbromide	−2·34		
	1-Bromadamantane	0·210	−2·02	1-Bromadamantane	−2·38		

* Corrected against half-wave potential of potassium $E_{1/2} = -1 \cdot 86$ V.

in this field are needed, not only for further critically selected model compounds, but also with more detailed experimental data (dependence of half-wave potentials and wave shapes on the concentrations of the depolariser and the supporting electrolyte, on the composition of the solvent, kind of cation used, temperature, *etc.*) to enable more dependable conclusions to be made.

ELECTROACTIVE GROUPS THAT FORM PART OF THE CYCLIC SYSTEM

In this section will be discussed systems in which during the electrode process either a bond in the ring system is reductively hydrogenated or a new bond in the ring system is formed. Both of these processes can be affected by the introduction of substituents, by the size of ring, by the position of the electroactive group, by the kind and extent of conjugation and by some other stereochemical factors. The systems involved are quinoid systems, α,β-unsaturated ketones, unsaturated hydrocarbons, vicinal dibromides, *etc.*

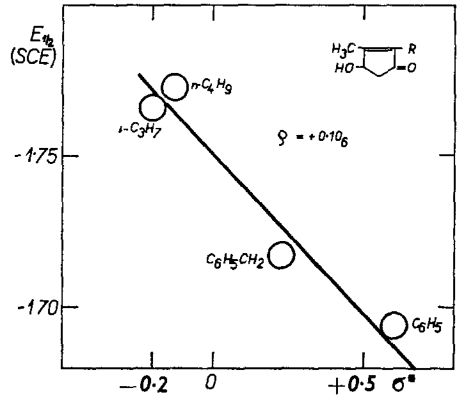
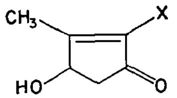


FIG. 8.—Dependence of half-wave potentials of substituted rethrolones on Taft polar substituent constants σ^* (half-wave potentials in 0·1*M* LiOH from reference 41).

Substituent effects

For rethrolones (LII) the half-wave potentials in 0·1*M* lithium hydroxide measured by Krupička[41] fit well equation (1) for X = C_4H_9, i-C_3H_7, $CH_2C_6H_5$ and C_6H_5 (Fig. 8).

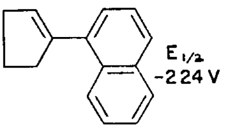


LII

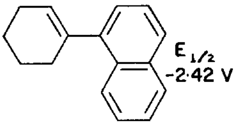
The value for C_6H_5 agrees well with the linear relationship so that it can be deduced that this group exerts predominantly a polar effect and that its conjugation is not of primary importance. The determined value $\rho^*_{\pi,\mathrm{R}} = +0{\cdot}10_6$ V allowed computation of the following approximate values of substituent constants:

$$\begin{aligned} \sigma^*_{\mathrm{CH=CH_2}} &= +0{\cdot}12 \\ \sigma^*_{\mathrm{(2\text{-}furyl)methyl}} &= +0{\cdot}29 \\ \sigma^*_{\mathrm{cyclohex\text{-}2\text{-}en\text{-}1\text{-}yl}} &= +0{\cdot}01 \\ \sigma^*_{\mathrm{cyclopent\text{-}2\text{-}en\text{-}1\text{-}yl}} &= -0{\cdot}01. \end{aligned}$$

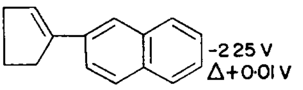
For naphthalene cycloalkenes[42] both the way in which the naphthalene ring acts as a substituent in the 1- or 2-positions and the size of the hydroaromatic ring can affect the half-wave potential. The latter effect is discussed under *Effect of size of ring* (p. 1370). Here only the exchange of α-naphthyl for β-naphthyl in LIII to LVI will be mentioned briefly:



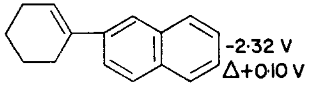
LIII



LIV



LV

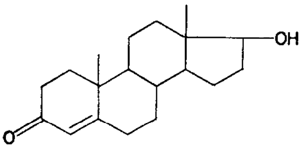


LVI

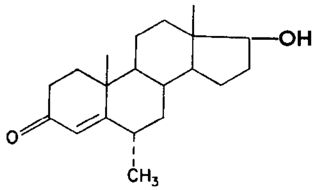
The difference in both magnitude and direction of the shift from this exchange for cyclopentene and cyclohexene is caused by steric hindrance of coplanarity, as proved in more detail on p. 1370.

The sequence of polarographic reducibility: LIII ≈ LV > LVI > LIV, is analogous to that observed for the rate of maleic anhydride addition in the Diels–Alder reaction, namely: LIII ≈ LV > LVI ≫ LIV. It is assumed[42] that this presents a proof that in the electroreduction a primary product with an exocyclic double-bond in the pivotal position between the naphthalene and the hydroaromatic ring is formed by 1,4-addition. The formation of this intermediate is thought to be hindered in compound LIV.

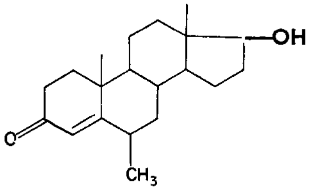
The most extensive data are available for substituent effects on half-wave potentials of α,β-unsaturated 3-oxosteroids. Here the effect of substitution in several positions can be followed. The effects of substituents in position 6 can be observed for compounds[11] LVII to LIX (in 50% ethanol, Britton–Robinson buffer pH 6·0):



LVII -1385 V

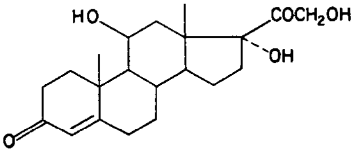


LVIII -1375 V

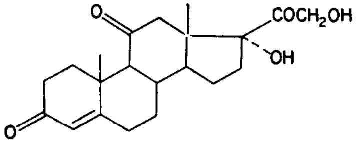


LIX -1355 V

Differences in half-wave potentials[4,5] can also be observed for substituents in position 11 (see LX and LXI; 90% ethanol, veronal buffer pH 8·5):

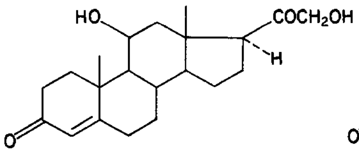


LX -1 50 V

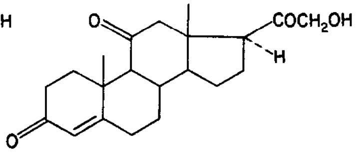


LXI -1·44 V and -1 65 V

On the other hand, compounds LXII and LXIII, studied[4] under the same conditions and differing only in the absence of the hydroxyl group in position 17, show a much less marked effect of the substitution in position 11:

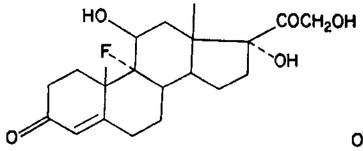


LXII -1·48 V and -1·68 V

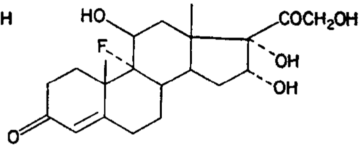


LXIII -1 49 and -1 64 V

The effect of a hydroxyl group in position 16 can also be considerable as shown by a comparison of substances[12] LXIV and LXV [dimethylformamide, 0·1*M* $N(C_4H_9)_4$ and 0·01*M* $N(C_2H_5)_4I$]:

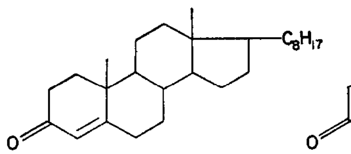


LXIV -1·66 V and -2 10 V

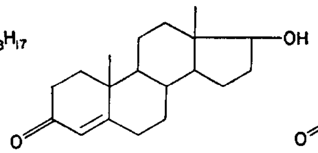


LXV -1 63 V and -2·11 V

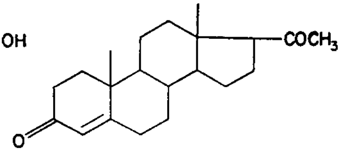
Greatest attention has been paid to the effect of substituents in position 17 on the shift of the half-wave potentials of Δ^4-3-ketosteroids.[3-5,7,11] In 50% ethanol containing triethylamine buffer[7] (pH 10·5) the effect is small; in 0·1*M* hydrochloric acid it is more marked (Table X). More considerable shifts were observed[4] in 90% ethanol containing a veronal buffer pH 8·5 (LXVI to LXVIII, and in the more complex systems



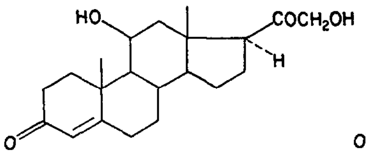
LXVI -1 55 V



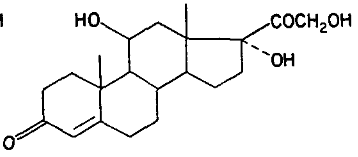
LXVII -1·49 V



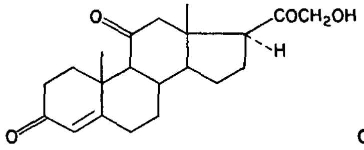
LXVIII -1 45 V



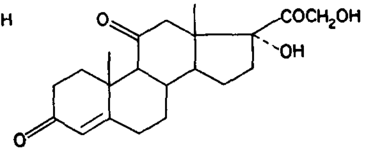
LXIX -1·48 V and -1·68 V



LXX -1·50 V

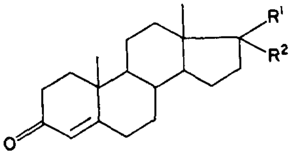


LXXI -1·49 V and -1·64 V



LXXII -1·44 V and -1·65 V

TABLE X.—EFFECT OF SUBSTITUENTS IN POSITION 17 ON THE HALF-WAVE POTENTIAL OF Δ^4-3-KETOSTEROIDS (50% ETHANOL, N.C.E.)

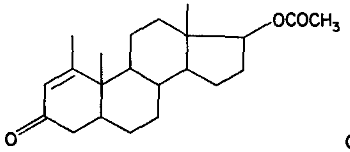


Compound	R^1	R^2	$E_{1/2}$ (*V*) 0·1*M* HCl	$E_{1/2}$ (*V*) pH 10·5*	$dE_{1/2}/dpH$
Progesterone	$COCH_3$	H	−1·11	−1·68	0·063
Testosterone	OH	H	−1·13	−1·69	0·061
Methyltestosterone	OH	CH_3	−1·13	−1·68	0·059
Testosterone propionate	$OOCC_2H_5$	H	−1·13	−1·68	0·060
17-Hydroxyprogesterone	$COCH_3$	OH	−1·14	−1·68	0·059
11-Deoxycorticosterone	$COCH_2OH$	H	−1·12	−1·67	0·059
11-Deoxycortisterone acetate	$COCH_2OOCH_3$	H	−1·11	−1·67	0·060
11-Deoxy-17-hydroxycorticosterone	$COCH_2OH$	OH	−1·15	−1·69	0·059

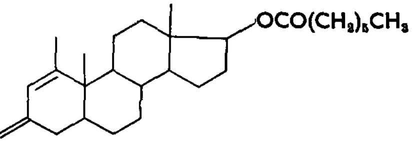
* Triethylamine buffer.

LXIX to LXXII), but under these conditions the effect of the proton transfer accompanying the electrode process cannot be excluded.

Even substituents in the side chain can affect the half-wave potentials[12] of Δ^1-3-ketosteroids [LXXIII and LXXIV; in dimethylformamide, 0·1*M* $N(C_4H_9)_4I$, 0·01*M* $N(C_2H_5)_4I$].

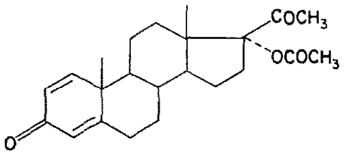


LXXIII -1·66 V

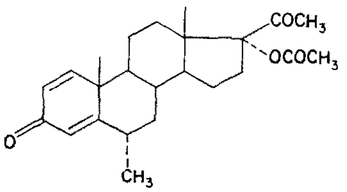


LXXIV -1·62 V

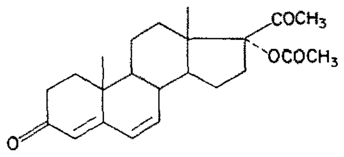
Similarly, the half-wave potentials of $\Delta^{1,4}$- and $\Delta^{4,6}$-3-ketosteroids can also be affected[11] by substituents in various positions, *e.g.*, 6 (LXXV to LXXVIII in 50% ethanol and Britton–Robinson buffer pH 6·0):



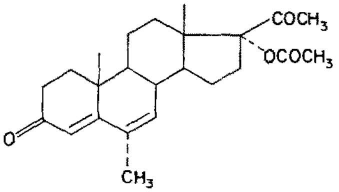
LXXV $-1{\cdot}22$ V



LXXVI $1{\cdot}22$ V

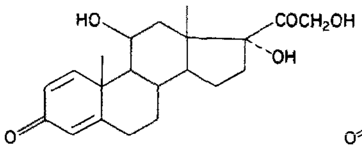


LXXVII $-1{\cdot}06_5$ V



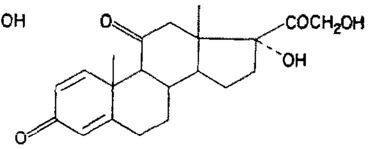
LXXVIII $-1{\cdot}09_5$ V

and in position 11 (LXXIX and LXXX, in 50% ethanol):



LXXIX

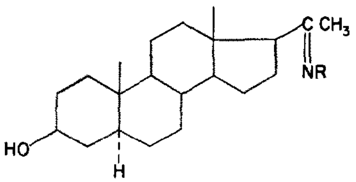
malonate pH 4·6: $-1{\cdot}21$ V
triethylamine pH 10·8: $-1{\cdot}59$ V



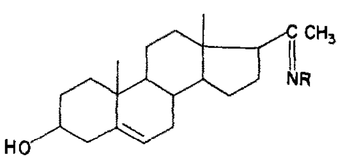
LXXX

malonate pH 4·6: $-1{\cdot}16$ V
triethylamine pH 10·8: $-1{\cdot}52$ V

However, not only the half-wave potentials of ketosteroids, but also of their derivatives can be affected by remote substituents. Most of the available data concerns the Girard derivatives, mainly the trimethylaminoglycyl hydrazides.[4] For derivatives of saturated ketones such an effect can be demonstrated in compounds containing a reducible C═N bond in position 20 and varied in ring B (LXXXI and LXXXII, in 90% ethanol containing veronal buffer pH 8·5):



LXXXI $-1{\cdot}51$ V



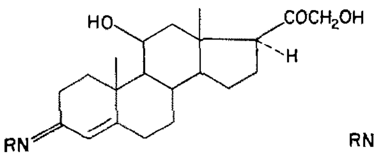
LXXXII $-1{\cdot}57$ V

where
R=NHCOCH$_2$N$^+$(CH$_3$)

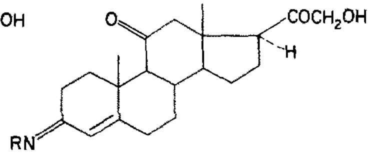
Among the steroids bearing a double-bond in the α,β-position with respect to the carbonyl group, effects have been observed[4] for derivatives of Δ^4-3-ketosteroids in the presence of substituents both in position 11 (comparison of LXXXIII with LXXXIV and of LXXXV with LXXXVIII) and in position 17 (comparison of

LXXXIII with LXXXV and of LXXXIV with LXXXVIII) [in 90% ethanol containing veronal buffer pH 8·5; R = $NHCOCH_2N^+(CH_3)_3$].

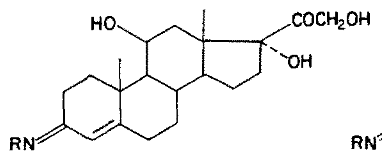
In contrast, the betainyl hydrazones of compounds LXVI to LXVIII all show in 90% ethanol at pH 8·5 the first reduction step at −1·34 V, even when they differ from the above compounds only by the absence of a substituent in position 11. There is no explanation available at present of the fact that the half-wave potentials of the betainyl hydrazones of LXVI to LXVIII are identical, whereas the half-wave potentials of the parent compounds are significantly different.



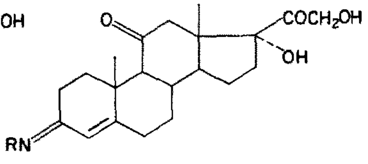
LXXXIII -1·35 V



LXXXIV -1·37 V



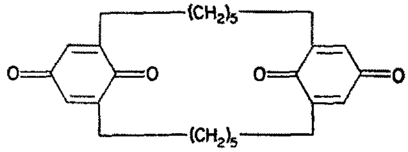
LXXXV -1·42 V



LXXXVIII -1·34 V

Effect of size of ring

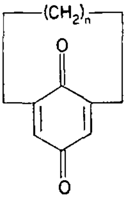
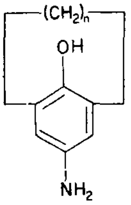
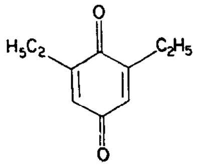
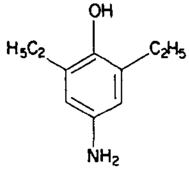
The effect of the size of ring on reversible redox systems has been studied systematically *via* reduction of the 2,6-polymethylene quinones and oxidation of 2,6-polymethylene-4-aminophenols[43,44] (Table XI). It has been shown that a decrease of the size of ring below n = 14 causes a shift of the redox potential towards negative values compared with the value for dialkyl derivatives. For smaller rings quinone is, therefore, relatively more stabilised when compared with hydroquinone. Two quinoid systems in a sixteen-membered ring show no mutual interaction, as was demonstrated by the coincidence of the half-wave potentials of bis-pentamethylene-(2,2,6,6)-bisbenzoquinone (LXXXIX) with that of the higher 2,6-polymethylenequinones.[45]



LXXXIX

Among the irreversible systems, unsaturated hydrocarbons will first be discussed. The half-wave potentials of the naphthyl alkenes[42,46] (Table XII) follow roughly the sequence found for the relative values of the conjugative power, C_t, as based on ultraviolet absorption spectra and on rates of addition of maleic anhydride in the Diels–Alder reaction. It is assumed[46] that the half-wave potentials rather than to be a function of the angle of the twist in the original molecule (ϑ) depend on the angle of twist at the moment of the electrode process (ϑ_p). The electrical field of the electrode will orientate the depolariser preferably in a flat position in the double-layer, so that $\vartheta_p < \vartheta$, if possible. An inspection of molecular models[46] indicates little or no hindrance to the attainment of coplanarity by naphthalenes bearing the substituent in position 2. For these compounds it is assumed that in the course of the electrode process they became virtually coplanar, *i.e.*, $\vartheta_p \approx 0°$.

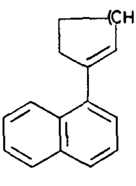
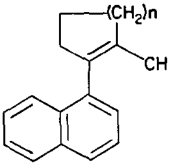
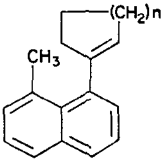
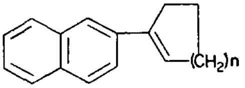
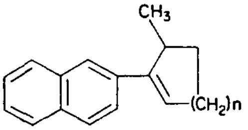
TABLE XI.—EFFECT OF SIZE OF RING ON REVERSIBLE REDOX POTENTIALS[43,44]
(10% acetic acid, 40% ethanol)

n		$E_{1/2}$ (*V*)	
9	−0·029		—
10	+0·026		+0·081
11	+0·086		—
12	+0·117		+0·178
13	+0·139		+0·200
14	+0·143		+0·192
15	+0·160		+0·211
16	+0·151		+0·205
17	+0·158		+0·202
18	+0·144		+0·190
19	+0·144		+0·200
	+0·140		+0·202

For cyclopentenylnaphthalenes there is only a small difference between the half-wave potentials of 1- and 2-substituted compounds. The direction of the observed shift towards more negative values for the 2-naphthyl derivative is in accordance with the prediction from C_t-values. Hence, it is assumed that in addition to the 2-naphthyl derivatives the molecule of 1-cyclopentenylnaphthalene is also able to achieve a practically planar arrangement during the electrode process ($\vartheta_p \approx 0°$). For the 1-cyclohexenyl and 1-cycloheptenyl derivatives the steric hindrance of rotation of the alkenyl group into coplanarity is no longer negligible and results in the shifts of the half-wave potentials of 1-naphthyl derivatives towards more negative values.[46]

Further evidence for such kinds of deduction can be drawn from the behaviour of methyl derivatives. The shifts caused by the introduction of the methyl group into the cycloalkenyl group (−0·07 V or −0·04 V, respectively) can give one a rough idea of the magnitude of the polar effect resulting from methyl substitution on the cyclopentenyl ring. For 1-cyclopentenylnaphthalene the observed shift (−0·17 V) can be

TABLE XII.—HALF-WAVE POTENTIALS OF NAPHTHYL ALKENES[42,44]
[75% dioxan–water, 0·1*M* $N(C_4H_9)_4I$]

Compound		$E_{1/2}$ (*V vs.* S.C.E.)				
	n	1	2	Δ*	3	Δ*
		−2·27	−2·46	−0·19	−2·41	−0·14
		(−2·42)	(−2·46)	(−0·04)	—	—
		−2·36	(−2·42)	(−0·06)	—	—
		−2·30	−2·38	−0·08	−2·35	−0·05
		−2·37	−2·42	−0·05	—	—

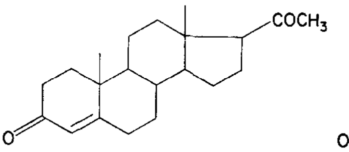
* Δ = Difference relative to cyclopentenyl derivative.

attributed partly to steric hindrance and partly to coplanarity. For 1-cyclohexenylnaphthalene the introduction of the methyl group is practically without effect, showing that in the unsubstituted 1-cyclohexenyl derivative there is a negligible contribution from conjugative interaction of the two rings. Similarly, only a slight effect is shown when a methyl group is introduced into position 8 of the naphthalene ring in 1-cyclohexenylnaphthalene. The greater shift (and towards more negative potentials) of —0·09 V caused by an 8-methyl group in 1-cyclopentenylnaphthalene indicates that this shift is at least partly caused by the steric hindrance of coplanarity, even when it is less effective than for the substitution of the methyl group in the cyclopentenyl ring.

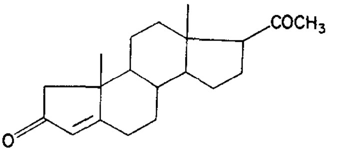
Whereas in the hydrocarbons discussed the reduction of the double bond occurs at more positive potentials in the cyclopentenyl ring than that in the cyclohexenyl ring, the reduction of the system COCH═CH, from which in the final product

$COCH_2CH_2$ is formed, follows the reverse order. Both in α,β-unsaturated ketones[12] such as XC and XCI [in dimethylformamide with 0·1*M* $N(C_4H_9)_4I$ and 0·01*M* $N(C_2H_5)_4I$] and in α,β-unsaturated lactones[47] (where the reduction of the double bond occurs at potentials about 0·4 V more positive than in the corresponding cardiac glycosides with an unsaturated five-membered lactone ring) the reduction of the six-membered compound occurs at more positive potentials than that of the five-membered compound.

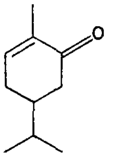
For monocyclic terpene ketones,[48,49] the difference between the five- and six-membered compounds is rather small [XCII to XCV, in 80% ethanol with 0·1*M* $N(C_2H_5)_4I$]; a direct comparison is, nevertheless, prevented by the two methyl groups on the double bond in isothujone (XCV) when compared with the one in XCII and XCIII. That the introduction of the second alkyl group can possess a considerable effect on the half-wave potentials is demonstrated by comparison of the half-wave potentials[49] of jasmone (XCVI) and isodihydrojasmone (XCVII):



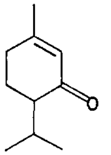
XC -1·66 V



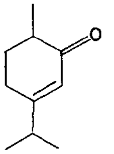
XCI -1·85 V



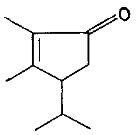
XCII
-1·77 V



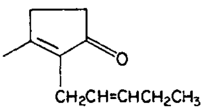
XCIII
-1·80 V



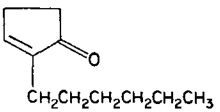
XCIV
-1·81 V



XCV
-1·81 V



XCVI
-2·00 V



XCVII
-1·87 V

As examples of those electrode processes that result in formation of a new bond, the reduction of vicinal dibromides is discussed next. Principally, these compounds are reduced[50] in one two-electron step. Because the main product of this step has been shown to be the unsaturated hydrocarbon, and because no other wave is apparent on the polarographic curve (which would correspond to the reduction of the monobromo derivative), it may be assumed that an elimination process takes place with the second bromine atom participating in the formation of the transition state.

How far this assumption is valid can be verified by an inspection of Table XIII. For monobromo derivatives, for which the two-electron process can be taken for granted, the value of the limiting current constant I varied under identical experimental conditions between 2·2 and 2·9. All values for I in Table XIII that are greater than about 3·2 seem to indicate that in addition to the two-electron elimination process a four-electron substitution can participate in the electrode process. A further indication of this type of process seems to be a remark[50] that controlled potential electrolysis of ethylene dibromide at a mercury pool electrode gives rise to some ethane in addition to ethylene. Controlled potential electrolysis and microcoulometry using the mercury dropping electrode would be of importance especially for checking these plots for compounds 5, 6, 7, 9 and 12 (Table XIII). The two-electron reduction of 1,6-dibromocyclodecanes (22 and 23) seems to indicate a transannular cyclisation to decalin.

TABLE XIII.—HALF-WAVE POTENTIALS OF VICINAL DIBROMIDES[18]

No.	Substance	cis			trans		
		$I \cdot 10^3$	$E_{1/2}$ (*V*)	$\frac{2{\cdot}3RT}{\alpha nF}$	$I \cdot 10^3$	$E_{1/2}$ (*V*)	$\frac{2{\cdot}3TR}{\alpha nF}$
1	4-t-Butyl-trans-3-cis-4-dibromocyclohexane	—	—	—	2·30	−0·86*	0·359
2	4-t-Butyl-cis-3-trans-4-dibromocyclohexane	2·89	−1·67*	0·180	—	—	—
3	2β,3α-Dibromo[9βH,10αH]decalin	—	—	—	3·27	−0·82*	0·374
4	exo-cis-2,3-Dibromobicyclo[2.2.1]heptane	3·32	−1·53	0·150	—	—	—
5	endo-cis-2,3-Dibromobicyclo[2.2.1]heptane	3·78	−1·21	0·200	—	—	—
6	trans-2,3-Dibromobicyclo[2.2.1]heptane	—	—	—	4·10	−1·56	0·216
7,8	2,3-Dibromobicyclo[2.2.2]octane	4·05	−1·28	0·186	2·82	−1·33$_5$	0·189
9	1,2-Dibromocyclopentane	—	—	—	3·60	−0·94	0·215
10, 11	1,2-Dibromocyclohexane	2·62	−1·64	0·182	2·98	−1·04	0·247
12	1,2-Dibromocycloheptane	—	—	—	3·25	−1·00	0·288
13	1,2-Dibromocyclo-octane	—	—	—	2·08	−1·05	0·346
14	5,5,8,8-Tetramethyl-trans-1,2-dibromocyclodecane	—	—	—	2·67	−1·15	0·313
15, 16	1,2-Dibromocyclododecane	2·13	−1·51	0·230	2·53	−1·44	0·182
17	1,2-Dibromocyclotetradecane	2·21	−1·33	0·312	—	—	—
18	1,2-Dibromocyclohexadecane	2·06	−1·21	0·440	—	—	—
19	Ethylene dibromide	3·28	−1·23*	0·185	—	—	—
20	Erythro-5,6-dibromodecane	3·01	−1·14	0·386	—	—	—
21	Threo-5,6-dibromodecane	—	—	—	2·71	−1·24	0·340
22, 23	1,6-Dibromocyclodecane	3·16	−1·78	0·210	2·52	−1·73	0·178

* The inclusion in this column is deliberate.

In a homologous series and for those reaction series in which the properties and shape of the molecule do not vary over too wide a range, it has been repeatedly proved that the value of the parameter 2·3RT/αnF varies relatively little. For vicinal dibromides, on the other hand, variation of this parameter is quite considerable (from 0·15 to 0·44: Table XIII). Because there is no correlation between this value and that for I, a change of the number of electrons (n) transferred in the potential-determining step does not seem the essential reason for this change. Nevertheless, a change in mechanism involving a change in the number of electrons in the potential-determining step seems only slightly probable, but cannot be completely excluded.

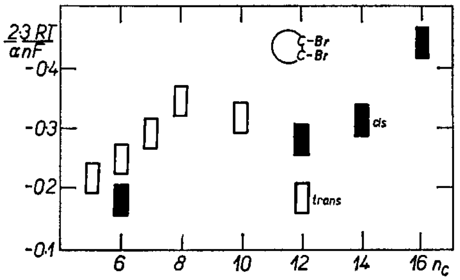


FIG. 9.—Dependence of 2·3 RT/αnF for reduction waves of cyclic vicinal dibromides on number of ring atoms: values of 2·3 RT/αnF from reference 19 for ☐ trans and ■ cis isomers.

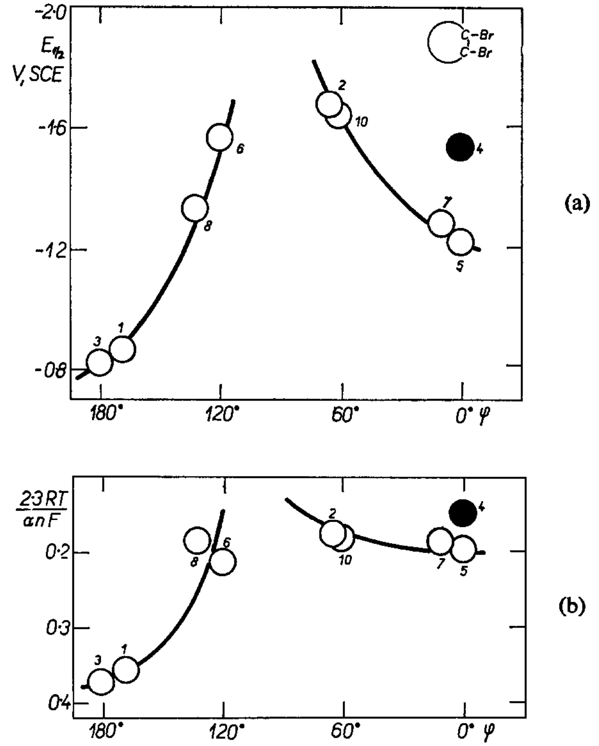


FIG. 10.—Dependence of (*a*) half-wave potentials and (*b*) values of 2·3 RT/αnF for reduction waves of cyclic vicinal dibromides on estimated value of torsion angle (φ) (half-wave potentials, values of 2·3 RT/αnF and estimated values of torsion angle from reference 19; numbering of compounds according to Table XIII; full points deviate).

A change in the value of the transfer coefficient α seems to be decisive. It can be assumed that this change is connected with the orientation of the electroactive substance or the adsorbability. Because there is no information available concerning the relation between the adsorbability and the chemical structure of compounds of the type discussed, this assumption can be considered only as tentative.

The values of 2·3RT/αnF form two groups—one at 2·3RT/αnF = 0·18 ± 0·04 and the second at $2{\cdot}3RT/\alpha nF = 0{\cdot}36 \pm 0{\cdot}07$. The dibromides of the first group largely, but not exclusively, are able relatively readily to attain an anti-periplanar arrangement of the bromine atoms, whereas for those belonging to the second group such an arrangement can be attained not at all or only with difficulty.[18] The dependence of the value of $2{\cdot}3RT/\alpha nF$ on the number of ring carbon atoms is given in Fig. 9.

As has been stressed several times in previous sections of this review, quantitative comparisons of half-wave potentials are permissible only in reaction series in which the value of αn remains constant. Because this condition is not fulfilled for vicinal dibromides, the discussion of structural effects on half-wave potentials (Table XIII) given below should be considered as a first approximation.

Compounds 1–8 (Table XIII) with a rigid structure, in which the torsion angle between the C—Br bonds is known, are considered first. Dependence of half-wave potentials on torsion angle φ (Fig. 10A) resembles the Karplus curve.[51] Most positive waves were observed for $\varphi \approx 180°$ (anti-periplanar arrangement) and 0° (synperiplanar arrangement), most negative for $\varphi \approx 60$–$120°$. Only the value for compound 4 does not follow a smooth curve. An analogous trend also shows the dependence of $RT/\alpha nF$ on the torsion angle (Fig. 10B).

Among the flexible dibromides, existing in equilibria of two or more forms, are those compounds for which it is known[18] that they are able readily to attain an anti-periplanar arrangement of the C—Br bond (9, 12–14, Table XIII), reduced at relatively positive potentials. They would correspond in rigid compounds to torsion angles of $\varphi > 150°$. On the contrary, those dibromides (11, 15, 16) which attain an anti-periplanar arrangement only with a great expenditure of energy[18] or not at all, are reduced at more negative potentials, which would correspond to rigid dibromides with $\varphi \approx 60°$.

The half-wave potentials of monocyclic, flexible vicinal dibromides, as well as of some rigid dibromides were an approximately linear function of the logarithms of the rates of homogeneous elimination reactions.[52] In agreement with the results obtained for bimolecular homogeneous reactions is the more positive reduction of erythro-isomer (20) than that of threo-5,6-dibromodecane (21, Table XIII).

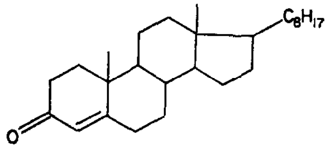
Effects of position and conjugation

Discussion in this section is restricted solely to the reduction of α,β-unsaturated ketosteroids and their derivatives.

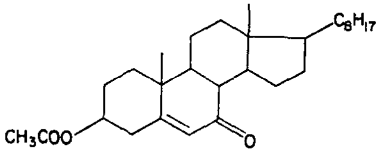
Whereas for ketosteroids considerable differences in half-wave potentials have been observed[4] according to the position of the COCH=CH system (XCVIII to CIII in 90% ethanol, veronal buffer pH 8·5), little difference has been found for the corresponding betainyl hydrazones[4] (CIV and CV).

The compounds CII and CIII (in toluene sulphonate pH 2·1, 80% ethanol[9]) differ more than in the position of the double bond; nevertheless, the effect of other changes is probably not predominant.

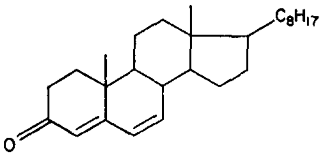
An increasing extent of conjugation shifts the half-wave potentials towards more positive values (Table XIV). $\Delta^{1,4}$-3-ketosteroids are reduced by some 0·16 V at more positive potentials, $\Delta^{4,6}$ by some 0·30 V than Δ^{4}-3-ketosteroids. The crossed conjugation is less effective than linear. The effect in betainyl hydrazones seems slightly less marked.



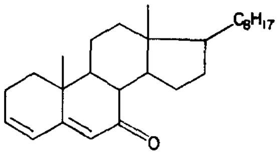
XCVIII -1·55 V



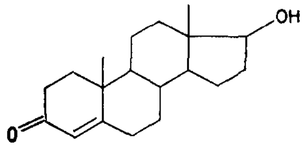
XCIX no wave



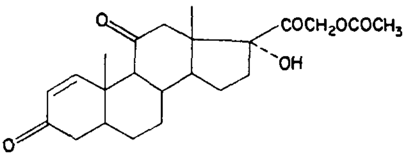
C -1·18 V



CI -1·24 V

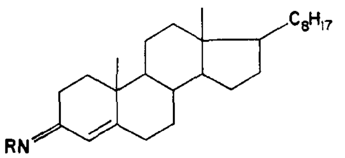


CII -1·16 V

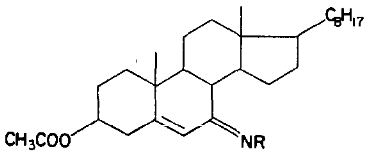


CIII 1·10 V

R=NH $COCH_2N(CH_3)_3Cl$



CIV -1·34 V



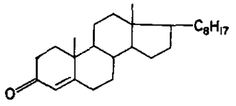
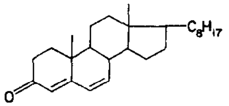
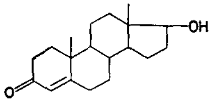
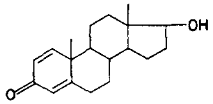
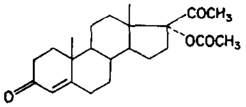
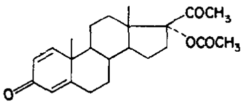
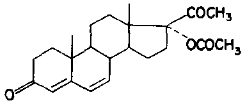
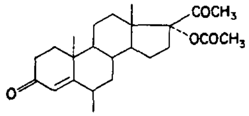
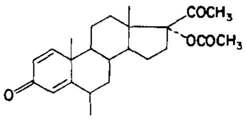
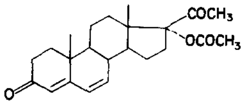
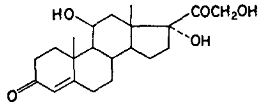
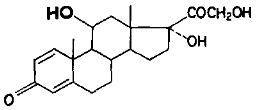
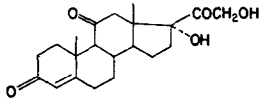
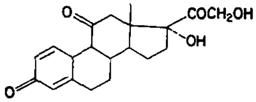
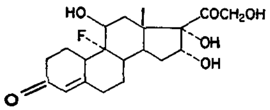
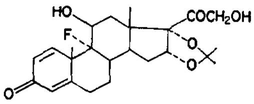
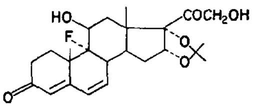
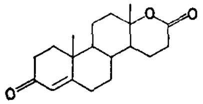
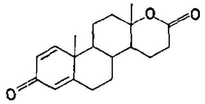
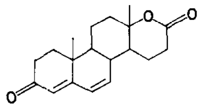
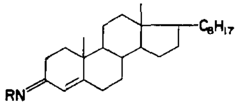
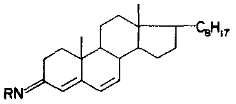
CV -1·34 V

Steric factors

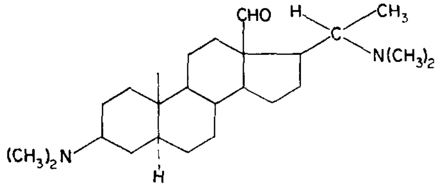
A few comments can be added concerning the polarographic reduction of polyhalogenated compounds.

Inspection of Table XIII shows that, of the available pairs of cis- and trans-isomers, in one case (7 and 8) the cis-isomer is reduced at more positive potentials than the trans-isomer, but in two cases (10 and 11; 15 and 16) the trans-isomer is reduced at more positive potentials. It has been shown under *Effect of size of ring* (p. 1375) that the case of the reductive elimination is better explained on the basis of torsion angles φ than on a comparison of isomeric pairs. Hence, one refrains from a more detailed discussion, for example, of results given in reference 53. Nevertheless, the particular case of hexachlorocyclohexane should be mentioned. This substance is reduced to benzene[53–57] with consumption of six electrons and liberation of six chloride ions. The γ-isomer is reduced at potentials by some 0·6 V more positive than the next most easily reducible isomer (α). This behaviour parallels the observations that this isomer possesses the greatest dipole moment, is more adsorbed at the mercury surface than other isomers and possesses much stronger insecticide activity than other isomers. The role of adsorption and dipole moment have also been discussed[57] in the case of other halogen derivatives.

TABLE XIV.—EFFECT OF CONJUGATION ON REDUCTION OF KETOSTEROIDS

Δ^4	Δ^{1,4}	Δ^{4,6}	Ref.
 -1·55 V		 -1·18 V (0·37 V)	4
 -1·38$_5$ V	 -1·23$_5$ V (0·15 V)		11
 -1·37$_5$ V	 -1·22 V (0·15$_5$V)	 -1·06$_5$V (0·31 V)	11
 1·38 V	 -1·22 V (0·16 V)	 -1·09$_5$ V (0·29 V)	11
 -1·37 V	 -1·21 V (0·16 V)		5
 -1·31 V	 -1·16 V (0·15V)		5
 -1·63 V	 -1·44 V (0·19 V)	 -1·26V (0·37 V)	12
 -1·66 V	 -1·44 V (0·22 V)	 -1·21 V (0·45)	12
 -1·34 V $R=NHCOCH_2N(CH_3)_3Cl$		 -1·12 V (0·22 V)	4

The adsorptivity of organic compounds can also be studied polarographically from capacity phenomena and even from suppression of maxima.[36] If the 3-amino group in hollarhimine (CVI) is in α-configuration, the compound is much more easily adsorbed at the surface of the mercury electrode than the β-isomer. It was deduced that adsorption occurs from the rear of ring A in the steroid molecule.



CVI

CONCLUSIONS

If quantitative treatments similar to those already made with other groups of compound are, in future, to be applied to alicyclic systems, it will be necessary to carry out in this field the polarographic research on an even broader scale than with other groups of compound because of the great variations in alicyclic systems. It was the aim of this review to demonstrate the possibilities of application of polarography in the solution of alicyclic problems and to expose gaps that exist in our present knowledge.

Zusammenfassung—Der Artikel bespricht die Polarographie alicyklischer Verbindungen.

Résumé—On présente une revue sur la polarographie des composés alicycliques.

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The Editorial Board and Publisher of TALANTA take pleasure in welcoming the following new members to the Advisory Board of the journal:

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Also, they would like to record their sincere thanks for the help given by

E. BISHOP
W. KEMULA
J. MITCHELL, JR.
D. H. WILKINS

who retire from the Advisory Board.

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NOTICES

BELGIUM

Saturday–Wednesday 10–21 *September* 1966: **XXXVIth International Congress on Industrial Chemistry:** *Fédération des Industries Chimiques de Belgique* and *Belgian Branch of Societé de Chimie Industrielle.* Brussels.

In Group II, *General Technical Problems of the Chemical Industry,* of the programme a Section will be devoted to *Analysis: Methods and Apparatus.* Further information may be obtained from Secrétariat Général du XXXVI^e Congrès International de Chimie Industrielle, 49 Square Marie-Louise, Brussels 4.

UNITED KINGDOM

Wednesday–Friday 5–7 *January* 1966: **Symposium on Thin-Layer Chromatography:** *Department of Textile Industries, University of Leeds* **and** *Society for Analytical Chemistry, Thin-Layer Chromatography Group.* University of Leeds.

The programme is as follows:

Wednesday 5 January	
Reproducibility of R_f-Values in Thin-Layer Chromatography.	M. S. J. DALLAS
Place of Thin-Layer Chromatography in Pesticide Residue Analysis.	J. THOMSON
Use of Radioactive Tracers in Analysis by Thin-Layer Chromatography.	D. A. LAMBIE
Thursday 6 January	
Fundamentals and Applications of Thin-Layer Electrophoresis.	J. D. R. THOMAS
Applications of Thin-Layer Chromatography in Anthraquinone Dyestuff Chemistry.	C. G. HAYNES
Applications of Thin-Layer Chromatography in Propellentry.	F. W. S. CARVER
Participants Contributions (Details to be announced later)	
Friday 7 January	
Value of Film Chromatography in Chemical Research.	E. V. TRUTER

Further information can be obtained from Secretary for University Extension Lectures, Department of Adult Education and Extramural Studies, University of Leeds, Leeds 2.

Wednesday 5 *January* 1966: Reading of **Elwell Award Papers:** *Society for Analytical Chemistry, Midlands Section.* University of Birmingham, Birmingham 15. 6.30 p.m.

Friday 7 *January* 1966: **Annual General Meeting** followed by **Initiation, Development and Testing of Analytical Methods in Industry,** J. HASLAM: *Society for Analytical Chemistry, Western Section.* Newport. 7.00 p.m.

Thursday 27 *January* 1966: Meeting on **Economics of Automatic Analysis:** *Society for Analytical Chemistry, Automatic Methods Group.* London.

Friday 28 *January* 1966: **Annual General Meeting:** *Society for Analytical Chemistry, Scottish Section.* Glasgow.

Saturday 29 *January* 1966: **Annual General Meeting** followed by **Thermal Analysis,** G. F. LONGMAN: *Society for Analytical Chemistry, North of England Section. Old Nag's Head Hotel,* Lloyd Street, Manchester. 2.30 p.m.

British Standards Institution has announced the following *Revised British Standard: B.S.* 1016: *Methods for the analysis and testing of coal and coke: Part* 3: 1965: *Proximate analysis of coal.* (Price: 7*s.* 6*d.*). The determination of moisture, volatile matter and ash in coal is detailed.

UNITED STATES OF AMERICA

Monday-Thursday 24–27 *January* 1966: **Nineteenth Annual Symposium on Modern Methods of Analytical Chemistry.** Louisiana State University, Baton Rouge, La.

Sunday 30 *January-Friday* 4 *February* 1966: **A.S.T.M. Committee Week:** *American Society for Testing and Materials.* Shoreham and Sheraton-Park Hotels, Washington D.C.

Monday-Friday 13–17 *June* 1966: **Fifth National Meeting:** *Society for Applied Spectroscopy.* Sheraton-Chicago Hotel, Chicago, Ill.

Original papers are being solicited in all areas of theoretical and applied spectroscopy and gas chromatography, including X-ray spectroscopy, arc-spark emission, flame emission, atomic absorption, infrared, ultraviolet, visible, Raman, far infrared, NMR-EPR, nuclear particle spectroscopy, activation analysis and solid state spectroscopy. Anyone wishing to submit a paper is encouraged to send a title and abstract (not more than 200 words) before 1 March to Dr. E. LANTERMAN, Borg-Warner Corp., Des Plaines, Ill. 60018.

American Society for Testing and Materials has announced the availability of the following publication:

Hydrocarbon Analysis—STP 389: 426*pp.* (Price: $8.50; to ASTM members: $5.95). Sponsored by Research Division IV of ASTM Committee D-2 on Petroleum Products and Lubricants, the book is divided into four sections:

(1) Where We Are and a Look Ahead;
(2) Potential Analytical Developments;
(3) Integrated Methods Approach;
(4) Hydrocarbon and Non-Hydrocarbon Impurities.

To closely link the programme of the NBS Office of Standard Reference Materials with research efforts in other laboratories, a publication series entitled *Standard Reference Materials* has been initiated as a medium for broad and rapid dissemination of the results of standard materials investigations at **National Bureau of Standards.**

The basic publication in this series, NBS Misc. Publ. 260, is subtitled *Catalog and Price List of Standard Materials Issued by the National Bureau of Standards.* This basic section is kept up to date quarterly by issuing supplementary insert sheets as new standards are prepared, old ones are exhausted, renewals issued and others are discontinued.

Other publications in this series are numbered as Misc. Publ. 260–1, Misc. Publ. 260–2, and so forth. Thus far the following publications have been issued: 260–1, *Preparation of NBS White Cast Iron Spectrochemical Standards;* 260–2, *Preparation of NBS Copper Base Spectrochemical Standards;* 260–3, *Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard;* 260–4, *Standard Reference Materials: Sources of Information;* 260–5, *Accuracy of Solution X-Ray Spectrometric Analysis, of Copper-Base Alloys; and* 260–6, *Methods for the Chemical Analysis of White Cast Iron Standards.* Several more publications in this Series are under way.

ERRATUM—Volume 11

Page 1353, Fig. 5: The legend should read as follows

FIG. 5.—Working curves for tellurium(IV):
——— $HClO_4$ system,
- - - - HCl system.

Talanta, 1965, Vol. 12, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

19–23 *June* 1967: **XIII Colloquium Spectroscopicum Internationale:** *Canadian Association for Applied Spectroscopy.* Ottawa.

Requests for information and offers of papers should be directed to the Secretary, XIII Colloquium Spectroscopicum Internationale, National Research Council, Ottawa 7, Canada.

UNITED KINGDOM

Wednesday 10 *November* 1965: Meeting on **ESR and Polarography:** *Polarographic Society.* National Physical Laboratory, Teddington. 2.30 p.m.

The following papers will be presented:

Recent Progress in Electrokinetics	G. Hills
Applications of ESR to Polarography of Oxygen in Aprotic Solvents.	M. E. Peover
Polarography in Intra-molecularly Hydrogen-bonded Systems.	R. Grinter and T. G. Edwards

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Wednesday 10 *November* 1965: Meeting on **Automatic Analysis:** *Society for Analytical Chemistry* Wellcome Building, Euston Road, London N.W.1. 3.00 p.m.

The programme will include the following papers:

Process Control with Gas Chromatography in the Chemical Industry.	H. Kienitz
Non-radiometric Instruments for Process Control in the Windscale Nuclear Fuel Reprocessing Plant.	C. R. McGowan
Data Processing Systems Incorporating Automatic Analysis.	C. W. Munday
Some Applications of Radioisotopes in Chemical Analysis.	J. K. Skrebowski

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During December, 1965, Professor W. Kemula will lecture on *Partition of Mixtures of Homologues and Isomers by Chromato-polarography* at the following places:—

7 December: Department of Chemistry, University of Nottingham: 5.00 p.m.
10 December: Department of Chemistry, University of Birmingham: 6.30 p.m.
13 December: School of Chemistry, University of Bristol: 5.30 p.m.
14 December: Department of Chemistry, University of Exeter: 5.15 p.m.
16 December: School of Pharmacy, Brunswick Square, London W.C.1: 6.00 p.m.

Thursday 2 *December* 1965: **Annual General Meeting** followed by Meeting on **Thermal Analysis in Relation to Composition of Evolved Gases,** D. Fitzgerald, S. C. Bevan and S. Thorburn: *Society for Analytical Chemistry, Thermal Analysis Group.* 14 Belgrave Square, London S.W.1. 6.30 p.m.

Saturday 4 *December* 1965: Meeting on **Training of the Analyst in Physical Methods,** A. G. Jones: and H. R. Jones: *Society for Analytical Chemistry, North of England Section.* City Laboratories, Mount Pleasant, Liverpool. 2.30 p.m.

Tuesday 7 *December* 1965: Discussion Meeting on **Effluent Analysis,** F. G. Broughall, S. H. Jenkins and N. T. Wilkinson: *Society for Analytical Chemistry, Midlands Section.* College of Advanced Technology, Birmingham 4. 7.00 p.m.

Thursday 9 *December* 1965: **Annual General Meeting** followed by a **Discussion Meeting:** *Society for Analytical Chemistry, Biological Methods Group. The Feathers,* Tudor Street, London E.C.4. 6.30 p.m.

Friday 10 *December* 1965: **Annual General Meeting** followed by **A Statistical Approach to Analysis** A. K. SOPER: *Society for Analytical Chemistry, Microchemical Methods Group.* Burlington London House, W.1. 6.45 p.m.

Friday 17 *December* 1965: **Atomic-Absorption Spectrophotometry,** H. PUGH: *Society for Analytical Chemistry, Western Section.* Cardiff. 7.00 p.m.

Monday–Thursday 18–21 *July* 1966: **Symposium on Some Newer Physical Methods for Structural Chemistry.** New College and the Clarendon Laboratory, Oxford.

The principal subjects will be mass spectrometry, optical rotatory dispersion and circular dichroism. Those wishing to give papers or attend the Symposium should communicate as soon as possible with *Laboratory Practice,* 9 Gough Square, London E.C.4.

British Standards Instutition has announced the following *New British Standard: B.S.* 3917: *Methods for the Analysis of manganese ores: Part* 1: 1965: *Manganese dioxide (active oxygen)* (4s.). This describes the reagents required, recommended methods of sampling and test procedure for the titrimetric determination of manganese dioxide in the range normally found in manganese ores. The method is substantially in line with that given in ISO Recommendation No. 312—Determination of active oxygen (conventially expressed as manganese dioxide).

Part 2: 1965: *Total manganese* (4s.). This describes the reagents required, recommended methods of sampling and test procedure for the titrimetric determination of manganese in the range normally found in manganese ores.

Part 3: 1965: (4s.). This describes the reagents required, recommended methods of sampling and test procedure for the titrimetric determination of iron in manganese ores in which the iron content exceeds 0.5%.

The following *Revised British Standard* has also been announced: *B.S.* 1756: *Methods for the sampling and analysis of flue gases: Part* 3: 1965: *Analysis by the Haldane apparatus* (10s.). This deals with the analysis of a flue gas sample with the Haldane apparatus.

UNITED STATES OF AMERICA

Thursday–Saturday 2–4 *December* 1965: **Southeast-Southwest Regional Meeting:** *American Chemical Society.* Hotel Peabody, Memphis, Tenn.

Monday 31 *January–Tuesday* 1 *February* 1966: **Conference on Progress in Gas Chromatography.** University of California, Los Angeles.

The following chemists will discuss *Progress in Gas Chromatography,* emphasising their own work: M. BEROZA, K. P. DIMICK, H. W. JOHNSON, JR., A. J. MARTIN, C. S. G. PHILLIPS, J. H. PURNELL, D. T. SAWYER and J. C. STERNBERG.

The Conference will be followed on 2–4 February by the **Eighth Short Course in Fundamental Principles of Gas Chromatography.** This is an up-dated version of previous courses aimed primarily to instruct personnel from industry, although it may be equally valuable to persons in academic or government laboratories.

Further information may be obtained from H. L. TALLMAN, Physical Sciences Extension, Room 6532 Engineering Building, University of California, Los Angeles, California 90024.

Seven new or renewed radioactivity standards have recently been announced by **National Bureau of Standards** and are now available from the Office of Standard Reference Materials, N.B.S., Washington, D.C., 20234: sodium-22, iron-55, zinc-65, yttrium-88, caesium-137/barium-137m, cerium-141 and americium-241.

Five other standards are currently out of stock. Two of these, iodine-125 and mercury-203, will be reissued in the near future. The other three, scandium-46, strontium-85 and niobium-95, may be available within a year.

American Society for Testing and Materials has announced the availability of the following publications:

X-Ray and Optical Emission Analysis of High-temperature Alloys: STP 376 ($2.50 or $1.75 to *ASTM members*).

X-Ray Emission Line Wavelength and Two-theta Tables: DS 37 ($20.00 *or* $14.00 *to ASTM members*).

ERRATA—Volume 12

Page 831, line 11 of Reagents: For *molar extraction coefficient* read *molar extinction coefficient.*

Page 901, reference 23: This should read

[23] M. I. Kabachnik, S.T. Ioffe and T. A. Mastryukova, *Zhur. obshchei Khim.*, 1955, **25**, 684.

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NOTICES

CANADA

Monday–Wednesday 18–20 *October* 1965: **Twelfth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa.

Papers are invited dealing with all fields of spectroscopy; investigations in which novel applications of spectroscopy were used; and applications of other techniques to problems in spectroscopy, such as electronic computers and high-speed photography.

Titles and brief abstracts of papers should be submitted as soon as possible to Mr. R. V. Baker, Aluminium Company of Canada Ltd., Arvida, Ottawa; the final date for acceptance of papers is June 15.

DEUTSCHE DEMOKRATISCHE REPUBLIK

28.9.–2.10. 1965: **2. International Symposium Reinststoffe in Wissenschaft und Technik:** *Chemische Gesellschaft in der DDR, Gesellschaft Deutscher Bergund Hüttenleute* und *Physikalische Gesellschaft in der DDR.* Dresden.

Sektion C: Reinststoff-Analytik

Bestimmung chemischer Verunreinigungen mit modernen physikalischen und chemischen Verfahren—Spezielle Berücksichtigung methodischer Weiterentwicklungen

Sektion D: Realstruktur

Nachweis von Kristallbaufehlern mittels Röntgen-, Elektroden- und Neutronenstrahlen sowie mit metallographischen Methoden—Entstehung, Verhalten und Eigenschaften von Gitterstörungen

Sitz des Organisationskomitees: Chemische Gesellschaft in der DDR, Berlin W8, Clara-Zetkin-Str. 105.

FRANCE

Mercredi 2-6-1965: Réunion commune avec la Section de Chimie Analytique de la Société de Chimie Industrielle.

Mecredi 2-6-1965: L'analyse fonctionnelle au service de la synthèse organique, par M. F. Pellerin, à 17 h 45, à la Faculté de Pharmacie de Paris.

GREECE

Sunday–Friday 19–24 *September* 1965: **Methods of Immediate Separation and Chromatography:** *Association of Greek Chemists* in collaboration with *Association for Development of Spectrographic Methods* (*G.A.M.S.*). Athens.

The principal subject will be Chromatography in the general sense, its theoretical aspects, apparatus and analytical applications. The following plenary lectures will be presented:

Some recent progress in chromatography.	E. Lederer
Identification of gas chromatographic fractions.	D. Ambrose
A comparison of thin layer and paper chromatography.	F. H. Pollard

Further information can be obtained from Professor G. Parissakis, Association of Greek Chemists, 27 Kaningos Road, Athens, Greece.

ÖSTERREICH

"**Symposium analytische Chemie**", Treffen jugoslawischer, ungarischer und österreichischer Chemiker. (Im Anschluß an die Hauptversammlung des Vereines Österreichischer Chemiker.)

Graz, 29. *September* bis 1. *Oktober* 1965.

Hauptvortrage: B. Kosta (Jugoslawien), E. Pungor (Ungarn), V. Gutmann (Wein).

Kolloquium für metallkundliche Analyse und Elektronenstrahlmikroanalyse, veranstaltet vom Institut für analytische Chemie und Mikrochemie der Technischen Hochschule in Wien und der Österreichischen Gesellschaft für Mikrochemie und Analytische Chemie.

Wein, 20. bis 23, *Oktober* 1965, *Technische Hochschule in Wien.*

UNITED KINGDOM

Monday–Thursday 6–9 *September* 1965: **First International Conference on Thermal Analysis.** Department of Natural Philosophy, University of Aberdeen, Old Aberdeen, Scotland.

As indicated previously [*Talanta*, 1965, **12** (1), ii], the theme will be

Thermal Techniques and Their Applicability

and the conference will have the following Sections:

1. Advances in instrumentation.
2. Organic materials, including polymers.
3. Inorganic materials and metallurgy.
4. Physical chemistry and quantitative aspects.
5. Minerals.
6. Applied sciences (building materials, ceramics, *etc.*).

The number of papers that has been offered is such that it will be necessary to hold two sessions of most, if not all, Sections. In consequence, it will be impossible to avoid simultaneous meetings, but in arranging such sessions attention will be paid to the numbers interested in each of the Sections.

Each session of each Section will be presided over by a prominent worker in the field and, at the invitation of the Organising Committee, Dr. J. P. REDFERN, Dr. C. B. MURPHY, Professor Dr. L. G. BERG and Professor Dr. R. BARTA will deliver opening lectures at the first sessions of Sections 1, 2, 3 and 6, respectively.

If not already paid, the registration fee of £5 sterling ($15.00 U.S. or 13 roubles) is now due and must be paid by 15 May, 1965. Further information may be obtained from Dr. R. C. MACKENZIE, Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland.

Wednesday–Friday 13–15 *October* 1965: **1965 Symposium on Automated Analytical Chemistry:** Technicon Instruments Company Ltd. London.

As in previous years, the Symposium will be on an International basis and original work by distinguished scientists from Europe and America will be presented, as well as contributions from workers in United Kingdom.

The *Society for Analytical Chemistry* has approved the formation of a *Thermal Analysis Group,* which will be concerned with methods of investigation normally performed under dynamic conditions of temperature.

The Officers of the first Committee of the new Group are:

Chairman: R. C. MACKENZIE
Vice-Chairman: J. P. REDFERN
Hon. Secretary: C. J. KEATTCH
Hon. Treasurer: A. A. HODGSON

Members of the Society for Analytical Chemistry may become members of the Group on request to the Secretary of the Society, 14 Belgrave Square, London S.W.1. Those who are not members of the Society may receive notices of the meetings of the Group on application to its Secretary, Mr. C. J. KEATTCH, John Laing Research and Development Ltd., Manor Way, Boreham Wood, Herts.

British Standards Institution has announced the following *Revised British Standard:*

B.S. 2690: *Methods of testing water used in industry: Part* 2: 1965: *Dissolved oxygen, hydrazine and sulphite.* This gives three methods for dissolved oxygen, one method for hydrazine and one method for sulphite. (*Price* 7s.6d.)

The following *Amendment Slip* is also announced:

B.S. 3762: 1964: *Methods of sampling and testing detergents. Amendment No.* 1: *PD* 5446. (*Gratis.*)

UNITED STATES OF AMERICA

Monday–Friday 7–11 *June* 1965: **International Carbon-14 and Tritium Dating Conference.** Washington State University, Pullman, Wash.

Wednesday–Friday 9–11 *June* 1965: **Summer Symposium on Bioanalytical Techniques:** *Division of Analytical Chemistry of American Chemical Society* and ANALYTICAL CHEMISTRY. University of Wisconsin, Madison, Wis.

Sunday–Friday 13–18 *June* 1965: **Sixty-Eighth Annual Meeting:** *American Society for Testing and Materials.* Purdue University, Lafayette, Ind.

Monday–Thursday 14–17 *June* 1965: **Sixteenth Mid-America Symposium on Spectroscopy.** Sheraton-Chicago Hotel, Chicago, Ill.

Monday–Tuesday 14–15 *June* 1965: **Twentieth Annual Northwest Regional Meeting:** *Pacific Northwest Sections of American Chemical Society.* Oregon State University, Corvallis, Ore.

Monday–Friday 14–18 *June* 1965: **Symposium on Molecular Structure and Spectroscopy.** Ohio State University, Columbus, Ohio.

Thursday–Saturday 24–26 *June* 1965: **Conference on Small-Angle X-Ray Scattering.** Syracuse University, Syracuse, N.Y.

Wednesday 29 *September–Friday* 1 *October* 1965: **Twelfth National Vacuum Symposium:** *American Vacuum Society.* Statler-Hilton Hotel, New York City, N.Y.

The Programme Committee solicits the submission of contributed papers for presentation at the Symposium. Abstracts should be submitted by 5 July to the Chairman: R. L. JEPSEN, Varian Associates, 611 Hansen Way, Palo Alto, California 94303, U.S.A.

Contributed papers should report significant results of new and original work, either experimental or theoretical in nature, in an area relating to production, measurement or application of vacuum. Papers dealing with *fundamental* aspects of vacuum production, vacuum measurement and behaviour of materials and surfaces in a vacuum environment are particularly welcome. Papers on new or improved vacuum components and vacuum systems are also welcome provided they are truly technical rather then commercial in nature.

Of special interest this year are papers on such "Space-Related Problems" as friction, sticking and wear under conditions of outer space, and measurements of densities and pressure of various molecular species at high altitudes. Another timely area is electron microscope inspection of microcircuits. Thin films, of course, constitute one of the most important applications of vacuum; it is, therefore, hoped that a large number of good papers will again be contributed in this area.

Following last year's procedure, the *Thin Film Division of the American Vacuum Society* plans to hold a special *Thin Film Division Symposium*, also at the Statler-Hilton Hotel, on September 28, the day preceding the National Vacuum Symposium. This special Symposium will consist exclusively of invited papers on such topics as nucleation and growth, dislocations, and low *energy electron diffraction studies.*

American Society for Testing and Materials has announced that the following publication is now available:

Techniques of Electron Microscopy, Diffraction and Microprobe Analysis: STP 372: 90 + *vi pp. with heavy paper cover.* ($3.75 or $2.60 to ASTM members.)

This presents new techniques and applications of electron microscopy, diffraction and microprobe analysis in research studies. It is well illustrated with photographs, drawings and charts.

UNGARN

8.6. bis 12.6.1965: *Budapest:* Konferenz des wissenschaftlichen Vereins für die Silicatindustrie und der Universität der chemischen Industrie, Veszprém.

Auskunft: Konferenzausschuß Budapest V (Ungarn), Szabadság-tér 17, Haus der Technik, Silikonf.

ERRATA

Volume 12

Page 186, Table I: The heading to the second column should read

$$\text{Na}_2\text{S}_2\text{O}_3,\\ ml$$

Page 401: The address of the authors should read *Faculty of Technical and Nuclear Physics.*
Page 405, line 2: for *tartarate* read *tartrate.*
Page 405, Table II: In the footnote read *interfering* for *interferring.*
Page 406, line 5 from bottom of page: For *interferring* read *interfering.*

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NOTICES

DENMARK

Saturday–Friday 14–20 *August* 1965: **Eighth European Congress on Molecular Spectroscopy:** *Dansk Forening for Molekylspektroskopi.* H. C. Ørsted Institute, Copenhagen, Denmark.

The following general and introductory lectures have been finalised:

Impact of wave-mechanical methods on interpretation of molecular spectroscopy.	R. Daudel
Michelson interferometers for far infrared spectroscopy and refractometry.	Th. Förster
Microwave spectroscopy in the region 0.4–4 mm.	W. Gordy
Infrared spectra of strongly hydrogen bonded systems.	D. Hadzi
Analysis of high-resolution NMR spectra.	R. A. Hoffman
Electronic spectra of aromatic hydrocarbon molecules and ions.	G. J. Hoijtink
Fortschritte bei der infrarotspecktroskopischen Analyse makromolekularer Systeme.	D. Hummel
The exciton model in molecular spectroscopy.	M. Kasha
Optische und elektrische Effekte an Systemen monomolekularen Schichten.	H. Kuhn
Electronic spectra of simple molecules by electron impact.	A. Kuppermann
Barriers to international rotation from infrared spectra.	H. C. Longuet-Higgins
Potential functions and coriolis interactions in polyatomic molecules.	I. M. Mills
Recoilless absorption of gamma-radiation and its application to electronic shielding in rare earths.	R. L. Mössbauer
Infrared detection of transient species produced by flash photolysis.	G. Pimentel
Formulae for chemical substitution shifts in conjugated spectra.	J. R. Platt
Approximative Potentialkurven für Moleküle.	H. Preuss
Recent results and future trends in microwave spectroscopy.	J. Sheridan
Molecular spectroscopy with optical masers.	B. Stoicheff
Raman spectra of some species in aqueous solution.	L. A. Woodward

Contributed papers have been accepted within the following areas of research and theory: Electron spin resonance; Far infrared spectra; High-resolution infrared spectra; High-resolution Raman spectra; High-resolution visible-ultraviolet spectra; Hydrogen bonding; Instrumentation; Microwave spectra; Novel analytical applications; Nuclear magnetic resonance; Solid state spectra; Solvent effects; Spectral intensities, Spectral theory; Spectra of matrix isolated and adsorbed molecules; Vibrational spectra (infrared and Raman); Visible-ultraviolet spectra; and also a few papers dealing with circular dichroism, electron impact spectroscopy, *etc.* No more contributed papers can be accepted.

Further information can be obtained from 8th European Congress on Molecular Spectroscopy, Universitetsparken 5, København ø, Denmark.

FRANCE

Mardi 27 *avril* 1965: **La recherche des substances étrangères dans les produits céréaliers (biologiques, minérales, organiques),** par M. J. Bure, 17 h 45, la Faculté de Pharmacie de Paris.

UNITED KINGDOM

Monday 29 *March–Friday* 2 *April* 1965: **Laboratory Apparatus and Materials Exhibition: LABEX 1–65:** *Scientific Instrument Manufacturers' Association of Great Britain.* Earls Court, London.

Tuesday 6 *April* 1965: **Inorganic applications of infrared spectroscopy,** R. J. Magee; **Examination of clays and slag materials,** P. S. Keeling: *Society for Analytical Chemistry, North of England and Midland Sections.* North Staffordshire College of Technology, Stoke-on-Trent, 7.15 p.m.

Tuesday–Friday 6–9 April 1965: Symposium on **Physical Methods of Structure Determination:** *The Chemical Society Anniversary Meetings.* Glasgow [see *Talanta*, 1965, **12**(2), ii].

Wednesday 7 *April* 1965: Symposium on **Pharmaceutical Screening of Drugs:** *Society for Analytical Chemistry, Biological Methods Group.* School of Pharmacy, University of London, Brunswick Square, London W.C.1.

Thursday–Friday 8–9 *April* 1965: **Spring Conference:** *Institute of Physics and Physical Society, X-Ray Analysis Group.* University of Edinburgh.

Friday–Saturday 9–10 *April* 1965: **Infrared Analysis,** D. M. W. Anderson, R. J. Magee, L. C. Thomas, H. A. Willis: *Society for Analytical Chemistry, Microchemical Methods and Special Techniques Groups.* University of Sussex, Brighton.

Tuesday 13 *April* 1965: Symposium on **Applications of A.E.I. MS10 Mass Spectrometer.** Imperial College, London.

Subjects include: General gas analysis; Isotopic measurement; Impurity in gases at the ppm level; Age determination of rocks; Vacuum monitoring; Gaseous diffusion through membranes; Applications in physical chemistry research; Analysis of small gas samples; Surface reaction studies; Process monitoring; Flame and combustion analysis; Vacuum fusion analysis.

Enquiries should be addressed to Mr. A. J. Bullough, Associated Electrical Industries Ltd., Barton Dock Road, Manchester 17.

Tuesday–Wednesday 13–14 *April* 1965: **Symposium on Thermal Analysis.** Northern Polytechnic, London [see *Talanta*, 1964, **11**(8), ii].

Wednesday 21 *April* 1965: **Automatic Methods of Analysis,** J. F. Marten and G. V. R. Mattock: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Lea Valley Section.* Luton and South Bedfordshire College of Further Education, 6.45 p.m.

At the *Annual General Meeting* of the **Western Section** of the **Society for Analytical Chemistry** held on 8 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: E. A. Hontoir
Vice-Chairman: L. E. Coles
Secretary/Treasurer: T. G. Morris, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

At the *Thirtieth Annual General Meeting* of the **Scottish Section** of the **Society for Analytical Chemistry** held on 22 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: J. K. McLellan
Vice-Chairman: D. M. W. Anderson
Secretary/Treasurer: J. W. Murfin, Boots Pure Drug Co. Ltd., Motherwell Street, Airdrie Lanarkshire.

At the *Annual General Meeting* of the **North of England Section** of the **Society for Analytical Chemistry** held on 30 January, 1965, the following Officers were elected for the forthcoming year:

Chairman: J. F. Clark
Vice-Chairman: W. Cule Davies
Secretary/Treasurer: G. F. Longman, Denegarth, Birkenhead Road, Meols, Wirral, Bi Cheshire.

At the *Twenty-First Annual General Meeting of the* **Microchemical Methods Group** of the **Society for Analytical Chemistry** held on 19 February, 1965, the following Officers were elected for the forthcoming year:

Chairman: R. GOULDEN
Vice-Chairman: T. R. F. W. FENNELL
Treasurer: F. H. OLIVER
Secretary: Mrs. D. E. BUTTERWORTH, National Chemical Laboratory, Teddington, Middlesex.

UNITED STATES OF AMERICA

Sunday–Friday 4–9 *April* 1965: **149th National Meeting**: *American Chemical Society*. Detroit, Michigan.

Monday–Wednesday 19–21 *April*: **Third National Biomedical Sciences Instrumentation Symposium**: *Instrument Society of America*. Dallas, Texas.

Monday–Thursday 19–22 *April* 1965: **1965 International Conference on Modern Trends in Activation Analysis.** College Station. Texas A and M University, Texas [see *Talanta*, 1965, **12**(2), iii].

Wednesday–Friday 21–23 *April* 1965: **Third Marine Sciences Instrumentation Symposium**: *Instrument Society of America*. Miami, Florida.

Monday–Thursday 4–7 *October* 1965: **Twentieth Annual International Conference and Exhibit**: *Instrument Society of America*. Los Angeles, California.

The theme of the 1965 meeting is **New Measures of Progress in Instrumentation.** Further information is available from Dr. E. M. GRABBE, 1965 Conference Programme Co-ordinator, c/o Instrument Society of America, 530 William Penn Place, Pittsburgh, Pa. 15219.

Monday–Thursday 11–14 *October* 1965: **Seventy-Ninth Annual General Meeting**: *Association of Official Agricultural Chemists*. Marriott Motor Hotel, Twin Bridges, Washington, D.C.

For information contact LUTHER G. ENSMINGER, A.O.A.C., Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

1965 *Book of ASTM Standards*: Issued periodically by **American Society for Testing and Materials** in 32 parts, it will contain approximately 3700 standards of which more than 1260 will be new or revised since publication of the 1964 Volume. Each of the parts, brought up-to-date and available on the same monthly schedule each year, covers a specific field of interest and includes a detailed index, table of contents and a numeric list of standards.

ERRATA—Volume 12

Page 134, first line: This should read . . . .*advantage of high hydrogen overvoltage*
Page 136, Table II: Heading to final column should read *Dietert furnace*
Page 136, line 6 from bottom: For *dimethylglyoxine* read *dimethylglyoxime*

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NOTICES

BUNDESREPUBLIK DEUTSCHLAND

Die Fachgruppen *Analytische Chemie* und *Lebensmittelchemie und gerichtliche Chemie* in der *Gesellschaft Deutscher Chemiker* veranstalten gemeinsam mit der *Gesellschaft für Physiologische Chemie* und der *Deutschen Gesellschaft für Klinische Chemie* in der Woche vom 15.–19. März 1965 eine Tagung zum Thema

Moderne analytische Methoden in der Lebensmittelchemie und der biologischen Chemie

Es werden folgende Hauptvorträge gehalten:

Enzymatische Analyse	H.-U. Bergmeyer
(Genaues Themo steht noch nicht fest)	
Die Bestimmung von Alkohol im Blut	R. Block
Moderne Methoden zur Bestimmung von Steroidhormonen	H. Breuer
Problem bei der Analyse von Ionen in Körperflüssigkeiten	E. Heinz
Neuere Entwicklungen der flammenfotometrischen Analysenverfahren	R. Herrmann
Chelatometrische Methoden in der klinschen Analyse	A. Holasek
Möglichkeiten und Grenzen in der Anwendung moderner biochemischer Verfahren	G. Pfleiderer
Ein Querschnitt über Aufbau und Technologie der im Lebensmittelverkehr verwendeten Kunststoffe.	H. Sutter

Des weiteren werden voraussichtlich noch Hauptvorträge zu den Themen

Moderne elektrometrische Methoden
Messung des Säure-Base-Haushaltes
Methoden der klinischen Gasanalyse

gehalten werden.

Weitere Auskunft ist bei der GOCh-Geschäftsstelle, 6000 Frankfurt/Main, Postfach 9075, Bundesrepublik Deutschland, zu erhalten.

CANADA

Monday 8 *February* 1965: **First Toronto Symposium on Thermal Analysis.** Seaway Towers Hotel, Toronto, Ontario [see *Talanta*, 1964, **11** (12), i].

DENMARK

Sunday–Friday 14–20 *August* 1965: **Eighth European Congress on Molecular Spectroscopy:** sponsored by *International Union of Pure and Applied Chemistry* and *Royal Danish Academy of Sciences.* H. C. Ørsted Institute, Copenhagen, Denmark.

The subjects of the meeting will be within the field of molecular spectroscopy, *viz.*

Raman and infrared spectra
Ultraviolet spectra
Microwave spectra
Nuclear magnetic resonance spectra
Electron spin resonance spectra
Spectral theory
Novel analytical applications

Further information may be obtained from 8th European Congress on Molecular Spectroscopy, Univseritetsparken 5, København Ø, Denmark.

FRANCE

Vendredi 19–2–1965: **Dosage du silicium par activation neutronique:** *Section de Chimie analytique de la Société Chimique de France*, à 17 h 30, à l'Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre Curie, Paris, 5^{e}.

INDIA

Wednesday–Saturday 27–30 *January* 1965: **Fifth Seminar on Electrochemistry:** Central Electrochemical Research Institute, Karaikudi.

More than 120 research papers have been submitted to be read at the Seminar, which will be attended by about 60 delegates from different scientific institutions and industry in India and abroad. The important technical sessions will be

1. Electrode Kinetics, Electrochemical Equilibria and Electroanalysis.
2. Electro-organic and -inorganic Products.
3. Electrothermics and Electrometallurgy.
4. Batteries.
5. Electrodeposition and Metal Finishing.
6. Corrosion.
7. Miscellaneous.

It is also proposed to hold a special session on *Aluminium.*

UNITED KINGDOM

Wednesday–Friday 6–8 *January* 1965: Conference on **Optics in process control:** *Institute of Physics and Physical Society.* Manchester College of Science and Technology.

Tuesday 2 *February* 1965: **pH and its Significance,** W. K. F. WYNNE-JONES: *Society for Analytical Chemistry, Midlands Section.* University of Birmingham, Edgbaston, Birmingham 15, 6.30 p.m.

Wednesday 3 *February* 1965: **New spectroscopic sources:** *Society for Analytical Chemistry, Special Techniques Group* and *Institute of Physics and Physical Society, Applied Spectroscopy Group.* Wellcome Building, Euston Road, London N.W.1, 3.00 p.m.

Thursday 11 *February* 1965: **Discussion Meeting:** *Society for Analytical Chemistry, Biological Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Tuesday 16 *February* 1965: **Precipitation from homogeneous solution,** M. WILLIAMS: *Society for Analytical Chemistry, Midlands Section.* Loughborough College of Advanced Technology, 7.00 p.m.

Friday 19 *February* 1965: Symposium and Exhibition on **Thin Layer Chromatography,** E. V. TRUTER, L. J. MORRIS, W. J. CRIDDLE, E. J. SHELLARD and P. J. STEVENS: *Society for Analytical Chemistry, Thin-Layer Chromatography Group* and *Western Section.* Welsh College of Advanced Technology, Cardiff.

Friday 19 *February* 1965: **Annual General Meeting** followed by **Address of Retiring Chairman,** D. W. WILSON: *Society for Analytical Chemistry, Microchemical Methods Group.* Burlington House, London W.1, 6.45 p.m.

Friday 26 *February* 1965: **Research work at the Government Laboratory,** D. T. LEWIS: *Society for Analytical Chemistry, Scottish Section.* University of Strathclyde, Glasgow, 7.15 p.m.

Saturday 20 *March* 1965: Symposium on **Identification of Drugs and Poisons:** *Pharmaceutical Society of Great Britain.* School of Pharmacy, University of London, Brunswick Square, London W.C.1.

In cases of poisoning, speed in identification of the causitive agent is essential, and the morning session will be devoted to discussing how this procedure may be improved. The afternoon session will be concerned with more fundamental aspects of analytical procedures.

Registration forms, together with full details, may be obtained from the Organising Secretary, Pharmaceutical Society of Great Britain, 17 Bloomsbury Square, London W.C.1.

Monday–Thursday 6–9 *September* 1965: **First International Conference on Thermal Analysis.** Aberdeen, Scotland.

The Conference will have as theme

Thermal Techniques and Their Applicability

and will cover all thermal methods, both dynamic and static. In addition, it will be interdisciplinal and papers which could be presented under one of the following headings are invited:

1. Advances in instrumentation (including new methods of general applicability).
2. Organic materials, including polymers.
3. Inorganic compounds and metallurgy.
4. Physical chemistry, including quantitative studies.
5. Minerals, ceramics, glass, refractories and building materials.

Further information may be obtained from Dr. R. C. Mackenzie, Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, Scotland.

Wednesday 15 *September* 1965: Symposium on **Thermometric Titrimetry:** *Society for Analytical Chemistry, Special Techniques Group* and *Midlands Section* with *Royal Institute of Chemistry, Birmingham and Midlands Section* and *Society for Chemical Industry, Birmingham and Midlands Section.* University of Birmingham, Edgbaston, Birmingham, 15.

Anyone who is interested in submitting a paper or demonstrating thermometric titrimetry apparatus should communicate with Mr. M. L. Richardson, John and E. Sturge Ltd., Kings Norton, Lifford Lane, Birmingham 30.

In July 1959, the **National Lending Library for Science and Technology** (Boston Spa, Yorkshire) published its first *List of Current Periodicals Received from China.* During the three years that followed (1960–62) very little material from China come into the Library. Only in 1963 did scientific and technical periodicals start to flow in again. The Library is currently receiving 64 titles, including 25 of the *Acta Sinica* series (figures from the first list were 89 and 27) and, in all, the *List of Scientific and Technical Periodicals Received from China* (July 1964) contains 155 titles.

British Standards Institution has announced the following *New British Standard: B.S.* 3804*: Methods for the determination of the calorific value of fuel gases: Part* 1*:* 1964*: Non-recording methods.* The method for the range 250–600 Btu/ft^3, using the Boys water-flow calorimeter, is based on the procedure in the General Directions to Gas Examiners, issued by the Ministry of Power. Modifications are described for the ranges 80–250 Btu/ft^3 and 600–3500 Btu/ft^3. The use of the bomb calorimeter for gases above 2200 Btu/ft^3 or, with modifications, for gases of lower calorific value, is also described. (*Price* 17s.6d.)

UNITED STATES OF AMERICA

Monday–Friday 25–29 *January* 1965: **Winter Gordon Research Conference on Electrochemistry: Electrode Processes.** Miramar Hotel, Santa Barbara, California.

The programme is as follows:

Monday 25 *January*	
Structure of the double layer at electrodes.	Roger Parsons
Comparative double layer studies.	D. M. Mohilner
Electrical double layer at amalgam electrodes.	J. N. Butler
Tuesday 26 *January*	
Anodic oxidation with special reference to hydrocarbons.	J. O'M. Bockris
Potential dependent adsorption of uncharged molecules on solid electrodes	E. Gileadi
Implications of magnetic and other methods for studying vapour phase adsorption on metals.	P. W. Selwood
Physical organic chemistry and organic polarography.	A. Streitwieser, Jr.
Wednesday 27 *January*	
Polarographic rate-controlled currents, volume reactions and influence of adsorption	J. Koryta
Experimental approaches to investigation of chemical reactions coupled to charge transfers.	I. Shain
New applications of EPR to organic electrode processes and homogeneous electron exchange reactions.	R. N. Adams
Thursday 28 *January*	
Techniques for non-aqueous electrochemistry.	W. B. Schaap
Interpretation of electrochemical measurements in non-aqueous solvents.	W. B. Schaap
Scale-dependent electrode phenomena.	C. W. Tobias
Friday 29 *January*	

Informal discussion, including round-table discussion, on *Fundamental Rate Equation of Electrochemical Kinetics, Interpretation of Potential Barriers,* and *Parameters of Electrode Kinetics.*

Further information is available from Dr. W. George Parks, Director, Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island, U.S.A.

Monday 1 *February* 1965: **Metropolitan Regional Meeting** of *American Chemical Society.* Stevens Institute of Technology, Hoboken, N.J.

Monday 1 *February* 1965: **Fourth Annual Metropolitan Regional Meeting,** *American Chemical Society.* Stevens Institute, Hoboken, New Jersey.

The programme for the Sessions on Analytical Chemistry is as follows:

Structural correlations of unsaturated sulphur compounds by NMR.	R. V. Moen
Determination of microstructures of cationically polymerised 3-methylbutene-1 by NMR.	B. E. Hudson

Symposium on molecular characterisation

Panel discussion featuring inter-relationships of NMR, IR, mass spectroscopy and microelemental analysis: R. Gore, T. S. Ma, E. Malinowski and B. King.

Application of thin-layer chromatography to the U.S.P. foreign steroid tests.	E. M. Cohen
Gas chromatographic behaviour of methandstenolone and related steroid tests.	C. R. Rehn and R. C. Luders
Determination of vitamin E in multi-vitamin tablets by GLC.	F. Mohn, V. Viswanathan, J. Arbigkit and B. Senkowski
Special gas chromatographic inlet system for handling volatile materials in solids.	E. R. Quiram
Characterisation of organic halogen compounds as 2,4-dinitrophenylhydrazones of methyl ketones prepared by reaction of organo-cadmium compounds with acetic anhydride.	E. J. Benjamin and J. G. Sharefkin
Low level analysis of polynuclear aromatics using mass spectroscopy.	J. M. Kelliher and R. E. Swarbrick
Application of modern instrumentation to classical methods for determining number average and weight average molecular weights of high polymers.	B. E. Hudson
Radio chromatographic determination of elements precipitated as phosphates.	G. A. Welford, R. S. Morse and E. L. Chiotis
Frontal solubilisation chromatography.	H. D. Spitz, W. Rieman III and H. L. Rothbart
Volumetric analysis of nitrato, nitro and nitramine compounds for chromous chloride reduction.	C. G. Jamison and D. J. Cragle
Study of diphenylpicrylhydrazyl as an organic analytical reagent—I: *Analysis of amines.*	G. J. Tapariello and M. A. M. Janish
Determination of colour temperature of flash lamps by spectrometry.	D. J. Bracco and S. Weisberger
An automated polymer fractionation unit.	B. Groten and W. Schulz
Determination of sodium, aluminium and manganese in soils by instrumental neutron activation analysis.	H. W. Naas and W. H. Wahl
Improved semiautomated analysis of fluorine in plant tissues.	J. Jacobson, L. Weinstein, D. McCune and A. E. Hitchcock

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Monday–Tuesday 1–2 *February* 1965: Research Conference on *Progress in Gas Chromatography.* UCLA Department of Chemistry, and Engineering Extension and Physical Sciences Extension, University of California Extension, Los Angeles, California.

Monday 1 *February*

Influence of surface effects on retention time and peak shape.	J. H. Purnell
Selective liquid phase interactions and gas chromatographic identification.	S. H. Langer

Tuesday 2 *February*

New developments in gas-solid chromatography.	C. S. G. Phillips
Recent advances in biomedical applications of gas chromatography.	S. R. Lipsky

Wednesday–Friday 3–5 *February* 1965: Course on **Fundamental Principles of Gas Chromatography.** UCLA Department of Chemistry, and Engineering Extension and Physical Sciences Extension, University of California Extension, Los Angeles, California.

Monday–Friday 8–12 *February* 1965: **Committee Week and Spring Meeting:** *American Society for Testing and Materials.* Statler Hilton Hotel, Cleveland, Ohio.

Talanta, 1965, Vol. 12, pp. i to ix. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

La Commission Internationale d'Analyses "C.I.A." du **COMITE INTERNATIONAL DE LA DETERGENCE "C.I.D."** a tenu sa 8ème réunion annuelle à Barcelone, les 22 et 23 Octobre 1964, sous la présidence du Prof. G. JACINI. Neuf pays y participaient.

Un des points principaux de l'ordre du jour était l'analyse générale des *produits non-ioniques*, qui est à l'étude par un Groupe de Travail spécial depuis 3 ans déjà, et qui fait l'objet d'une importante bibliographie. Certaines déterminations de cette analyse générale sont déjà particulièrement avancées, et l'on peut citer entre autres:

—le dosage des cendres, qui sera proposé à l'I.S.O. cette année,

—le dosage de l'eau, par les méthodes K. Fischer pour les teneurs en eau jusqu'à 10%, et Dean-Stark pour les teneurs supérieures,

—le dosage de l'oxyde d'éthylène potentiel dans ses condensats au moyen de l'acide iodhydrique, pour lequel trois méthodes sont actuellement retenues: deux classiques (Zeisel et Siggia) et une que l'on peut considérer d'avant-garde, la spectrographie infra-rouge. Trois nouvelles analyses circulaires seront effectuées cette année dans 7 pays, sur divers condensats oxyéthylénés et sur un condensat mixte oxyde d'éthylène/oxyde de propylène, selon la méthode Siggia,

—la caractérisation titrimétrique, qui est au point à l'heure actuelle mais que la C.I.A. désire compléter par des courbes représentatives des classes courantes de produits non-ioniques commerciaux,

—la détermination de l'indice d'hydroxyle: deux méthodes sont en présence (acétylation et phtalylation) et ont été expérimentées; il est envisagé d'étudier aussi une méthode à l'anhydride stéarique, où l'hydrolyse n'est pas à craindre,

—le dosage des polyglycols libres, où la méthode Weibull donne de bons résultats mais dans un domaine d'application limité. La C.I.A. effectuera une analyse circulaire dans 7 pays, en utilisant un procédé hollandais sur résines échangeuses d'ions accompagné d'un contrôle terminal faisant emploi de la chromatographie sur couche mince,

—le dosage des esters sulfuriques, qui sera confié à un groupe de travail spécialisé qui effectuera une analyse circulaire dans 3 pays.

Le Groupe de Travail Non-Ioniques poursuivra ses travaux sur la teneur en matière non transformée, la chromatographie sur papier, la séparation des hydrocarbures non sulfonés, et il étudiera un canevas général d'analyse des produits commerciaux non-ioniques.

La C.I.A a adopté définitivement une méthode d'analyse pour les *alkylsulfonates de sodium techniques* au moyen d'échangeurs d'ions, résultat de recherches hollandaises et allemandes; elle sera déposée à l'I.S.O. pour homologation.

L'analyse des *mélanges d'alkylsulfates primaires, d'alkylarène sulfonates, de non-ioniques et de savons*, au moyen d'échangeurs d'ions, se poursuit. Deux méthodes: hollandaise et suisse, sont retenues; elles feront l'objet d'une analyse circulaire entre 3 pays.

Enfin, la C.I.A. a mix aussi à son programme de travail le pH des agents de surface, et l'utilisation de 1£ chromatographie sur alumine dans l'analyse des produits tensio-actifs non-ioniques.

La prochaine réunion de la C.I.A. aura lieu les 30 Septembre et 1er Octobre 1965, aux Pays-Bas.

La 8ème réunion de la Commission Internationale d'Essais "C.I.E." du **COMITE INTERNATIONAL DE LA DETERGENCE** "C.I.D." a eu lieu à Londres, les 18 et 19 Mars 1965, sous la présidence du Dr. E. GÖTTE. Dix pays y participaient.

Parmi les 20 travaux différents inscrits à son ordre du jour, trois ont été adoptés définitivement et seront soumis à l'I.S.O. pour homologation internationale. Il s'agit de:

—la stabilité des agents de surface à l'eau dure, par appréciation visuelle,

—la préparation de l'eau dure,

—la détermination du point de trouble des agents de surface non-ioniques dérivant de l'oxyde d'éthylène, où l'on distingue trois cas: solutions se troublant à température ordinaire (emploi d'une solution de butyldiglycol), solutions se troublant entre 10 et 90° (emploi d'eau distillée), solutions se troublant au-dessus de 90° (tube scellé, ou solution saline).

Deux autres méthodes seront présentées à l'I.S.O. après vérification: propriétés de l'eau distillée, et masse volumique apparente des pâtes au remplissage.

Divers essais circulaires inter-laboratoires ont été décidés pour contrôler certaines méthodes, et citons entre autres:

—Pouvoir protecteur des agents de surface vis-à-vis des savons calcaires, qui sera étudié dans 7 pays en partant de la méthode Schönfeldt.

—Viscosité des agents de surface: deux appareillages sont proposés, l'un à tube capillaire, l'autre à système rotatif. Ils seront comparés dans 9 pays, avec deux produits différents (1 nonionique, 1 anionique).

—Contrôle de certains effets du blanchissage au moyen de tissu témoin non souillé; deux tissus standardisés seront utilisés pour des essais effectués dans 6 pays.

—Stabilité des solutions d'agents de surface; des essais seront effectués sur une méthode Epton simplifiée, dans 3 pays.

—Dishwashing test: une méthode proposée par le Royaume Uni sera expérimentée dans 7 pays, avec une salissure composée de 80% de suif neutre et 20% d'huile de coprah.

Par ailleurs, certains pays ont été chargés de poursuivre l'étude de méthodes d'essais pour:

—l'évaluation du pouvoir mouillant: deux méthodes sont en compétition (immersion, et pression capillaire); la question repose sur le choix d'un tissu témoin standardisé.

—la mesure de la couleur des agents de surface liquides ou en solution, préconisée par comparaison visuelle simple ou par spectrophotométrie. Pour une méthode subjective, les travaux de l'A.I.S. seront adoptés.

—le pouvoir détergent, qui est confié á un Groupe de Travail spécialisé, chargé d'effectuer une compilation des salissures artificielles existantes et de les analyser.

—la solubilité des agents de surface.

Enfin, les Commissions nationales ont été chargées d'étudier des textes nouveaux, concernant le pouvoir émulsionnant et la stabilité des émulsions, la concentration critique pour la formation des micelles, la tension d'adhésion, l'action des oxydants et l'influence sur les taches diverses, la pastillabilité des agents de surface et leur vitesse de dissolution.

La prochaine réunion de la C.I.E. aura lieu les 17 et 18 Mars 1965, à Bruxelles.

C'est à Lisbonne que la Commission Internationale de Terminologie "C.I.T." du **COMITE INTERNATIONAL DE LA DETERGENCE** "C.I.D." s'est réunie pour la 10ème fois, les 29 et 30 Avril 1965, sous la présidence de M. J. Combette.

Les travaux de la C.I.T. se sont inscrits dans les trois domaines suivants:

—*CLASSIFICATION DES AGENTS DE SURFACE:* outre le classement scientifique en cours d'homologation à l'I.S.O., le besoin d'une classification plus simple, mais inspirée de la première, s'est fait sentir et la C.I.T. a décidé d'établir un classement usuel. Un Groupe de Travail, réunissant 5 pays, s'est vu confier cette tâche.

—*ORDONNANCEMENT DU VOCABULAIRE*: Il est prévu d'inclure, dans ce cadre, toutes les définitions, actuelles ou à venir, de termes se rapportant aux agents de surface. Un Groupe de Travail, comprenant 4 pays, a également été chargé d'établir les différentes rubriques dans lesquelles entreront ces termes.

—*VOCABULAIRE DES AGENTS DE SURFACE*: Les travaux de la C.I.T. avancent rapidement dans ce domaine. De nouvelles définitions se trouvent ainsi acquises et la C.I.T. a chargé des Comités de Rédaction de la présentation définitive de ces définitions, pour envoi à l'International Organization for Standardization "I.S.O."; parmi celles-ci, citons:

—une nouvelle liste de *termes généraux*, comprenant des termes tels que: angle de raccordement, endophilie, exophilie, lipophilie, lipophobie, hystérésis de mouillage, etc.

—des *procédés et méthodes de fabrication*, tels que: amidification, estérification, hydrolyse, oxyéthylation, phosphatation, etc.

—des termes spéciaux tels que: charge, additif, adjuvant, renforçateur, dont les acceptions sont parfois différentes suivant les pays.

Enfin, la C.I.T. a examiné en 1ère lecture une longue liste de définitions du domaine des *produits auxiliaires textiles surfactifs*, élaborées en commun par les Commissions Française et Allemande.

La prochaine réunion de la C.I.T. est prévue en Allemagne les 21 et 22 Avril 1966.

BUNDESREPUBLIK DEUTSCHLAND

Hauptversammlung und Kekulé-Feier Bonn 1965 der *Gesellschaft Deutscher Chemiker vom* 13. bis 18. *Sept.* 1965 in Bonn/Rhein.

GDCh-Fachgruppe „ANALYTISCHE CHEMIE“
gemeinsam mit der GDCh-Fachgruppe „ANGEWANDTE ELEKTROCHEMIE“

Montag, 13. *September* 1965, 9.00 *Uhr*

Vortragstagung

„Elektroanalyse organischer und anorganischer Substanzen“

W. Huber
Neuentwicklungen bei Titrationen in nichtwäßrigen Lösungsmitteln.
G. Manecke, H. F. Förster und H. J. Panoch
Uber die potentiometrische Titration einiger molekular- und struktur-einheitlicher niedermolekularer Hydrochinon-Formaldehyd-Kondensate.
W. Simon
Säure-Base-Titrationen in flüssigem Ammoniak.
P. Zuman
Die Anwendung der Polarographie in der organischen Analyse.

Montag, 13. *September* 1965, 15.00 *Uhr*

N. Konopi
Zur Polarographie von Chinolacetaten.
H. W. Nürnberg und G. Wolff
Anwendungen der Pulse-Polarographie in der organischen Analyse.
G. F. Reynolds
Polarographic Studies of Azo Dyes.
O. Hockwin
Anwendung der polarographischen Adsorptionsanalyse zur Bestimmung des Pilocarpins im Kammerwasser des Auges.
H. Berg
Ergebnisse und Probleme der Photopolarographie.

Dienstag, 14. *September* 1965, 15.00 *Uhr*

P. Bersier und F. v. Sturm
Polarographische Bestimmung von Cu, Bi, Tl, Pb, Cd, Fe und Zn bei Arsenüberschuß.
C. C. Barker
Effects in polarography attributable to specific adsorption of reactants.
L. Gierst und P. Herman
Salt effects on the polarographic behaviour of pyridine.
G. Teske
Kontinuierliche Analyse insbesondere von Spurenkonzentration oxydierender und reduzierender Stoffe in Flüssigkeiten und Gasen mit Hilfe potentiostatischer Meßanordnungen.
D. Nebel
Potentiometrische und spektrophotometrische Untersuchungen zur Komplexbildung von Plutonium und einiger chemisch ähnlicher Elemente in wäßriger Lösung.

Donnerstag, 16. *September* 1965, 9.00 *Uhr*

D. Oeder, W. Seiler und H. Fischer
Potentialbestimmte Grenzflächen- und Elektrolytfilminhibition bei einer Redoxreaktion an Quecksilber.
J. Kůta
Die Ausnutzung der Adsorptionserscheinungen in der polarographischen Analyse.
H. Jehring
Der Einfluß von Molekülbau und Meßbedingungen auf das wechselstrompolarographische Verhalten grenzflächenaktiver Stoffe und die sich daraus ergebenden wissenschaftlichen und analytischen Möglichkeiten.
K. Cammann
Anwendung ionenspezifischer Glaselektroden und analytischer Brennstoffzellen.
R. Bertram und P. Lambrecht
Konduktometrische Messungen an geschmolzenen Metall-Salzsystemen unter Verwendung eines neuen ‚kontaktlosen‘ Hochfrequenzverfahrens.

W. HELBIG
Differentielle potentiometrische Tritration im Nanogrammbereich.
Organisationskomitee: Gesellschaft Deutscher Chemiker-Geschäftsstelle, 6 Frankfurt/Main 9, Postfach 9075.

Friday 24 *September-Friday* 1 *October* 1965: International Advanced Study Institute on **Optical Rotatory Dispersion and Circular Dichroism.** Bonn.

This is intended for research students and post-doctorals as well as industrial chemists. Several outstanding scientists in this field have agreed to act as lecturers. The official language will be English. Most of the commercially available instruments for measuring ORD and CD will be exhibited and demonstrated. Applicants are requested to contact Dr. G. SNATZKE, Organisch-Chemisches Institut der Universitat, 53 Bonn/West Germany, Meckenheimerallee 168.

CZECHOSLOVAKIA

6.9. bis 18.9.1965: **IV. Internationaler Polarographischer Kursus:** Institut für physikalische Chemie der Karlsuniversität und das Polarographische Institut der Tschechoslowakischen Akademie der Wissenschaften. Prag [*Talanta*, 1965, **12**(4), i].

DEUTSCHE DEMOKTATISCHE REPUBLIK

2. Internationales Symposium Reinstoffe in Wissenschaft und Technik: *die Chemische Gesellschaft in der DDR, die Gesellschaft Deutscher Bergund Hüttenleute und die Physikalische Gesellschaft in der DDR:* von 28. *September* bis 2. *Oktober* 1965 in Dresden.

Plenarvorträge

PROF. DR. H. SPECKER
Probleme und Möglichkeiten der Spurenanalyse in hochreinen Stoffen.

Sektion C1—REINSTSTOFF-ANALYTIK 1

Massenspektroskopie

H. HINTENBERGER
Massenspektrographische Festkörperanalyse
J. FRANZEN und K. SCHUY
Absolute massenspektroskopische Analyse fester Körper.
J. FRANZEN und K. SCHUY
Eine Ionenoptik für die genaue massenspektrographische Analyse von festen Körpern.
H. WAGNER, JENA und H. MAI
Die Schwärzungskurve photographischer Einkornschichten als Grundlage quantitativer massenspektrographischer Analysen.
H. MAI, DRESDEN und H. WAGNER
Die Massenabhängigkeit der Schwärzungswirkung von 20-keV-Ionen bei verschiedenen Typen von Einkornschichten.
M. S. CUPACHIN
Massenspektroskopische Untersuchung vielatomiger Molekülionen von Festkörpern und deren analytische Anwendung.
W. RIEPE
Quantitative Bestimmung von sehr kleinen Mengen Erdalkalien in Natriumsalzen durch Isotopenverdünnungsanalyse.

Statistische Methoden

K. DOERFFEL
Nachweisgrenze und Reinheitsgarantie.
D. M. SMITH and D. J. HOBBS
The application of statistics to trace analysis by emission spectrography.
R. A. GEITZ
Über einige Probleme der Spurenanalyse.
L. M. IVANCOV U. A
Zur Empfindlichkeitssteigerung direkter photoelektrischer Methoden der Spektralanalyse.

Spektralanalyse

P. W. J. M. BOUMANS
Zur Verbesserung der spektralanalytischen Nachweisgrenzen durch Zusätze.

G. Ehrlich, H. Engelhardt, H. Scholze und R. Gerbatsch

Verbesserung spektrographischer Spurenbestimmungen durch eine Anlage zur Nachreinigung von Spektralkohlen und zum Ausschluß von Verunreinigungen während der Probenvorbereitung.

A. V. Karjakin, M. V. Achmanova und V. A. Kajgorodov

Möglichkeiten zur Anwendung eines Impulslasers in der Spektralanalyse reiner Stoffe.

B. Gostkowska and H. Ekiert

Attempts of spectral determination of trace impurities in semiconductor materials using a high frequency plasma generator.

Ch. I. Zilberstejn, R. Gerbatsch, O. N. Nikitina, M. P. Semov und G. Artus

Zur empfindlichen Lösungsspektralanalyse mit Anregung des Trockenrückstandes auf Spektralkohleelektroden (Dauerbogenanregung).

V. Svoboda

Zur empfindlichen Lösungsspektralanalyse mit Anregung des Trockenrückstandes auf Spektralkohleelektroden (Impulsbogenanregung).

N. Krasnobaeva und N. Jordanov

Einfluß der Gasatmosphäre auf die spektralanalytische Bestimmung von Rheniumspuren nach einem Destillationsverfahren.

H.-P. Schramm und W. Beckert

Spektralanalytische Qualitätskontrolle in der Reinsttellurherstellung mit direkter Anregung metallischer Elektroden.

Ju. Charizanov und N. Krasnobaeva

Quantitative Spektralanalyse von Reinstblei unter Ausnutzung der fraktionierten Destillation.

H.-H. Rußmann

Die Spektralanalyse von Reinstgraphiten.

H. Nickel

Der Einfluß von Borcarbid in Graphitelektroden auf das Verdampfungsverhalten verschiedener Spurenelemente bei der Spektralanalyse im Lichtbogen.

L. Veesernyes

Spektrochemische Bestimmung von 11 Spurenelementen in SiCl$_4$ und SiHCl$_3$.

Lumineszenzanalyse

A. V. Karjakin und L. I. Anikina

Lumineszenzverfahren zur Bestimmung von Seltenerdelementen.

S. Terol

The detection of rare earths in solid solution by cathodoluminescence.

Sektion C2—REINSTSTOFF-ANALYTIK 2

Kinetische Analysenmethoden

K. B. Jacimirski

Gegenwärtiger Stand und Perspektiven der kinetischen Analysenmethoden.

Aktivierungsanalyse

I. P. Alimarin und Ju. V. Jakovlev

Aktivierungsanalytische Spurenbestimmung in Reinststoffen.

H. Rommel

Untersuchungen zur Borbestimmung in Silicium und Germanium durch Protonen- und Deuteronenaktivierung.

S. Niese

Die neutronenaktivierungsanalytische Bestimmung von Phosphor, Schwefel und Chlor in Arsen.

I. Kosa-Somogyi and R. Groh

Purity check of organics by physico-chemical analysis.

Photometrische Analysenverfahren und vergleichende Untersuchungen

J. Minczewski, J. Czakow, A. Foldzinska, H. Jaskolska, B. Kucharzewski, J. Malinowski, T. Nowicka-Jankowska, Z. Radwan, W. Rutkowski, B. Strzyzewska und W. Zmijewska

Präzision und Bestimmungsgrenzen bei Spurenbestimmungen in Reinststoffen.

J. Minczewski, R. Dybczynski, J. Malinowski, T. Nowicka-Jankowska, Z. Radwan, B. Strzyzewska, and L. Wodkiewicz.

The determination of traces of rare earth elements in some rare earths.

H.-G. Döge, G. Ehrlich, H. Große-Ruyken, O. Großmann und B. Neef

Spektrophotometrische und aktivierungsanalytische Bestimmung von Verunreinigungen in Wolfram und Molybdän.

O. Klug
Beiträge zur Trennung und Bestimmung einiger Spurenverunreinigungen in Reinstgallium.
Z. Marczenko
Die Anwendung der Kolorimetrie zur Spurenbestimmung in Reinststoffen.
M. Knizek
Einige Bemerkungen über die spektrophotometrische Bestimmung von Eisenspuren.
E. Jackwerth
Anreicherung und Bestimmung von Eisen- und Kobaltspuren in Nickel und Reinstnickelsalzen.
W. Angermann
Anwendung von Kollektoren zur Abtrennung von Begleitelementen aus Reinstmetallen.

Elektrochemische Analysenverfahren

R. Neeb
Neuere elektrochemische Methoden zur Spurenanalyse.
M. Geißler, C. Kuhnhardt und R. Lehmann
Ein neuer Rechteckwellenpolarograph und seine Anwendung in der Reinstmetallanalyse.
S. I. Sinjakova
Amalgampolarographische Spurenbestimmung in Reinststoffen mit Voranreicherung und Anwendung katalytischer Ströme.
W. Beckert und E. Weiße
Die Anwendung der anodischen Voltammetrie am hängenden Quecksilbertropfen zur Qualitätskontrolle in der Reinstgalliumherstellung.
J. Lovasi
Die Anwendung der Umkehrpolarographie in der Reinstmetallanalyse.

Gasbestimmung in Metallen

K. Friedrich
Möglichkeiten zur Bestimmung sehr geringer Gasgehalte in Reinstmetallen.
E. Fromm und H. Jehn
Fehlermöglichkeiten bei der Gasbestimmung nach dem Heißextraktionsverfahren mit Metallbad.
E. Lassner
Kritische Betrachtungen zur Sauerstoffbestimmung in Molybdän durch Entgasung in festem Zustand.
W. Fischer
Über den Einfluß des Oberflächenzustandes des Probenmaterials bei Nichtmetallbestimmungen in reinen Metallen.

Organisationskomitee: Sekretariat der Chemischen Gesellschaft in der DDR, 108 Berlin, Clara-Zetkin-Straße 105 (Verantwortlich: Dr. K. Reimer).

FRANCE

Thursday-Sunday 9–12 *September* 1965: **EUCHEM Conference on Mass Spectrometry.** Sarlat.

GREECE

Sunday–Friday 19–24 *September* 1965: **Methods of Immediate Separation and Chromatography:** *Association of Greek Chemists* in collaboration with *Association for Development of Spectrographic Methods (G.A.M.S.).* Athens [*Talanta,* 1965, **12**(5), i].

OSTERREICH

29. *September* bis 1 *Oktober* 1965: **Symposium analytische Chemie,** Treffen jugoslawischer, ungarischer und österreichischer Chemiker im Anschluß an die Hauptversammlung des Vereins Osterreichischer Chemiker. Graz.

UNITED KINGDOM

Monday–Thursday 6–9 *September* 1965: **First International Conference on Thermal Analysis,** Department of Natural Philosophy, University of Aberdeen, Old Aberdeen, Scotland [*Talanta,* 1965. **12**(5), ii].

Wednesday 15 *September* 1965: **Symposium on Thermometric Titrimetry (Enthalpimetry):** *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Birmingham and Midlands Section.* Department of Chemistry, University of Birmingham, Birmingham 15.

The programme is as follows:

Introduction to Thermometric Titrimetry.	L. S. Bark
Development of an Automatic Titration with Digital Read-Out.	M. Smith
Kodak's Apparatus for Recording Titration Curves.	W. S. Sebborn
Thermodynamic Background and Possible Application to Analytical Problems.	H. J. V. Tyrrell
Thermometric Titrations of Some Precipitation Reactions.	R. J.-N. Harries
Acetone as Solvent in the Automatic Titration of Acidic Substances.	G. A. Vaughan

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Tuesday–Wednesday 21–22 *September* 1965: **Mass Spectroscopy Conference:** *Mass Spectroscopy Group.* University College, London [*Talanta*, 1965, **12**(2), ii].

Thursday 30 *September* 1965: **Isotope Dilution and Neutron Activation—Some New Aspects:** J. Růžička and J. Starý: *Society for Analytical Chemistry, Midlands Section* and *Special Techniques Group; Royal Institute of Chemistry, Birmingham and Midlands Section* and *Society of Chemical Industry, Midlands Section.* Department of Chemistry, University of Birmingham, Birmingham 15, 6.30 p.m.

Friday 1 *October* 1965: Informal Discussion on **Neutron Diffraction as a Tool in Chemistry:** *Chemical Society.* Inorganic Chemistry Laboratory, South Parks Road, Oxford.

The provisional programme is as follows:

General Principles of the Applications of Neutron Diffraction to Chemistry.	G. E. Bacon
Neutron Crystallography of Very Small and Very Large Structures: UO_2 *and Vitamin* B_{12}.	B. T. M. Willis
Use of Thermal Neutrons to Investigate Covalent Bonding in Transition Ion Complexes.	W. Marshall
Investigation of Defects in Solids by Neutron Diffraction.	E. W. J. Mitchell

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Sunday–Saturday 4–10 *September* 1966: **Summer School in Spectroscopy:** *Royal Institute of Chemistry.* School of Pharmacy, Brunswick Square, London W.C.1 and Royal Free Hospital Medical School.

The 1966 Summer School will consist of comprehensive courses on *organic spectroscopy* (infrared and nuclear magnetic resonance) and *inorganic spectroscopy* (with particular reference to infrared). Full particulars and applications forms will be available early in 1966.

Monday–Wednesday 12–14 *September* 1966: **Conference on Spectroscopy:** *Institute of Petroleum.* Institution of Electrical Engineers, Savoy Place, London.

The Conference will be similar to those held previously. Sessions are planned on: Far Infrared Spectroscopy, Attenuated Total Reflectance, Electron Spin Resonance, Nuclear Magnetic Resonance, Absorption Spectroscopy, in the Organometallic Field, Ultraviolet and Vacuum Ultraviolet Spectroscopy, Fluorescence Spectroscopy, Optical Rotatory Dispersion, Application of Lasers to Spectroscopy and Spectral Documentation.

Further information may be obtained from Institute of Petroleum, 61 New Cavendish Street, London W.1.

British Standards Institution has announced the following *Revised British Standard:*

B.S. 1428: *Group A Combustion trains for the determination of elements: Part A5*: 1965: *Rapid method combustion tubes (Belcher and Ingram type) and absorption tube:* 5*s*. This includes constructional details and dimensioned drawings of Type 1 combustion tube and Flaschenträger absorption tube for carbon and hydrogen, and Type 2 combustion tube for halogens and sulphur. Recommendations are given for designs of absorbers for oxides of nitrogen and for halogens and sulphur.

Group D Volumetric apparatus: Part D1: 1965: *Burettes with pressure-filling device and automatic zero:* 5*s*. This includes constructional details, tolerances on capacity and delivery time, method of use and a dimensioned drawing of four special burettes for microchemical work.

UNITED STATES OF AMERICA

Monday 30 *August–Friday* 3 *September* 1965: **Fourth National Meeting of Society for Applied Spectroscopy.** Denver Hilton Hotel, Denver, Colo. [*Talanta*, 1965, **12**(7), iv].

Wednesday–Friday 8–10 *September* 1965: **1965 Technicon International Symposium on Automation in Analytical Chemistry:** Technicon Instruments Corp. Statler-Hilton Hotel, New York City.

Sunday–Friday 12–17 *September* 1965: **150th National Meeting:** *American Chemical Society.* Atlantic City, N.J.

Tuesday–Thursday 21–23 *September* 1965: **Sixteenth Testing Conference, TAPPI,** Netherland-Hilton Hotel, Cincinnati, Ohio.

Wednesday–Friday 22–24 *September* 1965: **Fourth Annual Meeting on Practice of Gas Chromatography:** *Committee E-*19 *on Gas Chromatography, A.S.T.M.* Sheraton-Jefferson Hotel, St. Louis, Mo.

Wednesday–Friday 22–24 *September* 1965: **Fourth Annual Pacific Conference on Spectroscopy, Instrumentation and Chemistry.** Huntington-Sheraton Hotel, Pasadena, Calif.

Monday–Tuesday 27–28 *September* 1965: **Fifth Informal Conference on Vacuum Microbalance Techniques.** The Nassau Inn, Palmer Square, Princeton, N.J. [*Talanta*, 1965, **12**(7), viii].

Tuesday–Thursday 12–14 *October* 1965: **Ninth Conference on Analytical Chemistry in Nuclear Technology:** *Analytical Chemistry Division of Oak Ridge National Laboratory.* Mountain View Hotel, Gatlinburg, Tennessee.

The Conference will be composed of six sessions embracing the following subjects:

Analytical Chemistry of Transuranium Elements,
Symposium on Role of Analytical Chemistry in Pure Materials Research,
Selected Papers on Bio-Analytical Techniques,
Miscellaneous Subjects.

Enquiries concerning the Conference should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37831.

National Bureau of Standards has announced the availability of the following *New Standards:*

Low-Alloy Steel Standards. Four new low-alloy steel standards, now available for use in X-ray spectrochemical analysis, have the same compositions as previously issued optical emission standards, but are in a different size suitable for X-ray analysis. The standards are NBS Nos. D803a, acid open hearth (0.06% of carbon); D805a, medium manganese; D807a, chromium-vanadium; and D809b, nickel.

Another new X-ray spectrochemical standard is NBS No. D820a, ingot iron.

Stainless Steel Standards. To meet industry's need for more stainless steel standards, the Bureau has prepared four new standard materials of the 18 Cr–8 Ni group. These standards (NBS Nos. 1151, 1152, 1153 and 1154) are in disk form, for use primarily in optical emission and X-ray spectrometric analysis.

Titanium-Base Alloy Standard. A new standard has been prepared by the Bureau to cover more adequately the range of commercial titanium-base alloys now available and to supplement other NBS titanium-base alloy standards. The new titanium alloy standard (NBS No. 176) has the following provisional certificate of analysis in percentages: Al—5.16, Sr—2.47, Fe—0.07_0, C—0.01_5, Ni—0.01_0, Cu—0.003, Mn—0.0008, and Mo—0.003.

Aluminium Brass Standards. Aluminum brass standards, previously issued only in chill-cast form, are now available in wrought form. The certificate of analysis of the extruded standards (NBS Nos. 1118, 1119, and 1120) are nearly identical to those of the cast form.

The following *Renewal Standards* have been issued to replace out-of-stock standards:

Titanium-base alloy No. 173A, which replaces No. 173, has the following provisional certificate of analysis in percentages: Al—6.47, V—4.06, Fe—0.15, Co—0.2_5, N—0.01_8, Si—0.03_7, Cu—0.002, and Mo—0.005.

Sibley Iron Ore Standard No. 27e, which replaces Mesabi Iron Ore Standard 27d, has the following provisional certificate of analysis (in percentages): Fe—66.6, SiO_2—3.64, and P—0.042.

Benzoic Acid Standard No. 39i, replaces No. 39h for calibrating calorimeters.

Potassium Hydrogen Phthalate No. 185d. a *p*H standard, replaces acid potassium phthalate No. 185c.

Butyl-Rubber Standard No. 388a replaces No. 388.

Barium Cyclohexanebutyrate No. 1051a, Ba—29.1%, replaces No. 1051.

Calcium 2-Ethylhexanoate No. 1074, Ca—13.4%, replaces calcium cyclohexanebutyrate No. 1054.

Cobalt Cyclohexanebutyrate No. 1055a, Co—17.4 and Ni—0.05%, replaces No. 1055.

Nickel Cyclohexanebutyrate No. 1065a, Ni—16.8%, replaces No. 1065.

Sodium Cyclohexanebutyrate No. 1069, Na—11.9%, replaces No. 1069.

American Society for Testing and Materials has announced the availability of the following publications:

ASTM Standards for General Testing Methods: Part 31, 1965 *Book of ASTM Standards on Metallography; Non-Destructive Testing; Radioisotopes and Radiation Effects; Industrial Chemicals; Emission, Absorption and Mass Spectroscopy.* 740 *pp.* 67 *Standards.* $13.00 or $9.10 (members).

Application of Advanced and Nuclear Physics to Testing Materials—STP 373. 140 *pp.* $6.25 or $4.35 (*members*). Directed primarily at technologists in the building materials field.

ERRATUM—Volume 12

Page 391, lines 5–8 from bottom: These should read *The* K_α *radiation in the first order was used except in the case when second order* K_α *radiation was used for the lower concentration range. The Ni* K_β *radiation interfered at low concentration of copper but the second order* K_α *was found to be more sensitive than the first order copper* K_β *radiation. It is possible . . .*

Talanta, 1965, Vol. 12, pp. i to v. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

DIVISION OF ANALYTICAL CHEMISTRY, COMMISSION ON MICROCHEMICAL TECHNIQUES

*International Investigation into Errors in Elementary Organic Microanalysis**

Approximately one year ago, a questionnaire was sent to microanalysts throughout the world for the purpose of collecting data in regard to the errors encountered in elementary organic microanalysis. Although the response seemed favourable, only a small percentage of the microanalysts throughout the world actually co-operated. The following table shows the number of participants and the number of reports from each country:

United States	6 Authors	7 Reports
France	5 Authors	17 Reports
United Kingdom	4 Authors	12 Reports
Italy	1 Author	1 Report
Japan	4 Authors	6 Reports
Netherlands	1 Author	7 Reports
Switzerland	5 Authors	7 Reports
U.S.S.R.	20 Authors	34 Reports

If the Commission's report is to be of the greatest possible value, it is necessary to have information from those countries from which there was no response. It is also obvious that from certain countries the response was poor. Consequently, the Commission is making another appeal to all microanalysts. Each person should list the problems with which he has had difficulty, and if possible, he should describe the manner in which these problems were solved. However, as much information as possible should be included, because this might yield clues which are insignificant to the analysts but valuable to the Commission.

The deadline for this information will be 1 January, 1966, and it should be sent to one of the following people:

Reports in ENGLISH to:	AL STEYERMARK, Head Microchemical Department Hoffmann-La Roche Inc. Nutley, New Jersey, U.S.A.
Reports in FRENCH to:	Dr. ROGER LÉVEY, Directeur Service Central de Microanalyse Laboratoire Municipal 39 bis, rue de Dantzig Paris, France
Reports in GERMAN to:	Dr. WOLFGANG SCHÖNIGER Microanalytical Laboratory Department of Pharmaceutical Chemistry Sandoz Limited Basle 13, Switzerland

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* The present investigation does not include trace analysis.

Reports in RUSSIAN to:	Dr. N. E. Gel'man Institute of Elemental Organic Compounds Academy of Sciences Moscow, RUSSIA
Reports in SLAVIC LANGUAGES and in HUNGARIAN to:	Mr. Jiři Körbl Analytical Laboratory Research Institute for Pharmacy and Biochemistry Czechoslovakian Academy of Science Kourimska 17, Prague, Czechoslovakia
Reports in LANGUAGES OTHER THAN THE ABOVE to:	Dr. Roger Lévey (see above address)

BUNDESREPUBLIK DEUTSCHLAND

8. 11. bis 12. 11. 1965: *Dortmund:* Seminar für Laborleiter, Leistungen und Anwendungsmöglichkeiten spektroskopischer Methoden (Emissions-, Molekül- und Massenspektroskopie). Vergleich mit anderen moderen Analysenmethoden. *Auskunft:* Institut für Spektrochemie, 4600 Dortmund, Postfach 778.

JAPAN

Thursday–Saturday 11–13 *November* 1965: **Third Conference on X-Ray Analysis:** Osaka.

SWITZERLAND

Monday–Saturday 17–22 *October* 1966: **Third International Exhibition of Laboratory Measurement and Automation Techniques in Chemistry** (ILMAC): Basle.

UNITED KINGDOM

Wednesday 6 *October* 1965: **Some Special, Sensitive and Selective Reactions in Inorganic Trace Analysis,** T. S. West: *Society for Analytical Chemistry.* Burlington House, London W.1. 7.00 p.m.

Friday 8 *October* 1965: **Poison Detection,** A. S. Curry: *Society for Analytical Chemistry, Western Section.* Cardiff. 6.30 p.m.

Wednesday 13 *October* 1965: Discussion Meeting on **Automatic Methods for the Determination of Carbon, Hydrogen and Nitrogen:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4. 6.30 p.m.

Wednesday 13 *October* 1965: **Analytical Methods in the British Museum Laboratory-Science and Archaeology,** H. Barker: *Chemical Society, Aberdeen and North of Scotland Section of Royal Institute of Chemistry* and *Society of Chemical Industry.* Marischal College, Aberdeen. 8.00 p.m.

Thursday 14 *October* 1965: **Some Recent Advances in Analytical Chemistry,** W. I. Stephen: *Royal Institute of Chemistry, Liverpool and North-Western Section.* Technical College, Brook Street, St. Helens. 7.30 p.m.

Thursday 14 *October* 1965: **Positive Identification of Pesticide Residues,** K. I. Benyon and **Analysis of Pesticide Residues,** K. E. Elgar: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Cambridge Sub-Section.* Cambridgeshire College of Arts and Technology, Collier Road, Cambridge. 7.30 p.m.

Thursday 21 *October* 1965: **Application of High-Voltage Paper Electrophoresis to Some Analytical Problems with Special Reference to Carbohydrates,** D. Gross: *Society for Analytical Chemistry, Scottish Region.* Heriot-Watt College, Edinburgh. 7.30 p.m.

Thursday 21 *October* 1965: **Photoluminescence as an Analytical Technique,** C. A. Parker: *Chemical Society* and *Royal Institute of Chemistry, Mid-Southern Counties Section.* College of Technology, Bournemouth. 7.30 p.m.

Thursday 21 *October* 1965: Discussion Meeting: *Society for Analytical Chemistry, Biological Methods Group. The Feathers,* Tudor Street, London E.C.4. 6.30 p.m.

Friday 22 *October* 1965: Meeting on **Atomic-Absorption Spectroscopy,** W. J. Price, L. Watson and R. A. White: *Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group* and *University of Cambridge Chemical Society.* Department of Chemistry, University of Cambridge.

Tuesday 26 *October* 1965: **Determination of Oxygen in Steel,** M. S. W. Webb, R. J. Webb and C. A. Baker: *Sheffield Metallurgical Association, Modern Methods of Analysis Group* and *Society for Analytical Chemistry, Special Techniques Group* and *North of England Section.* Sheffield. 7.00 p.m.

Wednesday 27 *October* 1965: **Atomic-Absorption Spectroscopy,** J. B. Dawson: *Royal Institute of Chemistry, Stirlingshire and District Section* and *Society of Chemical Industry.* Technical College, Falkirk. 7.30 p.m.

Friday 29 *October* 1965: **Some Modern Physical Methods of Analysis and Structural Diagnosis** M. St C. Flett: *Royal Institute of Chemistry, North Lancashire Section* and *Society of Chemical Industry.* Harris College, Preston. 7.30 p.m.

Friday 29 *October* 1965: **Twenty-First Anniversary Celebration Meeting** on **Microchemistry—Past, Present and Future,** R. Belcher, C. Whalley and C. L. Wilson: *Society for Analytical Chemistry, Microchemical Methods Group.* Imperial College, South Kensington, London S.W.7. 4.30 p.m.

Tuesday 2 *November* 1965: **Colouring Matter in Food,** J. B. Aldred: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, Huddersfield Section* and *Society of Dyers and Colourists, Huddersfield Region.* College of Technology, Huddersfield. 7.30 p.m.

Tuesday 2 *November* 1965: Debate on **Chemical Analysis—Is it Physics?** W. G. Cummings and A. R. Philpotts: *Royal Institute of Chemistry, Downland Section.* Distillers Co. Ltd., Epsom. 6.30 for 7.00 p.m.

Wednesday 10 *November* 1965: Meeting on **Automatic Analysis:** *Society for Analytical Chemistry.* Wellcome Building, Euston Road, London N.W.1. 3.15 p.m.

Friday 12 *November* 1965: **Analytical Requirements for Applied Geochemistry,** J. S. Webb: *Royal Institute of Chemistry, South-Western Counties Section.* College of Technology, Plymouth. 5.30 p.m.

Tuesday–Wednesday 16–17 *November* 1965: **Symposium on Physical Methods:** *Society of Cosmetic Chemists of Great Britain.* Grand Hotel, Brighton [see *Talanta*, 1965, **12**(9), iii].

Thursday 18 *November* 1965: **Analytical Aspects of Molecular Biology,** D. G. Smyth: *Royal Institute of Chemistry, Birmingham and Midlands Section* and *Society of Chemical Industry, Midlands Section* and *Association for Science Education, Midlands Branch.* Lancaster College of Technology, Coventry. 7.00 p.m.

Thursday–Friday 18–19 *November* 1965: **Conference on Computational Methods in Crystallography:** *Institute of Physics and Physical Society.* Institution of Electrical Engineers, London.

Tuesday 23 *November* 1965: **Annual General Meeting** followed by **Address of Retiring Chairman** L. Brealey: *Society for Analytical Chemistry, Special Techniques Group.* Burlington House, London W.1. 7.00 p.m.

Wednesday 24 *November* 1965: Discussion Meeting on **The Optimal Environment for Microchemical Analysis,** A. J. Cross: *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4. 6.30 p.m.

Friday 26 *November* 1965: **Separate or Calculate,** A. L. Glenn: *Society for Analytical Chemistry, Scottish Section.* University of Strathclyde, Glasgow. 5.30 p.m.

Tuesday 30 *November* 1965: **Atomic-Fluorescence Spectroscopy,** G. I. Goodfellow: *Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group.* Burlington House, London W.1.

British Standards Institution has announced the following *New British Standards: B.S.* 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 14: 1965: *Determination of nickel (gravimetric method)* (4*s.* 6*d.*). This describes the reagents required, recommended methods of sampling and test procedure for the gravimetric determination of nickel in aluminium and aluminium alloys having a nickel content in the range 0.2–3%.

B.S. 3630: *Methods for the sampling and analysis of zinc and zinc alloys: Part* 3: *Magnesium in zinc alloys (gravimetric method)* (4*s.*). This describes the reagents required, recommended methods of sampling and test procedures for the gravimetric determination of magnesium in zinc alloys having a magnesium content in the range 0.02–0.10%.

B.S. 3903: 1965: *Methods of test for suplhuric acid* (10*s.*). This describes the determination of sulphuric acid content, residue on ignition, sulphur dioxide, arsenic, ammoniacal nitrogen, nitrogen oxides, chloride, iron, lead, copper and aluminium, and the free SO_3 content for oleums.

B.S. 3907: *Methods for the analysis of magnesium and magnesium alloys: Part* 1: 1965: *Determination of aluminium in magnesium alloys* (*gravimetric method*) (4*s*.). This describes the reagents required, recommended methods of sampling and test procedure for the gravimetric determination of aluminium in magnesium alloys having an aluminium content in the range 1.5–12%.

B.S. 3908: *Methods for the sampling and analysis of lead and lead alloys: Part* 1: 1965: *Sampling of ingot lead, lead alloy ingots, sheet, pipe and cable sheathing alloys* (4*s*.). This describes the selection of ingots, preparation of surfaces, method of taking samples by sawing and precautionary methods against contamination of the sawings.

The following *Revised British Standard* has also been announced: *B.S.* 1756: *Methods for the sampling and analysis of the flue gases: Part* 4: 1965: *Miscellaneous analyses* (£1). This deals with the determination of moisture, sulphur dioxide and sulphur trioxide, sulphuric acid dew-point, carbon monoxide (less than 0.5%) and nitrogen oxides.

UNITED STATES OF AMERICA

Monday–Thursday 18–21 *October* 1965: **Third International Symposium on Advances in Gas Chromatography:** *University of Houston.* Sheraton-Hilton Hotel, Houston, Texas.

The programme is as follows:

Monday Morning, 18 *October*

Life Detection by Gas Chromatography.	J. E. Lovelock
Resolution of Optical Isomers by Gas Chromatography.	E. Gil-Av
Gas Chromatography of Volatile Metal Complexes.	R. E. Sievers
An Electrical Discharge Pyrolyser for Gas Chromatography.	J. C. Sternberg
Gas Chromatography of Isotopic Molecules by Open Tubular Columns.	A. Liberti

Monday Afternoon, 18 *October*

A Simple Approach to the Rate Theory of Gas Chromatography.	I. Halasz
Electrostatic Interactions in Gas-Solid Chromatography.	J. King, Jr.
Evidence for Turbulence and "Coupling" in Chromatographic Columns.	J. H. Knox
Correlation of Retention Data and Structural Parameters of Carboxyl Compounds.	J. F. Haken
Support Effects on Retention Volumes in Gas Chromatography: Practical and Theoretical Aspects.	P. Urone

Tuesday Morning, 19 *October*

Ultrasonic Velocity Instrumentation for Liquid and Gas Chromatography Effluent Detection.	K. Abel
Gas Chromatography Effluent Detection. Design and Operation of Gas-Phase Ionisation Detectors for Liquid Chromatography.	E. Haahti
A Liquid Chromatographic System for Analysis of Macromolecules.	J. Stouffer
A Flame Ionisation Detector for Liquid-Liquid Chromatography.	A. Karmen
Separation of Derivatives of Biogenic Amines.	E. C. Horning

Tuesday Afternoon, 19 *October*

Investigation of Formamide as a Useful Gas Chromatography Stationary Phase of Extreme Selectivity and without Flame Ionisation Signal.	J. Janak
Determination of Polarity of Stationary Phases Used in Gas Chromatography.	P. Chovin
Clean Gases for Chromatography.	B. Osborne
Preparative Scale Separation of Multicomponent Mixtures by Continuous Gas Chromatography.	P. E. Barker

Wednesday Morning, 20 *October*

Contempory Gas-Solid Chromatography.	C. G. Scott
Micro-Packed Columns for High Speed Gas Chromatography.	I. Halasz
High Resolution Capillary Adsorption Columns for Gas Chromatography.	R. D. Schwartz
Application of High Pressure Gas Chromatography to Micro-Packed Columns.	J. C. Giddings
High Speed Chromatography.	V. Pretorius

Wednesday Afternoon, 20 *October*	
Quality and Flavours of Wine, Rum and Brandy by Gas Chromatography.	E. Bayer
Gas Chromatographic Analysis of Steam Volatile Aroma Constituents: Application to Coffee, Tea and Cocoa Aromas.	D. Reymond
Gas Chromatography of Sesquiterpenoids.	R. Teranishi
Behaviour of Stationary Phases at Cryogenic Temperatures.	C. Merritt, Jr.
Thursday Morning, 21 *October*	
Efficiency of Molecule Separators in Gas Chromatography-Mass Spectrometry Instruments.	R. Ryhage
Micro Gas Chromatography.	W. F. Wilhite
A Specific Detector for Phosphorous and for Sulphur Compounds-Sensitive to Subnanogram Quantities.	S. S. Brody
New Column Systems for Gas Chromatography.	R. P. W. Scott

Wednesday–Friday 3–5 *November* 1965: **Twenty-Third Pittsburg Diffraction Conference.** Mellon Institute, Pittsburgh, Pa.

Friday–Monday 5–15 *November* 1965: **First Midwest Regional ACS Meeting.** University of Missouri, Kansas City, Mo.

Tuesday–Thursday 16–18 *November* 1965: **Atom Fair '65** held in conjunction with **Annual Conference of Atomic Industrial Forum** and **1965 Winter Meeting of American Nuclear Society:** Sheraton-Park Hotel, Washington, D.C.

Wednesday–Friday 17–19 *November* 1965: **Seventh Eastern Analytical Symposium.** Statler Hilton Hotel, New York City.

ERRATA—Volume 12

Page 764, Reagent No. 6 in Table 1: The reference should read *128* and not *297*.

Page 772, The following additional reference is necessary

[128] N. C. Sogani and S. C. Bhattacharyya, *Analyt. Chem.*, 1957, **29**, 397.

Page 836, line 3 of †† footnote to Table IV: For (*p. 7*) read (*p. 835*).

Page 857, line 3 of Experimental: For *hydrochorlic* read *hydrochloric*.

Talanta, 1965, Vol. 12, pp. i to vi. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

BUNDESREPUBLIK DEUTSCHLAND

15.–19. *Marz* 1965: **Moderne analytische Methoden in der Lebensmittelchemie und der biologischen Chemie:** Heidelberg (Die Hauptvorträge sind in *Talanta*, 1965, **12** (1), i, schon angedeutet worden).

FRANCE

Mardi 9 *mars* 1965: **Progrès récents de la chromatographie des macromolécules biologiques, par** M. R. L. MUNIER, à 17 h 45, à la Faculté de Pharmacie de Paris.

Vendredi 19 *mars* 1965: **Chimie Analytique générale:** Conférence: mise au point sur les recherches analytiques dans les sels fondus par M. G. DELARUE: Section de Chimie analytique de la Société Chimique de France, à 17 h 30, à l'Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre Curie, Paris, 5^e.

Mardi 23 *mars* 1965: **Réactions enzymatiques spécifiques et structure des polysaccharides,** par M. R. DEDONDER, à 17 h 45, à la Faculté de Pharmacie de Paris.

UNITED KINGDOM

Friday 5 *March* 1965: **Annual General Meeting** followed by **Address of Retiring President,** D. C. GARRATT: *Society for Analytical Chemistry.* Burlington House, London W.1, 3.00 p.m. Followed in the evening by the **Biennial Formal Dinner** at Merchant Taylors' Hall, London E.C.2.

Friday 5 *March* 1965: **Modern methods of analysis in the coal industry,** G. R. NELLIST: *Society for Analytical Chemistry, North of England Section.* County Hall Durham, 7.15 p.m. Preceded by afternoon tour of the County Hall and County Laboratories.

Friday 12 *March* 1965: **Annual General Meeting** followed by **Ladies Evening:** *Society for Analytical Chemistry, Midlands Section.* Department of Chemistry, University of Birmingham, Birmingham 15.

Wednesday 17 *March* 1965: **Discussion Meeting:** *Society for Analytical Chemistry Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Saturday 20 *March* 1965: Symposium on **Identification of Drugs and Poisons:** *Pharmaceutical Society of Great Britain.* School of Pharmacy, University of London, Brunswick Square, London W.C.1 (see *Talanta*, 1965, **12** (1), ii).

Tuesday 23 *March* 1965: **Use of the electron microprobe,** J. V. T. LONG and M. J. FLEETWOOD: *Society for Analytical Chemistry, Special Techniques Group and Midlands Section.* Department of Chemistry, University of Birmingham, Birmingham 15, 6.30 p.m. Preceded by afternoon visit at 2.30 p.m. to Mond Nickel Research Laboratories, Wiggin Street, Birmingham 16.

Friday 26 *March* 1965: **Determination of trace constituents in metallurgical samples,** W. T. ELWELL and **Principles of radioactivation analysis,** H. W. WILSON: *Society for Analytical Chemistry, Scottish Section.* Technical College, Falkirk, 7.15 p.m.

Sunday 29 *March–Thursday* 2 *April* 1965: **Laboratory Apparatus and Materials Exhibition:** Earls Court, London.

Tuesday 30 *March* 1965: **Analysis of sugars,** D. CROSS and R. BUTLER and **Characterisation of fats,** K. A. WILLIAMS and C. B. BARRETT: *Society for Analytical Chemistry, North of England Section* and *Midlands Section.* Boots Pure Drug Co. Ltd., Pennyfoot Street, Nottingham, 10.30 a.m.

Wednesday 31 *March* 1965: Meeting on **Food Analysis:** *Society for Analytical Chemistry.* Burlington House, London W.1, 7.00 p.m.

Tuesday–Friday 6–9 *April* 1965: **Anniversary Meetings:** *The Chemical Society*. Glasgow.

There will be three Symposia, of which that entitled **Physical Methods of Structure Determination** may be of interest to analytical chemists:

Wednesday Morning, 7 *April*

X-ray studies of natural products.	J. Monteath Robertson
Recent advances in structural chemistry of organometallics.	L. F. Dahl

Wednesday Afternoon, 7 *April*

Mass spectrometry of high molecular weight compounds.	F. W. McLafferty
Application of high resolution mass spectrometry to natural products.	K. Biemann

Friday Morning, 9 *April*

Applications of nuclear magnetic resonance in inorganic chemistry.	R. E. Richards
New techniques in proton resonance spectroscopy.	J. N. Shoolery

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Wednesday 7 *April* 1965: Symposium on **Pharmaceutical Screening of Drugs:** *Society for Analytical Chemistry, Biological Methods Group*. School of Pharmacy, University of London, Brunswick Square, London W.C.1.

For details apply to Mr. K. L. Smith, Boots Pure Drug Co. Ltd., Pennyfoot Street, Nottingham.

Tuesday–Wednesday 21–22 *September* 1965: **Mass Spectroscopy Conference:** *Mass Spectroscopy Group*. University College, London.

The meetings are open to all and will cover all aspects of mass spectroscopy. Those interested are invited to submit titles of short papers on current work before 26 February, 1965. The Organising Committee will also be grateful to receive suggestions for topics of special interest which might be given prominence or generally discussed at the meeting.

Further information is available from Mr. R. M. Elliott, Associated Electrical Industries Ltd., Scientific Apparatus Department, Barton Dock Road, Urmston, Lancs.

At the *Annual General Meeting* of the **Atomic Absorption Spectroscopy Group** of the **Society for Analytical Chemistry** held on 15 December, 1964, the following Officers were elected for the forthcoming year:

Chairman: W. T. Elwell
Vice-Chairman: J. B. Dawson
Secretary/Treasurer: D. Moore, Hilger and Watts Ltd., 98 St. Pancras Way, London N.W.1.

British Standards Institution has announced the following *New British Standards:*

B.S. 2073*: Methods of testing essential oils: Determination of Lead. Addendum No.* 1*:* 1964*: PD* 5393. Determination of lead (ppm) in essential oils, by absorptiometric measurement of lead dithizonate in solution, after removal of volatile components of the oil. Also, preparation of 'lead-free' reagents for the method. (*Price:* 2s. 6d.)

B.S. 3812*:* 1964*: Recommendations for estimating the dryness of saturated steam.* Basic requirements for apparatus; procedures, calculation. (*Price:* 6s.)

The following *Amendment Slip* is also announced:

B.S. 1756*: Methods for the sampling and analysis of flue gases: Part* 2*:* 1963*: Analysis by the Orsat apparatus. Amendment No.* 1*: PD* 5384. (*Gratis*)

UNITED STATES OF AMERICA

Monday–Friday 1–5 *March* 1965: **Sixteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.** Penn-Sheraton Hotel, Pittsburgh, Pa.

Wednesday–Friday 17–19 *March* 1965: **Fifteenth National Instrument Society of America Conference on Instrumentation for the Iron and Steel Industry.** Pick-Roosevelt Hotel, Pittsburgh, Pa.

Monday–Thursday 19–22 *April* 1965: 1965 **International Conference on Modern Trends in Activation Analysis:** *International Atomic Energy Agency, European Atomic Energy Community, United States Atomic Energy Commission and Texas A and M University.* College Station, Texas.

The programme is as follows:

Monday Morning, 19 *April*

Place of activation analysis in a research establishment dealing with pure materials.	A. A. SMALES

Session I—Nuclear Reactions

Variable energy neutron activation analysis.	E. L. STEELE
Measurement and utilisation of neutron capture gamma radiation.	J. L. BROWNLEE and W. G. LUSSIE
^{3}*He activation analysis.*	E. RICCI, R. L. HAHN, J. E. STRAIN and F. F. DYER
Use of semi-conductors for surface analysis be elastic scattering of accelerated charged particles.	M. PEISACH and D. O. POOLE
Determination of some light elements by secondary reactions.	H. J. BORN and D. C. AUMANN
Neutron activation analysis of iridium in osmium and experimental study of the second order reaction.	R. GIJBELS and J. HOSTE
Analysis of metalloids by activation with photons and charged particles.	C. ENGLEMANN and G. CABANA

Monday Afternoon, 19 *April: Session II—Radiochemistry*

Rapid radiochemical separation procedures for activation analysis indicators.	W. H. WAHL, V. J. MOLINSKI and H. ARINO
New developments of systematic analysis of high purity metals and especially of Al, Fe, Cu, Zr and Ni.	P. ALBERT
Design of apparatus for post-irradiation chemical treatments in activation analysis.	W. T. BURNETT, JR. and M. D. COHEN
Substoichiometric determinations in activation analysis.	J. RŮŽIČKA, J. STARÝ and A. ZEMAN
A new approach to neutron activation analysis through micro and submicro electro-separation techniques.	H. B. MARK, JR., F. J. BERLANOI and B. VASSOS
Use of a small-sized automated system, including a radiochemical step in activation analysis.	F. GIRARDI
Determination of impurities in high purity niobium and tantalum by radioactivation analysis.	T. KAWASHIMA

Monday Evening, 19 *April: Inaugural Banquet*

Analysis and measurement—The foundation of science and technology.	W. W. MEINKE

Tuesday Morning, 20 *April: Session III—Radiochemistry*

Analysis of a demascus steel by neutron and gamma activation.	A. F. VOIGT and A. ABU-SAMRA
Determination of trace amounts of tantalum and tungsten in metals.	A. F. VOIGT, A. L. JEWETT, E. C. JACOBSON and K. L. MALABY
Determination of trace arsenic in germanium and germanium oxide by neutron activation analysis.	J. HOSTE and D. DESOETE
Zinc and bromine in some meteorites by activation analysis.	R. H. FILBY
Removal of radiosodium interference in neutron activation analysis.	M. P. MENON and R. E. WAINERDI
Determination of indium and thallium in zinc and zinc salt.	D. GIBBONS and D. LAWSON
Determination of trace amounts of tellurium in N.B.S. standard reference materials by neutron activation analysis.	D. A. BECKER and F. W. SMITH

Neutron activation analysis of ^{18}O with chemical separation.	W. H. Ellis, G. J. Frite and I. G. Han

Tuesday Afternoon, 20 April: Session IV—(a) Chromatography, (b) General

Radioactivation analysis of silicon and silicon compounds with successive use of ion-exchange chromatography.	V. V. Moiseev, R. A. Kuznetsov and A. I. Kalinin
Chromatographic separation method for activation analysis.	W. Bock-Werthman
Some applications of ion-exchange resins in activation micro-analysis.	J. Laverlochere
Production of homogeneous biological material for inter-laboratory comparison of elementary analyses.	H. J. M. Bowen
Accuracy of radioactivation analysis.	J. P. Cali and J. R. Weiner
New activation analysis facilities at N.B.S.	G. W. Smith and J. R. DeVoe
Activation analysis programme of N.B.S.	J. R. DeVoe

Tuesday Evening, 20 April

Informal discussion groups: 1. *Determination of oxygen.*
2. *Neutron generators in industry.*
3. *Computer methods in activation analysis.*

Wednesday Morning, 21 April: Session V—Neutron Generators

Measurement of surface contamination of high purity beryllium samples.	K. R. Blake, T. C. Martin and I. L. Morgan
Non-destructive determination of silicon and oxygen in meteorities by fast neutron activation analysis.	J. R. Vogt and W. D. Ehmann
Liquid and plastic scintillation counting for oxygen by neutron activation analysis.	F. A. Iddings
Precision analysis with 14-MeV neutrons.	W. E. Mott and J. M. Orange
High-output neutron tubes.	J. E. Bounden, P. D. Comar and J. D. L. H. Wood
A fast neutron activation analysis system with industrial applications.	J. D. L. H. Wood and J. M. Bakes

Wednesday Afternoon, 21 April: Session VI—Instrumentation

Selective and sensitive analysis of activation products by multidimensional gamma spectrometry.	R. W. Perkins
A fast/sum coincidence spectrometer and sensitive compilation for activation analysis.	M. Wahlgren, J. Wing and J. Hines
A Cs–NaI dual crystal Compton reduction detector.	C. F. Lam and R. E. Wainerdi
Interfacing the teletype model 33-c ASR to nuclear instruments used for computer coupled activation analysis.	R. W. Schideler
Application of coincidence methods in activation analysis.	W. Schulze
A fast punched-card read-out system for pulse height analysers.	B. A. Euler, P. L. Phelps and D. F. Covell

Thursday Morning, 22 April: Session VII—Computer Methods

An analysis of the method of least squares as related to gamma ray scintillation spectroscopy.	J. R. Wolberg
Evaluation of computer programmes for gamma ray spectrometry in activation analysis.	J. F. Emery, F. F. Dyer, T. Alexander and E. Schonfeld
Improved accuracy in determination of radionuclide concentrations in solutions containing fast-delaying isotopes by least squares resolution of the gamma ray spectra.	E. Schonfeld

New developments in application of neutron activation analysis to problems in scientific crime detection.	D. E. Bryan, V. P. Guinn and D. M. Settle
Activation analysis applications of an on-line digital computer.	M. D. Cohan
Hair individualisation studies by neutron activation analysis.	A. K. Perkons and R. E. Jervis
Computer programmes to optimise times of irradiation and decay in multiple-element activation analysis.	T. L. Isenhovur, C. A. Evans, Jr. and G. H. Morrison

Thursday Afternoon, 22 *April: Sessions VIII and IX* (concurrently)

Session VIII—Biological Applications

Development and demonstration of use of ^{129}*I activation analysis for atmospheric tracing.*	B. Keisch and R. C. Koch
Determination of biosperic levels of ^{129}*I by neutron activation analysis.*	B. Keisch and R. C. Koch
Activation analysis of urine for zinc.	E. D. Bird, W. H. Ellis and W. C. Thomas, Jr.
Manganese and copper content in human body fluids.	T. Fields
Studies of gamma spectrum of neutron irradiated blood.	L. O. Plantin
Determination of selenium in human tissues by activation analysis.	R. H. Tomlinson and R. C. Dickson
Simultaneous determination of copper and zinc in human lung tissue by neutron activation analysis.	R. G. Keenan, J. H. Marcus and J. R. Devoe
Simple and rapid magnesium determination in biological samples by neutron activation analysis.	C. K. Kim and W. W. Meinke
Use of neutron activation analysis to determine biological availability of copper in soils.	J. R. Kline, S. S. Brar, P. I. Gustafson and R. H. Rust
Neutron activation analysis for plutonium mixed in soil.	R. K. Fuller and H. R. Lukens, Jr.

Session IX—Industrial Applications

Measurement of fibre blend variability by activation analysis.	A. A. Armstrong, J. F. Boydon and A. J. Chudoar
Fast neutron activation analysis in molten salt electrometallurgical research.	K. G. Broadhead and H. H. Heady
Nuclear analysis system for coal.	T. C. Morgan, I. L. Morgan and J. D. Hall
Industrial applications of neutron activation.	A. L. Gray
Correlation of physical properties of rubber with nitrogen content by neutron activation analysis.	L. J. Walker and V. L. Eggebraaten
A comparison of neutron activation analysis and vacuum fusion analysis of oxygen content of steel.	D. E. Wood and L. L. Pasztor

Further information may be obtained from Dr. R. E. Wainerdi, Activation analysis Research Laboratory, Texas A and M University, College Station, Texas, U.S.A.

Monday–Thursday 18–21 *October* 1965: **Third International Symposium on Advances in Gas Chromatography.** Sheraton-Lincoln Hotel, Houston, Texas.

An outstanding programme is being planned and it will include lectures by internationally known leaders in this field. New developments in detectors and columns for liquid chromatography will be included in the programme. There will also be an exhibition of new gas chromatographic instruments and accessories. Participation in the Symposium will be on the basis of invited contributions; however, a limited number of papers from U.S.A. and abroad are being solicited. Those who wish to make contributions are requested to submit an abstract of about 700 words (or the complete manuscript) by 1 June, 1965. Financial assistance for travel will be available for authors of papers accepted from abroad.

Abstracts of papers and enquiries concerning the Symposium should be directed to Professor A. Zlatkis, Department of Chemistry, University of Houston, Houston, Texas.

SUMMARIES FOR CARD INDEXES

Precision of the determination of copper and gold by atomic absorption spectrophotometry: H. KHALIFA, G. SVEHLA and L. ERDEY, *Talanta*, 1965, **12**, 703. (Institute for General Chemistry, Technical University, Budapest XI, Gellért tér 4, Hungary.)

Summary—Copper and gold can be determined by atomic absorption spectrophotometry using hollow cathode lamps which produce the resonance lines of 3247 Å and 2428 Å, respectively. Optimal experimental conditions have been ascertained. In the case of copper calibration curves are presented for 10–100 as well as for 100–700 ppm, and in that of gold for 5–50 as well as for 50–500 ppm. The influence of several cations and anions has been examined. Precision calculations have been made by a method suggested previously by the authors.

Application of circular thin-layer chromatography to inorganic qualitative analysis: M. H. HASHMI, M. A. SHAHID and A. A. AYAZ, *Talanta*, 1965, **12**, 713. (West Regional Laboratories, P.C.S.I.R., Lahore, West Pakistan.)

Summary—After separation of metal ions into Groups 1–5 of the classical hydrogen sulphide scheme of qualitative analysis, the metal ions in each Group are separated by circular thin-layer chromatography. Several solvents and spray reagents for the Group analyses are reported. The method is simple and convenient; development of a chromatoplate is complete within 2 min.

Substoichiometric determination of copper in high-purity metals by activation analysis: M. KŘIVÁNEK, F. KUKULA and J. SLUNEČKO, *Talanta*, 1965, **12**, 721. (Institute for Nuclear Research, Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia.)

Summary—A selective and very simple substoichiometric determination of copper in high-purity aluminium, silicon, iron, gallium, zinc and tin by activation analysis has been developed. The radiochemical procedure is based on the extraction of copper diethyldithiocarbamate into chloroform from an aqueous alkaline medium. The only interfering elements are mercury, palladium, silver, osmium and gold.

ТОЧНОСТЬ ОПРЕДЕЛЕНИЯ МЕДИ И ЗОЛОТА МЕТОДОМ АТОМНОЙ АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

H. KHALIFA, G. SVEHLA and L. ERDEY, *Talanta*, 1965, **12**, 703.

Резюме—Медь и золото можно определить методом атомной абсорбционной спектроскопии с использованием трубок с полым катодом, которые производят резонансные линии 3247 Å и 2428 Å, соответственно. Определены оптимальные условия опыта. В случае меди приведены стандартные кривы для областей концентрации 10–100 мг/л и 100–700 мг/л, а в случае золота для областей 5–50 мг/л и 50–500 мг/л. Исследовано влияние некоторых катионов и анионов. Калькуляции точности выполнены способом раньше предложенным авторами.

ИСПОЛЬЗОВАНИЕ МЕТОДА РАДИАЛЬНОЙ ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ В НЕОРГАНИЧЕСКОМ КАЧЕСТВЕННОМ АНАЛИЗЕ:

M. H. HASHMI, M. A. SHAHID and A. A. AYAZ, *Talanta*, 1965, **12**, 713.

Резюме—После разделения ионов металла в группы I–V классической схемы качественного анализа на основании сероводорода, ионы каждой группы разделяются методом радиальной тонкослойной хроматографии. Приводят несколько растворителей и реагентов для обнаружения пятен, применимых в анализе групп. Метод несложный и удобный; хроматограмма получается в 2 мин.

ПОДСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ В МЕТАЛЛАХ ВЫСОКОЙ ЧИСТОТЫ МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА.

M. KŘIVÁNEK, F. KUKULA and J. SLUNEČKO, *Talanta*, 1965, **12**, 721.

Резюме—Разработан избирательный и легко осуществимый подстехиометрический метод для определения меди методом радиоактивационного анализа в алюминии, кремнии, железе, галлии, цинке и олове высокой чистоты. Метод основывается на экстрагировании меди раствором диэтилдитиокарбамата в хлороформе из воднощелочной среды. Определению мешают только ртуть, палладий, серебро, осмий и золото.

Reduction of alkyl disulphides with triphenylphosphine: Ray E. Humphrey, Avis L. McCrary and Rodney M. Webb, *Talanta*, 1965, **12**, 727. (Department of Chemistry, Sam Houston State College, Huntsville, Texas, U.S.A.)

Summary—Alkyl disulphides are reduced to thiols by triphenylphosphine in aqueous methanol, with the phosphine being converted to the oxide. Water is believed to be the source of the hydrogen and oxygen required. The reductions are rather slow; heating for periods of several hours is necessary. Maximum yields of 70–80% are generally obtained, although some substituted alkyl disulphides, such as cystine and dithiodiglycolic acid, are quantitatively reduced. The principal analytical application of this reduction appears to be the determination of aromatic disulphides in the presence of alkyl disulphides, because the aromatic compounds are reduced at a much greater rate.

Spectrophotometric determination of platinum after extraction of the stannous-chloro complex by high molecular weight amines: M. A. Khattak and R. J. Magee, *Talanta*, 1965, **12**, 733. (Department of Chemistry, Queen's University, Belfast 9, N. Ireland.)

Summary—An investigation of the complex formed between platinum(IV) and tin(II) in hydrochloric acid solutions has been carried out, and its extractibility by various long-chain high molecular weight amines (HMWA) in organic solvents examined. The orange coloured platinum(IV)–tin(II) complex is quantitatively extractable from an aqueous phase into an organic phase of a wide range of high molecular weight amines in chloroform or benzene. On the basis of this extractability a method has been developed for the spectrophotometric determination of platinum in the presence of many other elements. Comparison of the absorption spectra of the coloured species in the aqueous and amine phases indicates the presence of the same absorption species in each medium. The extractability of the complex by HMWA suggests that the coloured species is anionic and not cationic as reported by earlier authors.

A critical evaluation of colorimetric methods for determination of the noble metals—III: Palladium and platinum: F. E. Beamish, *Talanta*, 1965, **12**, 743. (Department of Chemistry, University of Toronto, Toronto 5, Canada).

Summary—Spectrophotometric methods for palladium and platinum recorded subsequent to 1958 are critically reviewed. Associated with the descriptions of each metal there is included a table which identifies reagents recorded before 1958 together with pertinent references.

ВОССТАНОВЛЕНИЕ АЛКИЛДИСУЛЬФИДОВ ТРИФЕНИЛФОСФИНОМ:

R. E. Humphrey, A. L. McCrary and R. M. Webb, *Talanta*, 1965, **12**, 727.

Резюме—Алкилдисульфиды восстанавливаются трифенилфосфином в водном растворе метилового спирта; фосфин превращается в окись. Кажется что вода является источником водорода и кислорода требованного в реакции. Восстановление поступает медленно: надо нагревать через несколько часов. В большинстве случаев реакция достигает только 70–80% теории, хотя некоторые алкилдисульфиди, так как на пример цистин и дитиогликолевая кислота восстанавливаются количественно. Важнейшим применением этого восстановления в анализе является определение ароматических дисульфидов в присутствии алкилдисульфидов, с тех пор как скорость восстановления ароматических соединений гораздо больше.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПЛАТИНЫ ПОСЛЕ ЭКСТРАКЦИИ ХЛОРОКОМПЛЕКСА С ОЛОВОМ(II) ВЫСОКОМОЛЕКУЛЯРНЫМИ АМИНАМИ:

M. A. Khattak and R. J. Magee, *Talanta*, 1965, **12**, 733.

Резюме—Исследован состав комплекса платины(IV) с оловом(II) в солянокислых растворах и его экстрагирование растворами различных высокомолекулярных аминов длинной цепью (ВМА) в органических растворителях. Комплекс платины(IV) и олова(II) оранжевого цвета экстрагируется количественно из водной в органическую фазу, состоящуюся из раствора ряда высокомолекулярных аминов в хлороформе или бензоле. На основании этого поведения разработан метод для спектрофотометрического определения платины в присутствии многочисленных других элементов. Спектры светопоглощения водной и аминовой фазы показывают присутствие одного и того же абсорбирующего вещества в этих средах. На основании экстрагирования комплекса с ВМА считается что окрашенное вещество анионного, не катионного характера, как сообщено раньшими авторами.

КРИТИЧЕСКАЯ ОЦЕНКА КОЛОРИМЕТРИЧЕСКИХ МЕТОДОВ ДЛЯ ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ—III: ПАЛЛАДИЙ И ПЛАТИНА:

F. E. Beamish, *Talanta*, 1965, **12**, 743.

Резюме—Критически обсуждаются спектрофотометрические методы для определения палладия и платины, опубликованные после 1958 года. В описании каждого метода включена таблица реагентов регистрированных прежде 1958 г. вместе с литературными ссылками.

Spectrophotometric determination of selenium in technical sulphuric acid by *o*-phenylenediamine: K. Tōei and K. Itō, *Talanta*, 1965, **12**, 773. (Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan.)

Summary—*o*-Phenylenediamine reacts quantitatively with selenium to form piaselenol even when a large amount of sulphate is present. Piaselenol is extracted by toluene and the absorbance at 335 mμ measured to determine the amount of selenium in technical sulphuric acid. Interference from iron(III) and nitrous acid can be conveniently eliminated by adding EDTA and urea before colour development.

Reversible indicators for titrations with hypochlorite: R. Belcher, I. El-Khiami and W. I. Stephen, *Talanta*, 1965, **12**, 775.

Summary—Several sulphone-phthalein indicators have been examined to test their possible application as redox indicators in titrations with hypochlorite, bromate, iodate and chloramine-T. It was confirmed that Cerana's indicator, Bromothymol Blue, is an excellent reversible indicator for titrations with hypochlorite. Bromocresol Purple is possibly slightly better. Cresol Red, Xylenol Orange, Thymol Blue and Methyl Thymol Blue are also suitable, but there is little point in using them, because the first two are converted to Bromocresol Purple and the last two to Bromothymol Blue. In the remaining systems the indicators were inferior to or no better than conventional indicators.

Formal potential of tris(2,2′-dipyridyl)iron(II) sulphate: R. Belcher, J. N. Brazier and W. I. Stephen, *Talanta*, 1965, **12**, 778. (Department of Chemistry, University of Birmingham, Birmingham 15, England.)

Summary—The formal potential of tris(2,2′-dipyridyl)iron(II) sulphate has been redetermined and is now reported as 1·023 V in 1*F* sulphuric acid as against the generally accepted value of 0·97 V. This new figure accounts for the hitherto inexplicable behaviour of the indicator in the titration of iron(II) with dichromate.

3,3-Diphenylindane-1,2-dione dioxime as a highly sensitive precipitant for palladium: L. S. Bark and D. Brandon, *Talanta*, 1965, **12**, 781.

Summary—3,3-Diphenylindane-1,2-dione dioxime has been prepared and a preliminary investigation shows it to be more sensitive than indane-1,2-dione dioxime as a precipitant for palladium(II).

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЕЛЕНА В ТЕХНИЧЕСКОЙ СЕРНОЙ КИСЛОТЕ:

K. Toei and K. Ito, *Talanta*, 1965, **12**, 773.

Резюме—*o*-Фенилендиамин реагирует количественно с селеном образуя пиаселенол, даже в присутствии значительных количеств сульфат-иона. Концентрацию селена в технической серной кислоте определяют экстрагированием пиаселенола с толуолом и измерением светопоглощения при 335 ммк. Влияние железа(III) и азотистой кислоты можно легко исключить добавлением раствору ЭДТА и мочевины перед проявлением окраски.

ОБРАТИМЫЕ ИНДИКАТОРЫ ДЛЯ ТИТРОВАНИЙ С ГИПОХЛОРИТОМ:

R. Belcher, I. El-Khiami and W. I. Stephen, *Talanta*, 1965, **12**, 775.

Резюме—Исследована применимость некоторых сульфонофталеиновых индикаторов в качестве окислительно-восстановительных индикаторов при титрованиях с растворами гипохлорита, бромата, иодата и Хлорамина Т. Подтверждено что индикатор Церана-бромотимолсиний-представляет отличный обратимый индикатор для титрования с гипохлоритом. Бромкрезолпурпурный кажется даже несколько лучшим. Крезолкрасный, ксиленолоранжевый, тимолсиний и метилтимолсиний тоже подходящие, но использовать их не стоит потому что два первых превращаются в бромкрезолпурпурный, а два последних в бромтимолсиний. В остальных системах индикатори были хуже или не лучше чем обыкновенные индикаторы.

ФОРМАЛЬНЫЙ ПОТЕНЦИАЛ СУЛЬФАТА ТРИС(2,2′-ДИПИРИДИЛ)ЖЕЛЕЗА(II):

R. Belcher, J. N. Brazier and W. I. Stephen, *Talanta*, 1965, **12**, 778.

Резюме—Снова определен формальный потенциал трис(2,2′-дипиридил)железа(II); обнаруженный потенциал равен 1,023 V в 1 *F* серной кислоте, против общепринятой величины 0,97 V. Эта новая величина объясняет до сих пор необъяснимое поведение индикатора при титровании железа(II) бихроматом.

3,3-ДИФЕНИЛИНДАН-1,2-ДИОНДИОКСИМ ВЫСОКОЧУВСТВИТЕЛЬНЫЙ РЕАКТИВ ДЛЯ ОСАЖДЕНИЯ ПАЛЛАДИЯ:

L. S. Bark and D. Brandon, *Talanta*, 1965, **12**, 781.

Резюме—3,3-Дифенилиндан-1,2-диондиоксим был приготовлен и в предварительных опытах оказался более чувствительным от индан-3,2-диондиоксима в качестве осаждающего агента для палладия(II).

SUMMARIES FOR CARD INDEXES

Application of anodic stripping voltammetry to the determination of mercury in lithium sulphate: P. EMMOTT, *Talanta*, 1965, **12**, 651 (M.G.O. Inspectorates, Chemical Inspectorate, Royal Arsenal, Woolwich S.E.18, England).

Summary—The technique of anodic stripping voltammetry, using a carbon-paste electrode, has been applied to the determination of mercury in solutions of 1·8 M lithium sulphate. Over the range 0·08–2·5 μg/ml, the relationship between peak current and mercury content is linear. At the higher level, the standard deviation of the results is 0·1 μg/ml, falling to 0·04 μg/ml at the lower level. The interference of other cations has been studied and their effect overcome by the use of a standard addition procedure.

A study of the cobalt chloro-complexes in dimethylformamide and the use of one of them for the spectrophotometric determination of cobalt: LEROY PIKE and JOHN H. YOE, *Talanta*, 1965, **12**, 657. (Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia, Charlottesville, Virginia, U.S.A.).

Summary—Cobalt(II) forms deep-blue stable chloro-complexes in dimethylformamide. One of them, $(CoCl_4)^{2-}$, is used for the spectrophotometric determination of cobalt. Optimum analytical conditions have been established. Beer's law is obeyed between a cobalt concentration of 5 and 100 ppm; a wider concentration range was not investigated. Sensitivity of the colour reaction is 0·10 μg of cobalt per cm^2 for log $I_0/I = 0·001$. A large excess of many foreign ions can be tolerated; an ion-exchange separation is used when necessary. The method has been applied successfully to the determination of cobalt in steel, ferromanganese and a nickel-copper alloy.

Vanadium compounds in reductimetric titrations—I: Standardisation of vanadium(II) sulphate with iron(III) solution: K. L. CHAWLA and J. P. TANDON, *Talanta*, 1965, **12**, 665. (Department of Chemistry, University of Rajasthan, Jaipur, India).

Summary—Methods of standardisation of vanadium(II) sulphate against iron(III) sulphate are described. The standardisation can be carried out visually at a temperature of about 80° using acetylacetone, or meconic, salicylic or sulphosalicylic acids as internal indicators. The titration can be carried out at room temperature if copper(II) is used as a catalyst; the end-point can be detected with methylene blue, gallocyanine or potentiometrically as well as by the indicators listed above. The copper(II) catalyses the oxidation of vanadium(III) to vanadium(IV), which is slow at room temperature.

ПРИМЕНЕНИЕ АНОДНОЙ СТРИППИНГ ВОЛЬТАМЕТРИИ В ОПРЕДЕЛЕНИИ РТУТИ В СУЛЬФАТЕ ЛИТИЯ:

Р. Еммотт, *Talanta*, 1965, **12**, 651.

Резюме—Метод анодной стриппинг вольтаметрии, пользуясь угольным электродом в виде пасты, применен в определении ртути в 1,8 М растворах сульфата лития. В области 0,08–2,5 мкг/мл существует линейное отношение между пиковым током и количеством ртути. При высших концентрациях стандартная ошибка результатов равна 0,1 мкг/мг а при нижих концентрациях 0,04 мкг/мл. Изучены помехи других катионов и избегнуто их влияние использованием стандартной процедуры добавки.

ИЗУЧЕНИЕ ХЛОРО-КОМПЛЕКСОВ КОБАЛЬТА В ДИМЕТИЛФОРМАМИДЕ И ИСПОЛЬЗОВАНИЕ ОДНОГО ИЗ НИХ ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ КОБАЛЬТА:

LeRoy Pike and John H. Yoe, *Talanta*, 1965, **12**, 657.

Резюме—Кобальт(II) образует тёмно синие устойчивые хлорокомплексы в диметилформамиде. Одним из них-$(CoCl_4)^{2-}$-пользуются для спектрофотометрического определения кобальта. Установлени оптимальные условия. Закон Беера соблюдается в области концентрации кобальта 5 до 100 мг/л. Бопее широкая область концентрации не была исследована. Чствувительность цветной реакции 0,10 мкг кобальта/см^2 для $\log I_0/I = 0{,}001$. Множество ионов в большем избытке не мешают определению; в случае необходимого выделения пользуются ионообменным методом. Описанный выше метод был успешно применен для определения кобальта в стали, ферромарганце и сплаве никеля и меди.

ИСПОЛЬЗОВАНИЕ СОЕДИНЕНИЙ ВАНАДИЯ В ВОССТАНОВИТЕЛЬНЫХ ТИТРОВАНИЯХ—I: УСТАНОВКА ТИТРА СУЛЬФАТА ВАНАДИЯ(II) РАСТВОРОМ ЖЕЛЕЗА(III):

K. L. Chawla and J. P. Tandon, *Talanta*, 1965, **12**, 665.

Резюме—Описываются методы установки титра растворов сульфата ванадия(II) сульфатом железа(III). Титрование проводится при температуре около 80° с визуальным концем титрования, с использованием ацетилацетона, меконовой, салициловой или сульфосалициловой кислот в качестве внутренного индикатора. Титрование можно провести при комнатной температуре пользуясь медью(II) в качестве катализатора. Конец титрования обнаруживается метиленовым голубим, галлоцианином или потенциометрическим методом, или с использованием индикаторов перечисленных выше. Медь(II) катализует окисление ванадия(III) в ванадий (IV), которое поступает медленно при комнатной температуре.

Amperometry with two polarisable electrodes—VI: Chelometric determination of copper: J. Vorlíček and F. Vydra, *Talanta*, 1965, **12**, 671 (Analytical Laboratory, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia).

Summary—A study of the determination of copper by titration with EDTA, using biamperometric detection of the end-point with two stationary platinum electrodes, is reported. The influence of pH, applied potential, temperature and rate of stirring on the course and accuracy of the titration are examined. The selectivity of the titration is investigated and possible analytical applications discussed.

Determination of deactivated olefines on the submicro scale: R. Belcher and B. Fleet, *Talanta*, 1965, **12**, 677 (Department of Chemistry, University of Birmingham, Birmingham 15, England).

Summary—Olefines which do not undergo the normal addition reactions with electrophilic reagents can be reacted with the nucleophilic reagent morpholine to form a tertiary amine. A submicro method using this reagent has been developed. When the addition product is basic it is titrated after acetylation of the excess morpholine; when it is neutral the excess of morpholine is titrated.

Spectrophotometric determination of niobium(V) with Bromopyrogallol Red: R. Belcher, T. V. Ramakrishna and T. S. West, *Talanta*, 1965, **12**, 681 (Department of Chemistry, University of Birmingham, Birmingham 15, England).

Summary—Bromopyrogallol Red reacts with niobium(V) in a tartrate medium at pH 6·0 to form an intense blue coloured 3:1 reagent; metal complex ($\epsilon_{610\ m\mu} = 60{,}000$); the reaction is gelatin sensitised. In a medium made $10^{-2}M$ with respect to EDTA a 2:1 complex is formed and though the sensitivity decreases slightly ($\epsilon_{610\ m\mu} = 53{,}000$), the reaction becomes highly selective towards niobium. After the addition of masking agents to complex the few interfering ions, no interference is found from 1000-fold excesses of the 34 cations examined, including tantalum, tungsten, molybdenum, titanium, zirconium, beryllium and thorium, or from any of the common complexing anions, including phosphate and fluoride. The conditional stability constant for the 3:1 complex is $2{\cdot}7 \times 10^{18}$ and for the 2:1 complex, 1×10^{12}. The colour system is stable and reproducible and the proposed method seems to be the most sensitive visible-range spectrophotometric method so far proposed for niobium(V).

АМПЕРОМЕТРИЯ С ИСПОЛЬЗОВАНИЕМ ДВУХ ПОЛЯРИЗУЕМЫХ ЭЛЕКТРОДОВ—VI: ХЕЛАТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ:

J. Vorlíček and F. Vydra, *Talanta*, 1965, **12**, 671.

Резюме—Изучено определение меди титрованием с ЭДТА, с использованием биамперометрического индицирования конца титрования с двумя неподвижными платиновыми электродами. Исследовано влияние pH, приложенного потенциала, температуры и скорости перемешивания на течение и точность титрования. Исследована тоже избирательность титрования и обсуждается её применение в анализе.

ОПРЕДЕЛЕНИЕ ДЕЗАКТИВТРОВАННЫХ ОЛЕФИНОВ В СУБМИКРОАНАЛИТИЧЕСКОМ МАСШТАБЕ:

R. Belcher and B. Fleet, *Talanta*, 1965, **12**, 677.

Резюме—Олефины которые не подвергаются обыкновенными реакциями присоединения с электрофильными реагентами могут реагировать с нуклеофильным реагентом морфолином, с образованием третичного амина. Разработан метод в субмикроаналитическом масштабе пользующийся этим реагентом. В случае основного продукта присоединения титруют продукт после ацетилирования избытка морфолина; в случае нейтрального продукта титруют избыток морфолина.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИОБИЯ(V) С БРОМОПИРОГАЛЛОЛ КРАСНЫМ:

R. Belcher, T. V. Ramakrishna and T. S. West, *Talanta*, 1965, **12**, 681.

Резюме—Бромопирогаллол красный реагирует с ниобием(V) в виннокислой среде при pH 6,0 и образует интенсивно синий комплекс в отношении реагент:металл 3:1 ($\epsilon_{610\ \text{ммк}}$ = 60,000); реакция сенсибилизирована желатином. В растворе 10^{-3} M в отношении на ЭДТА образуется комплекс 2:1 и реакция становится высоко избирательной для ниобия, хотя чувствительность незначительно уменьшается ($\epsilon_{610\ \text{ммк}}$ = 53,000). После добавления маскирующих агентов не обнаружены помехи от 1000-кратного избытка 34 изученных катионов, включая тантал, вольфрам, молибден, титан, цирконий, бериллий и торий или от обыкновенных комплексообразующих анионов включая фосфат- и фторидионы. Условная константа устойчивости равна $2,7 \times 10^{18}$ для комплекса 3:1 и 1×10^{12} для комплекса 2:1, соответсвенно. Окраска устойчивая и повторяемая; кажется этот метод представляет до сих пор самый чувствительный спектрофотометрический метод в области видимого спектра для определения ниобия(V).

Analysis of metal chelates—IV: Simultaneous polarographic determination of metals and 8-hydroxyquinoline in metal 8-hydroxyquinolates: Y. Tanigawa, S. Minami and K. Takiyama, *Talanta*, 1965, **12**, 691 (Mukogawa Women's University, Nishinomiya, Japan).

Summary—Studies of the simultaneous determination of metal and 8-hydroxyquinoline in metal 8-hydroxyquinolates have been made by a.c. polarography, after precipitation of the chelates by a conventional procedure and re-solution in a suitable medium. Cadmium, copper, lead and bismuth may be determined, together with 8-hydroxyquinoline but the zinc peak cannot be distinguished from that of the 8-hydroxyquinoline under the conditions employed. Some aspects of the results are discussed.

Applications of chelatometry—XVII: Titrimetric determination of silver ions via reduction to the elemental state: C. Hennart, *Talanta*, 1965, **12**, 694 (Seraincourt, Val d'Oise, France).

Summary—Silver(I) ions are determined *via* their quantitative reduction with elemental copper; the copper(II) ions formed are titrated, without filtration, by EDTA using Murexide as indicator.

Spectrophotometric determination of palladium with pyridine-2-aldehyde-2-pyridylhydrazone: C. F. Bell and D. R. Rose, *Talanta*, 1965, **12**, 696. (Department of Chemistry, Brunel College, London, W.3., England.)

Summary—Palladium(II) and pyridine-2-aldehyde 2-pyridylhydrazone form a red complex in aqueous solution with maximum development of colour at pH values between 11·5 and 11·8 ($\lambda_{max} = 520$ mμ). A procedure is described for the accurate spectrophotometric determination of 1–10 μg of palladium. Only a few metal ions interfere and their interference can be prevented by the addition of EDTA.

АНАЛИЗ ХЕЛАТОВ МЕТАЛЛОВ—IV: ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ МЕТАЛЛОВ И 8-ОКСИХИНОЛИНА В 8-ОКСИХИХНОЛИНАТАХ МЕТАЛЛОВ:

Y. TANIGAWA, S. MINAMI and K. TAKIYAMA, *Talanta*, 1965, **12**, 691.

Резюме—Изучено одновременное определение металла и 8-оксихинолина в 8-оксихинолинатах металлов полярографическим методом при переменном токе, после осаждения хелатов обыкновенным методом и повторным растворением в подходящей среде. Можно определить кадмий, медь, свинец и висмут вместе с 8-оксихинолином, но в примененных условиях не удается различать пик цинка от пика 8-оксихинолина. Обсуждаются некоторые взгляды на результаты.

ПРИМЕНЕНИЕ ХЕЛАТОМЕТРИИ—XVII: ТИТРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИОНОВ СЕРЕБРА ПУТЕМ ВОССТАНОВЛЕНИЯ ДО ЭЛЕМЕНТАРНОГО СОСТОЯНИЯ:

C. HENNART, *Talanta*, 1965, **12**, 694.

Резюме—Ионы серебра(I) определяются путем количественного восстановления с металлической меди; Образованные ионы меди(II) титруются—без фильтрования—раствором ЭДТА, с использованием мурексида в качестве индикатора.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ ПИРИДИН-2-АЛЬДЕГИД-2-ПИРИДИЛГИДРАЗОНОМ:

C. F. BELL and D. R. ROSE, *Talanta*, 1965, **12**, 696.

Резюме—Палладий(II) образует с пиридин-2-альдегид-2-пиридилгидразоном комплекс красного цвета в водном растворе с максимальным проявлением окраски при pH 11,5–11,8 ($\lambda_{\text{макс}} = 520$ ммк). Описана процедура для точного спектрофотометрического определения 1–10 мкг палладия. Только немногие ионы металлов мешают определению и их влияние можно устранить добавлением ЭДТА.

Talanta, 1965, Vol. 12, pp. i to vi. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The **Commission for determination of Trace Elements in Food** of the **International Union of Pure and Applied Chemistry** has prepared methods for the determination of traces of lead [*Pure Appl. Chem.*, 1965, **10**(1), 71] and of mercury (*ibid.*, 77).

HUNGARY

Wednesday–Saturday 20–23 *April* 1966: **International Conference on Application of Physico-Chemical Methods in Chemical Analysis:** *Hungarian Chemical Society* under sponsorship of *Department for Chemical Sciences of Hungarian Academy of Sciences.* Budapest.

The Conference will be organised under the following sections:

Theoretical questions of chemical analysis
Electro-analysis
Thermal analysis
Chromatography
Spectrophotometry
Radiochemistry and activation analysis.

The official languages adopted will be: English, German, French, Russian and Hungarian. Lectures will be followed by discussions for which the necessary interpretation will be secured.

Further information may be obtained from Organising Committee of Analytical Chemistry Conference, c/o Magyar Kémikusok Egyesülete, Budapest V, Szabadság tér 17, Hungary.

UNITED KINGDOM

Monday–Tuesday 5–6 *July* 1965: **Conference on Low-level Radioactivity Measurements—Limitations and Techniques:** *Institute of Physics and Physical Society.* Imperial College, London.

The provisional programme is as follows:—

Monday, 5 July

Session I: Introduction

Survey papers will be presented by S. C. Curran and G. R. Martin

Session II: Techniques of Alpha-Particle Counting and Spectrometry

Topics dealt with will include limitations of current techniques of alpha-spectrometry and advances in the use of gas-flow counters and semiconductors.

Session III: Assay of Samples Emitting Beta-Particles

Part 1. Survey of developments in general counting techniques, including the use of scintillators, proportional counters and semiconductor detectors.

Part 2. Measurement of low concentrations of radionuclides emitting low energy beta-particles.

Tuesday, 6 July

Session IV: Analysis and Assay of Gamma-Ray Emitters

Topics considered will include investigations of sources of background, the use of computer programmes in the analysis of gamma-ray spectra, low energy gamma-ray spectrometry, the applications of coincidence techniques and the use of semiconductor detectors.

Session V: Chemical Techniques

Radiochemical separation and purification of radionuclides at low concentration.

Session VI: Accuracy and Low-Level Measurements

Special attention will be given to uncertainties arising in sampling, chemical processing and counting statistics.

Session VIII: Some Applications of Low-Level Counting

Part 1. Measurements of environmental radiation. Topics will include measurements of atmospheric radioactive xenon, the use of an activation technique in determining the dose rate in the upper atmosphere due to fast neutrons and investigations of radionuclides of very long half-life.

Part 2. Measurement of radioactivity in the human body. Topics will include the general design of body computers and in particular the use of proportional counters in measurements of plutonium-239.

Monday–Saturday 12–17 *July* 1965: **XII International Spectroscopy Colloquium.** University of Exeter [see *Talanta*, 1964, **11**(4), vi].

Monday–Friday 19–23 *July* 1965: **Society for Analytical Chemistry Conference 1965.** University of Nottingham, Nottingham.

The programme, subject to minor alterations, will be as follows:

Monday, July 19

Opening Address by A. A. Smales *Analytical Chemistry—Science or Technology?*

Session A—Afternoon

A Standard Biological Material for Elementary Analysis by H. J. M. Bowen

Examination and Determination of Cephaloridine by J. L. Martin and W. H. C. Shaw

Analysis of Phosphatides by Means of Potentiometric Titration in Non-aqueous Medium by P. Smits and J. Kuiper

Fundamental Studies in Automatic Digestion by J. F. Marten and G. Catanzaro

Session B—Afternoon

A Prototype X-Ray Milliprobe Analyser by F. W. J. Garton, J. T. Campbell and J. Watling

Determination of Microgram Amounts of Zirconium in Uranium and Steel by X-Ray Fluorescence Spectroscopy by B. L. Taylor

A Study of Silicon Determination in Organo-silicon Compounds by X-Ray Fluorescence with Vacuum Spectrograph by F. L. Chan

Analysis of Plastics Materials: X-Ray Fluorescence Examination of Volatile Liquids with the Philips PW1540 Spectrometer by D. C. M. Squirrell

Tuesday, July 20

Session A—Morning

Studies on the Relationship between Molecular Structure and Chromatographic Behaviour—IV: Behaviour of Some Nitrophenols Chromatographed by Partition Chromatography by L. S. Bark and R. J. T. Graham

Use of Thin-layer and Semi-preparative Gas-Liquid Chromatography in Detection, Determination and Identification of Organo-phosphorus Pesticide Residues by D. C. Abbott, N. T. Crosby and J. Thomson

Some Fundamental Aspects in the Practice of Thin-layer Electrophoresis by W. J. Criddle, G. J. Moody and J. D. R. Thomas

Quantitative Analysis of Fatty Alcohol-Ethylene Oxide Adducts by Thin-layer Chromatography by T. D. Heyes

Direct Conductimetric Titration of Acidic and Basic Compounds Resolved by Thin-layer Chromatography by W. Boardman and B. Warren

Session B—Morning

Determination of Some Light Elements by Charged-particle Activation Analysis and Measurement of Prompt Radiation by T. B. Pierce and P. F. Peck

Determination of Microgram Amounts of Fluoride by a Pyrohydrolytic Lanthanum-Alizarin Complexan Procedure Designed for Plutonium-containing Materials by A. G. Davies and J. K. Foreman

Determination of Tellurium in Gallium Arsenide and Germanium by Neutron Activation Analysis by K. W. Lloyd

Spectrochemical Analysis of Radioactive Materials—VIII: The Spectrographic Analysis of Minute Samples by V. Svoboda

Determination of Rare Earths in Substituted Yttrium Iron Garnets by Neutron Activation and γ-Ray Spectrometry by K. W. Lloyd and E. J. Millett

Session A—Afternoon

Analysis of n-Alcohol-Ethylene Oxide Adducts by Gas-Liquid Chromatography by W. Lazarus

Organic Trace Analysis by Measurement of Photoluminescence by C. A. Parker

Recent Advances in the Analysis of Poly(vinyl chloride) Compositions by L. H. Ruddle, S. D. Swift, J. Udris and P. E. Arnold

An Infrared Method for the Determination of Small Amounts of Acetaldehyde in Aqueous Solution by D. M. W. Anderson and J. F. Stoddart

Session B—Afternoon

Application of Controlled-potential Coulometry to Determination of Plutonium by G. PHILLIPS and G. W. C. MILNER

Electrophoresis on Cellulose Acetate Membrane in Strong Electrolytes: Determination of Electrophoretic Mobility of Some Actinide Elements in Hydrochloric and Nitric Acids by F. CLANET

Some Aspects of Spectrochemical Analysis of Actinide Elements by F. T. BIRKS

Determination of Some Constituents of Rocks and Minerals by Fast-neutron Activation Analysis by J. M. BLAKES, P. G. JEFFERY, D. W. DOWNTON and J. D. L. H. WOOD

Wednesday, July 21—Morning

Lecture by A. T. JAMES *Adventures in Chromatography*

Thursday, July 22

Session A—Morning

Titrimetric Quality (Q) of and Feasibility for Symmetrical Ion Combination Reactions having Products of Constant Activity by E. BISHOP

Aminoanthraquinone Indicator Dyes and their Application by I. KRAUSZ and Á. ENDRÖI-HAVAS

Determination of Trace Amounts of Silver with Diphenylthiocarbazone in High-purity Cobalt, Lead, Nickel, Zinc and Other Metallurgical Products by R. CARSON and E. G. WALLICZEK

Determination of Indium by Solvent Extraction Followed by EDTA Titration by J. A. CLEMENTS and T. DAVIES

A Kinetic and Titrimetric Study of Determination of Iron^{II} *with Potassium Bromate* by J. M. OTTAWAY and E. BISHOP

Session B—Morning

Thenoyltrifluoroacetone, a Fluorimetric Reagent for Europium and Samarium by R. E. BALLARD and J. W. EDWARDS

Determination of Commonly Used Non-ionic Detergents in Sewage Effluents by a Thin-layer Chromatographic Method by S. J. PATTERSON, E. C. HUNT and K. B. E. TUCKER

Determination of Total Chlorine Available in Waters by L. S. BARK and H. G. HIGSON

Factors Affecting Formation and Solvent Extraction of Complex of Nickel with Furil α-Dioxime by A. L. WILSON

Determination of Certain Trace Metals in Very Pure Waters by Automatic Analysis by F. A. POHL

Session A—Afternoon

Studies on Nickel^{II} *Dioximes of Analytical Importance* by R. J. MAGEE and L. GORDON

Determination of Microgram Amounts of Osmium with N-(4-Aminophenyl)morpholine by L. S. BARK and D. BRANDON

Control and Assessment of Systematic Errors by Routine Analytical Work by D. L. LYDERSEN

Some Applications of Polarography in Physiological Analysis by R. C. ROONEY

Session B—Afternoon

Construction and Applications of an Electrolytic Hygrometer by H. J. CLULEY and J. E. STILL

Voltammetric Studies with Different Electrode Systems—I: Molybdenum as Reference Electrode in Polarography by V. T. ATHAVALE, S. V. BURANGEY and R. G. DHANESHWAR

Electroanalytical Chemistry of Hot-water Solutions by A. J. ELLIS and G. J. HILLS

Differential Electrolytic Potentiometry—XVII: An Interpretation of DEP as a Linear Diffusion Process by E. BISHOP

Friday, July 23

Session A—Morning

Colorimetric Determination of Vanadate in Presence of Chromate, Molybdate, Tungstate and Nitrate with 4-(2-Pyridylazo)-resorcinol by W. J. GEARY and C. N. LARSSON

Organic-phase Spectrophotometric Determination of Iron^{III} *with Thiocyanate, after Extraction with Di-(2-ethylhexyl)orthophosphoric Acid from Chloride Solutions* by E. CERRAI and G. GHERSINI

Spectrofluorimetric Determination of Microgram Amounts of Scandium with Salicylaldehyde Semicarbazone by G. F. KIRKBRIGHT, T. S. WEST and C. WOODWARD

Automation of Anion-exchange Chromatography of Phosphorus Anoins by F. H. POLLARD, G. NICKLESS, D. E. ROGERS and D. L. CRONE

A Critical Evaluation of Differential Reaction-rate Methods Employed for the Simultaneous Analysis of Closely Related Mixtures—I: First-order and Pseudo First-order Methods by H. B. MARK, jun., R. A. GREINKE and L. J. PAPA

Session B—Morning

A Study of the Mechanism Underlying Separation of Rare-earth Elements by Paper Chromatography by D. I. RYABCHIKOV, G. M. VARSHAL and M. M. SENIAVIN

Encapsulation as a Technique for Determination of Hydrogen in Volatile Metals by F. R. COE, N. JENKINS and D. H. PARKER

Spectrophotometric Determination of Sub-microgram Amounts of Impurities in Semiconductor Materials by J. A. ROBERTS, J. WINWOOD and E. J. MILLETT

Use of Radionuclides to Study Adsorption of Cations on Carboxycellulose Ion Exchangers by E. KORÖS, ZS. REMPORT-HORVATH, A. LASZTITY and E. SCHULEK

A Rapid Method of Determining Soluble Silicates by B. M. MILWIDSKY and S. HOLTZMAN.

British Standards Institution has announced the following *New British Standards* —

B.S. 3338: *Methods for the sampling and analysis of tin and tin alloys.*

Part 9: 1965: *Method for the determination of arsenic in ingot tin, solders and white metal bearing alloys (photometric method).* 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of arsenic in ingot tin, solders and white metal bearing alloys having an arsenic content between 0.01 and 0.3%.

Part 13: 1965: *Method for the determination of antimony in solders and white metal bearing alloys (volumetric: potassium bromate method).* 3*s*. 6*d*. This describes the reagents required, recommended method of sampling and test procedure for the determination of antimony in solders and white metal bearing alloys having an antimony content between 0.2 and 17%.

Part 14: 1965: *Method for the sampling of white metal bearing alloy ingots.* 3*s*. 6*d*. This describes the selection of ingots, preparation of surfaces, method of raking samples by means of sawing and precautionary measures against contamination of the sawings.

Part 15: 1965: *Method for the determination of copper and lead in white metal bearing alloys (electrodeposition method).* 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of copper and lead in white metal bearing alloys having a copper content between 0.1 and 6% and a lead content between 0.1 and 5%.

Part 16: 1965: *Method for the determination of tin in white metal bearing alloys (nickel coil reduction method).* 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of tin in white metal bearing alloys having a tin content between 5 and 90%.

Part 17: 1965: *Method for the determination of cadium in solders and white metal bearing alloys (photometric method).* 3*s*. 6*d*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of cadmium in solders and white metal bearing alloys having a cadmium content up to 0.12%.

B.S. 3630: *Methods for the sampling and analysis of zinc and zinc alloys.*

Part 6: 1965: *The determination of aluminium in zinc alloys (volumetric method).* 4*s*. This describes the reagents required, recommended methods of sampling and test procedure for the determination of aluminium in zinc alloys having an aluminium content in the range 3 to 5%.

The following *Amendment Slips* have also been announced:—

B.S. 812: 1960: *Methods for the sampling and testing of mineral aggregates, sands and fillers. Amendment No.* 3: *PD* 5482. 2*s*. 6*d*.

B.S. 1715: 1963: *Methods of analysis of soaps and soap powders. Amendment No.* 1: *PD* 5478.

UNITED STATES OF AMERICA

Tuesday–Friday 8–11 *June* 1965: **Eighteenth Annual Summer Symposium on Analytical Chemistry—Bioanalytical Techniques:** *Division of Analytical Chemistry, American Chemical Society* and ANALYTICAL CHEMISTRY. University of Wisconsin, Madison, Wis.

The programme is as follows:—

Wednesday Morning, 9 *June*

Structural and chemical organisation of biological materials.	W. B. MASON
Scope and techniques of enzymatic analysis.	M. VANKO

Wednesday Afternoon, 9 *June*

Quantitative histochemical techniques.	D. GLICK
Microelectrophoresis of nucleotides from individually isolated cells.	M. L. MOSS
Microcolumn chromatography of amino acids and small peptides.	P. B. HAMILTON

Thursday Morning, 10 *June*

Starch gel electrophoresis.	O. Smithies
Acrylamide gel electrophoresis.	S. Raymond
Thin-layer chromatography.	H. K. Mangold

Thursday Afternoon, 10 *June*

Symposium on undergraduate chemical research.

Friday Morning, 11 *June*

Double labeling techniques in analysis of biological materials.	N. D. Lee
Iodine-131 *immunochemical assay of peptide hormones.*	J. Roth
Gas chromatographic techniques for biologically important steroids.	H. H. Wotiz

Friday Afternoon, 11 *June*

Direct readout systems in analytical chemistry.	E. A. Boling
Multiple automatic analysis.	L. T. Skeggs, Jr.

Sunday–Friday 13–18 *June* 1965: **Sixth-Eighth Annual Meeting:** *American Society for Testing and Materials.* Purdue University, Lafayette, Ind.

The following parts of the programme may be of interest to analytical chemists:—

SYMPOSIUM ON DETERMINATION OF NON-METALLIC COMPOUNDS IN STEEL

(Sponsored by ASTM Committee E-3 on Chemical Analysis of Metals)

Monday Afternoon, June 14

Isolation, separation and identification of microconstituents in steels	H. Hughes and K. W. Andrews
Application of differential thermal analysis-effluent gas analysis to determination of non-metallic compounds in steel	L. M. Melnick
Identification of inclusions with electron probe microanalyser	K. F. J. Heinrich
Isolation and determination of boron-nonmetallic inclusions in steel	L. C. Pasztor and R. M. Raybeck
Determination of stable oxide inclusions in low alloy steels using a combination of electrolytic and chemical separations	J. P. McKaveney, W. J. Rabar, G. L. Vassilaros and J. M. Snook
Isolation of oxide inclusions from carbon steels, using bromine-methyl acetate	R. M. Raybeck and L. C. Pasztor

SYMPOSIUM ON ANALYTICAL TECHNIQUES AS APPLIED TO HYDRAULIC CEMENTS AND CONCRETE

(Sponsored by ASTM Committee C-1 on Cement)

Tuesday Evening, June 15

Pathology of concrete	Bernard Erlin
Detection and identification of organic additives in cement and admixtures in concrete	W. G. Hime
Quantitative diffraction measurements by fast scanning	R. L. Handy
Substitution of alkali oxides in tricalcium aluminate	D. E. Day
Determination of acetate additions in cement by gas chromatography	A. S. Wexler and J. F. Coburn

SYMPOSIUM ON SOME APPROACHES TO PROBLEMS IN SPECTROCHEMICAL ANALYSIS

(Sponsored by ASTM Committee E-2 on Emission Spectroscopy)

Thursday Morning, June 17

Atomic absorption—problem areas, solutions and direction of future growth	Frederick Brech

Free-atom problem in flame atomic emission and absorption spectroscopy	R. N. Kniseley, W. E. L. Grossman and V. A. Fassel
New trends in atomic absorption instrumentation	Walter Slavin
Thursday Afternoon, June 17	
Unsolved problems in spectroscopy—"sampling"	C. M. Davis
"Unsolved" optical problems in spectrochemical analysis	L. O. Eikrem
Optomising accuracy and precision in DC ARC analysis	A. J. Mittel
Thursday Evening, June 17	
Point-to-plane gap geometry for emission spectrometric analysis of metals and alloys	J. K. Hurwitz
Preparation and excitation of powdered samples for spectrochemical analysis	J. E. Paterson
Spectroscopy of solutions	J. A. Norris
Friday Morning, June 18	
Problems in sampling and excitation of X-rays	K. F. J. Heinrich
Problems in X-ray dispersion and detection.	J. A. Dunne
Computing methods and X-ray fluorescence analysis	A. H. Gillieson

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Recently, to increase the value of certain standard samples to industry, the **National Bureau of Standards Office of Standard Reference Materials** has completed the certification of a number of trace elements; their values have now been added to the previously available certification of analyses covering the main constituents.

The 13 standards involved are 5 *NBS Cartridge Brass Spectrometric Standards* and 8 *NBS White Cast Iron Spectrometric Standards*. Two or more completely independent methods of analysis were employed for the determination of each newly certified element.

U.S.S.R.

Monday–Sunday 12–18 *July* 1965: **Xth International Congress on Pure and Applied Chemistry:** Organised on behalf of *International Union of Pure and Applied Chemistry* by *Academy of Sciences of U.S.S.R.* Moscow [see *Talanta*, 1964, **11**(8), iii].

Talanta, 1965, Vol. 12, pp. i to vii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Monday–Wednesday 4–6 *October* 1965: **Symposium on Industrial Organic Analysis:** *Chemical Institute of Canada, Analytical Subject Division.* Drawbridge Inn, Sarnia, Ontario.

The provisional programme is as follows:

Monday, 4 October

Session I—TRENDS IN INDUSTRIAL ANALYSIS

TRENDS IN INDUSTRIAL ANALYSIS.
Sidney Siggia

CATHODE-RAY POLAROGRAPHY: A NEW INSTRUMENTAL METHOD FOR THE SIMULTANEOUS DETERMINATION OF LEAD STYPHNATE AND TETRACENE IN PRIMER MIXTURES.
H. Zehnder

MODERN TRENDS IN WHISKY ANALYSIS.
W. H. Arison

Session II—ADVANCES IN APPLIED SPECTROSCOPY

ANALYTICAL APPLICATIONS OF LOW FREQUENCY INFRARED SPECTROSCOPY.
J. E. Katon

RECENT TRENDS IN INFRARED SPECTROSCOPY.
W. F. Ulrich

INTERNAL REFLECTION SPECTROSCOPY.
P. A. Wilks, Jr.

COMBINATION OF GAS CHROMATOGRAPHY WITH INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.
E. G. Brame, Jr.

SPECTROSCOPIC ANALYSIS OF RUBBER MATERIALS.
G. Rappaport

Session III—OTHER ANALYTICAL METHODS

ATOMIC ABSORPTION ANALYSIS OF TERPHENYL-TYPE NUCLEAR REACTOR COOLANT FOR IRON IMPURITY.
J. P. Mislan

ANALYSIS OF 4-BIPHENYL AND 4,4′-BIPHENYLDISULPHONIC ACID MIXTURES BY CONTINUOUS ELECTROPHORESIS SEPARATION AND ULTRAVIOLET SPECTROPHOTOMETRY.
N. E. Skelly

N.B.S. ORGANIC STANDARD REFERENCE MATERIALS: PRESENT & FUTURE.
T. W. Mears

ANALYSIS OF ORGANIC MATERIALS CONTAINING INORGANIC ELEMENTS BY THIN-LAYER CHROMATOGRAPHY AND ELECTRON PROBE MICROANALYSIS.
J. C. Barlow, W. F. Traber and R. C. Herrmann

THIN-LAYER CHROMATOGRAPHIC TECHNIQUES APPLICABLE TO INDUSTRIAL ORGANIC ANALYSIS.
E. A. Davies

Tuesday, 5 October

Session IV—CHARACTERISATION OF POLYMERS

EFFECT OF SOLVENT UPON HIGH RESOLUTION NMR SPECTRA OF POLYMERS.
Kermit C. Ramey

COLUMN FRACTIONATION AND DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION OF POLY (α-OLEFINS).
Wolfgang W. Schulz

SOME APPLICATIONS OF THE ULTRACENTRIFUGE TO MOLECULAR WEIGHT DISTRIBUTION STUDIES.
J. M. Hulme and R. M. B. Small

USE OF DIFFERENTIAL THERMAL TECHNIQUES IN POLYMER CHARACTERISATION.
Kenneth Casey

Session V—Panel Discussion "THE ROLE OF CLASSICAL METHODS IN MODERN INDUSTRIAL ANALYSIS"

Wednesday 6 *October*

Session VI—GAS CHROMATOGRAPHY

APPLICATIONS OF LARGE-SCALE PREPARATIVE GAS CHROMATOGRAPHY.
A. J. Martin, L. Mikkelsen and F. J. Debbrecht

DEVELOPMENTS IN ON-STREAM PROCESS GAS CHROMATOGRAPHY.
George S. Turner

INVESTIGATION OF TRACE IMPURITIES IN HELIUM BY GAS CHROMATOGRAPHY.
R. E. Leveque

GAS CHROMATOGRAPHIC ANALYSIS AT CRYOGENIC TEMPERATURES.
D. R. Rushneck (to be presented by P. F. Leigh-Mossley)

DETERMINATION OF ETHYLENE OXIDE IN AIR BY GAS CHROMATOGRAPHY.
T. Dumas

Monday–Wednesday 18–20 *October* 1965: **Twelfth Ottawa Symposium on Applied Spectroscopy.** Ottawa.

ITALY

Tuesday–Friday 20–23 *September* 1966: **Sixth International Symposium on Gas Chromatography.** *Institute of Petroleum, Gas Chromatographic Discussion Group.* Catholic University, Rome.

The Group invites the submission of papers for consideration for inclusion in the proceedings. Papers on the following groups of subjects will be considered:

(a) Principles, Techniques or Novel Applications of Gas Chromatography.
(b) The use of gas chromatography together with other techniques for the solution of analytical problems.
(c) Novel principles and techniques in connection with liquid chromatography or other kinds of chromatography.
(d) Theoretical or experimental studies involving use of or comparison of more than one kind of chromatography.

Abstracts (not more than 500 words long) of proposed papers should be sent not later than January 1st, 1966, to the Editor: Dr. A. B. Littlewood, School of Chemistry, The University, Newcastle upon Tyne, 1, England.

ÖSTERREICH

20.10. bis 23.10. 1965: **Kolloquium für metallkundliche Analyse und Elektronenstrahlmikroanalyse:** Institute für Analytische Chemie und Mikrochemie der Technischen Hochschule, Wien.

UNITED KINGDOM

Friday–Saturday 24–25 *September* 1965: **Meeting on Trace Analysis:** *Society for Analytical Chemistry, Microchemical Methods Group* and *Western Section.* University of Exeter.

The programme is as follows:

Friday, 24 *September*

Morning visit to Marine Biological Station, Plymouth, with lecture on

Current Work on Biophysics and Radioactive Tracer Techniques by	T. I. Shaw

Evening session as follows:

Determination of Micro-Constituents of Sea Water.	F. A. J. Armstrong
Use of Stationary Mercury Drop Electrode for Trace Analysis.	J. F. C. Tyler
Sub-Nanogram Region.	E. Bishop

Saturday, 25 *September*

Afternoon session as follows:

Determination of Trace Contaminants in Peroxygen Compounds.	C. Whalley
Determination of Some Impurities in Beryllium by Differential Cathode-Ray Polarography.	G. C. Goode and J. Herrington
Application of Some Ternary Complexes in Trace Analysis.	R. M. Dagnall
Evening discussion on *Trace Analysis in Aqueous Media* introduced by	L. H. N. Cooper

Tuesday–Wednesday 16–17 *November* 1965: **Symposium on Physical Methods:** *Society of Cosmetic Chemists of Great Britain.* Grand Hotel, Bristol.

The scientific programme will include eleven lectures by authors from Great Britain and Germany, as follows—

Spectrophotometric methods for the rapid evaluation of the inactivation of anti-microbial agents.	M. Brown
Thin-layer chromatographic techniques in residue analysis.	J. Thomson
Particle size analysis using Coulter counters.	R. W. Lines
Infrared spectroscopy of aqueous detergent solutions.	M. A. Puttnam
Spectral slit width and other sources of error in ultraviolet spectrophotometry.	A. R. Rogers
Rheological studies of new cream bases with the Brookfield synchroletric viscometer.	F. Neuwald
Analysis of aerosol propellants.	R. J. Brook and B. D. Joyner
Fluorescent antibody studies in dermatology.	N. R. Rowell
Preparative gas chromatography.	G. R. Fitch
Techniques for assessing the rheological properties of toiletry and cosmetic products.	P. Sherman
The relation between structure and properties in plastics used in packaging.	A. Sharples

Symposium periods will be devoted to discussion of these papers, which will be circulated beforehand to registered participants. Registration forms, together with full details, can be obtained from the General Secretary, Mrs. D. Mott, 18 Warner Close, Harlington, Middlesex.

Wednesday–Friday 14–16 *September* 1966: **Particle Size Analysis Conference 1966:** *Society for Analytical Chemistry.* Loughborough College of Technology, Loughborough, Leicestershire.

Papers and discussions will describe original work in the field covered by the review of *Particle Size Analysis* published in *The Analyst,* 1963, **88,** 156. Critical comparison of methods and descriptions of new techniques will be welcome, but review articles will not be appropriate. Intending authors are asked to submit titles and 100-word summaries of their papers to the Editor of *The Analyst* by 8 November, 1965. Further information may be obtained from the Conference Hon. Secretary, Mr. D. Soul, 14 Belgrave Square, London S.W.1.

The **Society for Analytical Chemistry** has approved the formation of an *Automatic Methods Group*, concerned with "mechanised and automatic methods and equipment in analytical chemistry". Members of the Society may become members of the Group on request to the Secretary of the Society, 14 Belgrave Square, London S.W.1. Those who are not members of the Society may receive notices of the meetings, *etc.*, on application to Mr. D. C. M. SQUIRRELL, Imperial Chemical Industries Ltd., Plastics Division, Bessemer Road, Welwyn Garden City, Herts.

British Standards Institution has announced the following *New British Standard:*
B.S. 3900: *Methods of test for paints.* This includes *Group B: Tests involving chemical examination of liquid paints and dried paint films.*
Part B1: 1965: *Determination of water by the Dean and Stark method* (1s.).
Part B2: 1965: *Determination of volatile matter and non-volatile matter* (1s.).
Part B3: 1965: *Determination of 'soluble lead'* (2s.).

The following *Amendment Slip* has also been announced:
B.S. 1756: *Methods for the sampling and analysis of flue gases: Part* 2: 1963: *Analysis by the Orsat apparatus. Amendment No.* 2: *PD* 5534.

UNITED STATES OF AMERICA

Monday–Thursday 4–7 *October* 1965: **Twentieth Annual Conference and Exhibit:** *Instrument Society of America.* Los Angeles, Calif.

The following part of the programme may be of interest to analytical chemists:

Monday Afternoon, 4 *October—Analysis Instrumentation*

Applications of Electrolytic Titration to Trace Sulphur Analysis in Atmospheric Pollution and Hydrogen Catalytic Reforming.	R. R. AUSTIN
Mass Spectroscopy and Gas Chromatography Correlated for Leak Rate Measurement.	G. R. TALBOTT
Analysis Instrumentation: A Successful Method of Application and Utilisation.	R. S. NEWMAN
An Automatic Tristimulus Colorimeter and Spectrophotometer.	J. H. GARFUNKEL, J. KILLPATRICK and H. G. SPERLING
Design of a Vapour Detector using the Ultraviolet Absorption Principle.	L. N. BOLMGREN and L. L. HILL

Monday–Thursday 4–7 *October* 1965: **Annual Research Equipment Exhibit and Instrument Symposium:** National Institutes of Health, Bethesda, Md.

Monday–Thursday 11–14 *October* 1965: **Seventy-Ninth Annual Meeting:** *Association of Official Agricultural Chemists.* Marriott Twin Bridges Motor Hotel, Washington, D.C.

Tuesday–Thursday 12–14 *October* 1965: **Ninth Conference on Analytical Chemistry in Nuclear Technology:** *Oak Ridge National Laboratory, Analytical Chemistry Division.* Mountain View Hotel and Hotel Greystone, Gatlinburg, Tennessee.

The preliminary programme is as follows:

Tuesday Morning, 12 *October*

Session 1: *ANALYTICAL CHEMISTRY OF THE TRANSURANIUM ELEMENTS*

PREPARATION AND DETERMINATION OF THE TRANSURANIUM ELEMENTS.
Sherman Fried

SOLID STATE COUNTERS FOR IMMEDIATE ANALYSIS DURING COLUMN CHEMISTRY.
James T. Haley, *Robert J. Walker* and *Tommy R. Corbin*

DETERMINATION OF AMERICIUM BY CONTROLLED POTENTIAL COULOMETRY.
René Berger and *G. Koehly*

CONTRIBUTION OF ALPHA-GAMMA AND BETA-GAMMA COINCIDENCES USING A SIMPLE DEVICE TO THE ANALYSIS OF PLUTONIUM-AMERICIUM, NEPTUNIUM-PLUTONIUM, RUTHENIUM-ZIRCONIUM-NIOBIUM MIXTURES.
Raymond Pottier and *René Berger*

THE SRL NEUTRON COUNTER AND ITS ANALYTICAL APPLICATIONS.
H. P. Holcomb and *T. R. Herold*

DETERMINATION OF NEPTUNIUM-239 IN FALLOUT BY GAMMA SPECTROSCOPY.
Seymour Gold and *J. M. Hardin*

Tuesday Morning, 12 *October*

Session 2: *SYMPOSIUM—ROLE OF ANALYTICAL CHEMISTRY IN PURE MATERIALS RESEARCH*

ANALYTICAL REQUIREMENTS OF THE PURE MATERIALS RESEARCHER.
J. W. Cleland

STANDARD REFERENCE MATERIALS: REQUIREMENTS AND AVAILABILITY.
W. W. Meinke

MASS SPECTROMETRY IN PURE MATERIALS ANALYSES.
R. E. Honig

MASS SPECTROMETRY: ACCURACY AND PRECISION STUDIES.
G. H. Morrison

Tuesday Afternoon, 12 *October*

Session 3: *ANALYTICAL CHEMISTRY OF THE TRANSURANIUM ELEMENTS*

ADJUSTABLE α-CONTAINMENT BOX FOR HOT CELLS AND SOME METHODS FOR PURIFICATION AND DETERMINATION OF TRANSURANIUM ELEMENTS.
J. Kooi, J. M. Gandolfo, W. Kraak and *J. C. Post*

SYNTHESIS AND EVALUATION OF SEVERAL POLYAMINOPOLYCARBOXYLIC ACIDS FOR GROUP SEPARATION OF TRANSPLUTONIUM FROM LANTHANIDE ELEMENTS BY SOLVENT EXTRACTION.
R. D. Baybarz

ANALYTICAL SUPPORT FOR THE Am–Cm EXTRACTION PROCESS.
E. K. Dukes

DETERMINATION OF PLUTONIUM AND URANIUM IN CERAMIC FUEL MATERIALS.
V. M. Sinclair, J. L. Drummond and *W. Davies*

USE OF ALCOHOLIC HCl AND HNO_3 ANION COLUMN IN STUDY OF DEBRIS FROM UNDERGROUND NUCLEAR EXPLOSIONS.
Richard J. Morrow

Tuesday Afternoon, 12 *October*

Session 4: *SYMPOSIUM—ROLE OF ANALYTICAL CHEMISTRY IN PURE MATERIALS RESEARCH*

ANALYSIS OF PURE MATERIALS WITH THE ION MICROPROBE SOLIDS MASS SPECTROMETER.
A. E. Barrington

ELECTRICAL TEST METHODS IN PURE MATERIALS ANALYSES.
L. R. Weisberg

PARTICLE ACCELERATORS IN PURE MATERIALS ANALYSES.
R. L. Hahn

REQUIREMENTS OF A GENERAL ANALYTICAL LABORATORY IN PURE MATERIALS ANALYSES.
S. J. Adler

AN ANALYTICAL FACILITY FOR PREPARATION AND STUDY OF ULTRA-PURE MATERIALS.
C. M. Bradford

Wednesday Morning, 13 *October*

Session 5: *ANALYTICAL CHEMISTRY OF THE TRANSURANIUM ELEMENTS*

UNITED STATES TRANSURANIUM RESEARCH PROGRAMME.
A. Chetham-Strode

QUANTITATIVE ELECTRODEPOSITION OF ACTINIDES IN AQUEOUS AND ORGANIC SAMPLES.
M. Y. Donnan and *E. K. Dukes*

ISOTOPIC ANALYSIS OF TRANSURANIUM ELEMENTS BY MASS SPECTROMETRY.
R. E. Eby

DETERMINATION OF LOW CONCENTRATIONS OF URANIUM AND PLUTONIUM BY ISOTOPE DILUTION ANALYSIS AND ALPHA-RAY SPECTROMETRY.
L. C. Nelson, Jr.

ALPHA RADIATION EFFECTS ON CONCENTRATED SOLUTIONS OF LITHIUM CHLORIDE CONTAINING HYDROCHLORIC ACID.
D. A. Costanzo, R. D. Baybarz and *J. E. Bigelow*

Wednesday Morning, 13 *October*

Session 6: *SYMPOSIUM—ROLE OF ANALYTICAL CHEMISTRY IN PURE MATERIALS RESEARCH*

DETERMINATION OF MINUTE QUANTITIES OF SELECTED ELEMENTS IN HIGH PURITY BERYLLIUM.
W. M. Henry and *E. R. Blosser*

APPLICATIONS OF ORNL SPARK SOURCE MASS SPECTROGRAPH TO HIGH PURITY MATERIALS ANALYSIS.
J. R. Sites

EXAMPLES OF ANALYSIS OF HIGH PURITY MATERIALS ON MASS SPECTROGRAPH—ZINC, TANTALUM, PLATINUM, GOLD.
Paul Paulsen

ANALYTICAL CHEMISTRY IN SEMI-CONDUCTOR MATERIALS RESEARCH.
P. F. Kane

SOME APPLICATIONS OF SPARK SOURCE MASS SPECTROGRAPHY TO ANALYSIS OF ALLOYS IN PURE ELEMENTS.
J. C. Franklin and *E. B. Griffin*

APPLICATIONS OF CORNELL UNIVERSITY SPARK SOURCE MASS SPECTROGRAPH.
G. H. Morrison

Wednesday Afternoon, 13 *October*

Session 7: *GENERAL*

THE NATURE OF LIGHT.
J. W. Robinson

MICRODETERMINATION OF NIOBIUM, TANTALUM, TITANIUM, VANADIUM AND ZIRCONIUM IN URANIUM COMPOUNDS.
O. A. Vita and *C. F. Trivisonno*

URANIUM ISOTOPE ANALYSIS BY OPTICAL EMISSION SPECTROSCOPY USING THE JARRELL–ASH 3.4 METER SPECTROMETER.
J. A. Leys and *R. E. Perkins*

A 12-INCH, 90-DEGREE SECTOR, SINGLE FOCUSING MASS SPECTROMETER FOR ANALYSIS OF CORROSIVE GASES.
R. N. Stover, E. G. Kerfoot and *M. M. Michlik*

MASS SPECTROMETRIC ANALYSIS OF BORON TRIFLUORIDE.
J. C. Horton

REVERSED-PHASE CHROMATOGRAPHIC SEPARATION OF RARE EARTHS USING METHYLENEBIS(2-ETHYLBUTYLPHOSPHINE OXIDE) AND METHYLENEBIS-(2-ETHYLHEXYLPHOSPHINE OXIDE) AS STATIONARY PHASES.
J. W. O'Laughlin, G. J. Kamin, J. W. Ferguson and *C. V. Banks*

Thursday Morning, 14 *October*

Session 8: *GENERAL*

ZONAL CENTRIFUGE DEVELOPMENT.
N. G. Anderson

AUTOMATED CARBOHYDRATE ANALYSER.
J. G. Green and *N. G. Anderson*

AUTOMATED NUCLEOTIDE ANALYSER.
N. G. Anderson and *J. G. Green*

CONTINUOUS MOISTURE ANALYSER MONITORS HYDROGEN FLUORIDE OFF-GASES DURING OXIDE REMOVAL AT MOLTEN SALT REACTOR EXPERIMENT.
W. S. Pappas

PHOTON ACTIVATION ANALYSIS.
Jacob Spira

DETERMINATION OF FLUORINE IN PRESENCE OF OXYGEN BY FAST NEUTRON ACTIVATION.
L. C. Nelson, Jr. and *H. Bussell*

A SIMPLE TECHNIQUE FOR RAPID ANALYSIS OF RADIOACTIVE GASES BY LIQUID SCINTILLATION COUNTING.
Mary L. Curtis, Sandra L. Ness and *L. L. Bentz*

ANALYSIS OF CARBON IN SODIUM.
V. M. Sinclair, J. L. Drummond and *A. W. Smith*

Thursday Morning, 14 *October*

Session 9: *SYMPOSIUM—ROLE OF ANALYTICAL CHEMISTRY IN PURE MATERIALS RESEARCH*

ANALYSIS OF HIGH PURITY ALKALI METALS.
S. J. Rodgers

ANALYSIS OF HIGHLY PURIFIED PLUTONIUM METAL.
C. F. Metz

ABSORBANCE SPECTRA OF SINGLE CRYSTALS.
J. P. Young and *G. W. Clark*

APPLICATION OF DIFFERENTIAL CATHODE-RAY POLAROGRAPH TO DETERMINATIONS OF TRACE IMPURITIES IN HIGH PURITY BERYLLIUM.
G. C. Goode and *J. Herrington*

SIMPLIFIED PRECISION COULOMETRY.
E. L. Eckfeldt and *E. W. Shaffer*

Monday–Thursday 18–21 *October* 1965: **Third International Symposium on Advances in Gas Chromatography.** Sheraton-Lincoln Hotel, Houston, Texas.

Tuesday–Thursday 19–21 *October* 1965: **Twenty-Fifth Ananachem Conference.** Embassy Hotel, Detroit, Mich.

Sunday 31 *October–Friday* 5 *November* 1965: **Fifth Pacific Area National Meeting and Fourth West Coast Materials Testing Exhibit:** *Association for Testing and Materials.* Olympic Hotel, Seattle, Washington.

Talanta, 1965, Vol. 12, pp. i to vii. Pergamon Press Ltd.

NOTICES

AUSTRALIA

Monday 31 *May–Wednesday* 2 *June* 1965: **Fifth Australian Spectroscopy Conference:** *Australian Academy of Sciences.* Perth, W. Australia.

CANADA

Wednesday–Friday 26–28 *May* 1965: **Eleventh National ISA Analysis Instrumentation Symposium,** jointly with **Sixth National ISA Chemical and Petroleum Instrumentation Symposium with Section Exhibit.** Sheraton-Mount Royal Hotel, Montreal.

Monday–Wednesday 4–6 *October* 1965: Meeting on **Industrial Organic Analysis:** *Chemical Institute of Canada, Analytical Chemistry Division.* Drawbridge Inn, Sarnia, Ontario.

Sessions are being planned in: Trends in Industrial Analysis; Advances in Analytical Spectroscopy; Characterisation of Polymers. There will be three additional sessions, one of which will be devoted to Gas Chromatography.

Further information may be obtained from R. M. SMALL, Research Department, Polymer Corporation Ltd., Sarnia, Ontario, Canada.

CZECHOSLOVAKIA

IV. Internationaler Polarographischer Kursus

In der Zeit vom 6.9. bis 18.9.1965 veranstaltet das Institut für physikalische Chemie der Karlsuniversität und das Polarographische Institut der Tschechoslowakischen Akademie der Wissenschaften einen Lehrgang in Polarographie. Dieser Kursus besteht aus Vorlesungen über die Grundlagen der Polarographie, die in deutscher Sprache abgehalten werden, und einem entsprechenden Praktikum. Der Lehrgang ist für Hochschulabsolventen gedacht, spezielle Vorkenntnisse der Polarographie sind jedoch nicht Bedingung. Die Zahl der Teilnehmer wird auf 20 begrenzt. Dieser Lehrgang wird vorbereitet unter Schirmherrschaft von Professor Dr. J. Heyrovský, die Vorlesungen und das Praktikum liegen in den Händen von Fachkräften der Karlsuniversität und des Polarographischen Institutes. Die Teilnahmgebühr beträgt Kčs 500.—einschliesslich eines Ausfluges in die Umgebung Prags und eines gemeinsamen Abendessens am Abschlusstage des Lehrganges, Unterbringung in Studentenheimen zu mässigen Preisen wird gewährleistet.

Vorläufige Anmeldungen mit Angabe von Titel, Name und Adresse sind an das Institut für physikalische Chemie der Karlsuniversität, Prag 2, Albertov 2030, bis spätestens 1. Juni 1965 zu richten.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die Unterkommission für Gas-Chromatographie veranstaltet im Mai 1965 in Berlin ihr

V. Symposium über Gas-Chromatographie

Wegen einer Überschneidung hat sich der in früheren Ankündigungen mitgeteilte Termin als ungünstig erwiesen. Die Tagung wurde deshalb auf die Zeit

vom 18. bis 21. Mai 1965

verlegt

Das Symposium steht nicht unter einem speziellen Thema, sondern es sollen gleichermaßen
die Theorie der Trennung,
das Verhalten der flüssig-stationären Phase,
Probleme der Adsorption,
Fragen der Detektion und Auswertung,
methodische Arbeiten und
spezielle Anwendungen der Gas-Chromatographie

behandelt werden. Diese Absicht spiegelt sich in den bereits vorliegenden und weiter unten aufgeführten Vortragsmeldungen wider.

In Anbetracht der zu erwartenden starken ausländischen Beteiligung und der Fülle des vorliegenden Materials scheint es angezeigt, dem V. Symposium über Gas-Chromatographie den Charakter einer Diskussionstagung zu geben. Es sollen daher alle Beiträge als Manuskript gedruckt den Tagungsteilnehmern vor Beginn der Veranstaltung zugesandt werden.

Eingegangene Vortragsmeldungen

Zur Theorie der Trennung

G. Schay

Zum gegenwärtigen Stand der Theorie der Gas-Chromatographie (Hauptvortrag)

O. Grubner und E. Kučera

Ergebnisse der Theorie der statischen Momente und ihre Bedeutung für Gas-Chromatographie

A. Pethö

Bemerkungen zum Begriff der Trennstufe

M. S. Wigdergaus

Über einige Fragen der Theorie der Gas-Chromatographie

Die flüssig-stationäre Phase

H. Kelker

Neue Ergebnisse mit flüssig-kristallinen Schmelzen als stationäre Phasen (Hauptvortrag)

M. Krejči, H. Dubsky, M. Rusek und K. Tesařik

Theoretische Aspekte der Benetzung von Trägern durch Trennflüssigkeit in der Gas-Chromatographie

C. Kehrer, H. G. Struppe und E. Leibnitz

Zum Einsatz polarer Trennflüssigkeiten in Kapillarsäulen

W. Ecknig, H. Rotzsche und H. Kriegsmann

Über Zwischenmolekularkräfte und Auswahl von Trennflüssigkeiten

E. A. Kruglow, K. M. Weißberg und S. I. Abramowitsch

Gebrauch von Pentaerythritäthern in der Gas-Chromatographie als stationäre Phase

F. Falk

Verwendung von Äthylenglykol-γ-Ketopimilatpolyester als GC-Flüssigphase in der Fettchemie

Fragen der Detektion und Auswertung

G. Schomburg

Moderne Detektoren für die Gas-Chromatographie (Hauptvortrag)

O. Piringer und E. Tătaru

Der Elektrolytleitfähigkeitsdetektor, Konstruktion, Arbeitsweise und Anwendung

H. Dubský

Ein Beitrag zu den in der Gas-Chromatographie angewandten Verbrennungsmethoden

J. Leonhardt und H.-K. Bothe

Der Nachweis anorganischer Gase mit dem Argon-Ionisationsdetektor

G. Gnauck und H. Schön

Neue Ergebnisse des Nachweises von permanenten Gasen mit β-Strahlen-Ionisationsdetektoren

S. Matoušek

Argondetektor mit zwei Ausgangssignalen für den Anschluß einer automatischen Auswerteeinrichtung

H.-K. **Bothe**, H. **Hilbig** und P. **Popp**

Die Identifizierung gas-chromatographisch getrennter Substanzen auf Grund ihres Elektronenanlagerungsvermögens

M. **Wurst**

Die gas-chromatographische Analyse von Organosiliciumverbindungen unter Verwendung einer Gasdichtewaage

G. **Garzó** u. a.

Die Anwendung des Flammenionisationsdetektors bei der Analyse von siliciumorganischen Verbindungen

H. **Holzhäuser**

Studien zur quantitativen Auswertung gas-chromatographischer Analysen

Z. **Typlt**

Auswerteeinrichtung für schnellaufende Gas-Chromatographie

G. **Schubert**

Ein volltransistorisiertes Bausteinsystem eines Schwingkondensatorverstärkers und dessen Einsatzmöglichkeiten in der Gas-Chromatographie

B. **Petzelt**

Neuer Universalchromatograph in Bausteinweise

V. **Kusky** und V. **Prochazka**

Erfahrungen mit der automatischen Betriebschromatographie für die Analyse von gasförmigen und flüssigen Produkten

E. **Grimm**

Über Prozeßchromatographie

Beiträge zur Methodik

G. **Guiochon**

Temperaturprogrammierte Analyse mit Kapillarsäulen (Hauptvortrag)

A. A. **Shuchowizki**

Betrachtung zur Vakanto- und trägergaslosen Chromatographie

J. **Novák**, V. **Vašák** und J. **Janák**

Eine neue chromatographische Methode für die Bestimmung der Konzentration von Spurenkomponenten in Gasen

J. **Franc**, F. **Mikeš** und M. **Pikeš**

Identifizierung organischer Substanzen mit Hilfe der Gas-Chromatographie an Hand chromatographischer Septren

K. **Höppner**, U. **Prösch** und H.-J. **Zöpfl**

Präparative Gas-Chromatographie von Methyl- und Äthylzinnverbindungen

M. **Šingliar**

Identifizierung organischer Stoffe durch Hydrierung

W. G. **Bereskin** und A. T. **Swiatoschenko**

Untersuchungen an gefüllten Kapillarsäulen

K. M. **Weißberg** u. a.

Untersuchung der Zusammensetzung der bicyclischen aromatischen Kohlenwasserstoffe mit Hilfe der Gas-Chromatographie und Molekularspektroskopie

F. LANGE, J. ERPENBECK, U. PRÖSCH und H.-J. ZÖPFL

Gas-chromatographische Untersuchuungen über die präparative Gastrennung durch Zirkulardiffusion

Spezielle Anwendungen

M. FILIPESCU u. a.

Die Anwendung der Gas-Chromatographie zur Feststellung des absoluten Alters von Gesteinen nach der Ar-K-Methode

H. SACKMANN, A. LOSSE und J. WILKE

Beitrag zur Gas-Chromatographie der Tetrachloride von Silicium, Zinn und Titan

K. TESAŘIK

Die Bestimmung der Spurenkonzentrationen von COS und CS_2 *in der Atmosphäre*

H. W. SCHULZE und H.-K. BOTHE

Gas-Chromatographie radioaktiv markierter Substanzen

D. A. WIACHIREW

Qualitative und quantitative gas-chromatographische Untersuchung von Verunreinigungen in Methylmetacrylat und in Methylacrylat

M. PETER und L. TORKOS

Gas-Chromatographie Analyse der bei Aromatengewinnungsversuchen entstandenen Extrakte

N. I. LULOWA u. a.

Gas-chromatographische Untersuchungen des durch katalytische Hochtemperaturcrackung erhaltenen Benzins

J. CABAL

Analyse hochsiedender paraffinischer Produkte

A. G. WERESTSCHAGIN

Identifikation und quantitative Bestimmung höherer Fettsäuren durch Verteilungs-Gas-Chromatographie

K. RÜHLMANN und G. MICHAEL

Neue Versuche zur Gas-Chromatographie der Aminosäure-Silylderivate

Probleme der Sorption und Modifizierung

A. V. KISELEV

Die Rolle der geometrischen und chemischen Faktoren der Struktur der Adsorbentien und Träger für die Gas-Chromatographie (Hauptvortrag)

D. A. WIACHIREW

Adsorption und gas-chromatographische Eigenschaften des mit Kalilauge behandelten Kieselgels und dessen Verwendung zur Analyse von Kohlenwasserstoffgemischen

N. P. DIMOV

Chromatographie der leichten Gase auf metallersetzbaren Silikagelen

K. I. SAKODYNSKI

Präparative Trennung auf modifizierten Adsorbenten

G. GNAUCK

Beitrag zur Anwendung von porösen Gläsern in der Gas-Chromatographie

K. D. STSCHERBAKOWA

Einfluß der Dehydroxylierung der Oberfläche breitporiger Silikagele auf das chemische Modifizieren und die Gas-Chromatographie

I. A. Mussaew und P. I. Sanin

Untersucung fester Träger für die Gas-Chromatographie

O. Grubner und R. Vespalec

Die Messung der Sorptionsisothermen von organischen Dämpfen durch eine modifizierte Methode von Glueckauf

H. Beyer und G. Schay

Bestimmung von Adsorptionsisothermen und Oberflächengrößen nach einer modifizierten Sorptiometermethode

E. Smolková, O. Grubner und L. Feltl

Bestimmung kleiner Oberflächen von pulverförmigen Stoffen mit der Methode der Wärmedesorption

O. Piringer und E. Tătaru

Die Anwendung der Gas-Chromatographie zu Chemisorptionsuntersuchungen des Wasserstoffs an Metallen

R. Komers

Untersuchung der Sorption von organischen Verbindungen durch eine dynamische Pulsmethode

L. Feltl, O. Grubner und E. Smolková

Messung der Sorption von organischen Dämpfen an pulverförmigen porosen Sorbenten durch die Methode der frontalen Gas-Chromatographie

Weitere das Symposium betreffende Anfragen richten Sie bitte an die

Unterkommission für Gas-Chromatographie—Sekretariat
705 LEIPZIG, Permoserstraße 15, Deutsche Demokratische Republik

FRANCE

Vendredi 7 *mai* 1965: Journée de Chimie Analytique dans le cadre de l'Assemblée annuelle de la Sociéte Chimique.

Mardi 11 *mai* 1965: **Le phénomène de fluorescence et ses applications analytiques,** par M. R. Bourdon, à 17 h 45, à la Faculté de Pharmacie de Paris.

Mardi 25 *mai* 1965: **L'analyse instrumentale: développements récents. Perspective d'avenir,** par M. J. C. Lefebvre, à 17 h 45, à la Faculte de Pharmacie de Paris.

UNITED KINGDOM

Friday–Saturday 9–10 *April* 1965: **Infrared Spectroscopy:** *Society for Analytical Chemistry, Microchemical Methods Group* and *Special Techniques Group.* University of Sussex, Falmer, Brighton.

The programme is as follows:

Friday Evening

Some Advances and Trends in Infrared Spectroscopy.	D. M. W. Anderson
Study of Chelate Compounds by Infrared Spectroscopy.	R. J. Magee
Infrared Spectroscopy applied to Very Small Quantities.	H. A. Willis

Saturday Morning

Infrared Spectra of Inorganic Materials.	D. F. Evans
Application of Long-path (40m) Gas Cells to Analysis of Atmospheric Pollution.	L. C. Thomas
Infrared Analysis by Attenuated Total Reflectance.	N. A. Puttnam

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Wednesday 14 *April* 1965: **Commercial Absorption Apparatus Meeting:** *Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group.* Sheffield College of Technology, Pond Street, Sheffield 1.

There will be a demonstration of commercial apparatus starting at 10.00 a.m. followed by a discussion at 7.00 p.m.

Tuesday 4 *May* 1965: **Some Problems in Water Conservation,** F. Law and L. R. Bays: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, North Lancashire Section.* Harris Technical College, Preston, 7.15 p.m.

Wednesday 5 *May* 1965: Contributions from Research Workers in Universities and Colleges of Advanced Technology. Bradford Institute of Technology, 2.30 p.m.

Wednesday 26 *May* 1965: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Wednesday 30 *March* 1966: **Symposium on Nuclear Magnetic Resonance and Electron Spin Resonance:** *Society for Analytical Chemistry, Midlands Section* and *Special Techniques Group; Royal Institute of Chemistry, Birmingham and Midlands Section; Society for Chemical Industry, Midlands Section.* University of Birmingham.

Anyone wishing to attend the meeting or to receive further information should communicate with Mr. M. L. Richardson, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30.

Tuesday–Thursday 14–16 *September* 1966: **Conference on Particle Size Analysis.** Loughborough College of Technology, Leicestershire.

Papers and discussions will describe original work in the field.

At the *Annual General Meeting* of the **Society for Analytical Chemistry,** held on Friday, 5 March, 1965, the following were elected Officers and Members of Council for the forthcoming year:

President: A. A. Smales
Past Presidents serving on Council: A. J. Amos, R. C. Chirnside, D. C. Garratt, J. H. Hamence
Vice-Presidents: A. G. Jones, C. Whalley
Hon. Treasurer: D. T. Lewis
Hon. Secretary: S. A. Price
Hon. Assistant Secretaries: B. S. Cooper (programmes), D. W. Wilson

At the *Annual General Meeting* of the **Midlands Section** of the **Society for Analytical Chemistry,** held on Friday, 12 March, 1965, the following were elected Officers for the forthcoming year:

Chairman: W. T. Elwell
Vice-Chairman: H. E. Brookes
Hon. Secretary: M. L. Richardson, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30
Hon. Treasurer: G. Ingram
Hon. Assistant Secretary: R. Adkins

British Standards Institution has announced the following *New British Standards:—B.S.* 3727: *Methods for the analysis of nickel for use in electronic tubes and valves: Part* 11: 1965: *Determination of silicon* 0.001–0.020% (*photometric method*). *Part* 13: 1965: *Determination of titanium* (*photometric method*). For each part of the reagents required, the test procedure and the necessary details are specified for each determination. (*Price:* 4s. each)

The following *Amendment Slips* are also announced:

B.S. 1673: *Methods of testing raw rubber and unvulcanised compounded rubber: Part* 2: 1954: *Methods of chemical analysis. Amendment No.* 5. *PD* 5408.

B.S. 1902: *Methods for testing refractory materials: Part* 2 *A:* 1964: *Chemical analysis of high silica and aluminosilicate materials. Amendment No.* 1. *PD* 5427.

B.S. 3210: 1960: *Methods for the analysis of water-soluble coal-tar dyes permitted for use in foods. Amendment No.* 1. *PD* 5430.

UNITED STATES OF AMERICA

Tuesday–Friday 4–7 *May* 1965: **Spring Meeting,** including **Symposium on Physical and Chemical Testing:** *American Chemical Society, Division of Rubber Chemistry.* Fontainebleau Hotel, Miami Beach, Fla.

Wednesday–Saturday 5–8 *May* 1965: **Sixth International Pulp and Paper Instrumentation Symposium:** *Instrument Society of America.* Hotel Northland, Green Bay, Wis.

Thursday–Saturday 6–8 *May* 1965: **Conference on Purification of Materials.** Waldorf Astoria Hotel, New York City.

Wednesday–Thursday 12–13 *May* 1965: **National Forum on Control of Water Quality:** *American Society for Testing and Materials.* ASTM Headquarters, Philadelphia, Pa.

Sunday–Friday 16–21 *May* 1965: **Thirteenth Annual Conference on Mass Spectrometry and Allied Topics:** *American Society for Testing and Materials, Committee E-*14 *on Mass Spectrometry.* Sheraton-Jefferson Hotel, St. Louis, Missouri [see *Talanta*, 1964, **11**(12) ii].

Wednesday–Friday 25–27 *August* 1965: **Fourteenth Annual Conference on Applications of X-Ray Analysis:** *Metallurgy Division, Denver Research Institute, University of Denver.* Albany Hotel, Denver, Colorado.

Sessions are planned on X-Ray Diffraction, -Emission Spectroscopy, -Microprobe Analysis, -Absorption and Microscopy, -Instrumentation, -Topography and -Small Angle Scattering. There will be special sessions on Soft X-Rays and Effects of Chemical Combination on X-Ray Spectra.

Papers are invited, of which titles and abstracts are due on 16 April.

Thursday–Friday 3–4 *February* 1966: **First Middle Atlantic Regional Meeting:** *American Chemical Society.* Sheraton Hotel, Philadelphia, Pa.

This Meeting will be the first of an annual series, replacing the former Delaware Valley and Metropolitan Regional Meetings. The cosponsoring ACS local sections are Delaware, Lehigh Valley, Monmouth County, New York, North Jersey, Philadelphia, Princeton, South-Eastern Pennsylvania, South Jersey and Trenton.

There will be nine scientific divisions for the presentation of papers, including one on *Analytical Chemistry* (Chairman: Mr. O. I. Milner, Socony Mobil Oil Co.). Further information may be obtained from Dr. Walter Clavan, Pennsalt Chemicals Corporation, Technological Center, King of Prussia, Penna. 19406.

Monday–Friday 9–13 *August* 1965: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire.

The programme is as follows:

Monday, 9 *August*

Applications of NMR to Polymer Structure Determination.	W. M. Ritchey
Cation-Sensitive Electrodes: Theory and Practice.	G. A. Rechnitz

Tuesday, 10 *August*

Applications of Differential Thermal Analysis to Polymers.	B. Wunderlich
General Applications of Differential Scanning Calorimetry.	A. P. Gray
Applications of Differential Thermal Analysis to Non-polymeric Systems.	P. D. Garn

Wednesday, 11 *August*

Modernisation of Microanalytical Methods.	H. Malissa
Use of Group Frequency Shifts in Interpreting Infrared Spectra.	W. J. Potts
Applications of Infrared Spectroscopy to Bio-Medical Analytical Problems.	D. Erley

Thursday, 12 *August*

Advances in Spark Source Mass Spectrometry.	A. J. Ahearn
Open Session.	

Friday, 13 *August*

Analytical Problems in Drug Metabolism Studies.	A. J. Glazko

Further information may be obtained from Dr. W. George Parks, University of Rhode Island, Kingston, Rhode Island.

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NOTICES

DENMARK

Saturday–Friday 14–20 *August* 1965: **Eighth European Congress on Molecular Spectroscopy:** *Dansk Forening for Molekylspektroskopi.* H. C. Ørsted Institute, Copenhagen, Denmark [see *Talanta,* 1965, **12**(3), i].

PUERTO RICO

Sunday–Sunday 1–8 *August* 1965: **IX Latin American Chemical Congress.** San Juan, Puerto Rico. One section of the Congress is devoted to Analytical Chemistry.

UNITED STATES OF AMERICA

Monday–Friday 2–6 *August* 1965: **Second Instrument Society of America Research Conference on Instrumentation Science.** William Smith College, Geneva, N.Y.

Monday–Friday 9–13 *August* 1965: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire [see *Talanta,* 1965, **12**(4), vii].

Sunday–Friday 22–27 *July* 1965: **1965 International Symposium on Microchemical Techniques:** *American Microchemical Society* with sponsorship of *I.U.P.A.C., Commission on Microchemical Techniques, Division of Analytical Chemistry.* Pennsylvania State University, University Park, Pennsylvania.

The following lectures will be presented:

Plenary Lectures

P. Elving	*Microchemistry: The Present and the Future*
H. A. Flaschka	*Photometric Titrations*
O. Kovaćs	*Techniques in Organic Microsynthesis*
M. Kuhnert-Brandstätter	*Present Status and Future of Chemical Microscopy*
P. L. Kirk	*Recent Microtechniques in Forensic Science*
T. Mitsui	*Organic Microanalysis in Japan—Past and Future*
E. Sawicki	*Identification and Determination of Unusual Functional Groups*

Session Speakers and Topics

C. Baret	*Purification of C-14 Labeled Compounds by Preparative Gas Chromatography*
M. T. Beck	*Determination of Mercury(II) Based on Catalytic and Inhibition Effects*
R. Belcher and G. Ingram	*Some Observations on Microdetermination of Oxygen in Organic Materials*
G. Bernath	*Experiences in Teaching Theory and Practice of Organic Micropreparative Technique*
F. Bermejo-Martínez	*Photometric Determination of Copper with DTPA*
A. G. Blas	*Spectrophotometric Determination of Chromium with DTPA*
L. I. Braddock	*Use of Reflectance Spectra for Estimation of Barbiturates by Spot Test Techniques*
L. Brancone	*Applications of Differential Thermal Analysis in Examination of Synthetic Organic Compounds*
W. B. Burton	*Microsynthesis of Radioactive Vinyl Phosphates*
K. L. Cheng	4,4′-*Bis(dimethylamino)thiobenzophenone as a Sensitive Reagent for Mercury and Palladium*
F. W. Cheng	*Microdetermination of Oxyethylene Groups in Glycols and Ethylene Oxide Adducts*

C. W. Childs	*A Study of the Pregl Carbon-Hyarogen Determination*
P. Close	*Potentiometric Titration of Micro Amounts of Iron(II) with Very Dilute Cerium(IV) Sulphate*
R. Condon	*A New Automatic Organic Elemental Microanalyser*
J. Corliss	*A Flexible Procedure for Karl Fischer Microtitrations*
G. Crossman	*Some Macro and Microscopic Applications of Dispersion Staining as Applied to Industrial Hygiene and Air Pollution*
S. S. Cruikshank	*Oxygen Determination on Compounds Containing Loosely Bound Water or Volatile Solvents*
A. K. Dey	*Chromotrope 2B as a Chromogenic Reagent for Photometric Determination of Rare Earths*
H. Diehl	*Further Work on Nature and Uses of Calcein*
M. Dimbat	*Use of Pyrolysis Gas-Liquid Chromatography for Determination of Submicrogram Quantities of Polymer*
M. I. Fauth	*Microdetermination of Nitrogen in Explosives*
R. W. Fennell	*Analysis of Organic Materials on Centrigram Scale: Mechanisation, Instrumentation, and Automation of Laboratory Analysis*
J. Fildes	*Submilligram Determination of Sulphur in Organic Compounds by Hot-Flask Combustion Method*
M. Fujimoto	*Detection of Minute Amounts of Tungsten with Ammonium Thiocyanate and Tin(II) Chloride Using Anion-Exchange Resin Beads*
L. W. Gamble	*Comparison of Two Rapid Techniques for Determining Molecular Weight Distribution of Polymers*
C. Georgescu	*Protein and Amino Acid Metabolic Disturbances in Certain Collagen Diseases*
H. W. Gerarde	*Unopette System in the Clinical Laboratory*
C. E. Gleit	*Recovery and Chemical Analysis of Submicrogram Particles*
G. Gorbach	*Methods of Microchromatography on Torsion Balances of High Efficiency*
B. W. Grunbaum	*A Self-Contained and Portable Microchemical Laboratory*
W. Guldner	*Flash Pyrolysis—A Demonstration*
G. M. Gustin	*New Absorption-Weighing Techniques for Micro Carbon and Hydrogen Methods*
J. B. Headridge	*Polarographic Determination of Lead in Steels and High-Temperature Alloys*
G. E. Heinze	*Determination of Menthol in Lozenges by Gas Chromatography*
R. Hofstader	*Application of the "Auto-Analyzer" to Automation of Some Microchemical Procedures: Microdetermination of Trace Quantities of Organic Chloride by a Micro Coulometric Technique-Application to Low Boiling Liquids*
A. Holasek	*A Continuous Recording of Colloidal Substances Passing Separation Columns, A High Precision Weighing Pipette for Milliliter Amounts*
Z. Holzbecher	*Fluorimetric Determination of Scandium and Gallium with Derivatives of Salicylaldehyde*
F. D. Houghton	*Thin-Layer Chromatographic Methods Applied to Inorganic Microanalysis*
K. Hozumi	*An Instrumental Method for Simultaneous Microdetermination of Carbon, Hydrogen, and Nitrogen*
L. K. Hunt	*Pyridylalpyridylhydrazine, A New Reagent for Cobalt*
S. S. Israelstam	*A Rapid and Simple Semimicro Method for Determining Carbon and Hydrogen in Organic Compounds*
S. Jacobs	*Determination of Amino Acids in Food Hydrolysates Using a Stabilised Indanetrione Hyrdate Reagent*
S. Jarmell	*A New Low Cost Differential Thermal Analyser*
J. Jordan	*Micro-calorimetric Titrations and Injection Enthaplimetry*
J. Kabara	*Occurrence of Natural and Artificial Methyl Esters in Lipid Extracts*
W. Kemula	*Application of Chromatopolarography to Analysis of Mixtures of Organic Compounds*
G. Kainz	*Determination of C-14, H-3, and S-35 after Combustion of the Organic Sample at a System of Nozzles*
M. T. Kelley	*Controlled-Potential Polarography and Coulometry as Micro Analytical Techniques: Determination of Trace Quantities of Uranium by Controlled-Potential DC Polarography of a Trioctyl Phosphine Oxide Extract*
W. J. Kirsten	*Ultramicro Determination of Phosphorus*

D. Liederman	*A Modified Wickbold Combustion Apparatus for Determination of Sulphur in Liquid Hydrocarbons*
T. S. Ma	*Micro Separation and Determination of Isomeric Phenolic Compounds*
L. Machherndl	*A Statistical Study of the Oxygen-Filled Flask Methods for the Determination of Halogen, Sulphur and Phosphorus in Organic Samples*
R. J. Magee	*Determination of Trace Amounts of Nickel in Presence of Large Amounts of Associated Elements by Colloid Absorption Spectrophotometry*
H. K. Mangold	*Thin-Layer Chromatography as an Analytical and Preparative Tool in Lipid Radiochemistry*
R. K. Maurmeyer	*Microdetermination of Primary Amino Groups*
W. C. McCrone	*Devices for Dispersion Staining, A Demonstration: Micro Melting Points*
C. D. Miller	*A New High Speed Analyser for Accurate Determination of Carbon and Hydrogen*
O. I. Milner	*Application of Atomic Absorption Spectroscopy to Trace Analysis of Petroleum*
G. Müller	*Automation of the Kinetic* V_2O_5 *Determination*
S. Natelson	*Instrumentation for Concentrating Trace Components of a Mixture for Gas Chromatography: Determination of Ethanol, Methanol, and* 2-*Propanol in Blood*
E. Pell	*Recent Results in Relative Conductometric Elemental Microanalysis*
F. H. Pollard	*Critical Examination of Use of Thin-Layer and Paper Chromatography of Inorganic Compounds, Especially Species of Phosphorus and Sulphur*
A. Ringbom	*A Spectrophotometric Method for Simultaneous Determination of Small Amounts of Magnesium and Calcium*
R. C. Rittner	*Simultaneous Microdetermination of Carbon, Hydrogen, and Sulphur*
Roth, M.	*Light-Scattering Techniques in Use in Biological Microchemistry*
C. A. Rush	*Microdetermination of Molecular Weight by a Modified Signer Method*
F. Salzer	*General Range of Application of Rapid Combustion Apparatus with Electric Indication for Determination of Carbon and Hydrogen*
E. Sawicki	*Chromatographic Separation and Spectral Analysis of Polynuclear Aromatic Amines and Heterocyclic Imines*
H. F. Schaeffer	*Chemical Microscopy of the Platinum Metals and Gold: Reactions with Acridine and* 1-*Adamantanamine*
H. H. O. Schmid	*Characterisation of Organic Compounds by Their Critical Solution Temperatures*
G. Schneider	*Microscale Synthesis of Some Substituted* 1,3-*Dioxenium*
E. Seoane	*Demonstration of Functional Groups in Indole Compounds by Microscale Reactions*
R. M. Silverstein	*Spectrometric Identification of Organic Compounds in the Milligram Range*
W. Simon	*Structural Elucidation with a Thermal Fragmentation—Gas Chromatography—Mass Spectrometry Combination Thermoelectric (Vaporometric) Determination of Molecular Weight on* 0·001 M *Solutions: A New Detector for Liquid Chromatography*
H. Spitzy	*A New Type of Radiometric Titration: Redox and Chelometric Microtitrations: Separation and Determination of Thyroid Hormones in the Nanogram Range by means of the Sorption Properties of Sephadex*
A. Strickler	*Continuous Micro-fractionation of Particle Mixtures by Electrophoresis*
W. Stuck	*Determination of Micro Quantities of Carbon in Aqueous Phases by a Differential Conductometric Method*
L. Szekeres	*Determination of Arsenic(III) Compounds by Precipitation Titration*
M. L. Tefft	*Improved Combustion Techniques for Microdetermination of Nitrogen in Organic Compounds with an Automatic Analyser*
C. Tiedcke	*Micro Carius Bombtube Method*
R. D. Tiwari	*Determination of Acetic Anhydride in Presence of Acetic Acid*
G. Toelg	*Methods of Organic Elemental Analysis with Microgram Amounts of Sample*
K. Ueno	*Application of a Zone Refining Technique to Inorganic Microanalysis*

M. Večeřa	*Study of Some Basic Reactions Used in Organic Analysis'*
J. R. Wagner	*A Technique for Microdetermination of Melting and Boiling Points*
W. Walisch	*An Automatic Submicro Method for Determination of Alkoxyl Content Ultra Micro C—H—N Analysis with Liquids and Hygroscopic Solids*
J. Wiberley	*Chemistry in Capillaries*
C. L. Wilson	*Teaching for Instrumentation*
M. Zamfirescu-Gheorghiu	*Ceruloplasmine Clinical Analysis: Characterisation After Microelectrophoresis and in Specific Immune Precipitates*
J. Zýka	*Microtitrations with Iron(II) Sulphate in Alkaline Solutions of Triethanolamine*

Monday 30 *August–Friday* 3 *September* 1965: **Fourth National Meeting of Society for Applied Spectroscopy.** Denver Hilton Hotel, Denver, Colo.

Activation Analysis

Use of neutron-activation analysis to determine trace elements in hair:	L. C. Bate and F. F. Dyer
Some recent measurements in applicability of neutron-activation analyses to detection of variations in abundances of stable isotopes:	James T. Corless
Requirements for activation analysis research laboratories:	D. E. Wood
Precision neutron-activation analysis of zinc and titanium oxides in organic coating pigments	V. L. Eggebraaten and L. E. Miller

Arc-Spark

Applications of microspark emission spectrography	Leo. J. Garbini, John B. Mooney and Carl Schoder
Evaluation of vacuum cup electrode system for spectrochemical analysis of solutions:	L. Zane McCulley
A comparison of performance and characteristics of accurately timed spark and of internal voltage stabilised spark as spectrochemical light sources:	A. Strasheim and I. K. A. Kovacs
Design, adjustment and operation of an off-axis Schmidt spectrograph for plasma applications:	Eugene B. Turner and E. John Eastmond
Spectroscopic properties and some analytical applications of an induction-coupled plasma discharge:	Richard H. Wendt and Velmer A. Fassel
A device for measuring spectral line widths:	Paul R. Barnett
Our present understanding of transition probability for optical transitions:	Ray Hefferlin
Determination of lead in whole urine by emission spectrography:	Richard L. Kuntz
Determination of colour temperatures of commercial flashbulbs by emission spectrographic techniques:	D. J. Bracco and S. Weisberger
Thermography of spectroscopic electrodes	C. J. Leistner and G. T. Sermon
An automatic discriminating print-out system for quantometric analysis:	John W. Theiring and Charles E. Pepper
Determination of organically bound arsenic in surface waters—wet chemical versus spectrographic:	Jon F. Koop, Morris E. Gales and Donna Lee Ferris
Spectroscopic properties of arcs of extreme power density:	F. Walter

Atomic Absorption

Selection of wavelengths for atomic absorption spectroscopy:	Marvin Margoshes
Partial analysis of rocks by atomic absorption:	Charles Banks Belt, Jr
Atomic absorption methods for analysis of natural waters:	Marvin J. Fishman

Atomic absorption determination of strongly emitting elements: Robert O. Brace

Spectral references in atomic absorption spectrometry: S. R. Koirtyohann and Edward E. Pickett

Atomic absorption analysis of caesium in graphite: C. W. Gullikson, R. W. Lamb, and D. W. Seegmiller

Extension of atomic absorption limits: W. Slavin

Atomic absorption behaviour of rhenium: W. G. Schrenk, D. A. Lehman and Lorin Neufeld

A comparison of automated calcium determinations by atomic absorption spectroscopy and colorimetric analysis: Paul P. Waring, Richard S. Harding, Jack A. Moorman and Zigmund S. Ziporin

Chromatography

Gas chromatographic behaviour of polar solutes on polar substrates: Paul Urone and Jon F. Parcher

Trace elements in NBS standards as determined by radiochromatography: George A. Welford, Robert S. Morse and Elias L. Chiotis

A study of the reaction between magnesium and potassium chlorate using gas chromatography and thermonanalysis: Francis R. Taylor and Clement Campbell

Performance of a universal, recording detector for liquid-elution chromatography: Richard E. Poulson

A new type of argon-ionisation, helium-electron capture detector for gas chromatography: K. F. Sporek

DTA TGA

Differential thermal analysis of polymers: C. F. Courtney, R. M. Curlee, D. Richard Anderson and J. M. Holovka

Calorimetric measurements by differential thermal analysis: I. M. Sarasohn

Rapid determination of specific heats by differential scanning calorimetry: Michael J. O'Neill

Thermal decomposition studies of propellants using differential thermal analysis: Jack M. Pakulak, Jr

Direct measurement of thermal diffusivity: Erwin L. Dosch

General

Separation and identification of basic nitrogen compounds in Wilmington petroleum by use of chromatography and NMR, UV, MASS and IR spectroscopy: C. F. Brandenburg and D. R. Latham

Application of spectroscopy in polymer research: Max Kronstein

Contamination analysis in aerospace systems: Russell G. Lundy

Infrared

Infrared spectra of new terpenes and terpene alcohols: Bernard M. Mitzner

Infrared spectra of two crystal forms of 1,3-*poly*-3-*methyl*-1-*butene:* J. J. Elliott and J. P. Kennedy

Far infrared studies of hydrogen bonding: R. J. Jakobsen and J. W. Brasch

Infrared spectra of hydroxy-bridged copper(II) compounds: John R. Ferraro and W. R. Walker

Effect of oxidation on morphology of hexagonal polyoxymethylene by X-ray diffraction and infrared spectrophotometry: Louis B. Jassie and Paul G. Kelleh

A study of hydrogen bonding by far infrared spectroscopy: R. E. Witkowski, G. L. Carlson and W. G. Fateley

*Infrared spectra of polybutene-*1 *polymorphs:* J. P. Luongo and R. Salovey

A method for continuous analysis of unsaturates in motor vehicle emissions: E. W. Lard, H. A. Brown and R. L. Thrift

Low-frequency infrared spectra of unsaturated carbonyl compounds: W. R. Feairheller and J. E. Katon
Analysis of a double base solid propellant: Irwin D. Smith
Minerals in the far infrared: Teddy L. Barber
Infrared spectrum of deuterated toluene: M. C. Goldberg and R. L. Wershaw
High sensitivity infrared analysis for detection of glycol and glycol degradation products in lubricants: Brenton H. Madison

Laser and Electron Probe

Electron microprobe applications to glass technology: William P. Whitney
Recent developments in electron probe microanalysis: Arno Arrak
Corrections for interelement effects in electron probe microanalysis: G. R. Lachance and R. J. Traill
Applications of microprobe in technical and service laboratory: H. T. Dryer and V. E. Shull
Recent advances in scanning electron probe microanalysis: P. W. Wright and I. K. Openshaw
Quantitative investigation with electron microprobe of exsolution, mantling and zoning in calcium, magnesium, iron, aluminium silicates: Paul W. Weiblen and Glen R. Himmelberg
Electron probe analysis in a service laboratory: Selby E. Summers
Microprobe examination of irradiated nuclear fuel materials: William F. Zelezny
Electron probe analysis of coatings for columbium base alloys: P. Lublin and W. J. Sutkowski
A new electron microprobe microanalyzer: H. B. Merrill, Jr
Affects of metal constituents of carbides and oxides on carbon and oxygen X-ray intensities: D. E. Fornwalt and A. V. Manzions
High performance organic mass spectrometer, modified CEC 21–103C: A. L. Burlingame and F. C. Walls
Response of photographic emulsions to photons and kilovolt-energy charged particles: J. M. McCrea
On the problem of selective vaporisation in spark source mass spectrography: W. Reuter and J. D. Kuptsis
Appliication of a dual emulsion technique in spark source mass spectrography: W· Reuter and J. C. Webber
Ionisation probabilities in a spark source mass spectrometer: Arthur J. Socha and Robert K. Willardson
Analysis of surface layers by spark source mass spectrometry : Thomas H. Briggs

Microwave

Applied microwave spectroscopy: R. H. Bauhaus and H. W. Harrington
Applications of microwave spectroscopy in aerospace life support research: W. F. White

NMR EPR

Manganese(II) interactions in KF Wm. J. Veigele
EPR and NMR data analysis using digital computers: J. R. Singer
NMR spectra of pyridines found in shale oil: F. R. McDonald and G. L. Cook
NMR study of solvent-solute interaction between Lowry-Bronsted bases and aliphatic alcohols: C. A. Glass

Raman

Applications of lasers in raman spectroscopy: S. P. S. Porto
Sample techniques and problems in laser excitation of raman spectra: R. C. Hawes, D. C. Nelson and K. P. George

UV Visible

An automated ultraviolet spectrophotometric method for determination of lactic acid by enzymatic assay: Jack A. Moorman and Richard S. Harding

Accessories for a new precision spectrophotometer	James J. Chisolm
Performance evaluation of spectrophotometer:	W. Kaye
A multiple purpose flame accessory for UV visible spectrophotometers:	Juan Rameriz-Munoz, August Hell and Norman Shifrin
Identification of some anthraquinone derivatives by flourescence spectrometry:	Francis R. Taylor and David A. Anderson
Flourescence spectroscopy: progress in 1964:	Hugh K. Howerton
Diffraction of a diverging beam:	Ellis E. Whiting
A new moving-object scanning spectrometer for ballistic-range radiometry:	Ellis E. Whiting

X-Ray Emission and Absorption

Semimicro X-ray fluorescence techniques as applied to geochemical problems:	Harry J. Rose, Jr and Frank Cuttitta
Determination of total bromine in brines by XRF:	Polly J. Dunton
Detectors for soft X-rays:	W. L. Baun and D. W. Fischer
Applications of an X-ray pulse spectroscope:	L. Seifert and George A. Brown
Rapid analysis with X-ray polychromators:	E. Davidson, A. W. Gilkerson and W. G. Shequen
Absorptiometry with beta-excited X-ray photons:	L. E. Preuss and C. Mizgala
A compilation of X-ray spectra of the beta-excited source:	L. E. Preuss and C. Mizgala
Energy dispersion for quantitative X-ray spectrochemical analysis—I: mathematical technique:	R. J. Labrie, J. W. Criss and L. S. Birks
Energy dispersion for quantitative X-ray spectrochemical analysis—II: experimental results:	L. S. Birks, R. J. Labrie and J. W. Criss

Symposium: Geologic Applications of Mass Spectrometry

High resolution mass spectrometry: application to organic geochemistry:	A. L. Burlingame and Pat Haug
Measurement and application of delta C^{13} values by ratio mass spectrometry:	Doris Hulse

Symposium: Spectroscopy of Nuclear Materials

X-ray absorption edge determination of plutonium in nitric acid solutions:	E. A. Hakkila, R. G. Hurley and G. R. Waterbury
Emission spectrochemical analysis of high-purity plutonium by the anion exchange-graphite spark technique:	James F. Murphy
Spectrochemical determination of yttrium in tantalum and tantalum-tungsten alloys:	Oliver R. Simi
Rare earth analysis by a rotating platform silver spark technique:	T. R. Lyon
Present status of description and analysis of optical spectra of uranium:	David W. Steinhaus
The determination of silicon in plutonium:	Roy Ko

Smyposium: Application of Spectroscopy to Semiconductor Materials

Analysis of semiconductors by spark source mass spectrometry:	A. J. Ahearn
Determination of epitaxial film thickness using an IR ellipsometer:	A. Ray Hilton and Charlie E. Jones
Determination of composition of epitaxial III–V alloys by reflection spectroscopy:	Charlie E. Jones, Jr
Quantitative trace analysis in submicrogram region: NBS plans for standard reference materials:	W. Wayne Meinke

Symposium: Time-Resolved Spectroscopy

Correlation of temperatures and third partner effects in time resolved spark discharges:	A. Strasheim, L. Krauss and A. J. Boettcher
Combustion of Zirconium droplets studied by flash heating and time-resolved spectroscopy:	L. S. Nelson

A multiple scan rapid spectrograph:	Ronald A. Hill
Time-resolved spectroscopy of air fluorescence produced by a high-altitude nuclear explosion:	S. Stone, H. Hoerlin and D. R. Westervelt
A new electromechanical shutter for time-resolved spectroscopy using the induction force principle:	Paul A. Kendall
Time-resolved spectroscopy in the far-vacuum ultraviolet (100–500Å)*:*	N. J. Peacock, G. A. Sawyer and K. S. Thomas
Study of fast gas reactions by high resolution absorption spectroscopy and flash photolysis:	Rolf Engleman, Jr
Applications of time-resolved spectroscopy to spectrochemical analysis:	Harold M. Burnett

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Wednesday–Friday 25–27 *August* 1965: **Annual Denver Research Institute X-Ray Conference.** Denver, Colorado.

Wednesday–Saturday 25–28 *August* 1965: **Twenty-Third Annual Meeting:** Electron Microscopy *Society of America.* Statler-Hilton Hotel, New York City.

Sunday 29 *August–Thursday* 2 *September* 1965: **Seventeenth Annual Meeting:** *American Association of Clinical Chemists.* Sheraton-Park Hotel, Chicago, Ill.

Monday 30 *August–Friday* 3 *September* 1965: **Fourth National Meeting:** *Society for Applied Spectroscopy.* Denver-Hilton Hotel, Denver, Colorado.

Monday–Tuesday 27–28 *September* 1965: **Fifth Informal Conference on Vacuum Microbalance Techniques.** *The Nassau Inn,* Palmer Square, Princeton, N.J.

Papers are invited on the following topics: Theory, New Types of Balance, Difficulties, Associated Equipment, Other Microweighing Methods, Applications. Title and abstract of about 150 words must be submitted by 30 July to Dr. Klaus H. Behrndt, Bell Telephone Laboratories, Murray Hill, N.J.

This Conference immediately proceeds the **Twelfth National Vacuum Symposium** [see *Talanta,* 1965, **12**(5), iii].

Monday–Thursday 11–14 *October* 1965: **Seventy-Ninth Annual Meeting:** *Association of Official Agricultural Chemists.* Marriott Motor Hotel, Twin Bridges, Washington, D.C.

Plans are underway to have six noted scientists give key addresses on such topics as statistics, modern instrumentation, laser beam applications, and organoleptic techniques. Over 200 other scientific papers on analytical methods will be presented on a variety of topics, including antibiotics, cosmetics, drugs, feeds, food additives, fertilisers, sanitation analysis, microbiological assays and flavous.

Additional information is available from Luther G. Ensminger, A.O.A.C., Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

Monday–Friday 21–25 *February* 1965: **Seventeenth Pittsburgh Conference on Analytical Chemstry and Applied Spectroscopy.** Penn-Sheraton Hotel, Pittsburgh, Pennsylvania.

About 250 papers on all phases of analytical chemistry and spectroscopy will be presented. Symposia on the following subjects are being arranged:

1. Combined gas chromatographic-mass spectrometric techniques.
2. Fast reaction kinetics.
3. Electron spin resonance.
4. Electron microprobe.
5. Process control X-ray spectrometry.
6. Atomic absorption.
7. Coblenz Society Symposium.
8. Gas chromatography utilising pyrolytic techniques.
9. NMR spectra of polymeric materials.
10. Nuclear magnetic double resonance.
11. Magnetic optical rotatory dispersion.
12. Analytical instrumentation in the space programme.
13. New instrumentation techniques.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed in the programme. Three copies of this abstract, with a letter listing the names of the authors, *etc*., should be addressed to Dr. R. E. Hein, Mellon Institute, 4400 Fifth Avenue, Pittsburgh, Pennsylvania, 15213. The final date for receipt of abstracts is 1 *October*, 1965.

U.S.S.R.

Monday-Sunday 12–18 *July* 1965: **XXth International Congress of Pure and Applied Chemistry:** *Academy of Sciences of U.S.S.R.* on behalf of *I.U.P.A.C.* Moscow State University.

The programme for the **Section on Analytical Chemistry is as follows:**

Tuesday Morning, 13 *July—Physical and Physicochemical Methods of Analysis*

Use of atomic spectroscopy for solving problems of automation of analysis.	B. V. L'vov
Determination of some heavy metals by atomic absorption spectroscopy.	L. Erdey and G. Svehla
Spectroscopic observations on the interconal zone of pre-mixed, fuel-rich, oxyacetylene flames.	V. A. Fassel, R. N. Kniseley, V. M. Mossotti, T. C. Cowley and D. Golightly
Atomic absorption spectrophotometry using metal complexes in organic solvents.	S. Gomiŝćek and H. Malissa
Investigations of the mechanism of the effect of certain organic reagents in flame spectrophotometry.	I. A. Voinovitch, M. Hameau, J. Legrand and L. Katz
Use of bisolvents in atomic absorption spectroscopy.	J. W. Robinson

Tuesday Morning, 13 *July—Methods of Separation and Concentration of Elements*

Systematic analysis by solvent extraction.	R. Chalmers
Extraction of some tervalent metal chlorides by tertiary and quaternary amines.	A. S. Kertes, G. Scibona, J. F. Byrum, K. Kimura, S. Basol and J. W. Irvine, Jr.
Solvent extraction studies with 2-*thenoyltrifluoracetone.*	A. De
Concentration and separation of indium, gallium, thallium, antimony and bismuth by extraction with alkyl phosphoric acids.	I. S. Levin, A. A. Shatalova, T. G. Azarenko, I. A. Vorsina and N. A. Burtovaya
Distribution constants of certain 8-*quinolinols and their copper chelates in a series of solvent pairs.*	H. Mottola and H. Freiser
Estimation of heterogenous extraction constants by an indirect way.	H. Specker
Solvent extraction of chelate compounds of elements with 1-*phenyl*-3-*methyl*-4-*benzoylpyrazolone*-5.	Yu. A. Zolotov, V. G. Lambrev, M. K. Chmutova and N. T. Sizonenko
On the role of the hydrogen bond in alkylamine extraction processes.	V. M. Vdovenko and A. A. Lipovsky

Wednesday Evening 14 *July—Physical and Physicochemical Methods of Analysis*

Use of spectral methods for determination of isotopic composition in analytical chemistry.	A. N. Zaidel
Some applications of the d.c. plasma jet to analysis, with special reference to the elimination of matrix effects.	M. S. W. Webb
On the concept of analytical accuracy.	S. M. Raysky
Sensitivity increase of direct spectral analysis.	Yu. I. Belyaev, L. M. Ivantsov, B. I. Kostin and V. V. Shemet
On the problem of increase in sensitivity of emission spectral analysis.	V. V. Nedler
Some techniques for raising the sensitivity and precision of emission spectral analysis.	Ya. D. Raikhbaum
Investigation of the scintillation method of spectral analysis.	Yu. I. Stakheyev
Application of some radar methods for increasing the sensitivity of emission spectral analysis.	V. I. Maslov

Wednesday Evening, 14 *July—Organic Reagents in Analytical Chemistry*

Hydrogen bridges and donor π-bond in the salicylaldoxime complexes of transition metals: Effect of electrophilic and nucleophilic substituents.	K. Burger, F. Ruff, I. Ruff and I. Egyed

New spectrophotometric inorganic reagents of very high selectivity and sensitivity.	T. S. West
Complex salts of 8-*mercaptoquinoline and its derivatives*	Yu. A. Bankovski and A. F. Yevin'ch
Influence of substituents on properties of metal reagents with phenolic hydroxyl groups.	G. Ackermann and D. Hesse
Analytical application of arsenazo III and its analogues—2,2-*bis-azo-derivatives of chromotropic acid.*	S. B. Savvin
Some new analogues of arsenazo III.	B. Budešinsky

Wednesday Evening, 14 *July—Methods of Separation and Concentration of Elements*

Separation procedures for substoichiometric determination of traces of metals.	J. Růžička, J. Starý and A. Zeman
The method of concentration-dependent distribution in the use of radioisotopes in quantitative analysis.	M. Kyrs
Concentration and separate determination of alkaline earth elements with azo-azoxy compounds.	F. P. Gorbenko
Separation and purification of protactinium-231 *and* -233.	A. V. Davydov, B. F. Myasoedov, Yu. P. Novikov, P. N. Paley and E. S. Palschin
Diagrams of distribution and separation on extraction.	A. V. Nikolaev
Anion exchange in acetate buffer medium: Adsorption and separation of some metallic elements, especially uranium(VI).	B. Tremillon and M. Vaissiere
Investigation of ion-exchange chromatographic separation of high-valency elements.	B. I. Nabivanets and L. N. Kudritskaya
Concentration of rare earth impurities of high grade rare earth samples using partition chromatography.	J. Bosholm, H. Grosse-Rüycken, N. A. Lebedev, E. Herrmann, and V. A. Halkin

Thursday Morning, 15 *July—Physical and Physicochemical Methods of Analysis*

Trace element determination in mercury and high purity acids by spark source mass-spectrometry.	C. Cherrier, M. Nalbantoglu and P. C. Pechney-Saint-Gobain
Chromato Mass Spectrometry.	V. L. Talrose, G. D. Tantzyrev, V. I. Gorshkov and S. T. Kozlov
Comparison of theoretically calculated and practically measured line intensities in X-ray fluorescence analysis.	K. H. Grothe and G. Krause
Quantitative analysis of highly radioactive materials: Spectrochemical and X-ray techniques.	C. Feldman
Electron probe measurements of impurity reactions in solid state diffusion.	L. S. Birks and D. J. Nagel
X-ray spectral quantitative analysis of complex substances of constant qualitative composition.	M. A. Blokhin
Quantitative X-ray microanalysis without a standard.	N. P. Ilyin and L. E. Loseva
X-ray determination of technetium and uranium.	F. Lux, F. Ammentorp-Schmidt, C. Herget and W. Opavsky

Thursday Morning, 15 *July—Organic Reagents in Analytical Chemistry*

Spectrophotometric determination of traces of gallium and indium with 1-(2-*pyridylazo*)-2-*naphthol* (*PAN*).	K. L. Cheng and B. L. Goydish
Spectrophotometric characteristics and choice of organic reagents.	M. K. Akhmedli, E. L. Gluschenko and P. B. Granovskaya
Photometric determination of rare earths with ammonium aurintricaroxylate (*aluminon*).	A. K. Dey, K. N. Munshi, S. P. Sangal and S. N. Sinha
Spectrofluorimetric determination of submicrogram amounts of aluminium and beryllium.	G. F. Kirkbright, T. S. West and C. Woodward

New method for spectrophotometric determination of super microamounts of copper.	Y. Kakita, M. Namiki and H. Gotô
Perspectives of dioxyazo compounds in analytical chemistry of rare elements: Some reagents for zirconium.	D. I. Ryabchikov and Yu. M. Dedkov
Use of some anabasine derivatives in analytical chemistry.	R. H. Dzanbaeva and Sh. T. Talipov

Thursday Morning, 15 *July—Methods of Separation and Concentration of Elements*

Preconcentration of trace elements by precipitation ion exchange.	G. H. Morrison, F. Tera and R. Ruch
Choice of conditions of chromatographic separation of mixtures of ions.	M. M. Senyavin
Silica gel as a cationite.	V. Marková and F. Vydra
Use of cellulose base ion-exchangers for concentration of organic ions.	E. Schulek, Zs. Remport-Horváth, A. Lasztity and E. Körös
Anion exchange in hydrofluoric acid solutions and its application for separation of elements.	V. S. Paholkov
Use of redox exchangers in analytical chemistry.	B. Sansoni
Development of partition chromatography of inorganic substances.	B. K. Preobrajensky, L. N. Moskvin and G. S. Katychin

Thursday Evening, 15 *July—Physical and Physicochemical Methods of Analysis*

The state and determination of water content in solutions and some extractive systems.	A. V. Karyakin, A. V. Petrov and Yu. B. Gerlit
Raman spectra excited by a laser emission at 6328 Å.	Cagnard, Cossard, Otto, Taieb and Troyanowsky
Application of Raman spectra for investigation of dispersed media.	M. M. Sushchinsky and A. S. L'vova
Gas and vapour analysis by infrared unresolved spectra.	B. S. Neporent
Use of thermogravimetry and infrared spectroscopy to follow reactions in the solid state.	C. Duval
Qualitative and quantitative analysis of organic compounds by quasi-linear spectra.	E. V. Shpolsky
Use of impulse heating for rapid determination of oxygen in refractory materials and metals.	Z. M. Turovtzeva and A. M. Vasserman
Some recent advances in atomic absorption spectroscopy.	A. Walsh

Thursday Evening, 15 *July—Organic Reagents in Analytical Chemistry*

Attempts to synthesise and study spray reagents for inorganic chromatography.	G. Nickless and F. H. Pollard
Some means of raising the selectivity of organic analytical reagents and their reactions.	N. N. Basargin
Designing reagents specific for palladium.	L. S. Bark and D. Brandon
A selective and sensitive colour of fluorescence reaction for silver.	R. M. Dagnall
Mechanism of interaction of hydroxylic organic reagents with ions of polyvalent metals.	V. A. Nazarenko
Chelates of germanium(IV).	R. L. Benoit and A. Beauchamp
Mechanism of interaction of antipyrine derivatives with inorganic ions and their use in analytical chemistry.	A. I. Busev, S. I. Gusev and V. P. Zhivopistsev

Thursday Evening, 15 *July—Methods of Separation and Concentration of Elements*

Separation, concentration and selective filtration of heavy metal ions on chelating ion-exchange resins.	R. Hering
Pyridine-2,6-dicarboxylic acids as chelating resins for separation of Ca^{2+}/Sr^{2+}.	E. Blasius and B. Brozio
Separation of ferrous and ferric ions by ion exchange.	B. Sagortchev

Separation of nickel and cobalt by ion exchange.	F. Burriel-Marti and Carmen Alvares-Herrero
Ion-exchange separation of germanium from vanadium and titanium.	D. A. Shishkov and S. Petyeva-Iordanova
Feasibility of volatile metal β-diketone complexes applied to alloy analysis by gas chromatography.	R. W. Moshier and J. E. Schwarberg
Paper thermochromatography.	C. Liteanu and S. Gocan

Friday Morning, 16 *July—Physical and Physicochemical Methods of Analysis*

N.M.R. studies using the ^{71}*Ga nucleus.*	N. N. Greenwood
Changes in nucleus magnetic relaxation times used inorganic analysis.	A. A. Popel
Vacuum emission spectrometric determination of oxygen in iron and steel.	Sh. Ikeda, H. Gotô and M. Suzuki
Spectrophotometric determination of uranium(VI) with halogeno derivatives of acetic acid.	P. Spacu, F. Popea and C. Tohăneanu
Spectral polarimetric analysis.	V. M. Potapov, A. P. Terent'yev and E. G. Rukhadze
Colour index observable by means of spectrophotometric measurements.	Ju. Sancho, A. Serna and C. Merin

Friday Morning, 16 *July—Organic Reagents in Analytical Chemistry*

Highly sensitive photometric determination by means of boron containing reagents.	F. Umland, D. Thierig and C. Schleyerbach
Comparative investigations of analytical reactions of new quadridentate chelants.	V. M. Dziomko, I. A. Krasavin and I. N Kremenskaya
Some pyridyl dioximes as analytical reagents.	W. Stephen and S. Thompson
Selective polydentate complexons.	R. P. Lastovsky, N. M. Dyatlova, I. D. Kolpakova and V. Ya. Tyomkina
Determination of copper(II) with bis-(2-quinolidene)-1,3-propylenediamine.	B. Kirson
Determination of thiocyanate and iodide by means of rhodamine-β.	A. Roig and A. H. Guerrero
Determination of titanium and niobium with N-furoylphenylhydroxylamine.	A. T. Pilipenko and E. A. Shpak

Friday Morning, 16 *July—Methods of Separation and Concentration of Elements*

Nucleation in precipitation from homogeneous solution.	R. Fisher
New use of organic coprecipitants for concentration of small amounts of elements.	V. I. Kuznetsov
Concentration of elements in connection with problems of coprecipitation theory.	N. A. Rudnev, G. I. Malofeeva and A. A. Loginov
Some properties of highly diluted solutions.	I. M. Korenman
Some problems of separation of trace quantity of elements by precipitation.	E. Upor and G. Nagy
Methods of chemical concentration for spectropolarographic of high purity metals.	A. G. Karabash, Sh. I. Peisulaev, L. S. Bondarenko, R. L. Slyusareva, F. L. Babina, M. M. Privalova, N. P. Sotnikova, G. G. Morosova, L. I. Kondrateva, V. L. Lobanova, N. N. Kuznetsova, G. D. Pavlova and Z. P. Moseeva

Friday Evening, 16 *July—Physical and Physicochemical Methods of Analysis*

Metrological aspects of analytical chemistry.	T. Plebanski
The reorganised standard reference materials programme of National Bureau of Standards.	W. W. Meinke
A statistical criterion of the classification of standard substances.	A. Rokosz
Standard rocks of the Central Geological Institute,	H. Grassmann
Directed search and improvement of catalytic reactions for kinetic methods of analysis.	K. B. Yatsimirsky

The tape machine and its applications.	A. Danielsson.
Comparison of modern methods of trace analysis (Mass spectrometry, isotopic dilution, activation).	E. Roth
An international comparison of accuracy and precision of some routine analytical techniques for trace elements.	G. B. Cook, M. B. Crespi and L. Kosta

Saturday Morning, 17 *July—Organic Reagents in Analytical Chemistry*

Precipitation of nickel and palladium dimethylglyoximates from homogeneous solution.	L. Gordon, O. E. Hileman and P. R. Ellefsen
Application of oximes in analysis.	V. M. Peshkova, V. M. Savostina and E. K. Astakhova
Precipitation from homogeneous solution: Precipitation of cupferrates and nitrosonaphtholates.	A. H. A. Heyn, N. G. Dave and Cheng-Yin Cheng
Anthranyl-N,N'-diacetic acid complexes with some tervalent metals.	C. Dragulescu, S. Policec and T. Simonescu
New research in the field of luminescent analysis.	E. A. Bozhevolnov, E. A. Solovyov and S. U. Kreingold
Fluorimetric determination of some individual rare earths in form of complexes.	N. S. Poluektov and L. I. Kononenko
Titrimetric methods of analysis of inorganic compounds in organic solvents.	A. P. Kreshkov

Saturday Morning, 17 *July—Methods of Separation and Concentration of Elements*

Mutual influence of components in amalgam methods of concentration and separation of metals.	A. I. Zebreva and M. T. Koslowsky
Combined physicochemical method of analysis and separation of elements.	P. N. Kovalenko and K. N. Bagdasarov
Calculation of optimum conditions for electrophoretic separation of cations.	W. Krey and H. Klamberg
Production of ultrapure materials by repeated normal freezing and analysis of impurity content by activation analysis.	J. E Powers
Application of zone melting to concentration of impurity in pure material analysis.	Sh. I. Peisulaev and E. E. Konovalov
Concentration of trace elements by zone melting of metal chelates.	K. Ueno
Phase analysis of alloys.	Yu. A. Klyachko

ERRATA—Volume 12

Page 427, line four of third paragraph: For *these questions* read *the question.*

Page 427, line five of third paragraph: For *or whether they are* read *and.*

Page 427, first sentence of fourth paragraph: This should read *Undoubtedly, nearly every erudite reader could have presented his own "account" to the authors, but it would hardly be possible for them to satisfy all possible claims of this type.*

British Standards Institution has announced the following *Revised British Standard: B.S.* 1016: *Methods for the analysis and testing of coal and coke: Part* 3: 1965: *Proximate analysis of coal.* (Price: 7*s.* 6*d.*). The determination of moisture, volatile matter and ash in coal is detailed.

UNITED STATES OF AMERICA

Monday-Thursday 24–27 *January* 1966: **Nineteenth Annual Symposium on Modern Methods of Analytical Chemistry.** Louisiana State University, Baton Rouge, La.

Sunday 30 *January-Friday* 4 *February* 1966: **A.S.T.M. Committee Week:** *American Society for Testing and Materials.* Shoreham and Sheraton-Park Hotels, Washington D.C.

Monday-Friday 13–17 *June* 1966: **Fifth National Meeting:** *Society for Applied Spectroscopy.* Sheraton-Chicago Hotel, Chicago, Ill.

Original papers are being solicited in all areas of theoretical and applied spectroscopy and gas chromatography, including X-ray spectroscopy, arc-spark emission, flame emission, atomic absorption, infrared, ultraviolet, visible, Raman, far infrared, NMR-EPR, nuclear particle spectroscopy, activation analysis and solid state spectroscopy. Anyone wishing to submit a paper is encouraged to send a title and abstract (not more than 200 words) before 1 March to Dr. E. LANTERMAN, Borg-Warner Corp., Des Plaines, Ill. 60018.

American Society for Testing and Materials has announced the availability of the following publication:

Hydrocarbon Analysis—STP 389: 426*pp.* (Price: $8.50; to ASTM members: $5.95). Sponsored by Research Division IV of ASTM Committee D-2 on Petroleum Products and Lubricants, the book is divided into four sections:

(1) Where We Are and a Look Ahead;
(2) Potential Analytical Developments;
(3) Integrated Methods Approach;
(4) Hydrocarbon and Non-Hydrocarbon Impurities.

To closely link the programme of the NBS Office of Standard Reference Materials with research efforts in other laboratories, a publication series entitled *Standard Reference Materials* has been initiated as a medium for broad and rapid dissemination of the results of standard materials investigations at **National Bureau of Standards.**

The basic publication in this series, NBS Misc. Publ. 260, is subtitled *Catalog and Price List of Standard Materials Issued by the National Bureau of Standards.* This basic section is kept up to date quarterly by issuing supplementary insert sheets as new standards are prepared, old ones are exhausted, renewals issued and others are discontinued.

Other publications in this series are numbered as Misc. Publ. 260–1, Misc. Publ. 260–2, and so forth. Thus far the following publications have been issued: 260–1, *Preparation of NBS White Cast Iron Spectrochemical Standards;* 260–2, *Preparation of NBS Copper Base Spectrochemical Standards;* 260–3, *Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard;* 260–4, *Standard Reference Materials: Sources of Information;* 260–5, *Accuracy of Solution X-Ray Spectrometric Analysis, of Copper-Base Alloys; and* 260–6, *Methods for the Chemical Analysis of White Cast Iron Standards.* Several more publications in this Series are under way.

ERRATUM—Volume 11

Page 1353, Fig. 5: The legend should read as follows

FIG. 5.—Working curves for tellurium(IV):
—— $HClO_4$ system,
- - - - HCl system.

Talanta, 1965, Vol. 12, p. iii Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Photometric determination of niobium with azo compounds: I. P. ALIMARIN and S. B. SAVVIN. (7 *October* 1965)

Some new heterocyclic compounds as analytical reagents: F. H. POLLARD, G. NICKLESS and R. G. ANDERSON. (7 *October* 1965)

Amperometry with two polarizable electrodes—XI: Determination of bismuth by EDTA titration: F. VYDRA and J. VORLÍČEK. (7 *October* 1965)

Contributions to the basic problems of complexometry—XXI: Determination of nickel in the presence of cobalt: R. PŘIBIL and V. VESELÝ. (7 *October* 1965)

Determination of gold by X-ray fluorescence methods: A. CHOW and F. E. BEAMISH. (8 *October* 1965)

A study of 3-methylthiazolidine-2-thione as a reagent for spectrophotometric determination of copper: J. A. CORBETT. (13 *October* 1965)

pH calculations for aqueous solutions of monofunctional acids and bases: U. A. Th. BRINKMAN. (14 *October* 1965)

A new method for titrimetric determination of perchlorate: G. ARAVAMUDAN and V. KRISHNAN. (14 *October* 1965)

A new method for spectrophotometric determination of supermicroamount of copper: YACHIYO KAKITA, MICHIKO NAMIKI and HIDEHIRO GOTO. (16 *October* 1965)

Preparation of iodic acid by direct oxidation of iodine with perchloric acid dihydrate: JOHN M. HAYES, HARVEY DIEHL and G. FREDERICK SMITH. (20 *October* 1965)

Spectrofluorimetric determination of submicrogram amounts of aluminium using salicylidene-*o*-aminophenol: R. M. DAGNALL, R. SMITH and T. S. WEST. (22 *October* 1965)

Qualitative and quantitative analysis of mixtures of 2,4-toluilene diamine and 2,4-toluilene diurea by infrared spectroscopy: K. EROSS, G. SVEHLA, L. ERDEY and E. VAZSONYI. (25 *October* 1965)

Investigation of thermal aging of barium sulphate precipitate by electron microscope: E. BUZAGH-GERE. F. PAULIK and L. ERDEY. (25 *October* 1965)

Use of gas-liquid and thin-layer chromatography in characterising air pollutants by fluorometry: E. SAWICKI, T. W. STANLEY, S. MCPHERSON and M. MORGAN. (26 *October* 1965)

"Stability" of acidified aqueous chloramine-T: C. G. R. NAIR. (25 *October* 1965)

A critical review of gravimetric and titrim etricreagents for the noble metals—II: F. E. BEAMISH, (26 *October* 1965)

An automatic recording titrator and its applications: SHINGO MIYAKE. (2 *November* 1965)

Sunday–Friday 13–18 *June* 1965: **Sixty-Eighth Annual Meeting:** *American Society for Testing and Materials.* Purdue University, Lafayette, Ind.

Monday–Thursday 14–17 *June* 1965: **Sixteenth Mid-America Symposium on Spectroscopy.** Sheraton-Chicago Hotel, Chicago, Ill.

Monday–Tuesday 14–15 *June* 1965: **Twentieth Annual Northwest Regional Meeting:** *Pacific Northwest Sections of American Chemical Society.* Oregon State University, Corvallis, Ore.

Monday–Friday 14–18 *June* 1965: **Symposium on Molecular Structure and Spectroscopy.** Ohio State University, Columbus, Ohio.

Thursday–Saturday 24–26 *June* 1965: **Conference on Small-Angle X-Ray Scattering.** Syracuse University, Syracuse, N.Y.

Wednesday 29 *September–Friday* 1 *October* 1965: **Twelfth National Vacuum Symposium:** *American Vacuum Society.* Statler-Hilton Hotel, New York City, N.Y.

The Programme Committee solicits the submission of contributed papers for presentation at the Symposium. Abstracts should be submitted by 5 July to the Chairman: R. L. JEPSEN, Varian Associates, 611 Hansen Way, Palo Alto, California 94303, U.S.A.

Contributed papers should report significant results of new and original work, either experimental or theoretical in nature, in an area relating to production, measurement or application of vacuum. Papers dealing with *fundamental* aspects of vacuum production, vacuum measurement and behaviour of materials and surfaces in a vacuum environment are particularly welcome. Papers on new or improved vacuum components and vacuum systems are also welcome provided they are truly technical rather then commercial in nature.

Of special interest this year are papers on such "Space-Related Problems" as friction, sticking and wear under conditions of outer space, and measurements of densities and pressure of various molecular species at high altitudes. Another timely area is electron microscope inspection of microcircuits. Thin films, of course, constitute one of the most important applications of vacuum; it is, therefore, hoped that a large number of good papers will again be contributed in this area.

Following last year's procedure, the *Thin Film Division of the American Vacuum Society* plans to hold a special *Thin Film Division Symposium*, also at the Statler-Hilton Hotel, on September 28, the day preceding the National Vacuum Symposium. This special Symposium will consist exclusively of invited papers on such topics as nucleation and growth, dislocations, and low *energy electron diffraction studies.*

American Society for Testing and Materials has announced that the following publication is now available:

Techniques of Electron Microscopy, Diffraction and Microprobe Analysis: STP 372: 90 + *vi pp. with heavy paper cover.* ($3.75 or $2.60 to ASTM members.)

This presents new techniques and applications of electron microscopy, diffraction and microprobe analysis in research studies. It is well illustrated with photographs, drawings and charts.

UNGARN

8.6. bis 12.6.1965: *Budapest:* Konferenz des wissenschaftlichen Vereins für die Silicatindustrie und der Universität der chemischen Industrie, Veszprém.

Auskunft: Konferenzausschuß Budapest V (Ungarn), Szabadság-tér 17, Haus der Technik, Silikonf.

ERRATA

Volume 12

Page 186, Table I: The heading to the second column should read

$Na_2S_2O_3$,
ml

Page 401: The address of the authors should read *Faculty of Technical and Nuclear Physics.*
Page 405, line 2: for *tartarate* read *tartrate.*
Page 405, Table II: In the footnote read *interfering* for *interferring.*
Page 406, line 5 from bottom of page: For *interferring* read *interfering.*

At the *Twenty-First Annual General Meeting of the* **Microchemical Methods Group** of the **Society for Analytical Chemistry** held on 19 February, 1965, the following Officers were elected for the forthcoming year:

Chairman: R. GOULDEN
Vice-Chairman: T. R. F. W. FENNELL
Treasurer: F. H. OLIVER
Secretary: Mrs. D. E. BUTTERWORTH, National Chemical Laboratory, Teddington, Middlesex.

UNITED STATES OF AMERICA

Sunday–Friday 4–9 *April* 1965: **149th National Meeting**: *American Chemical Society*. Detroit, Michigan.

Monday–Wednesday 19–21 *April*: **Third National Biomedical Sciences Instrumentation Symposium**: *Instrument Society of America*. Dallas, Texas.

Monday–Thursday 19–22 *April* 1965: **1965 International Conference on Modern Trends in Activation Analysis.** College Station. Texas A and M University, Texas [see *Talanta*, 1965, **12**(2), iii].

Wednesday–Friday 21–23 *April* 1965: **Third Marine Sciences Instrumentation Symposium**: *Instrument Society of America*. Miami, Florida.

Monday–Thursday 4–7 *October* 1965: **Twentieth Annual International Conference and Exhibit**: *Instrument Society of America*. Los Angeles, California.

The theme of the 1965 meeting is **New Measures of Progress in Instrumentation.** Further information is available from Dr. E. M. GRABBE, 1965 Conference Programme Co-ordinator, c/o Instrument Society of America, 530 William Penn Place, Pittsburgh, Pa. 15219.

Monday–Thursday 11–14 *October* 1965: **Seventy-Ninth Annual General Meeting**: *Association of Official Agricultural Chemists*. Marriott Motor Hotel, Twin Bridges, Washington, D.C.

For information contact LUTHER G. ENSMINGER, A.O.A.C., Box 540, Benjamin Franklin Station, Washington, D.C. 20044.

1965 *Book of ASTM Standards*: Issued periodically by **American Society for Testing and Materials** in 32 parts, it will contain approximately 3700 standards of which more than 1260 will be new or revised since publication of the 1964 Volume. Each of the parts, brought up-to-date and available on the same monthly schedule each year, covers a specific field of interest and includes a detailed index, table of contents and a numeric list of standards.

ERRATA—Volume 12

Page 134, first line: This should read . . . .*advantage of high hydrogen overvoltage*
Page 136, Table II: Heading to final column should read *Dietert furnace*
Page 136, line 6 from bottom: For *dimethylglyoxine* read *dimethylglyoxime*

LIST OF CONTENTS

Volume 12

SUBJECT INDEX

Talanta, 1965, Vol. 12, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Analysis of Ancient Metals: EARLE R. CALEY (*International Series Monographs on Analytical Chemistry*, Vol. 19). Pergamon Press, Oxford, 1964. Pp. xi + 176. 70s.

Introduction. The Heterogeneity of Ancient Metals and the Sampling Problem. Preliminary Observations and Measurements, Qualitative Tests and Choice of Quantitative Method. Gold and its Alloys. Silver and its Alloys. Copper and its Alloys. Various Non-ferrous Metals and their Alloys. Iron and Steel. The preparation of Reports. Index.

Kinetics of Precipitation: ARNE E. NEILSEN (*International Series of Monographs on Analytical Chemistry*, Vol. 18). Pergamon Press, Oxford, 1964. Pp. x + 153. 40s.

Energetics of Nucleation. Kinetics of Nucleation. Diffusion Controlled Growth. Nucleation Controlled Growth. Dislocation Controlled Growth. Compound Growth Mechanisms. Precipitation with Homogeneous Nucleation. Precipitation with a Generating Process. Secondary Growth. Seeding and Dissolution. Particle Shape. Adsorption. Appendix. References. Author Index. Subject Index.

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

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"Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique" by F. Girardi.

"Separation of Transplutonium Elements" by J. Starý.

"Differential Spectrophotometry" by G. Svehla.

Single copies of the **Heyrovský Honour Issue of Talanta,** December 1965, may be obtained from Journals Dept., Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at £2 or $6.50 per copy on a cash with order basis only.

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Talanta, 1965, Vol. 12, p. ix. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATION RECEIVED

Open Tubular Columns in Gas Chromatography: L. S. Ettre. Plenum Press, New York, 1965. Pp. xix + 164. $4.95.

Introduction. Origins; Nomenclature; Terms and Definitions: Characterisation of a Peak, Partition Process, Peak Separation, Column Efficiency, Flow Rate and Gas Velocity. *Theory and Practice.* Basic Golay Equation; Practical Conclusions from Golay Equation: Column Efficiency, Carrier Gas Flow, Selection of Carrier Gas, Liquid-Film Thickness; Comparison with Packed Columns: Influence of β Values on Column Characteristics, Changes in Necessary Column Efficiency, Influence of Column Permeability, Performance Index, Modified Expressions related to Plate Number Concept, Practical Applications; Influence of Temperature; Sample Capacity; Open Tubular Columns of Various Diameters. *Preparation of Open Tubular Columns.* Tubing: Plastic Tubing, Glass Tubing, Metal Tubing; Coating of Column Tubing: Cleaning of Column Tubing, Dynamic Coating Method, Static Coating Method, Elimination of Secondary Adsorption Effects of Column Tubing, Column Conditioning and Storage, Recoating of Open Tubular Columns; Testing of Open Tubular Columns: Use of "Polarity Mixture" for Testing, Determination of "Air Peak" Time; Increase of Inside Surface Area of Column Tubing: Chemical Treatment of Inside Wall of Tubing, Deposition of Porous Support Layer on Inside Wall of Tubing; Adsorption-Type Open Tubular Columns: Plating Methods, Adsorption Columns with Chemically Modified Inside Wall, Open Tubular Columns Coated with an Adsorptive Layer, Modification of Van Deemter-Golay Equation for Open Tubular Adsorption Columns. *Gas Chromatographic System.* Sample Introduction: Sample Introduction Systems, Split Systems; Pneumatic System: Carrier Gas Regulation, Connecting Tubes; Column Heating: Isothermal Operation, Programmed-Temperature Operation, Applications of Temperature-Programmed Open Tubular Columns, Compensation of Liquid-Phase Bleeding during Temperature Programming; Detection and Recording: Commonly used Detectors, Auxiliary Detectors, Recording Systems. *Bibliography. Supplements.* Calculation of "Air Peak" Time: Method of Peterson and Hirsch, Method of Gold; Instrumentation.

Butyl-Rubber Standard No. 388a replaces No. 388.

Barium Cyclohexanebutyrate No. 1051a, Ba—29.1 %, replaces No. 1051.

Calcium 2-Ethylhexanoate No. 1074, Ca—13.4 %, replaces calcium cyclohexanebutyrate No. 1054.

Cobalt Cyclohexanebutyrate No. 1055a, Co—17.4 and Ni—0.05 %, replaces No. 1055.

Nickel Cyclohexanebutyrate No. 1065a, Ni—16.8 %, replaces No. 1065.

Sodium Cyclohexanebutyrate No. 1069, Na—11.9 %, replaces No. 1069.

American Society for Testing and Materials has announced the availability of the following publications:

ASTM Standards for General Testing Methods: Part 31, 1965 *Book of ASTM Standards on Metallography; Non-Destructive Testing; Radioisotopes and Radiation Effects; Industrial Chemicals; Emission, Absorption and Mass Spectroscopy.* 740 *pp.* 67 *Standards.* $13.00 or $9.10 (members).

Application of Advanced and Nuclear Physics to Testing Materials—STP 373. 140 *pp.* $6.25 or $4.35 (*members*). Directed primarily at technologists in the building materials field.

ERRATUM—Volume 12

Page 391, lines 5–8 from bottom: These should read *The* K_α *radiation in the first order was used except in the case when second order* K_α *radiation was used for the lower concentration range. The Ni* K_β *radiation interfered at low concentration of copper but the second order* K_α *was found to be more sensitive than the first order copper* K_β *radiation. It is possible . . .*

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"Recent Uses of Liquid Ion Exchanges in Inorganic Analysis" by H. Green.

Talanta, 1965, Vol. 12, pp. ix to x. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Coulometric Analysis: K. ABRESCH and I. CLAASSEN, translated by L. L. LEVESON. Chapman & Hall, London, 1965. Pp. xi + 275. 36s.

Part I. Principles, Apparatus and Instrumentation: Introduction; Section 1, Electrochemical Theory—Ohm's law, Faraday's laws, E.m.f. of galvanic cells, Polarisation, Electrode potential, Nomenclature; Section 2, Principles of Coulometry—Controlled, constant potential coulometry (potentiostatic coulometry), Uncontrolled potential and constant current (coulometric titration), Constant potential and constant current, Continuously varying potential; Section 3, Current Efficiency; Section 4, End-point Detection—Colorimetric and spectrophotometric end-point detection, Electrometric end-point detection; Section 5, Interpretation of Current-voltage Curves; Section 6, Electrolysis Apparatus—Electrodes, Diaphragms, Electrolysis cells; Section 7, Measurement of Quantity of Electricity—Weight coulometers, Mercury coulometers, Gas coulometers, Titration coulometers, Colorimetric coulometers, Coulometric coulometers, Electromechanical coulometers, Electronic coulometers; Section 8, Control of Potential (Potentiostats)—Manual control, Electromechanical potentiostats, Electronic potentiostats; Section 9, Control of Current—Indirect regulation, Direct regulation; Section 10, Time Measurement; Section 11, Automatic Titrators—Controlled addition of titrant, Coulometric generation of reagents, Continuous titration; Section 12, Pulse Coulometry—Constant current pulses, Constant potential pulses.

Part II. Analytical Applications: Section 1, Potentiostatic Coulometry—Direct determinations, Indirect determinations, Table 1, Potentiostatic-Coulometric Determinations; Section 2, Coulometric Titrations—Acid-base titrations, Redox titrations, Precipitation and complex titrations, Table 2, Coulometric Titrations; Section 3, Miscellaneous—Determination of film thickness, Voltammetry, Table 3, Coulometric Dissolution with Continuously Changing Potential, Determination of polarographic n-values, Internal electrolysis, Determination of oxygen, Determination of water, Reaction kinetics, Other methods.

References. Index.

Die komplexometrische Titration: GEROLD SCHWARZENBACH und HERMANN FLASCHKA. Ferdinand Enke Verlag, Stuttgart, 1965. Pp. xvi + 339.

Teil I. Allgemeines über Titrationsmittel, Indikatoren und Instrumentelle Endpunktsindikation: Titration mit Komplexbildnern; Aminopolycarbonsäuren; Bildung und Stabilität der Komplexe; Titrations-kurven der Komplexometrie; Farben- und Fluoreszenzindikatoren der Komplexometrie—Farbschwache Indikatoren, Metallochrome Indikatoren, Fluoreszenzindikatoren, Redoxindikatoren, Herkunft, Reinheit und Benennung der Indikatoren; Der Farbwechsel metallochromer Indikatoren—pH- und pM-Indikatoren, pH-Abhängigkeit der Indikatorkonstanten, Indikatorkonstanten, Umschlagskurven, Sichtbarkeit des Farbwechsels; Instrumentelle Endpunktsanzeige—Photometrische Titrationen, Potentiometrische Titrationen, Konduktometrische Titrationen, Hochfrequenztitrationen, Amperometrische Titrationen, Coulometrische Titrationen, Chronopotentiometrische Titrationen, Thermometrische Titrationen, Radiometrische Titrationen; Titrationsarten und erzielbare Genauigkeit—Direkte Titration, Rücktitration, Substitutionstitration Summen- und Selektivtitration, Komplexometrie in Kombination mit Fällungsreaktionen, Cyanidmethoden, Amalgam-Methoden, Alkalimetrischkomplexometrische Titration; Selektivität—Trennungen, Maskieren, Demaskieren, Folgetitrationen, Indirekte Analyse.

Teil II. Titrationsverfahren und Arbeitsvorschriften: Maßlösungen, Indikatorzubereitungen, Puffergemische, Weitere Chemikalein, Lithium, Natrium, Kalium (Rb, Cs), Beryllium, Magnesium und Calcium, Barium und Strontium, Bor, Aluminium, Scandium, Yttrium und Seltene Erden (=SE), Plutonium, Titan, Zirkon (Hafnium), Thorium, Vanadium, Niob und Tantal, Chrom, Molybdän, Wolfram, Uran, Mangan, Rhenium, Eisen, Kobalt, Nickel, Platinmetalle, Kupfer, Silber, Gold, zink, Cadmium, Quecksilber, Gallium, Indium, Thallium, Kohlenstoff-Derivate, Silizium, Germanium, Zinn, Blei, Stickstoff-Derivate, Phosphor, Arsen, Antimon, Wismut, Sauerstoff, Schwefel-Derivate, Selen, Fluor, Halogene (ohne Fluor).

Literaturver-zeichnis, Autorenverzeichnis, Sachregister.

International Series of Monographs on Analytical Chemistry, Vol. 9: Analytical Chemistry of the Actinide Elements: ALFRED J. MOSES. Pergamon Press, Oxford, 1963. Pp. vii + 137. 45s.

Introduction; Nuclear properties and synthesis of the actinides; Nuclear instrumentation; Preliminary treatment of samples; Separations; Nuclear methods; Spectrophotometric methods; Emission spectroscopy and mass spectrometry; Electrochemical, X-ray and fluorimetric methods; Non-instrumental methods; Isotopic analysis of uranium and some other actinides; Miscellaneous methods; Nuclear data on actinides; The radioactive series; Thermal neutron activation and fission cross sections; Laboratory standards; Standard oxidation potentials of actinides; Abbreviations; List of general references; Subject index.

Spectroscopic Techniques in Organic Chemistry: Spectroscopy in Education, Vol. 2: A. J. BAKER and T. CAIRNS. Heyden & Son Limited, London, 1965. Pp. iv + 87.

Infrared Spectroscopy: Introduction, Experimental, Correlation tables, Interpretation of infrared spectra; Nuclear Magnetic Resonance Spectroscopy: Introduction, Tables, Interpretation of proton magnetic resonance spectra; Mass Spectrometry: Introduction, Interpretation of mass spectra; Ultraviolet Spectroscopy: Introduction, Experimental, Chromophores, Interpretation of ultraviolet spectra; Bibliography: General, Infrared spectroscopy, Nuclear magnetic resonance spectroscopy, Mass spectrometry, Ultra-violet spectroscopy.

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Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

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"Radiometric Titrations" by T. Braun and J. Tölgyessy.

"Recent Uses of Liquid Ion Exchangers in Inorganic Analysis" by H. Green.

"Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry" by B. D. Flockhart and R. C. Pink.

"A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum" by F. E. Beamish.

"A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold" by F. E. BEAMISH.

"Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals" by Rudolf Pribil.

Wednesday Afternoon, 20 *October*	
Quality and Flavours of Wine, Rum and Brandy by Gas Chromatography.	E. Bayer
Gas Chromatographic Analysis of Steam Volatile Aroma Constituents: Application to Coffee, Tea and Cocoa Aromas.	D. Reymond
Gas Chromatography of Sesquiterpenoids.	R. Teranishi
Behaviour of Stationary Phases at Cryogenic Temperatures.	C. Merritt, Jr.
Thursday Morning, 21 *October*	
Efficiency of Molecule Separators in Gas Chromatography-Mass Spectrometry Instruments.	R. Ryhage
Micro Gas Chromatography.	W. F. Wilhite
A Specific Detector for Phosphorous and for Sulphur Compounds-Sensitive to Subnanogram Quantities.	S. S. Brody
New Column Systems for Gas Chromatography.	R. P. W. Scott

Wednesday–Friday 3–5 *November* 1965: **Twenty-Third Pittsburg Diffraction Conference.** Mellon Institute, Pittsburgh, Pa.

Friday–Monday 5–15 *November* 1965: **First Midwest Regional ACS Meeting.** University of Missouri, Kansas City, Mo.

Tuesday–Thursday 16–18 *November* 1965: **Atom Fair '65** held in conjunction with **Annual Conference of Atomic Industrial Forum** and **1965 Winter Meeting of American Nuclear Society**: Sheraton-Park Hotel, Washington, D.C.

Wednesday–Friday 17–19 *November* 1965: **Seventh Eastern Analytical Symposium.** Statler Hilton Hotel, New York City.

ERRATA—Volume 12

Page 764, Reagent No. 6 in Table 1: The reference should read *128* and not *297*.

Page 772, The following additional reference is necessary

[128] N. C. Sogani and S. C. Bhattacharyya, *Analyt. Chem.*, 1957, **29**, 397.

Page 836, line 3 of †† footnote to Table IV: For (*p. 7*) read (*p. 835*).

Page 857, line 3 of Experimental: For *hydrochorlic* read *hydrochloric*.

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PAPERS RECEIVED

Some new colorimetric reagents for the determination of platinum metals: Krishna K. Saxena, Kailash N. Munshi and Arun K. Dey. (3 *March* 1965)

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Simultaneous determination of $^{65}_{30}$Zn and $^{32}_{15}$P in shellfish by radiochemical techniques: J. L. Setser and T. C. Rozzell. (8 *March* 1965)

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Precipitation of metal-cupferron complexes from homogenous solution—II: Titanium: Arno H. A. Heyn and Natwar G. Dave. (12 *March* 1965)

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A survey of the potentialities of liquid-liquid, discontinuous, counter-current solvent extraction for determination of trace constituents in geoloical materials—I: Extraction with solvents lighter than water: R. R. Brooks. (1 *December* 1964)

A survey of the potentialities of liquid-liquid, discontinuous, counter-current solvent extraction for determination of trace constituents in geological materials—II: Extraction with solvents heavier than water: R. R. Brooks. (1 *December* 1964)

Separations of protactinium from niobium, tantalum and other elements by solvent extraction using *N*-benzoyl-*N*-phenylhydroxylamine: S. J. Lyle and A. D. Shendrikar. (2 *December* 1964)

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Determination of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals with PAN: Elsie M. (Penner) Donaldson and W. R. Inman. (30 *August* 1965).

The mechanism of paper chromatography—A new explanation: P. B. Janardhan and Agnes Paul. (3 *September* 1965)

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Derivatives of pyrazolone as reagents for the extractive-spectrophotometric determination of tellurium: A. I. Busev and N. L. Babenko. (6 *September* 1965)

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ERRATA—Volume 11

Page 1307, line 2: For *though* read *through*.

Page 1311, reference 46: This should read 1963, **18**, 18.

Page 1607, line 8: This should read *hydriodic acid and stannic tetra-iodide* . . . .

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Page 127: The German and French summaries are as follows

Zusammenfassung—Einige 4-substituierte 1,2-Phenylendiamine wurden untersucht, um festzustellen, ob sie bei der spektralphotometrischen Bestimmung von Selen(IV) empfindlicher seien als 1,2-Phenylendiamin. 3,4-Dichlor-1,2-phenylendiamin ist anscheinend das empfindlichste unter den studierten Reagentien.

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Page 130, last line of *Selectivity group*: For $\overset{\alpha}{X}$ read ${}^{\alpha}X$.

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PUBLICATIONS RECEIVED

Les séparations par les résines échangeuses d'ions: B. TRÉMILLON. Gauthier-Villars, Paris, 1965. Pp. viii + 400.

PREMIERE PARTIE—*Propriétés Fondamentales des Résines Echangeuses d'Ions:* Introduction; Les équilibres entre une résine échangeuse d'ions et des solutions aqueuses; Influence de réactions chimiques; Les échangeurs d'ions dans les solvants autres que l'eau; Applications générales des échangeurs d'ions.

SECONDE PARTIE—*Fonctionnement et Applications des Colonnes d'Echangeurs d'ions:* Introduction; Fixation dans une colonne d'échangeur d'ions; Les séparations à des fins analytiques: le développement par élution; Les séparations à des fins préparatives: le développement par déplacement; Principes des colonnes d'échangeurs d'ions à contre-courant; Applications électrochimiques des résines échangeuses d'ions;

Appendice-Bases de la technique expérimentale des échangeurs d'ions. Annexe-Valeurs expérimentales des coefficients-limites de partage des éléments métalliques. Bibliographie générale, Notations et abréviations utilisées, Index alphabétique.

Gravimetric Analysis: Part II: LASZLO ERDEY. Pergamon Press, Oxford. Pp. xv + 796. £6.

Group I Cations: Silver, Lead, Mercury, Copper, Bismuth, Cadmium; Group II Cations: Arsenic, Antimony, Tin, Germanium, Gold, Platinum and Platinum Metals, Selenium, Tellurium; Group III Cations: Aluminium, Iron, Chromium, Nickel, Cobalt, Zinc, Manganese, Titanium, Zirconium and Hafnium, Thorium and the Rare Earths, Scandium, Niobium and Tantalum, Molybdenum, Tungsten, Vanadium, Uranium, Thallium, Indium, Gallium, Beryllium; Group IV Cations: Calcium, Strontium, Barium; Group V Cations: Magnesium, Sodium, Potassium, Lithium, Ammonium Ion; Methods of Separation of the Cations of the Alkali Metal Group; Author Index; Subject Index.

Radiochemistry of Rhodium: Monograph in the Series on the Radiochemistry of Elements: JAMES C. ARMSTRONG, JR. and GREGORY R. CHOPPIN. Subcommittee on Radiochemistry, National Academy of Sciences—National Research Council, U.S.A., NAS-NS-3008 (Rev. 1965). Pp. vi + 75. $1.00.

General references on the inorganic and analytical chemistry of rhodium; Rhodium separation bibliography; Isotopes of rhodium; Review of the chemistry of rhodium; Separation chemistry; Biological aspects of rhodium; Activation analysis; Counting techniques; Collection of detailed radiochemical procedures.

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Interlingua: FORREST F. CLEVELAND. (23 *April* 1965)

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ERRATA

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Page 1307, line 2: For *though* read *through*.

Page 1311, reference 46: This should read 1963, **18**, 18.

Page 1353, Fig. 5: The legend should read as follows

FIG. 5.—Working curves for tellurium(IV): —— $HClO_4$ system, – – – – HCl system.

Page 1607, line 8: This should read *hydriodic acid and stannic tetra-iodide* . . . .

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PUBLICATION RECEIVED

Chemical Analysis, Vol. XX—Amperometric Titrations: JOHN T. STOCK. Interscience Publishers, New York, London and Sydney, 1965. Pp. 730. $25.00.

PART I—Principles, Apparatus and General Techniques: Introduction; Limiting current at a voltammetric microelectrode; Location of equivalence point in amperometric titration; Biamperometric and bipotentiometric titration; Theoretical aspects of biamperometric titration; Techniques involving use of alternating current; Rotating and other solid indicator electrodes; Dropping and other mercury indicator electrodes; Reference electrodes and titration cells; Electrical equipment.

PART II—Combination Reactions: General introduction to applications; Acid-base reactions; Methods that involve silver—A. Cyanide, halides and miscellaneous reactants; Methods that involve silver—B. Sulphur-containing species; Methods that involve mercury—A. General; Methods that involve mercury species—B. Sulphydryl and other sulphur-containing species; Methods that involve Group III cations; Methods that involve lead; Miscellaneous inorganic titrants for anions; Methods that involve ferrocyanide or ferricyanide; Methods that involve anions derived from chromium, molybdenum or tungsten; Miscellaneous inorganic titrants for cations; Methods that involve organic compounds—A. Carbon–hydrogen–oxygen compounds; Methods that involve organic compounds—B. Ethylenediaminetetra-acetic acid or related agents and ions of Groups I and II; Methods that involve organic compounds—C. Ethylenediaminetetra-acetic acid or related agents and ions other than of Groups I and II; Methods that involve organic compounds—D. Oximes and nitroso compounds; Methods that involve organic compounds—E. Heterocyclic nitrogen compounds; Methods that involve organic compounds—F. Miscellaneous nitrogen compounds; Methods that involve organic compounds—G. Sulphur compounds; Methods that involve organic compounds—H. Miscellaneous compounds.

PART III—Oxidation-Reduction Reactions: Introduction to applications that involve oxidation-reduction reactions; Methods that involve iron(II) and cerium(IV), vanadate, dichromate or manganese species; Use of iron(II) in the analysis of mixtures of ions and in miscellaneous titrations. Methods that involve iron(III); Methods that involve the ferricyanide-ferrocyanide system; Non-ferrous reactions that involve cerium, titanium and vanadium species; Non-ferrous reactions that involve chromium and manganese species; Reactions that involve chlorine species; Methods that involve bromine species and inorganic substances; Methods that involve bromine species and organic substances; Iodine–thiosulphate methods; Methods that involve iodine species and those of arsenic, antimony and tin; Miscellaneous methods that involve iodine species; Determination of water by the Karl Fischer technique and related methods; Miscellaneous oxidation–reduction methods; Author index; Subject index.

The tape machine and its applications.	A. Danielsson.
Comparison of modern methods of trace analysis (Mass spectrometry, isotopic dilution, activation).	E. Roth
An international comparison of accuracy and precision of some routine analytical techniques for trace elements.	G. B. Cook, M. B. Crespi and L. Kosta

Saturday Morning, 17 *July—Organic Reagents in Analytical Chemistry*

Precipitation of nickel and palladium dimethylglyoximates from homogeneous solution.	L. Gordon, O. E. Hileman and P. R. Ellefsen
Application of oximes in analysis.	V. M. Peshkova, V. M. Savostina and E. K. Astakhova
Precipitation from homogeneous solution: Precipitation of cupferrates and nitrosonaphtholates.	A. H. A. Heyn, N. G. Dave and Cheng-Yin Cheng
Anthranyl-N,N′-diacetic acid complexes with some tervalent metals.	C. Dragulescu, S. Policec and T. Simonescu
New research in the field of luminescent analysis.	E. A. Bozhevolnov, E. A. Solovyov and S. U. Kreingold
Fluorimetric determination of some individual rare earths in form of complexes.	N. S. Poluektov and L. I. Kononenko
Titrimetric methods of analysis of inorganic compounds in organic solvents.	A. P. Kreshkov

Saturday Morning, 17 *July—Methods of Separation and Concentration of Elements*

Mutual influence of components in amalgam methods of concentration and separation of metals.	A. I. Zebreva and M. T. Koslowsky
Combined physicochemical method of analysis and separation of elements.	P. N. Kovalenko and K. N. Bagdasarov
Calculation of optimum conditions for electrophoretic separation of cations.	W. Krey and H. Klamberg
Production of ultrapure materials by repeated normal freezing and analysis of impurity content by activation analysis.	J. E Powers
Application of zone melting to concentration of impurity in pure material analysis.	Sh. I. Peisulaev and E. E. Konovalov
Concentration of trace elements by zone melting of metal chelates.	K. Ueno
Phase analysis of alloys.	Yu. A. Klyachko

ERRATA—Volume 12

Page 427, line four of third paragraph: For *these questions* read *the question.*

Page 427, line five of third paragraph: For *or whether they are* read *and.*

Page 427, first sentence of fourth paragraph: This should read *Undoubtedly, nearly every erudite reader could have presented his own "account" to the authors, but it would hardly be possible for them to satisfy all possible claims of this type.*

ERRATA

Volume 11

Page 1307, line 2: For *though* read *through*.

Page 1311, reference 46: This should read 1963, **18**, 18.

Page 1353, Fig. 5: The legend should read as follows

FIG. 5.—Working curves for tellurium(IV): —— $HClO_4$ system, – – – – HCl system.

Page 1607, line 8: This should read *hydriodic acid and stannic tetra-iodide* . . . .

Volume 12

Page 127: The German and French summaries are as follows

Zusammenfassung—Einige 4-substituierte 1,2-Phenylendiamine wurden untersucht, um festzustellen, ob sie bei der spektralphotometrischen Bestimmung von Selen(IV) empfindlicher seien als 1,2-Phenylendiamin. 3,4-Dichlor-1,2-phenylendiamin ist anscheinend das empfindlichste unter den studierten Reagentien.

Résumé—On a étudié quelques 1,2-phénylènediamines substituées en 4 afin de vérifier si elles offrent, par rapport à la 1,2-phénylènediamine, une sensibilité accrue dans le dosage spectrophotométrique du sélénium(IV). Le plus sensible des réactifs étudiés se révèle être la 3,4-dichloro-1,2-phénylènediamine.

Page 130, last line of *Selectivity group*: For $\overset{\alpha}{X}$ read ${}^{\alpha}X$.

Page 134, first line: This should read . . . *advantage of high hydrogen overvoltage*

Page 136, Table II: Heading to final column should read *Dietert furnace*

Page 136, line 6 from bottom: For *dimethylglyoxine* read *dimethylglyoxime*

Page 186, Table I: The heading to the second column should read

$Na_2S_2O_3$,
ml

Page 391, lines 5–8 from bottom: These should read *The K_α radiation in the first order was used except in the case when second order K_α radiation was used for the lower concentration range. The Ni K_β radiation interfered at the low concentration of copper but the second order K_α was found to be more sensitive than the first order copper K_β radiation. It is possible . . .*

Page 401: The address of the authors should read *Faculty of Technical and Nuclear Physics.*

Page 405, line 2: For *tartarate* read *tartrate.*

Page 405, Table II: In the footnote read *interfering* for *interferring.*

Page 406, line 5 from bottom of page: *For interferring* read *interfering.*

Page 427, line four of third paragraph: For *these questions* read *the question.*

Page 427, line five of third paragraph: For *or whether they are* read *and.*

Page 427, first sentence of fourth paragraph: This should read *Undoubtedly, nearly every erudite reader could have presented his own "account" to the authors, but it would hardly be possible for them to satisfy all possible claims of this type.*

Page 764, Reagent No. 6 in Table I: The reference should read *128* and not *297.*

Page 772, The following additional reference is necessary

[128] N. C. Sogani and S. C. Bhattacharyya, *Analyt. Chem.*, 1957, **29**, 397.

Page 831, line 11 of Reagents: For *molar extraction coefficient* read *molar extinction coefficient.*

Page 832, legend to Fig. 2: For *80% substoichiometry* read *80% stoichiometry.*

Page 833, column one of Table I: For *Antimony(III)(2mg)* and *Arsenic(III)(2 mg)* read *Antimony(III)(2 mg)*‡ and *Arsenic(III)(2 mg)*‡.

Page 834, column one of Table II: For *Total activity added, counts/10 sec* read *Total activity added, counts/50 sec.*

Page 834, column one of Table II: For *Activity of substoichiometric extract, counts/10 sec* read *Activity of substoichiometric extract, counts/50 sec.*

Page 834, Table II: Only the activities recorded for ${}^{109}Pd$ are actually in *counts/10 sec.*

Page 836, line 3 of †† footnote to Table IV: For (*p. 7*) read (*p. 835*).

Page 857, line 3 of Experimental: For *hydrochorlic* read *hydrochloric.*

Page 901, reference 23: This should read

[23] M. I. Kabachnik, S. T. Ioffe and T. A. Mastryukova, *Zhur. obshchei Khim.*, 1955, **25**, 684.

Page 1012, line four from bottom: This should read *photometer* (*see Table V*). *0·25% Solutions . . .*

Page 1013, Table V: The second value in the column headed *Standard deviation* should read 30 and not 74.

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PAPERS RECEIVED

Ion-exchange resins in non-aqueous solvents—I: Sorption rates of *p*-nitroaniline and effects of small amounts of water: Donald J. Pietrzyk. (3 *May* 1965).

Preparation and properties of tetramethyldipicrylamine: Carl E. Moore, Thomas S. Meyer and J. Walter Hudson. (3 *May* 1965).

Spectrophotometric determination of iron(III) with ω-amino-acetophenone-*N*,*N*-diacetic acid oxime: Takeshi Ando and Keihei Ueno. (4 *May* 1965).

Non-aqueous titration of hydroxamic acids: T. W. Stamey, Jr. and Robert Christian, Jr. (5 *May* 1965).

Spectrophotometric determination of small amounts of tellurium with Bismuthiol II: H. Yoshida M. Taga and S. Hikime. (7 *May* 1965).

Phase titrations—V: Nitroalkanes: Improving the phase titration end-point: D. W. Rogers, D. Lillian and I. D. Chawla. (7 *May* 1965).

Development and publication of new spectrophotometric methods of analysis: G. F. Kirkbright. (8 *May* 1965).

Comparison of methanol with water as a solvent in potentiometric titration of halides: Helene T. Havacek and William B. Swann. (10 *May* 1965).

Formal potential of tris(2,2'-dipyridyl)iron(II) sulphate: R. Belcher, J. N. Brazier and W. I. Stephen. (14 *May* 1965).

Polarographie chinoider verbindungen: H. Berg and K. Kramarczyk. (15 *May* 1965).

A phosphorimetric investigation of a number of alkaloids: Henry C. Hollifield and James D. Winefordner. (17 *May* 1965).

Selectivity index: R. A. Geitz. (20 *May* 1965).

Investigations on different alloys using the Weisz ring oven—I: Introduction of a simplified sampling technique: investigations on gold alloys and silver alloys: Y. A. Gawargious, L. J. Ottendorfer and S. S. M. Hassan. (21 *May* 1965).

Detection and determination of chlorophenols and chlorophenoxyacetic acids by instrumental analysis: L. Lechner, A. Somogyi and L. Biro. (24 *May* 1965).

Dithiocarbaminoacetic acid as a masking agent in complexometry: O. Budevsky, E. Russeva and B. Mesrob. (24 *May* 1965).

Application of polarography in co-ordination chemistry: J. Mašek. (24 *May* 1965).

Transition potentials of some triphenylmethane dyestuffs: R. Belcher, J. N. Brazier and W. I. Stephen. (25 *May* 1965).

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Substoichiometric separation using ion-association extraction systems: Jaromír Růžička and Adolf Zeman. (2 *June* 1965).

Determination and differentiation of nitrilotriacetic acid and ethylenediaminetetra-acetic acid: D. L Fuhrman, G. W. Latimer, Jr. and Jacqueline Bishop. (2 *June* 1965).

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"**Recent Uses of Liquid Ion Exchangers in Inorganic Analysis**" by H. Green.

"**Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry**" by B. D. Flockhart and R. C. Pink.

"**A Critical Evaluation of Colorimetric Methods for Determination of Nobel Metals—III: Palladium and Platinum**" by F. E. Beamish.

Talanta, 1965, Vol. 12, pp. xv to xvi. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Radiochemistry of Chromium: Monograph in the Series on the Radiochemistry of Elements: J. PIJCK. Subcommittee on Radiochemistry, National Academy of Sciences, National Research Council, U.S.A., NAS-NS-3007 (Rev. 1964), Pp. v + 64. $0.75

General reviews of the inorganic and analytical chemistry of chromium; General reviews of the radiochemistry of chromium; Table of isotopes of chromium; Review of those features of chromium chemistry of chief interest to the radiochemist: General: Separation reactions: Dissolution; Hazards and precautions; Counting techniques; Separation procedures; References.

Structure and Function in Biological Membranes: Volume II: J. LEE KAVANAU. Holden-Day, Inc. San Francisco, 1965. Pp. x + 323–760. $14.75.

Factors inducing Movement of Matrix. Transformations between Open and Closed Configurations: Cationic Displacements, Proton Activity, Site-Binding *versus* Electrostatic Interactions, Pathways of Cationic Displacements, Outline of Transition Events. Protoplasmic Streaming: Matrix Pumping by Simple Tubular Elements, Tubular *versus* Lamellar Elements, Propagation of the Transformation, Matrix Pumping by Complex Membranous Networks, Matrix Pumping in Systems of Double-Membrane Lamellae, Protoplasmic Streaming in Fungal Hyphae, Cyclosis of Plant Protoplasm, Protoplasmic Streaming During Aster Formation, Filament Streaming. Membrane Coalescence and Fragmentation, Contraction and Expansion, and Growth and "Degrowth": Coalescence of Membrane-Bounded Organelles, Fragmentation of Membrane-Bounded Organelles, Contraction and Expansion, Growth, Degrowth. Ameboid Locomotion: Principal Mechanisms Involved in Ameboid Locomotion, Outline of the Theories, Circulation of Matrix, Hyaline-Cap Formation, Hyaline-Cap Consolidation, Cortical Reticulum and Plasmalemma, Streaming Phenomena and Pseudopodium Retraction. Effects of Pressure and Temperature on Protoplasm: Effects of Pressure and Temperature on Ameboid Locomotion, Effects of Pressure on Cyclosis in Plant Cells, Effects of Pressure on Nerve Impulse Conduction, General Discussion of Pressure and Temperature Effects, Specific Effects of Pressure and Temperature. Activated Diffusion, Facilitated Diffusion, Active Transport and Impulse Conduction: Activated Diffusion, Facilitated Diffusion, Active Transport, Impulse Conduction. Electron-Optical Evidence for Membrane Substructure: Bacterial Cell Wall, Plasma Membranes, Intracellular Membranes, Future Studies. Bibliography. Author Index. Subject Index.

Industrial Isotope Techniques: LARS G. ERWALL, HANS G. FORSBERG and KNUT LJUNGGREN, assisted by ARNE HEDGRAN and STIG JOHANSSON. Munksgaard, Copenhagen, Denmark, 1964. Pp. 338.

Atomic Nuclei and Nuclear Radiation: Structure of the Atom, Periodic Table, Radioactivity, Nuclear Radiation, Interaction of Radiation with Matter. Nuclear Chemistry and Isotope Production: Isotope Effect and Isotope Separation, Nuclear Reactions, Sources for Neutrons and Particle Radiation, Production of Radioactive Isotopes, Labelling with Radioactive Isotopes. Measurement of Nuclear Radiation: Introduction, Detectors, Auxiliary Electronic Equipment, Practical Measuring Techniques, Instrumentation for Special Purposes. Technical Use of Nuclear Radiation Sources: Introduction, Nuclear Radiation Sources, Radioactive Gauges, Radiography and Radioscopy, Applications based on Effects of Radiation. Industrial Tracer Techniques: Introduction, Studies of Chemical Reactions, Measurements Using Installed Sources, Transport of Intact Sources, Transport Studies with Open Sources, Mixing Studies, Wear and Material Transfer, Metallurgical Tracer Techniques, Radioactive Tagging of Products, General Aspects on Use of Tracers. Radioactive Methods in Analysis: Introduction, Analysis by Means of Natural Radioactivity, Checking Analytical Methods, Radioactive Indicators and Precipitants, Chemical Exchange Analysis, Isotope Dilution Analysis, Radiometric Analysis, Activation Analysis, Nuclear Reaction Analysis. Radiation Protection in Industrial Use of Radioisotopes: Nature of Radiation Hazards, Internal and External Exposure, Dose Units, Maximum Permissible Doses, Assessment of Exposures, Legal Aspects of Radiation Work. References. Bibliography. Appendices: Data for Radioactive Nuclides of Importance to Isotope Techniques, Useful

Data for Radiation Measurement, Activation Analysis, Radiation Protection Data, Planning of Isotope Investigations. Subject Index.

Chimie Analytique—I: Généralités: B. TRÉMILLON: Librairie Armand Colin, 1965. Pp. 198.
Introduction—Généralités. Prévision des réactions en solution. Déplacement des équilibres par action chimique. Réactions dans les solvants autres que l'eau. Réactions de partage. Réactions électrochimiques. Bibliographie Sommaire.

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