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SIMULTANEOUS DETERMINATION OF ARSENIC, MANGANESE, AND SELENIUM IN BIOLOGICAL MATERIALS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A new method was developed for the simultaneous determination of arsenic, manganese, and selenium in biological material by thermal-neutron activation analysis. The use of ^{81m}Se as indicator for selenium permitted a reduction of activation time to 1 hr for a 1 g sample, and the possibility of loss of volatile compounds during irradiation could be dismissed. No pretreatment of the sample is required, and the radiochemical separation scheme is based on simple chemical operations, completed in less than 3 hr. A systematic experimental investigation of the performance characteristics of the method was carried out, including studies of the accuracy of the results. The actual precision achieved in routine application of the method in the analytical laboratory was in good agreement with the calculated precision, and the results are therefore well suited for statistical evaluation of differences at the ppM level in samples of biological tissue.

The possible development of abnormal trace element concentrations in uraemic patients undergoing regular peritoneal dialysis has been suggested as a factor in the evolution of uraemic polyneuropathy.[1]

The observation by Brune *et al.*[2] that uraemic patients show elevated concentrations of arsenic in blood, focused attention on this element, and the unique metabolic antagonism between arsenic and selenium[3] made the simultaneous determination of both these elements desirable. Manganese was included because the concentrations of manganese appear to be regulated by a homeostatic mechanism which does not depend on excretion through the kidneys.[4]

Reliable measurement of possible deviations from normal levels of these elements in human tissue requires analytical techniques capable of determining concentrations at the ppM (parts per milliard) level with good precision and accuracy.

Manganese can be determined in small biological samples with sufficient sensitivity by the catalytic oxidation of leucomalachite green with periodate,[5] while selenium can be determined by fluorometry of the 2,3-diaminonaphthalene complex.[6] For arsenic, colorimetric measurement of the reaction of arsine with silver diethyldithiocarbamate[7] is satisfactory for larger samples only, while small samples require the use of neutron-activation analysis.[8]

Any of the three elements can be determined by neutron-activation analysis. Selenium may be determined instrumentally after intense irradiation and several weeks of decay, by the measurement of ^{75}Se with a Ge(Li)-detector,[9] or, in dialysed samples, by a very short irradiation followed by the measurement of ^{77m}Se with a scintillation detector;[10] comparable sensitivity is achieved by β-counting of ^{81}Se after rapid radiochemical separation,[11] while the highest sensitivity and precision are reached by combining radiochemical separation with the measurement of ^{75}Se.[12] Attempts to utilize ^{79m}Se[13] or ^{81m}Se[14] have so far been unsuccessful for achieving a satisfactory limit of detection. Neither arsenic nor manganese has been determined in biological samples with satisfactory precision by purely instrumental analysis, but only relatively simple radiochemical separations are needed before measurement of ^{76}As[15] or ^{56}Mn.[16]

A combined determination of all three elements is possible with the automatic group-separation system developed by Samsahl,[17] but it requires the use of special apparatus not available in most laboratories.

An analytical procedure employing standard laboratory equipment was therefore developed for the simultaneous determination of arsenic, manganese and selenium in biological material by neutron-activation analysis.

EXPERIMENTAL

Methods of analysis

The absence of reagent blanks characteristic of activation analysis is limited to the post-irradiation treatment of the sample, and operations before irradiation should be restricted to the bare minimum necessary for sampling; radiochemical separation thus becomes necessary for all three elements.

Irradiation. Intense reactor irradiation of biological samples leads to radiolysis of the sample material and is often accompanied by a temperature rise, both of which may result in volatilization of elements such as arsenic and selenium. Mild irradiation conditions are thus preferable together with irradiation times at the minimum needed for satisfactory sensitivity.

The pneumatic tube system of the Danish reactor DR 2 offers a thermal-neutron flux density of 7×10^{12} neutron/cm^2/sec, and the energy absorption in biological tissue from the accompanying fast neutrons and γ-irradiation is about 5 Mrad/hr, corresponding to a maximum decomposition loss of well below 0·5% per hr of irradiation.

Experimental sensitivities reported by Yule[18] show that, for an irradiation time of 1 hr, ^{81m}Se is the most sensitive indicator for selenium, apart from ^{77m}Se which leaves no time for chemical separation. Counting yields observed for ^{76}As and ^{56}Mn produce satisfactory sensitivities for arsenic and manganese as compared with selenium.

It was found that satisfactory precision for all three elements in biological material could be achieved with a 1-hr irradiation in the pneumatic tube system and a sample size of about 1 g. The surface temperature of the sample during irradiation did not exceed 42°, and the total activity at the end of irradiation was less than 2 mCi. No special precautions were therefore called for in the transfer and handling of the irradiated sample.

Radiochemical separation. Incorporation of separation procedures for manganese and selenium into an existing method for the separation of arsenic[15] led to a simple method for the combined separation of all three elements.

Selenium was precipitated with ascorbic acid immediately after decomposition of the sample and before the cupferron scavenging. Manganese can be determined after the precipitation of arsenic with thioacetamide and the removal of sodium with hydrated antimony pentoxide.[16]

Further purification of selenium by dissolution and extraction into methyl isobutyl ketone[19] proved necessary, whereas no separation of manganese was required.

The separation procedure is shown schematically in Fig. 1; it is completed within 3 hr after the end of irradiation.

Detection and measurement. Satisfactory sensitivity required counting in well-type NaI(Tl) scintillation detectors for up to 80 min, and for ^{81m}Se an additional counting period of the same length some hours later was needed to eliminate the influence of ^{75}Se and other long-lived activities.

Counting times were small compared with the half-lives of ^{56}Mn and ^{76}As, but for ^{81m}Se the counting time exceeded one half-life, and a correction was necessary for decay during the counting period.

Counting data from the multi-channel analysers were produced on punched paper tape and processed *via* a teletype terminal in a GE 265 time-sharing computer system.

Peak areas were calculated from a smoothed spectrum generated by a five-point polynomial convolution of the counting data with the technique described by Savitzky and Golay.[20] Peak boundaries for both sample and comparator were decided by the method of Yule,[21] except that the sign changes of the first derivative were determined from a third degree polynomial convolution of the smoothed sample spectrum.

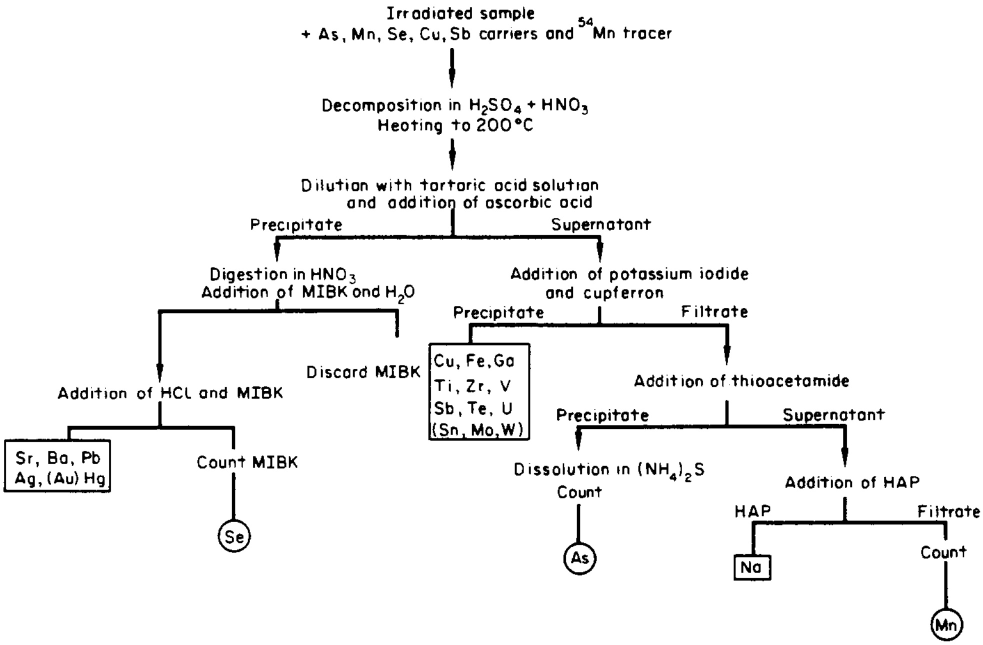

Fig. 1. Radiochemical separation scheme for arsenic, manganese, and selenium.

All samples and standards were counted for 1·0 ml of solutions in half-dram* polethylene vials, so as to eliminate differences in counting geometry.

Chemical yield. Determination of chemical yield by re-irradiation has several advantages over other methods of yield determination. No transfer from the counting vial takes place, and when identical indicators are used for both analysis and yield, differences in self-absorption between sample and standard are automatically compensated for.

In addition, positional differences in neutron flux during the simultaneous irradiation of sample and comparator may be neutralized, and the influence of interfering elements may be reduced.[15]

The yield of selenium was determined by re-irradiation for 10 sec and counting under exactly the same conditions as in the analytical determination of ^{81m}Se. The arsenic yield was measured after 10 min re-irradiation in a γ-ionization chamber for the determination of ^{76}As.[22]

The manganese yield was determined as the recovery of ^{54}Mn tracer added to the manganese carrier, by counting the sample after the decay of ^{56}Mn. The practically identical γ-energies of 0·84 MeV give the same compensation for differences in self-absorption as that achieved by re-irradiation.

Apparatus

Danish reactor DR 2 operating at 5 MW with pneumatic tube system extending into a thermal-neutron flux density of 7×10^{12} n/cm^2/sec.

Nuclear Data multi-channel pulse height analysers with Harshaw 3 × 3 in. and 2 × 1¾ in. well-type NaI(Tl) scintillation detectors.

Vibron Electrometer connected to Solartron Digital Voltmeter with National Physical Laboratory ionization chamber.

Reagents

Sulphuric acid 97–98%
Nitric acid 100%
Hydrochloric acid 37%
Methyl isobutyl ketone (MIBK)
Thioacetamide
Hydrated antimony pentoxide (HAP)
Ascorbic acid

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* The U.S. dram, or 1/8 U.S. fluid ounce or about 3·7 ml. Not to be confused with the Scottish dram!

Ammonium sulphate solution, 50% w/v
Ammonium sulphide solution, 40%
Tartaric acid solution, 1% w/v
Potassium iodide solution, 15% w/v
Cupferron, 6% w/v solution, prepared weekly

Carriers

Se-carrier, 10 mg/ml as Se(IV) in aqueous solution
As-carrier, 10 mg/ml as As(III) in 0·15*M* ammonia solution
Mn-carrier, 10 mg/ml as Mn(II) in 4*M* nitric acid, plus ^{54}Mn activity of 2 μCi/ml
Cu-carrier, 10 mg/ml as Cu(II) in aqueous solution
Sb-carrier, 10 mg/ml as Sb(III) in 1*M* citric acid and 0·25*M* oxalic acid solution

The carrier solutions are stable systems that can be stored in rubber-stoppered glass bottles for long periods of time. Accurately prepared carrier solutions, with concentrations verified by chemical analysis, are used for the preparation of reference standards by dilution with redistilled water.

Reference standards

Se, 50 μg Se/ml
As, 0·5 μg As/ml
Mn, 0·2 μg Mn/ml

The reference solutions were stored in screw-cap polyethylene bottles, and the changes in concentration were found to be about 1% per month for Mn and significantly less for As and Se.

Procedures

Irradiation. Samples of about 1 g are weighed into half-dram polyvials* and stored in a deep freezer until activation. Reference standards of about 1·2 ml of Se, As, and Mn are transferred to half-dram polyvials. All polyvials are heat-sealed and placed in a polyethylene bag which is also heat-sealed, and subsequently transported in a polyethylene rabbit to the irradiation position, where neutron activation takes place for 1 hr.

Decomposition. In a 50-ml beaker 2 ml of Cu-carrier, 0·1 ml of Sb-carrier, and 100 μl of Mn-carrier are dried at 110°. After cooling, 500 μl of Se-carrier and 100 μl of As-carrier are added, followed by 2·5 ml of conc. sulphuric acid. Identical volumes of Se-, As-, and Mn-carrier are transferred to separate half-dram polyvials and diluted to 1·0 ml; the vials are heat-sealed and set aside for yield determination. The irradiated sample is transferred to the beaker, care being taken to moisten all sample material with the sulphuric acid carrier mixture. The beaker is placed on a hot-plate at 130°, and nitric acid is added dropwise to prevent charring while the plate temperature is slowly raised to 250°. After complete destruction of organic matter, heating is continued until fumes of sulphuric acid evolve.

Separation of selenium. After cooling, the solution is poured slowly into a 40-ml centrifuge tube containing 5 ml of tartaric acid solution, and 10 ml of water are added. Selenium is precipitated by addition of 0·5 g of ascorbic acid, followed by stirring for at least 3 min. After centrifugation the supernatant liquid is transferred to another centrifuge tube for subsequent separation of arsenic.

The selenium precipitate is washed twice with water and dissolved in 15 drops of nitric acid. Addition of 0·5 ml of MIBK is followed by up to 10 drops of water to bring about the separation of two layers. After centrifugation the MIBK layer is discarded, 2·0 ml of hydrochloric acid and 1·1 ml of MIBK are added, and selenium is extracted by stirring for 1 min. After centrifugation the aqueous layer is discarded, and the MIBK phase is washed 3 times by stirring with three 2-ml portions of ammonium sulphate solution. Finally, the MIBK is transferred to a half-dram polyvial which is then heat-sealed.

Counting of selenium-81m. A reference standard is made by transferring 1000 μl of the irradiated Se-standard to a half-dram polyvial. The selenium sample is counted for 80 min live time beginning 90 min after the end of irradiation in a 2 × 1¾ in. well-type scintillation detector at a gain of 3·3 keV/channel. The reference standard is then counted for 4 min under the same conditions.

Both sample and standard are re-counted under identical conditions 2 hr later.

Yield of selenium. The separated selenium sample and the Se-carrier sample set aside for yield determination are irradiated together in the reactor for 10 sec. About 3 hr after the end of irradiation each sample is counted for 4 min under the same conditions as above. The chemical yields of selenium averaged 75%.

Calculation of result. Selenium is determined from the area of the 103-keV peak in the difference spectrum between the first and the second counting, correction being made for deviations in decay and counting time between sample and reference. With decay corrections referring to the mid-point of the counting period, a factor of 0·96 must be applied to the results from the 80-min countings. The chemical yield is calculated in the same way from the direct spectra of the re-irradiated sample and carrier.

The selenium content, corrected for chemical yield, is calculated in ng.

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* Olympic Plastics Corporation, Los Angeles.

Separation of arsenic. To the supernatant liquid from the selenium precipitation are added 4·0 ml of potassium iodide solution and 2·5 ml of cupferron solution with vigorous stirring. Stirring is continued for 3 min, and after at least 1 hr the slurry is filtered on a dense filter.* About 100 mg of thioacetamide are added to the filtrate, and arsenic is precipitated as the sulphide by gentle heating on a water-bath. After centrifugation the supernatant liquid is transferred to another centrifuge tube for subsequent separation of manganese.

The precipitate is washed three times with water, dissolved in 1·0 ml of ammonium sulphide solution, and finally transferred to a half-dram polyvial which is then heat-sealed.

Counting of arsenic-76. A reference standard is made by transferring 1000 μl of the irradiated As-standard to a half-dram polyvial.

The arsenic sample is counted for 80 min live time 24 hr after the end of irradiation in a 3 × 3 in. well-type scintillation detector at a gain of 6·7 keV/channel. The reference standard is counted for 8 min under the same conditions.

Yield of arsenic. The separated arsenic sample and the As-carrier sample set aside for yield determination are irradiated together in the reactor for 10 min. About 24 hr after the end of irradiation the samples are measured in the NPL ionization chamber with a polarizing voltage of 90 V, the voltage drop across a 100 GΩ resistor being read 3 times with 20 sec interval for each sample. The chemical yields of arsenic averaged 85%.

Calculation of result. Arsenic is determined from the 559-keV peak areas of sample and reference, corrected for differences in decay and counting time. The chemical yield is determined directly as the ratio between the average ionization-chamber readings of the re-irradiated sample and carrier.

The arsenic content, corrected for chemical yield, is calculated in nanograms.

Separation of manganese. To the supernatant liquid from the arsenic sulphide precipitation is added 0·5 g of HAP, and the mixture is stirred for 5 min. After centrifugation 1·0 ml is transferred to a half-dram polyvial, which is then closed.

Counting of manganese-56. A reference standard is made by transferring 1000 μl of the irradiated Mn-standard to a half-dram polyvial. The manganese sample is counted for 40 min live time no later than 5 hr after the end of irradiation with a 3 × 3 in. scintillation detector at a gain of 6·7 keV/channel. The reference standard is counted for 4 min under the same conditions.

Counting of manganese-54. The separated manganese sample and the Mn-54 carrier sample set aside for yield determination are counted not earlier than 24 hr after the end of irradiation, under the same conditions as above.

Calculation of result. Manganese is determined from the area of the 847-keV peak in the difference spectrum between the first and the second counting of the sample corrected for deviations from the reference in decay and counting time. The chemical yield is calculated in the same way from the 835-keV peak of the sample and carrier and should always be close to 4%.

The manganese content, corrected for chemical yield, is calculated in nanograms.

ANALYTICAL EVALUATION

Though neutron-activation analysis shares with other analytical methods a number of possible errors such as interference from other elements, an investigation of its performance-characteristics[23] must include parameters of its own, whereas others, such as range, may be excluded.

A sharp distinction between random and non-random errors is not always relevant, because a proper design of analytical procedure permits cancellation of systematic errors so that their effect is randomized and may influence the precision, but not the accuracy, of the analytical results.

In the present method re-irradiation yield-determinations of arsenic and selenium result in cancellation of errors from differences in self-absorption and irradiation position between sample and reference, and with optimum carrier composition[15] may even result in randomization of interference from other elements.

The accuracy of the method also depends on complete exchange of activated nuclides with their respective carriers, and on the absence of a blank value.

The precision of the analytical results is affected by counting statistics and by random variations in neutron fluence between sample and reference.

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* Schleicher and Schüll, type 602 eh

Interferences

Interference from other elements is expressed as the ratio between a quantity of a particular element and the corresponding error of the analytical result. Interference in activation analysis is therefore the product of a separation factor[24] S and an effective value f of the interfering element irradiated and counted as a sample, and calculated by reference to a comparison standard of the element to be determined.

The experimental determination of a separation factor is carried out in two steps: measurement of a decontamination factor D, followed by determination of chemical yield y, where $Dy = 1/S$.

The decontamination factor was determined by adding 10–100 μCi of a radioactive tracer of the highest possible specific activity of the interfering element to an unirradiated sample which was then processed according to the specified procedure. The ratio between the added activity and the activity of the separated sample is D.

The chemical yields of arsenic and selenium were determined by re-irradiation, while a fixed yield of 4% was assumed for manganese.

The effective value was determined by irradiating an aqueous sample of the interfering element for 1 hr along with reference standards. A known quantity m of the irradiated interfering element was transferred to a half-dram polyvial and diluted to 1·0 ml with water; this sample was counted along with a reference standard according to the specified counting procedure, and calculations were made to produce the apparent quantity of the element to be determined, m^*. The effective value f is the ratio m^*/m, and may be negative.

The error arising from the interference can now be expressed as fS μg of As, Mn and Se per μg of interfering element present, or its reciprocal Dy/f expressing the concentration of interfering element not to be exceeded to keep the error in the determination of As, Mn and Se below 1 ppM.

The choice of interfering elements selected for investigation was made on the basis of expected effective values >0·01 or comparatively poor separation factors. Experimentally determined interferences for the elements arsenic, selenium and manganese are listed in Tables 1–3.

Table 1. Experimentally determined interferences in arsenic analysis

Interfering element	Radioactive tracer	Activity μCi	Mass μg	Separation factor S	Effective value f	*ppm* of element ≡ 1 *ppM* of As
Cu	^{64}Cu	300	*	$2·3 \times 10^{-5}$	0·29	150
Br	^{80m}Br	100	3	$1·1 \times 10^{-3}$	0·09	10
Sb	^{122}Sb	1	*	$5·3 \times 10^{-3}$	0·72	0·25
W	^{187}W	20	0·1	$7·2 \times 10^{-3}$	−0·29	0·5

* Irradiated carrier.

Table 2. Experimentally determined interferences in manganese analysis

Interfering element	Radioactive tracer	Activity μCi	Mass μg	Separation factor S	Effective value f	*ppm* of element ≡ 1 *ppM* of Mn
Na	^{24}Na	*		$1·0 \times 10^{-2}$	$1·6 \times 10^{-4}$	600
K	^{42}K	*		1	$0·2 \times 10^{-5}$	500
Ga	^{72}Ga	200	7	$5·8 \times 10^{-3}$	$5·8 \times 10^{-4}$	300
Br	^{80m}Br	100	3	$1·2 \times 10^{-1}$	$2·0 \times 10^{-3}$	4

* Irradiated sample.

Table 3. Experimentally determined interferences in selenium analysis

Interfering element	Radioactive tracer	Activity μCi	Mass μg	Separation factor S	Effective value f	*ppm* of element $\equiv$ 1 *ppM* of Se
Cl	^{38}Cl	*		$2{\cdot}0 \times 10^{-5}$	−0·01	5000
Br	^{80m}Br	100	3	$5{\cdot}6 \times 10^{-4}$	−0·01	>40
Mo	^{99}Mo	60	12	$2{\cdot}1 \times 10^{-5}$	0·05	800
Ba	^{140}Ba	90	<0·1	$0{\cdot}9 \times 10^{-5}$	0·16	>300
Dy	^{165}Dy	5000	5	$3{\cdot}7 \times 10^{-7}$	1200	2
Au	^{198}Au	0·7	0·001	$1{\cdot}9 \times 10^{-1}$	−0·53	0·01
Hg	^{203}Hg	0·8	0·2	$1{\cdot}4 \times 10^{-2}$	0·11	0·6

* Irradiated sample.

Carrier exchange

Complete isotopic exchange between activated nuclides and carrier is usually brought about by quantitative oxidation or reduction to a common ionic species. Thus all forms of As are oxidized to As(V) during the nitric–sulphuric acid decomposition, and all Mn is reduced to Mn(II) by the addition of ascorbic acid. However, Se(IV) is partly oxidized to Se(VI) by nitric acid, and Se(VI) is not reduced by ascorbic acid; the accuracy of the selenium analysis therefore depends on the complete exchange between Se(IV) and Se(VI).

This was checked by adding 0·5 μCi of ^{75}Se as selenate(VI) to an unirradiated sample, which was then processed according to the specified procedure; the separated selenium sample was counted, and the chemical yield determined by re-irradiation. The recovery of ^{75}Se and the chemical yield agreed well within counting statistics, proving that complete exchange between Se(IV) and Se(VI) had taken place during sample decomposition.

Blank

The blank value was determined by analysis of redistilled water according to the specified procedure; while no arsenic or selenium could be detected, small quantities of Mn were invariably observed.

The polyethylene vials used for irradiation contain about 20 ppM of Mn, and it was found that up to 10% of this could be released to the water during irradiation, thereby giving rise to a manganese blank.

The limited contact between a tissue sample and the container wall makes a tissue blank lower than that of water, and the blank value is assumed to be <3 ppM.

PRECISION AND ACCURACY

Calculated precision

Random variations in neutron fluence between samples and reference standards were determined by simultaneous irradiation of several standards, and the relative standard deviation of the neutron fluence was found to be 2·5%.

The ratio between the fluence experienced by sample and reference therefore has a standard deviation of 3·5%, which represents the limiting precision for single determinations of manganese. For arsenic and selenium, where a single determination requires 2 irradiations, the limiting precision corresponds to a standard deviation of 5%.

The precision expected from counting statistics is calculated from counting data on the assumption that the covariances between channels are zero,[25] and its contribution is included in the calculated total standard deviation of a single determination.

Measured precision

Experimental determination of precision was made by repeated analysis of biological materials covering the range of interest. Observed and calculated weighted average standard deviations are given in Table 4 and they show satisfactory agreement.

The calculated standard deviation of a single determination is therefore a reasonable estimate of the actual precision of the result.

Table 4. Precision of analysis of biological samples

Element determined	Number of		Range, *ppM*	Average standard deviation, *ppM*		Detection limit *ppM*
	results	materials		experimental	calculated	
As	30	11	4–20	0·6	0·5	1
Mn	24	9	30–300	5	9	*
Se	27	9	70–500	9	10	20

* Determined by the sodium content of the sample

Limit of detection

The *a priori* detection limit according to Currie,[26] with errors of the first and the second kinds both equal to 5%, is 3·29 times the standard deviation of a blank.

The detection limit is here based on the standard deviation from counting statistics only, using the lowest results among the samples analysed. The resulting limits are given in Table 4, but the ultimate limit of detection may be slightly lower.

For manganese the limit of detection is determined by the concentration of sodium in the sample, but the ultimate detection limit is estimated at 10–20 ppM.

Accuracy

With a manganese blank of less than 3 ppM, all three elements have blank values well below the detection limit for actual samples, and no detectable bias in the results can be expected. Interferences from other elements at the levels expected in biological tissue are below the detection limit for all the elements investigated, and the significance of observed differences between analytical results can safely be tested on the basis of calculated standard deviations.

In the absence of suitable reference material of biological tissue, dried plant material was chosen for analysis, and results for kale and orchard leaves are presented in Table 5. The concentrations of arsenic and manganese far exceed those encountered in biological tissue, and reduction of sample weight yields poor precision of selenium results. The agreement with published values for kale is entirely satisfactory, while the results for As in orchard leaves are not consistent with the preliminary value given by the National Bureau of Standards.

Table 5. Analytical results for plant reference material

Material	Number of samples	Weight *mg*	This work			Recommended values			Reference
			ppm As	*ppm* Mn	*ppm* Se	*ppm* As	*ppm* Mn	*ppm* Se	
Kale	4	500	0·114 ± 0·003	14·6 ± 0·3	0·132 ± 0·008	0·14	14·9	0·15	*
Orchard leaves	4	500	8·7 ± 0·2	87·1 ± 1·6	0·088 ± 0·007	14	100	0·08	†

* H. J. M. Bowen. *Advan. Activation Analysis*, 1969, 1, 101.

† National Bureau of Standards, Reference Material 1571, 1971.

CONCLUSION

Simultaneous determination of arsenic, manganese, and selenium at the ppM level in biological tissue can be carried out by neutron activation followed by radiochemical separation. No treatment of the sample material before activation is required, so contamination of the sample is avoided, and only moderate irradiation is employed so the loss of volatile elements is negligible. The radiochemical separation is based on simple chemical operations and requires no precise control; its robustness makes it a reliable routine method in the analytical laboratory. Conventional photo-peak integration was shown to yield accurate results with satisfactory precision for biological tissue. Good agreement between experimental and calculated precision makes the results directly amenable to statistical evaluation.

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Zusammenfassung—Ein neues Verfahren zur gleichzeitigen Bestimmung von Arsen, Mangan und Selen in biologischem Material durch Aktivierungsanalyse mit thermischen Neutronen wurde entwickelt. Die Verwendung von ^{81m}Se als Indikator für Selen erlaubte eine Verminderung der Aktivierungszeit auf 1 hr für eine 1 g-Probe; die Möglichkeit des Verlustes flüchtiger Verbindungen während der Bestrahlung konnte ausgeschaltet werden. Die Probe braucht nicht vorbehandelt zu werden; das radiochemische Abtrennungsschema beruht auf einfachen chemischen Operationen und ist in weniger als 3 hv beendet. Die Leistungsfähigkeit der Methode wurde systematisch experimentell untersucht, darunter auch die Richtigkeit der Ergebnisse. Die bei der routinemäßigen Anwendung der Methode im analytischen Laboratorium erzielte tatsächliche Genauigkeit stimmte gut mit der berechneten Genauigkeit überein. Die Ergebnisse sind daher gut zur statistischen Auswertung von ppM-Unterschieden in biologischen Gewebsproben geeignet.

Résumé—Une nouvelle technique a été développée pour la détermination simultanée de l'arsenic, du manganèse et du sélenium dans les matères biologiques par analyse d'activation neutron-thermique. L'emploi du ^{81m}Se comme indicateur de sélenium a permis une réduction du temps d'activation à 1 heure pour un échantillon de 1g, et la possibilité d'une perte de produits volatis au cours de l'irradiation pouvait être négligée. Aucun prétraitement de l'échantillon n'était nécessaire et la méthode de séparation radiochimique était fondée sur des opérations chimiques simples, complétées en moins de 3 heures. Une étude expérimentale systématique des caractéristiques de performance de la méthode a été menée, comprenant des études de la précision des résultats. La précision obtenue au cours de l'emploi normal de la méthode en laboratoire était en bon accord avec la précision calculée, et les résultats sont par conséquent valables pour l'évaluation statistique de différences des niveaux de ppM dans les échantillons de tissu biologique.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM WITH 1,10-PHENANTHROLINE

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Summary—A simple and sensitive spectrophotometric method for the determination of vanadium based upon the reaction of vanadate with 1,10-phenanthroline in the presence of sodium dithionite in ammoniacal solution is described. The absorbance of the complex measured at 645 nm follows Beer's law for solutions containing 30–400 μg of vanadium in 100 ml of solution. A 10-fold excess of molybdenum, tungsten, phosphorus or chromium does not interfere. The molar absorptivity is $8{\cdot}0 \times 10^3$ l mole^{-1} cm^{-1}. The complex is shown to be tris-1,10-phenanthroline vanadium(II). The method has been applied successfully to the determination of vanadium in bauxite.

1,10-Phenanthroline (Phen) has been used in the determination of vanadium by oxidation of quadrivalent vanadium with ferric iron in the presence of Phen, the concentration of the resultant ferroin being determined spectrophotometrically.[1] Vanadium in the quinque- and tervalent states forms precipitates with Phen,[2] while quadrivalent vanadium form mono- and di-Phen complexes.[3] The blue chelate formed between vanadium(II) and Phen was observed by Schaefer and introduced as an indicator for use with strongly reducing titrants such as chromium(II).[4] The molar absorptivity of the complex was found to be $8{\cdot}0 \times 10^3$ l mole^{-1} cm^{-1} at 645 nm. A review article describes vanadium(II)-Phen as intensely blue-violet.[5] A dark blue cationic tri-Phen vanadium(II) complex has been obtained by controlled electrolytic reduction of vanadate in presence of Phen in an atmosphere of nitrogen.[6]

Phen is used in the present work as a chromogenic reagent for direct spectrophotometric determination of vanadium(II) obtained by reduction of vanadate with sodium dithionite in ammoniacal medium. Very good precision was obtained by using this method for determining vanadium in bauxites.

EXPERIMENTAL

Reagents

Standard vanadium solution. Pure vanadium pentoxide (1·785g), previously ignited at 500°, was dissolved in a slight excess of sodium hydroxide and then excess of sulphuric acid was added and the solution diluted to 1000 ml. Working standards were prepared by dilution of this solution.

1,10-Phenanthroline monohydrate solution, 0·2%.

Fluoroboric acid solution. Solid boric acid was added to concentrated hydrofluoric acid in a polythene beaker with stirring, until some boric acid remained undissolved. It was allowed to stand overnight and the supernatant liquid was filtered into a polythene bottle.

Ammonium chloride solution, 20%.

Sodium dithionite solution, 20%. Solutions of dithionite must be freshly prepared. Except in the studies of the coloured complex, solid dithionite was used.

Procedure

An aliquot of standard solution containing 0·1–0·2 mg of vanadium is transferred into a 100-ml beaker, followed by 2–3 ml of fluoroboric acid solution, 5 ml of ammonium chloride solution and 20 ml of Phen solution. The solution is diluted to 60 ml, heated to 80–90° and made distinctly ammoniacal. Five ml of dithionite solution are introduced into the solution, which is then cooled rapidly and transferred into a 100-ml volumetric flask. The solution is diluted to volume, shaken and allowed to stand for one hour at room temperature. Then the absorbance is measured at 645 nm against a reagent blank.

RESULTS

Characteristics of the complex

The absorbance spectra of the reagent blank and the vanadium(II)–Phen complex are shown in Fig. 1. The vanadium complex has a well-defined maximum at 645 nm, and Beer's law is obeyed over the range of concentration 0·3–4 μg/ml. The molar absorptivity is $8{\cdot}0 \times 10^3$ l mole^{-1} cm^{-1}, in agreement with Schaefer's results.[4]

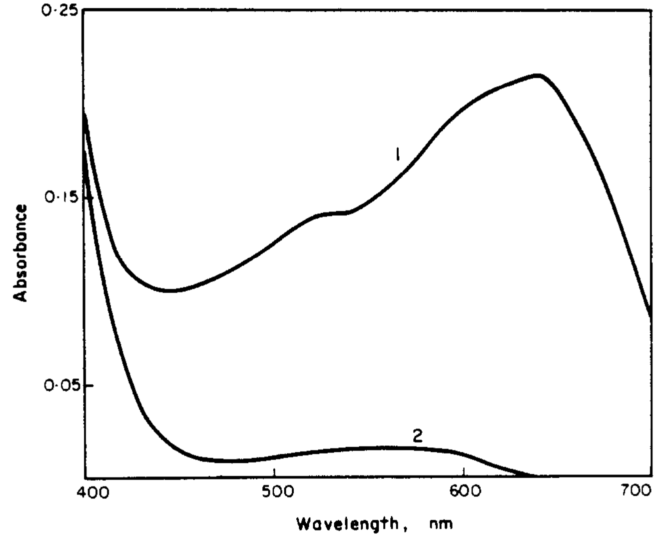

Fig. 1. Absorption spectra of vanadium(II)–Phen complex (1) and reagent blank (2) against water. C_V = 200 μg/100 ml.

The optimum pH range is 6·8–9·0. If the absorbance is measured within 3–4 hr, a pH up to 10·5 is permissible, but pH less than 6·5 should be avoided, because of the instability of dithionite.

The recommended procedure was repeated with different amounts of reagent and it was found that a molar ratio of Phen to vanadium of at least 10 : 1 is required. Further excess of reagent has no effect.

Various amounts of a freshly prepared solution of dithionite were added to test solutions with other conditions as detailed in the procedure. The minimum amount required for maximum colour development was 0·5 g, but 1·0–1·5 g of dithionite was found to be most suitable. Increasing the concentration of dithionite facilitates the formation of the coloured complex and the solution and colour of the complex become more stable.

The effect of heating and time on the formation of the complex is very important. Formation of the vanadium(II) complex is always slow at room temperature. A rapid and quantitative development of the colour was achieved by first heating the solution, followed by reduction of vanadate with dithionite. The colour intensity is unaffected by small variations in the prescribed temperature but heating for a long period after addition of dithionite causes a reduction of colour. When the effect of time of heating was studied it was found that the absorbance decreased when heating was continued for more than 30 min after addition of dithionite. Heating accelerates the decomposition of dithionite present in the solution and thus decreases the stability of the complex. If heating is omitted a 2-hr standing period is required.

The colour of the solution remains unchanged for about 24 hr in volumetric flasks, if direct contact with air is avoided. In direct contact with air, the colour of the complex starts fading within 3–4 hr after the reaction. A pinch of dithionite added to the solution after the reaction protects against colour fading for a prolonged period.

Fluoroboric acid affects the formation of the vanadium complex at high concentrations. The colour intensity is also sensitive to the fluoroboric acid concentration. The colour of the complex formed in presence of comparatively large amounts of fluoroboric acid decreases more rapidly. It was found satisfactory to use 2–3 ml of fluoroboric acid solution in a total volume of 100 ml when no metallic cations other than vanadium were present. The effect of fluoroboric acid is more pronounced with decreasing concentration of vandium. A larger excess of dithionite somewhat decreases the effect of fluoroboric acid on the vanadium complex. Fluoroboric acid has been found not to change the nature of the vanadium(II)–Phen complex. In the absence of fluoroboric acid a much smaller amount of dithionite can reduce vanadate to vanadium(II).

Nature of the complex

The empirical formula of the vanadium(II) complex in solution was studied by the continuous variation method of Job,[7] as modified by Vosburgh and Cooper[8] and showed the complex to be $[V(Phen)_3]^{2+}$, in agreement with Fujita *et al.*[6] (Fig. 2).

Like ferroin, the vanadium(II) complex is extractable as the fluoroborate into 1,2-dichloroethane and chloroform but fades rapidly on standing in the organic extract.[10] The coloured complex formed by reduction of vanadyl ion with sodium dithionite in presence of Phen has the same absorptivity.

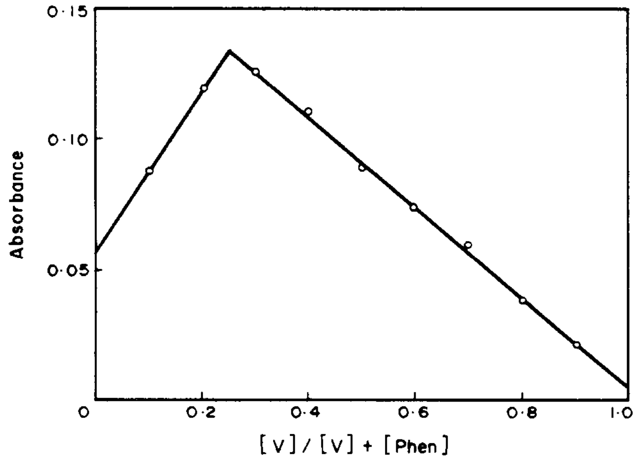

Fig. 2. Composition by Job's method.
V = Phen = $1 \times 10^{-3}M$; $\lambda = 645$ nm.

Interference studies

Solutions containing 100 μg of vanadium and varying concentrations of each ion to be tested were prepared. The vanadium was then determined by the recommended procedure except that the solutions were heated for 5–10 min after addition of dithionite. The limiting value of the concentration of foreign ions was taken as that which caused an error of not more than 2% in the absorbance. The results are summarized in Table 1.

Iron interferes in the determination of vanadium; titanium reacts with the reagent to give a yellow colour. Common complexing anions, *i.e.*, citrate, tartrate, oxalate, nitrilotriacetic acid, ethylenediaminetetra-acetic acid and 1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid completely inhibit the colour reaction; fluorides interfere seriously. A large excess of nitrate, chloride, sulphate or perchlorate does not interfere.

Table 1. Effect of various ions on the V(II)–Phen system

Ion	Added as	Amount of ion added, *mg/100 ml*	Absorbance at 645 nm	Amount of ion permissible, *mg/100 ml*
			0·159	
Fe(III)	$FeNH_4(SO_4)_2 \cdot 12H_2O$	0·05	0·157	0·05
*Al(III)	$Al_2(SO_4)_3 \cdot 18H_2O$	25·0	0·156	25
*Ti(IV)	TiO_2	0.10	0·157	0·1
Cr(VI)	$K_2Cr_2O_7$	5·0	0·156	5
Mo(VI)	MoO_3	10·0	0·166	5
W(VI)	$Na_2WO_4 \cdot 2H_2O$	10·0	0·156	10
PO_4^{3-}	NaH_2PO_4	50·0	0·157	50
†U(VI)	$UO_2(NO_3)_2 \cdot 6H_2O$	1·0	forms turbidity	0
CN^-	KCN	0·10	0·156	0·1
BF_4^-	Prepared fluoroboric acid soln.	5 ml/100 ml	0·150	3 ml/100 ml

* 4–5 ml of the prepared fluoroboric acid solution should be used when aluminium is present; 50 mg of aluminium can be tolerated when aluminium is added after acidifying a solution of sodium aluminate obtained by fusing alumina with sodium carbonate. If aluminium or titanium is present, the solution must be gently heated for some time after addition of dithionite, because the reaction is slow. If the solution is very concentrated aluminium fluoroborate may precipitate before addition of dithionite and co-precipitate some vanadium causing low results.

† Uranium forms an insoluble precipitate under the experimental conditions. The absorbance may be measured after filtering off the precipitate but the values for vanadium are then 4–6% low.

Application of the method

Determination of vanadium in bauxite. A 0·1–0·5-g sample was fused with 3–6 g of anhydrous sodium carbonate for 45–60 min in a platinum crucible. The fused mass was cooled and extracted with water, the extract was filtered, and the residue washed with hot 1% sodium carbonate solution. The resulting solution was diluted to about 100 ml, acidified with nitric acid, and heated to boiling, and 5–15 ml of fluoroboric acid solution were added, depending on the amount of sample. The solution was then made distinctly ammoniacal and the insoluble silica and any other precipitate filtered off. The solution was heated to boiling after addition of 5 ml of ammonium chloride solution and 30 ml of Phen solution. Then 1 g of solid dithionite was introduced into the solution, which was then gently heated for 5–10 min. The solution turned blue, owing to formation of the vanadium complex, and was cooled and transferred into a 200-ml volumetric flask. A pinch of dithionite was added, the volume made up to the mark and the absorbance measured at 645 nm against a blank carried through the procedure.

Calibration curves were obtained by using different amounts of a standardized solution of vanadium, without addition of fluoroboric acid, or from standard vanadium solution added to a solution of sodium aluminate obtained by fusing suitable amounts of alumina with sodium carbonate and proceeding as described.

Determination of vanadium in basalt. A 0·5-g sample was fused with sodium carbonate, and the cooled melt was leached with water, and acidified with nitric acid, as detailed above. The resulting solution was then evaporated to dryness, the residue baked for one hour, then leached with nitric acid, the insoluble residue filtered off and the colorimetric procedure applied, with gentle heating for 20–30 min instead of 5–10 min after addition of dithionite, for complete formation of the complex.

Some results for determination of vanadium are given in Tables 2 and 3.

Table 2. Determination of vanadium in artificial mixtures containing 95% Al_2O_3 and 5% SiO_2

V taken, *μg*	V found, *μg*	Sample taken, *g*	Error, %
450	451	0·2	+0·2
350	352	0·2	+0·6
200	197	0·2	−1·5
100	98	0·2	−2·0

Table 3. Determination of vanadium in bauxites and basalt

Material to be analysed	Sample, *g*	HBF_4 used, *ml*	V found by standard methods, *μg*	V found by proposed method, *μg*	Error, %
*Bauxite					
6	0·20	5·0	1000	1010	+1·0
12	0·20	5·0	1200	1215	+1·2
18	0·20	5·0	1000	1010	+1·0
24	0·20	5·0	1100	1100	0
30	0·20	5·0	1000	1020	+2·0
70	0·20	5·0	900	900	0
71	0·10	5·0	1900	1920	+1·0
21	0·50	12·0	260	270	+3·8
†Basalt	0·50	12·0	384	377	−2·0

* Source: Madhya Pradesh.

† Source: U.S. Geological Survey, BCR-1, Split 26, Position 7.

Precision test

A number of equal amounts of two bauxite samples containing between 1000 and 2000 *μg* of vanadium were analysed by the procedure given. The results of 10 determinations gave a standard deviation of 1 *μg* of vanadium.

DISCUSSION

The fusion with sodium carbonate and leaching of the product with water is necessary to effect an initial separation of vanadium from iron and titanium. Because of the instability of dithionite the colour reaction cannot be applied in acidic solution, but aluminium interferes seriously by precipitation as hydroxide at higher pH values if no complexing agent is used. In strongly alkaline solution, aluminium inhibits the reaction completely. Common complexing agents also completely inhibit the colour reaction. This difficulty was circumvented by the use of fluoroboric acid which, like hydrofluoric acid, forms stable complexes with a number of metal ions and has been put to analytical use in solvent extractions.[9,10] In the recommended pH range, it is possible, with fluoroboric acid, to mask traces of iron. Metals which hydrolyse easily and do not form very stable complexes with Phen can be masked with fluoroboric acid. Fluoroboric acid apparently forms crystalline precipitates with aluminium in small volumes of solution, and low values are obtained for vanadium present. This difficulty was overcome simply by dilution of the solution. The total volume of the solution before neutralization with ammonia should be between 100 and 150 ml. The amount of fluoroboric acid to be added depends on the amount of sample taken.

Vanadium(II) reacts with Phen between pH 4 and 6 in triethanolamine–hydrochloric acid buffer, but at higher pH triethanolamine itself interferes. The coloured complex also forms in sodium or potassium hydroxide media.

Enough Phen must be added to complex any interfering elements that can react with it, and to leave sufficient to react with vanadium. In view of the instability of the coloured complex, a pinch of dithionite is added to the volumetric flask before diluting to volume. The volumetric flasks should always be stoppered to avoid direct contact with air, in which the complex is less stable. In the applications of the method, addition of solid dithionite is preferred because of instability of its aqueous solution. The blue-violet colour which has been observed by some workers presumably results from a reaction of Phen with an excess of vanadium(II) (see Fig. 2).

The role of the ammonium chloride added to the solution before development of the colour is not very clear, but is probably that of a buffering agent. The addition is necessary.

Slightly high results may be obtained when the sample absorbance is compared with a calibration curve obtained by using pure vanadium solutions in presence of fluoroboric acid, if the recommended procedure is not strictly followed. This troublesome feature is avoided by using a calibration curve obtained with standard vanadium solutions containing no fluoroboric acid, and the 1-hr standing period is then not necessary.

The procedure is manipulatively simple and the concentrations of reagents are not critical above the specified values. The method, although lacking the sensitivity of some of the procedures previously described, is capable of determining vanadium in the usual concentrations met in ores and minerals.

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Zusammenfassung—Eine einfache und empfindliche spektrophotometrische Methode zur Bestimmung von Vanadium wird beschrieben, die auf der Reaktion von Vanadat mit 1,10-Phenanthrolin in Gegenwart von Natriumdithionit in ammoniakalischer Lösung beruht. Die bei 645 nm gemessene Extinktion des Komplexes befolgt bei Lösungen mit 30–400 μg Vanadium in 100 ml Lösung das Beersche Gesetz. Ein 10-facher Überschuß von Molybdän, Wolfram, Phosphor oder Chrom stört nicht. Der molare Extinktionskoeffizient beträgt $8{\cdot}0 \,.\, 10^3 \,\mathrm{l\,mol^{-1}\,cm^{-1}}$. Es wird gezeigt, daß der Komplex Tris-1,10-phenantholin-vanadium(II) ist. Die Methode wurde mit Erfolg auf die Bestimmung von Vanadium in Bauxit angewandt.

Résumé—On décrit une méthode spectrophotométrique simple et sensible pour le dosage du vanadium, basée sur la réaction du vanadate avec la 1,10-phénanthroline en la présence de dithionite de sodium en solution ammoniacale. L'absorbance du complexe mesurée à 645 nm suit la loi de Beer pour des solutions contenant 30–400 μg de vanadium dans 100 ml de solution. Un excès 10 fois plus grand de molybdène, tungstène, phosphore ou chrome ne gêne pas. On a trouvé que le coefficient d'absorption moléculaire est de $8{,}0 \times 10^3 \,\mathrm{l\,mole^{-1}\,cm^{-1}}$. On a montré que le complexe est le tris-1,10-phénanthroline-vanadium(II). On a appliqué la methode avec succès au dosage du vanadium dans la bauxite.

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USE OF THE TITANIUM(IV) CHELATE OF SALICYLIC ACID FOR A SELECTIVE ABSORPTIOMETRIC DETERMINATION OF TITANIUM

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Summary—Titanium(IV) forms a 1:1 chelate with salicylic acid in 40% aqueous ethanolic solution. The chelate is extractable into chloroform. A selective extraction method for the estimation of titanium in the presence of a variety of commonly interfering species is described. The addition of pyridine is found to increase the sensitivity and selectivity and makes it unnecessary to use alcohol in the extraction. The extracted species is a pyridine adduct of the titanium-salicylic acid chelate.

The chemistry of the titanyl ion (TiO^{2+}) in coexistence with iron(II) and iron(III) is of particular significance in studies of titaniferous materials such as ilmenite and rutile. The extensive literature on the analytical chemistry of titanium include procedures for its separation and determination by gravimetric, titrimetric, colorimetric and instrumental methods, such as precipitation with cupferron, tannin,[1] cinnamic acid,[2] and salicylhydroxamic acid,[3] redox titration after reduction with the Jones reductor,[4] formation of the complexes with hydrogen peroxide or sulphosalicylic acid,[5] solvent extraction involving thiocyanate,[6] dibutyl hydrogen phosphate[7] and molybdophosphate.[8]

However, the procedures hitherto described are not suitable in the presence of all metals, and considerable interference can occur, particularly in the presence of appreciable quantities of iron and vanadium. A serious criticism is that they cannot generally be directly applied to the determination of titanium in most titaniferous materials such as ilmenite.

Sudarikov and Smirnov[9] have reported that in sulphate medium titanium(IV) reacts with salicylic acid to yield fine biaxial crystals which give sodium and ammonium salts with compositions of $MR(TiR_2) \cdot 3H_2O$ and $M(TiR'_2R) \cdot 3H_2O$ where R and R′ are singly and doubly charged salicylate ions respectively, and M is Na^+ or NH_4^+. However, no studies have been reported on the use of this reaction for analytical purposes. Ziegler and Glemser[10] have used sulphosalicylic acid for a colorimetric procedure for titanium, but report serious interference in the presence of Al, Mn, Ca, Mg and Fe.

The addition of an acid solution of titanium(IV) to an aqueous ethanolic solution of salicylic acid gives immediately a yellow colour which is stable for over 72 hr. This solution is characterized by a broad absorption maxima around 360 nm. The Vosburgh and Cooper method[11] indicates the presence of only one absorbing species. The ratio of titanium to salicylic acid is found to be 1 : 1 by the Job[12] and slope-ratio[13] methods.

The titanium salicylate chelate is found to be extractable into chloroform in the presence of excess of the reagent. The molar absorptivity of the extracted species is

5·9 × 10^3 l·mole^{-1}·cm^{-1} (extraction pH 2·3). The salicylate complex of iron(III), λ_{max} = 530 nm and ε_{max} = 2·2 × 10^3 l·mole^{-1}·cm^{-1} in aqueous ethanol, is not extractable into chloroform. No interference is caused by the presence of Fe(III), Fe(II), Ca, Mg, Zn, Co(II), Mn(II), Ba, V(IV), Ni, and Al. Interference by F^- and $C_2O_4^{2-}$ is probably due to the formation of stable Ti(IV) complexes. Tolerance limits for various ions which commonly occur in conjunction with titanium, are shown in Table 1.

Table 1. Tolerance limits for foreign ions in procedures (*i*) and (*ii*)
(Titanium present = 7·6 μg)

		Tolerance, *ppm*	
Ion	Added as	Procedure (*i*) (alcohol)	Procedure (*ii*) (pyridine)
$C_2O_4^{2-}$	potassium oxalate	0·2	50
F^-	sodium fluoride	0·4	50
Mn(II)	sulphate	11	9000
V(IV)	sulphate	13	40
Fe(III)	chloride	13	22
Ba(II)	chloride	30	2000
Mg(II)	sulphate	50	400
Al(III)	sulphate	55	
Ni(II)	sulphate	60	
Ca(II)	chloride	80	
Fe(II)	sulphate	110	
Co(II)	chloride	120	
Zn(II)	sulphate	130	

The method is shown to be applicable to samples of ilmenite and the results show good recoveries and agree well with those obtained by classical gravimetric techniques. As oxalate was found to interfere, the fusion product of ilmenite with potassium bisulphate was extracted with sulphuric acid, instead of ammonium oxalate solution as in the tannin method[1] for titanium in ilmenite. However, extensive dilution is required, even with a 0·1-g sample of ilmenite, to obtain a concentration suitable for the procedure. Table 2

Table 2. Estimation of titania in ilmenite

	TiO_2 found, %			
Method of obtaining titanium in solution	from complex in aqueous ethanol	from $CHCl_3$ extract of complex, procedure (*i*)	from $CHCl_3$ extract of complex, procedure (*ii*)	from precipitation with tannin[1]
H_2SO_4 extraction of fusion product of ilmenite with $KHSO_4$	600*	54·2	53·8	37·1
Ammonium oxalate extraction of fusion product of ilmenite	10·8	0·2	53·1	54·6

* Apparently a result of interaction of Fe(III) and Ti(IV), and being further investigated. Similar observations were reported for Fe(II) and Ti(IV) by J. Beukenkamp and K. D. Herrington, *J. Am. Chem. Soc.* 1960, **82**, 3022.

shows the results obtained by both procedures. The procedure has also been satisfactorily applied to determination of the titanium and iron content of various samples from research on ferrotitanium alloys.[14]

The advantages of the procedure over methods for titanium are shown in Table 3.

Table 3. Methods for the estimation of titanium

Methods	Sensitivity	Interferences and disadvantages	pH
Gravimetric methods			
Tannin-oxalate[1]	0·1 g TiO_2	Ca	acidic
Cupferron[1]	—	Fe, V (use of H_2S)	acidic
5,7-Dibromo-oxinate[15]	up to 10 mg	Fe, V, Cu	acidic
Volumetric methods			
Jones reductor[15]	0·12–0·15 g Ti	V, Cu	acidic
Liquid zinc amalgam[15]	0·1–0·2 g Ti	V, reducible ions	—
Jones reductor/silver[4] reductor	up to 8 mg	V, instability of Ti(III)	—
Colorometric methods			
Hydrogen peroxide[5]	0·07 μg/cm^2 (400 nm)	Co, Ni, Cu, Zn, Fe, Mn	acidic
Chromotropic acid[16]	0·0026 μg/cm^2 (400 nm)	Fe, F^-, V	4–6
Tiron[16]	0·0036 μg/cm^2 (410 nm)	Fe, V, Al, Ca	3–10
Sulphosalicylic acid[12]	0·006 μg/cm^2 (445 nm)	Al, Mn, Ca, Mg, Fe	3–5
Diantipyrylmethane[18,19]	0·1 μg/cm^2 (380 nm)	V, Fe	acidic
Thymol[18]	0·009 μg/cm^2 (440 nm)	V, F^-	—
Solvent extraction methods			
Thiocyanate[6]	no details reported	no details available	—
Dibutyl hydrogen phosphate[7]	no details reported	no details available	—
Molybdophosphate[8]	no details reported	no details available	—
Thiocyanate–tri–n–octylphosphine oxide[20]	0·00012 μg/cm^2(432 nm)	Nb, nitrate	acidic
Thenoyltrifluoroacetone[21]	(430 nm)	Co, Ni, Mn, V, Fe, Cu, F^-	acidic
Cupferron[22]	—	V	6·0
Present procedure (*i*)	0·00082 μg/cm^2 (380 nm)	F^-; $C_2O_4^{2-}$	2–3
Present procedure (*ii*)	0·00065 μg/cm^2 (366 nm)	—	3·5–4·5

Although the low solubility of salicylic acid in water necessitated the use of an aqueous ethanolic medium, it was found that the presence of alcohol was also required for the chloroform extraction. In investigation of the role of the alcohol it was observed that the addition of even a small amount of pyridine enhanced the extraction of the titanium salicylic acid chelate into chloroform and that the alcohol was then not necessary. The use of pyridine was also found to increase the sensitivity (0·64 ng/cm^2 at 366 nm) and selectivity and provided a higher pH range (3·8–4·5) for optimum absorbance ($\varepsilon = 7{\cdot}3 \times 10^3$ l·mole^{-1}·cm^{-1} at 366 nm in chloroform at a pH of extraction = 3·9). Absorption spectra of the titanium salicylic acid chelate in 40% aqueous ethanol and its chloroform extract in the presence of ethanol or pyridine are shown in Fig. 1.

The "pyridine" method with extraction at pH 3·9 was used to assess interference by other ions. There was a marked increase in the tolerances for these ions, compared with those for the "alcohol" procedure, especially for oxalate and fluoride, which are the commonly interfering ions in most determination of titanium (Table 1).

Nature of the extracted species

Isolation of the complex and its analysis for titanium, salicylic acid and pyridine have shown that the extracted species contains these components in ratio 1 : 1 : *n* where *n* varies with the amount of pyridine used in preparation of the solid.

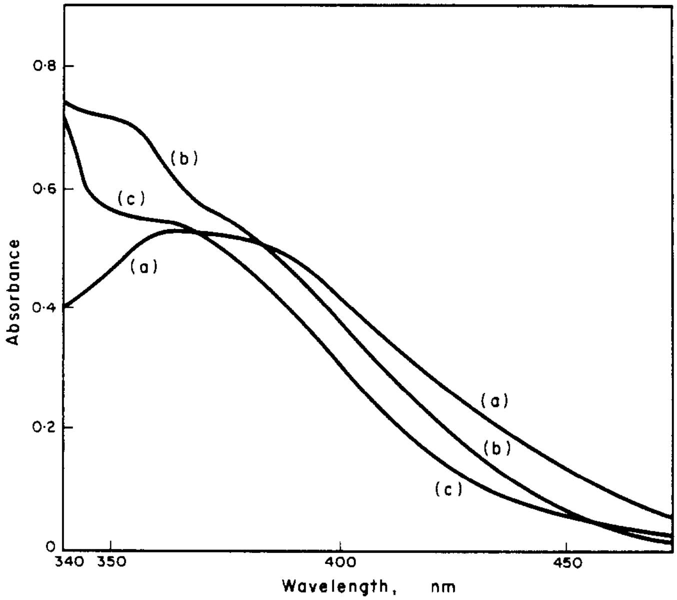

Fig. 1. Absorption spectra.
(*a*) Titanium-salicylic acid chelate ($1·04 \times 10^{-3}M$) in 40% v/v aqueous ethanol.
(*b*) Titanium-salicylic acid chelate ($1·00 \times 10^{-4}M$) extracted into $CHCl_3$ from 40% v/v aqueous ethanolic solution.
(*c*) Pyridine adduct of titanium-salicylic acid chelate in $CHCl_3$ ($2·97 \times 10^{-5}M$).

The infrared spectrum obtained for this pure solid in KBr discs was compared with that of the ligand. The band at 830 cm^{-1} was attributable to the Ti=0 stretching frequency. Similar assignments for $\nu_{Ti=0}$ have been reported for other titanyl complexes.[23,24] The bands at 1590 cm^{-1} and 595 cm^{-1} are due to unco-ordinated pyridine (co-ordinated pyridine gives higher frequencies).

The deformation frequencies of the CH groups of the pyridine ring, at 990, 1030 and 1145 cm^{-1}, reported by Sas *et al.*[25] in their studies on scandium-SCN^--pyridine complexes, remain unaltered in the infrared spectrum of our compound, again showing the presence of unco-ordinated pyridine in the solid. The extracted species is therefore a pyridine adduct of the Ti(IV)-salicylic acid chelate. However, studies[26] in these laboratories on a VO^{2+}-thiosalicylic acid-pyridine compound showed that these frequencies were shifted to 1015, 1042 and 1160 cm^{-1} respectively, which was taken as evidence for the existence of a V-pyridine co-ordinated bond *via* the nitrogen atom in the VO^{2+}-thiosalicylic acid-pyridine (1 : 2 : 1) ternary complex.

EXPERIMENTAL

Reagents

Analytical-grade chemicals were used throughout. Solvents and pyridine were redistilled.

Titanium(IV) solutions. Prepared from 99·6% pure TiO_2 by fusion with potassium bisulphate and extraction with 5% sulphuric acid, standardized by the cupferron method and by the use of a Jones reductor, and diluted accordingly, or prepared from air-dried potassium titanyl oxalate.

Buffers in 40% aqueous ethanol, the pH of which was determined from e.m.f. measurements with a quinhydrone electrode, were used to calibrate the pH meter for use with aqueous ethanolic solutions.

Recommended procedures

(*i*) *Extraction with chloroform in the presence of aqueous ethanol.* An aliquot of Ti(IV) solution was placed in a separating funnel together with 25 ml of 40% aqueous ethanolic solution of salicylic acid (0·1*M*), the pH adjusted to the desired value (2·3) with ammonia solution and sulphuric acid, and the solution diluted to 35 ml with water. Then 5 ml of chloroform were added and the solution was equilibrated by shaking. The organic extract was withdrawn and centrifuged and its absorbance measured at 380 nm against a reagent blank in chloroform.

(*ii*) *Extraction with chloroform in the presence of pyridine.* To 4 ml of 1*M* aqueous pyridine solution, 20 ml of sodium acetate–acetic acid buffer (pH 3·90) were added followed by an aliquot of Ti(IV) solution (prepared from potassium titanyl oxalate) and the solution was diluted with water to 30 ml. Then 5 ml of 0.1*M* salicylic acid in chloroform were added, the mixture was shaken, the organic phase was withdrawn and centrifuged, and the absorbance measured at 366 nm against a reagent blank in chloroform.

Analysis of alloys and slag containing iron, aluminium and titanium

Estimation of titanium. A 0·1-g sample was fused with 5 g of potassium bisulphate and extracted with 50 ml of 5% sulphuric acid and made up to 250 ml with 5% sulphuric acid. A known volume of this solution was diluted to 100 ml in water. An aliquot of this diluted solution was then treated according to procedures (*i*) and (*ii*).

Estimation of iron. An aliquot of the solution in 5% sulphuric acid, prepared as above, was boiled for a few minutes with 1–2 ml of concentrated nitric acid to convert all the iron into Fe(III), and the solution was made up to a known volume in water. An aliquot was treated by procedure (*i*) to determine titanium. The absorbance of the aqueous ethanolic phase after equilibration with chloroform was measured at 530 nm against a reagent blank, and the iron concentration obtained from a calibration curve.

Table 4. Analysis of alloy and slag samples containing titanium

Procedure	Sample	Titanium found, %	Iron found, %
i	No. 1	53·3	6·1
i	No. 2	23.4	46·1
ii	No. 1	52·1	
ii	No. 2	22·9	

Solid Ti(IV)-salicylic acid–pyridine product

A yellowish orange solid, m.p. 210–212°, was obtained by removal of solvent from a chloroform extract of a solution containing titanyl sulphate, pyridine and salicylic acid. The solid was purified by repeated extraction with diethyl ether containing increasing quantities of 60–80° petroleum ether to remove excess of salicylic acid. Analysis for the pyridine by Kjeldahl determination gave values for pyridine which varied with the concentration of pyridine used in preparation of the product.

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Zusammenfassung—Titan(IV) bildet mit Salicylsäure in 40% wäßrig-äthanolischer Lösung ein 1 : 1-Chelat. Das Chelat läßt sich in Chloroform extrahieren. Es wird eine selektive Extraktionsmethode zur Bestimmung von Titan in Gegenwart einer großen Anzahl verschiedener sonst störender Spezies angegeben. Es zeigt sich, daß die Zugabe von Pyridin die Empfindlichkeit und Selektivität weiter verbessert und die Verwendung von Alkohol bei der Extraktion unnötig macht. Die extrahierte Spezies ist ein Pyridinaddukt des Chelats aus Titan und Salicylsäure.

Résumé—Le titane (IV) forme un chélate 1 : 1 avec l'acide salicylique en solution hydroéthanolique à 40%. Le chélate est extractible en chloroforme. On décrit une m´thode d'extraction sélective pour l'estimation du titane en la présence d'une variété d'espèces communément gênantes. On a trouvé que l'addition de pyridine accroît la sensibilité et la sélectivité et rend inutile l'emploi d'alcool dans l'extraction. L'espèce extraite est un composé d'addition de la pyridine avec le chélate titane-acide salicylique.

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APPLICATION OF FLOW MICROCALORIMETRY TO ANALYTICAL PROBLEMS—I

DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES BY INHIBITION OF CHOLINESTERASE

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Summary—Flow microcalorimetry has been applied to the determination of organophosphorus pesticides by inhibition of cholinesterase. One direct inhibitor (TEPP) and one latent inhibitor (parathion) were investigated. The former is determinable at concentrations of about $10^{-6}M$ and the latter at about $10^{-4}M$. The inhibitory power of parathion is increased if methanol is used as solvent.

In flow microcalorimetry measurement is made of the heat generated by a reacting solution flowing through a calorimeter chamber, or by a reaction between two flowing streams meeting within the chamber. The technique is particularly suited to the study of enzyme-catalysed systems. It has been shown theoretically[1] and experimentally[2] that for an enzyme reaction that is zero-order in substrate (*i.e.*, [substrate] $\gg K_m$, where K_m is the Michaelis–Menten[3] constant) the heat-output rate, dq/dt, will give a steady recorder deflection which is proportional to enzyme activity. Inhibitor concentrations may be determined from the degree to which they inhibit the enzyme[4] and hence reduce heat-output rate.[1,2,5,6] This paper describes the application of flow microcalorimetry to the determination of organophosphorus pesticides *via* their inhibition of cholinesterase.

Anticholinesterase compounds have been reviewed[7,8] and the inhibiting effect of organophosphorus materials discussed.[8-10] Dimefox has been determined by the microcalorimetric technique.[11] Current non-enzymic methods are non-selective, the methods yielding total phosphorus being the most extreme examples, particularly when materials of biological origin are investigated. The enzymic methods are more selective and at least as sensitive as the chemical methods. In the main, only organophosphorus materials are detected by systems based upon cholinesterase. Selectivity may be introduced by use of cholinesterase from different sources.[12]

The flow microcalorimetric method is simple and reasonably rapid, the time for one experiment being about 35 min, and about 15 min for serial work. Other advantages are that the method of sample preparation is less important, the calorimeter will accept suspensions[13,14,15] (*e.g.*, soil, blood, algae) and optical purity is not required.

EXPERIMENTAL

Apparatus

The LKB Flow Microcalorimeter was equipped[1,2] with a flow-through cell and operated at 25°.

Materials

Enzyme (horse serum cholinesterase) solutions were prepared in "tris" buffer [tris-2-amino-2-(hydroxymethyl)-1,3-diol] adjusted to pH 8. Substrate solutions, (0·1*M* acetylcholine chloride and 0·02*M* butyrylcholine iodide) were prepared in the same buffer solution.

The enzyme solutions were stored at 0° before use.

The pesticides investigated were TEPP (tetraethyl pyrophosphate) and parathion.

Preliminary investigations

General procedure. An instrumental base-line was established by pumping substrate solutions (*e.g.*, 25 ml of 0·02*M* butyrylcholine iodide in "tris" buffer at pH 8) through the calorimeter. After exactly 5 min the appropriate enzyme solution was added rapidly, with vigorous stirring, to the remaining bulk of substrate solution. This reacting mixture (always zero-order kinetics with respect to substrate) then entered the calorimeter. The calorimetric response (arbitrary scale units) was the difference between the new scale-reading and the base-line value.

After each series of experiments all vessels and lines were cleaned by pumping through 5% sodium hydroxide solutions, followed by detergent and finally distilled water.

The grade of cholinesterase used was stated by the manufacturers to hydrolyse butyrylcholine three times as fast as it does acetylcholine. Hence acetylcholine chloride and butyrylcholine iodide were compared as substrates. At pH 8 and with 0·4 ml of 0·5 mg/ml enzyme solution added as described to 0·02*M* butyrylcholine iodide solution a calorimetric response of 47 units was observed, whereas 0·1*M* acetylcholine chloride produced a response of only 23. In all subsequent experiments butyrylcholine iodide was used as substrate.

The conditions for optimal heat-output rate may not be those for optimum substrate turnover,[1] because of the possible enhancement from secondary reactions, *e.g.*, protonation of buffer solutions occurring as a result of enzyme/substrate reaction. In the case of butyrylcholine iodide the reaction is butyrylcholine iodide + enzyme → butyric acid + choline-enzyme complex. The butyric acid (p*K* 4·83) will react with the buffer solution (pH 8) and the enthalpy of neutralization will supplement the enzyme/substrate reaction enthalpy and give a larger calorimetric response. It was found that pH 8 gave the highest calorimetric response (pH 7·0—55, pH 8·0—70, pH 9·0—65). In all substrate experiments "tris" buffer at pH 8 was used. The pH optimum for substrate turnover by cholinesterase lies in the range[16,17] 7·0–7·4 although pH 8 has been reported[18] for the system cholinesterase–TEPP. The relationship between enzyme activity and calorimetric response was found to be linear for 0·06–0·3 mg of enzyme added in 1 ml of buffer as described in *General procedure*. Englehard *et al.*[19] have shown that inorganic cations, especially sodium and bivalent cations, affect the equilibrium constants of the cholinesterase–substrate complex and the substrate-inhibited complex by increasing the activity of the enzyme. The final recommendations were to use solutions of sodium and magnesium chlorides. Comparison of calorimetric response in solutions (25 ml of substrate, 1 ml of 0·3 mg/ml enzyme) is given in Table 1.

Table 1

Added	Calorimetric response (mean of three experiments)
—	52
1 ml 0·15*M* NaCl + 1 ml 0·02*M* $MgCl_2$	52
1 ml 0·15*M* NaCl	42
1 ml 0·02*M* $MgCl_2$	62
1 ml 0·1*M* $AlCl_3$	41
1 ml 0·1*M* $CoCl_3$	56

Thereafter 1 ml of 0·02*M* magnesium chloride was added to each aliquot of substrate before addition of enzyme.

Inhibition experiments. The duration of incubation of enzyme with pesticide affects the level of inhibition. Incubation of enzyme solution alone for 5–120 min at 25° produced an increase in the calorimetric response from 52 to 72, but incubation of enzyme with pesticide decreased the response, the decrease becoming constant for incubation times longer than about 20 min (Fig. 1).

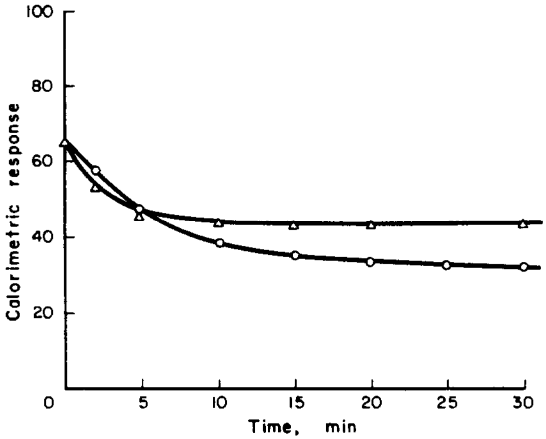

Fig. 1. Relationship between calorimetric response and incubation time for inhibition reaction. ⊙ Parathion in dioxan; △ TEPP in dioxan.

Procedure. Pesticide solutions were diluted to the required concentration in methanol or dioxan and 0·2 ml of solution was added to a sample tube containing 1 ml of 0·3 mg/ml enzyme solution and the mixture was incubated at 25° for 20 min. The general procedure was then followed.

RESULTS AND DISCUSSION

The results for the pesticide-inhibited runs are shown in Tables 2 and 3. Most results quoted are the average of three experiments.

The mechanism of the inhibiting action of organophosphorus compounds has been discussed by O'Brien,[16] Stubbs,[17] and Wilson[20] and reveals two broad types of inhibitor, latent and direct. The latter, more potent, inhibitors require to be present in 10^{-5}–$10^{-9}M$ concentration to cause 50% inhibition,[21] and the former in 10^{-1}–$10^{-4}M$ concentration *in vitro*. The latent inhibitors are activated *in vivo* to give direct inhibitors, *e.g.*, parathion

Table 2. Parathion as inhibitor

[Parathion], $10^{-4}M$	Response for parathion in					
	Dioxan	P*	Methanol	P*	Methanol/Br_2 water	P*
43·5	11	15·7	—		—	
34·5	11	15·7	—		—	
26·0	14	20·0	—		—	
17·4	19	27·2	—		—	
13·0	—		—		13	18·6
8·69	32	45·7	11	15·7	14	20·0
6·99	—		—		15	21·5
5·20	—		—		18	25·7
4·35	46	65·5	11	15·7	19	27·2
2·60	—		14	20·0	27	38·5
1·74	—		18	25·7	—	
0·87	—		30	42·8	43	61·4
0·44	—		45	64·0	50	71·5
0·0	70	100	70	100	70	100

* Percentage enzyme activity remaining after inhibition, calculated as

$$P = \frac{\text{Response for pesticide-inhibited experiment}}{\text{Response for unhibited experiment}} \times 100$$

Table 3. TEPP as inhibitor

[TEPP], $10^{-6}M$	Response for TEPP in			
	Dioxan	P*	Methanol	P*
6·30	12	17·2	—	
4·16	14	20·0	4	5·7
3·35	18	25·7	6	8·6
2·50	22	31·5	10	14·3
1·65	30	42·8	21	30·0
0·84	39	55·8	35	50·0
0·42	48	68·5	45	64·2
0·0	70	100	70	100

* Defined as in Table 2.

is oxidized *in vivo* to paraoxon, a direct inhibitor. This paper reports investigation of one latent and one direct inhibitor and of paraoxon obtained from parathion by oxidation with bromine water.

Since the organophosphorus compounds used are hydrolysed by water, stock solutions were made in both dioxan and methanol. The volume of either solvent actually used in the inhibition experiments produced no effect upon the calorimetric response. Dioxan is inert as solvent towards both pesticides. However both the organophosphorus materials studied are ethoxy compounds and, in methanol, will undergo methanolysis. This results in a mixed ethoxy-methoxy compound, and, in the case of parathion this yields a more potent inhibitor and hence leads to a more sensitive determination of parathion (see Tables 2 and 4).

Table 4 summarizes the analytical results obtained.

Table 4. Summary of analytical results

Pesticide	Solvent	Lowest determinable concentration, *μg/ml*	Range, *μg/ml*
parathion	dioxan	50	50–800
parathion	methanol	5	5–100
parathion/Br_2 water	methanol	5	5–160
TEPP	dioxan	0·05	0·05–1
TEPP	methanol	0·02	0·02–1·2

Selectivity was not investigated in this work but Guilbault[12] has shown that cholinesterases from different sources (*e.g.*, quail, beetle, dog, *etc*) have a markedly different response to a variety of pesticides. However, selectivity may be introduced by the use of different solvent systems, since, in the cases reported here, TEPP shows little variation in its inhibitory powers in dioxan and methanol whereas parathion shows a tenfold increase in inhibitory action in methanol relative to dioxan. In dioxan there is a factor of 10^3 in the sensitivity of the enzyme to the two pesticides.

Conversion of the latent inhibitor parathion into the direct inhibitor paraoxon is achieved by oxidation with bromine water.[16,17] However, in the experiments reported here there is only a small change in inhibitory power on oxidation of parathion in methanol solution. Methanolysis apparently confers direct and hence increased inhibitory powers on parathion.

As an analytical technique the flow microcalorimetric method is relatively rapid and certainly simple in operation. The sensitivity is high especially for direct inhibitors. Its sensitivity and precision are comparable with extant methods.[10,17] Flow methods have many advantages[2,22] and are simply automated—an advantage in modern analytical practice.

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Zusammenfassung—Die Durchfluß-Mikrokalorimetrie wurde auf die Bestimmung von phosphorhaltigen organischen Pestiziden durch Inhibition von Cholinesterase angewandt. Ein direkter (TEPP) und ein latenter Inhibitor (Parathion) wurden untersucht. Ersterer läßt sich bei Konzentrationen von etwa 10^{-6}M, letzterer bei etwa 10^{-4}M bestimmen. Die Inhibitorwirkung von Parathion (E 605) wird bei Verwendung von Methanol als Lösungsmittel gesteigert.

Résumé—On a appliqué la microcalorimétrie d'écoulement au dosage des pesticides organophosphorés par inhibition de la cholinestérase. On a étudié un inhibiteur direct (TEPP) et un inhibiteur latent (parathion). Le premier est dosable à des concentrations d'environ 10^{-6}M et le second à environ 10^{-4}M. Le pouvoir inhibiteur pour le parathion est accru si l'on utilise le méthanol comme solvant.

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ELECTRONIC ABSORPTION AND FLUORESCENCE OF CINCHOPHEN, CINCHONINIC ACID AND THEIR METHYL ESTERS; BIPROTONIC PHOTOTAUTOMERISM OF THE SINGLY-PROTONATED SPECIES

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Summary—The pH and Hammett acidity dependences of the absorption and fluorescence spectra of cinchoninic acid (quinoline-4-carboxylic acid), cinchophen (2-phenylquinoline-4-carboxylic acid) and their methyl esters, were studied. The predominant uncharged ground-state species derived from the free acids are zwitterions. Prototropic equilibria are too slow to compete with fluorescence for deactivation of the excited state at hydrogen ion concentrations represented by the pH scale. However, fluorescence shifts accompanying protonation indicate that the carboxyl group is more basic than the ring nitrogen atom in the excited state. In the Hammett acidity range the singly-charged cations of all the compounds studied undergo phototautomerism in the lowest excited singlet state. The rate of this process is acidity dependent. In very concentrated sulphuric acid solutions doubly-charged cations are formed in the excited state but not in the ground state. The intense emissions of these compounds in moderately concentrated sulphuric acid may be suitable for quantitative analysis if great care is taken to control solution acidity.

There has been considerable study of the electronic spectra of aromatic acids and bases which are either monofunctional or bifunctional with one functional group having electron-withdrawing and the other having electron-donating properties. In monofunctional molecules electron-withdrawing groups such as —COOH and a heterocyclic nitrogen atom in six-membered rings are generally found to become more basic or less acidic in the lowest electronically excited π,π^* states, resulting in red shifts upon protonation or blue shifts upon dissociation, of the fluorescence, phosphorescence and long-wavelength absorption spectral bands. Conversely, electron-donating groups such as —OH and —NH_2 become more acidic or less basic in the lowest excited π,π^* states, resulting in blue shifts upon protonation or red shifts upon dissociation, of the electronic spectra.[1,2] In bifunctional molecules containing an electron-donating and an electron-withdrawing group, qualitatively similar results are observed. However, the spectral shifts tend to be exaggerated as a result of charge transfer from the electron-donating group to the electron-withdrawing group, upon excitation.[3] This is the well-known auxochromic effect. Occasionally, the gain in acidity of an electron-donating group and the gain in basicity of an electron-withdrawing group, in the same electronically excited molecule, is so great that the order of ionization of the two groups is reversed with respect to the normal order observed in the ground state.[4-7] For example, β-methylumbelliferone in the ground electronic state exists in dilute acid solutions as a neutral, undissociated, phenolic lactone. However, in the lowest excited singlet state, the stable uncharged species derived from β-methylumbelliferone is a zwitterion having the phenolic group dissociated and the carbonyl group protonated. The change in structure between ground and excited states of β-methylumbelliferone is termed phototautomerism because it involves a protonic isomerization subsequent to excitation. In β-methylumbelliferone, where the electron-withdrawing and electron-donating groups are widely separated, phototautomerism is biprotonic since it must entail dissociation of the phenolic group and protonation of the carbonyl group. In molecules having the electron-withdrawing and electron-donating groups situated *ortho* to one another, however, phototautomerism may occur by proton transfer across an intramolecular hydrogen bond between the two groups, as for example, in salicylic acid.[4] This phenomenon is termed intramolecular phototautomerism.

Notwithstanding the information that has been gathered on molecules having electron-donating and electron-withdrawing groups, little systematic study has been undertaken of excited-state protonation and fluorescence phenomena of bifunctional molecules in which both functional groups are electron-donating or electron-attracting. It would be particularly interesting to observe the competition between two groups showing similar electromeric effects.

In this paper, we consider the acidity dependences of the absorption and fluorescence spectra of two pharmaceutically significant molecules, quinoline-4-carboxylic acid (cinchoninic acid) and its 2-phenyl derivative (cinchophen). Each of these molecules has two electron-attracting groups; the carboxylic acid group and the heterocyclic nitrogen atom. In order to simplify the characterization of the prototropic equilibria involved in this study, the methyl esters of these compounds were prepared and also subjected to fluorimetric analysis.

EXPERIMENTAL

Apparatus

Absorption spectra were recorded with a Beckman DB-GT spectrophotometer. Fluorescence spectra were recorded with a Perkin-Elmer MPF-2A fluorescence spectrophotometer having monochromators which were calibrated against the xenon line-emission spectrum; the output was corrected for instrumental response by means of a Rhodamine B quantum counter. The pH measurements were made on an Orion Model 801 pH meter employing a Beckman silver–silver chloride–glass combination electrode.

Reagents

Quinoline-4-carboxylic acid and 2-phenylquinoline-4-carboxylic acid were obtained commercially and purified by repeated recrystallizations from 75% ethanol–water solutions. The methyl esters of both quinoline-4-carboxylic acids were prepared according to the procedure of Elderfield and Siegel.[8] The melting points of the esters were in agreement with those reported in the literature.[9,10]

Analytical-reagent grade sulphuric acid was diluted with distilled demineralized water to prepare the solutions used to study the Hammett acidity region. The corrected Hammett acidity scale of Jorgenson and Hartter[11] was employed to calibrate the sulphuric acid solutions. Citrate and phosphate buffers and sodium hydroxide solutions in distilled demineralized water were used in work at higher pH values.

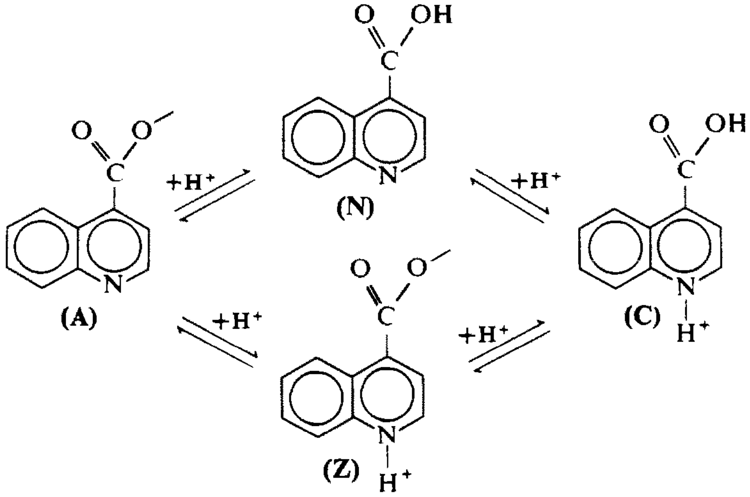
Each sulphuric acid or buffer solution, in a 10-ml volumetric flask, was injected with 100 μl of $1 \times 10^{-3}M$ stock solution of cinchophen or cinchoninic acid immediately before the recording of spectra, in order to minimize decomposition errors.

RESULTS AND DISCUSSION

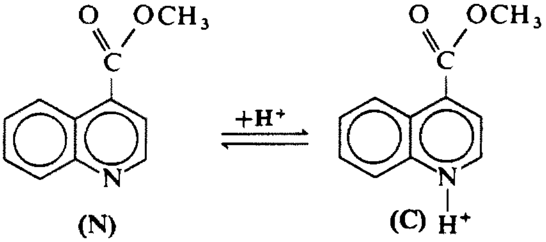
Absorption spectra and ground state ionization phenomena

The possible ionization phenomena of cinchoninic acid, on going from alkaline to dilute acid media, are represented in scheme 1.

Scheme 1



For the methyl ester, which is essentially a non-dissociating model of the neutral molecule (N) the only possible ionization within this pH region is represented in scheme 2.
Scheme 2



The long-wavelength absorption maxima as well as the fluorescence maxima of cinchoninic acid, cinchophen and their methyl esters at various acidities are presented in Table 1. In alkaline solutions cinchoninic acid demonstrates an absorption spectrum similar in appearance to that of quinoline[12,13] but differing in that the ^1L_a band of the 4-carboxylate group lies at a frequency some 1500 cm^{-1} lower than that of unsubstituted quinoline (Fig. 1). In the methyl ester of cinchoninic acid the ^1L_a band has shifted still further towards the red and overlaps the short-wavelength side of the ^1L_b band (Fig. 1). In dilute acid solutions (pH 2·5) the absorption spectrum of cinchoninic acid is similar to that of the quinolinium cation.[12,13] At pH 0 the absorption spectrum of cinchoninic acid and its methyl ester appear essentially identical, and gaussian, and at lower frequencies than the absorption spectrum of cinchoninic acid at pH 2·5. The absorption spectrum of cinchoninic acid in alkaline solutions is assigned to the anion (**A**). The red shift of the ^1L_a band of this species relative to that of quinoline is indicative of substitution in the 4-position of quinoline, which corresponds to an α-position in naphthalene, the parent hydrocarbon from which quinoline may be thought to be derived. Because of the quinolinium-like appearance of the uncharged species derived from cinchonic acid (pH 2·5) and its lack of identity with the methyl ester, the protonation of the anion is believed to occur at the ring nitrogen atom, resulting in the zwitterion (**Z**). The

Table 1. Low frequency absorption ($\bar{\nu}_a$) and fluorescence ($\bar{\nu}_f$) maxima of cinchoninic acid, cinchophen and their methyl esters. Spectral maxima are reported in $cm^{-1} \times 10^{-4}$, and ε in $l. mole^{-1} \cdot cm^{-1} \times 10^{-3}$

		$\bar{\nu}_{^1L_a}$	$\log \varepsilon_{^1L_a}$	$\bar{\nu}_{^1L_b}$	$\log \varepsilon_{^1L_b}$	$\bar{\nu}_f$
Cinchoninic acid	pH 10·0	3.46	4.96	3·17	3·68	2·56
	pH 2·5	—*		3·17	6·66	2·53
	pH 0	—*		3·10	5·94	—†
	H_0 −4·7	—*		3·10	5·94	2·11
	H_0 −10·0	—*		3·07	5·94	1·89
Cinchoninic acid methyl ester	pH 10·0	—*		3·16	2·28	2·39
	pH 0	—*		3·09	3·40	—†
	H_0 −5·8	—*		3·05	3·40	2·13
	H_0 −10·0	—*		3·05	3·40	1·90
Cinchophen	pH 10·0	—*		3·09	4·09	2·63
	pH 2·5	—*		2·94	9·61	2·46
	pH 0·0	—*		2·86	9·14	—†
	H_0 −3·4	—*		2·79	9·20	2·21
	H_0 −10·0	—*		2·68	9·20	1·87
Cinchophen methyl ester	pH 10·0	—*		2·96	3·12	2·42
	pH 0·0	—*		2·81	9·14	—†
	H_0 −4·7	—*		2·76	9·57	2·21
	H_0 −10·0	—*		2·70	9·57	1·86

* The ^1L_a band is degenerate with the ^1L_b band.
† No fluorescence is observed at pH 0.

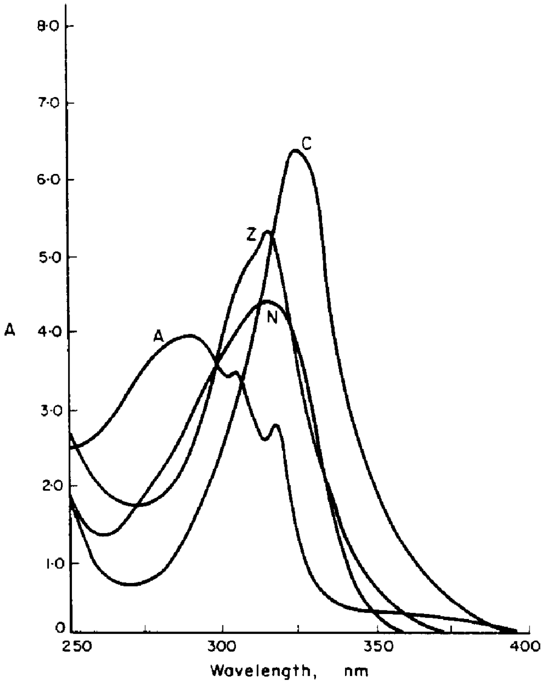


Fig. 1. Absorption spectra of cinchoninic acid (A at pH 10·0, Z at pH 2·5) and its methyl ester (N at pH 10·0, C at pH 0).

Table 2. Protolytic ground ($\mathrm{p}K_a$) and excited ($\mathrm{p}K_a{}^*$) state dissociation constants determined by absorptiometric and fluorimetric titrations, respectively, of cinchoninic acid, cinchophen and their methyl esters. $\mathrm{p}K_{\mathrm{ZA}}$ and $\mathrm{p}K_{\ \mathrm{Z}}$ correspond to the equilibria between the zwitterions derived from the free acids and the respective anions and cations. $\mathrm{p}K_{\mathrm{CN}}$ corresponds to the cation-neutral species equilibria of the methyl esters. $\mathrm{p}K^*_{\mathrm{DC'}}$ corresponds to the doubly-protonated–singly-protonated (at the carboxyl group) cation equilibria in the excited state.

	$\mathrm{p}K_{\mathrm{ZA}}$	$\mathrm{p}K_{\mathrm{CZ}}$	$\mathrm{p}K_{\mathrm{CN}}$	$\mathrm{p}K^*_{\mathrm{DC'}}$
Cinchoninic acid	4·6	1·1		−6·3
Cinchoninic acid methyl ester			3·2	−7·1
Cinchophen	4·8	1·1		−5·4
Cinchophen methyl ester			2·8	−6·3

dissociation constant for the interconversion between the anion and zwitterion was evaluated spectrophotometrically and found to be 4·6 (Table 2). In more concentrated acid solutions both the uncharged species and the methyl ester derived from cinchoninic acid were protonated. The identical absorption spectra obtained for the protonated species of each of these reactions indicates that the cation (C) is formed in each case. However, the $\mathrm{p}K_a$ value for the interconversion between the cation and the uncharged species derived from cinchoninic acid is 1·1 while that for the interconversion between the cation and neutral species derived from the methyl ester is 3·2. This is further evidence that the uncharged species derived from cinchoninic acid does not correspond in its electronic structure to the neutral methyl ester [the model of the neutral species (N)] and that the assignment of the zwitterion structure to the former is correct. That the absorption spectra of both cations and the neutral methyl ester are unstructured and that the ^1L_a bands have shifted towards the red to such a great extent in these species suggests that the neutral carboxylic acid group (or carbomethoxy group) is conjugated and coplanar with the aromatic ring in the ground and Franck-Condon excited states and that the absorption spectra have considerable charge-transfer character.

In concentrated sulphuric acid solutions the absorption spectra of both cinchoninic acid and its methyl ester demonstrate a small red shift with increasing sulphuric acid concentration. Although carboxylic acids derived from carbocyclic aromatic rings are known to protonate in the ground state at Hammett acidities near −8,[14] the changes in the absorption spectra of cinchoninic acid and its methyl ester were not sufficient to indicate that a prototropic reaction was occurring even in the most concentrated sulphuric acid solution ($H_0 = -10$) used. This is likely due to the positive charge already residing on the singly protonated cations being delocalized onto the carboxyl groups, reducing their basicities. The small red shifts found when acid solutions are used are likely due to hydrogen bonding of the carbonyl oxygen atom and differences in the dielectric strength between water and sulphuric acid.

Unlike cinchoninic acid, cinchophen does not show well-resolved vibrational structure in the absorption spectrum of its own anion (Fig. 2). Moreover, the ^1L_b band of the cinchophen anion lies at lower frequencies than that of the cinchoninate anion and the ^1L_a band for the former is obscure. The spectrum of the neutral methyl ester of

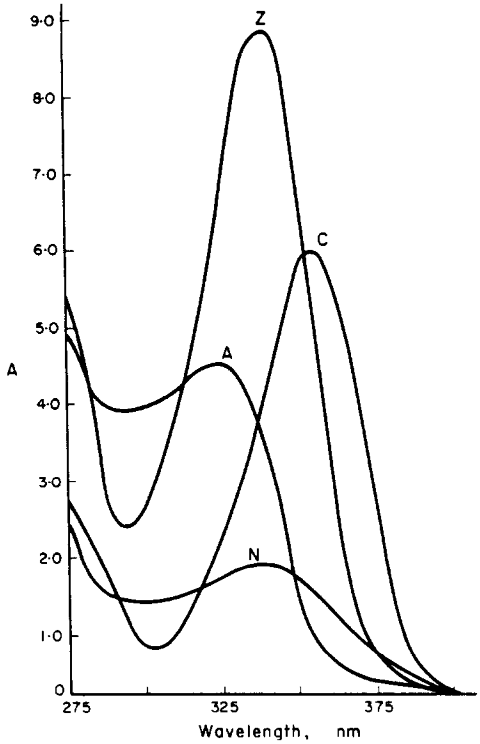


Fig. 2. Absorption spectra of cinchophen (A at pH 10·0, Z at pH 2·5) and its methyl ester (N at pH 10·0, C at pH 0).

cinchophen is similar to that of the anion of cinchophen but lies at lower frequencies. The two successive protonations of the anion derived from cinchophen result in successive red shifts of the low-frequency absorption band (which is probably a composite of the ^1L_a and ^1L_b bands). The pK_a values for interconversions between the anion and uncharged species and between the uncharged species and the cation are 4·8 and 1·1, respectively, while that for interconversion between the neutral species and cation derived from the methyl ester of cinchophen is 2·8. Because of the similarities between corresponding dissociation constants of cinchoninic acid and cinchophen and between the methyl esters of these compounds, it can be concluded that the prototropic species derived from cinchophen and present in any given pH region correspond exactly to those derived from cinchoninic acid (*i.e.*, the zwitterion is the predominant uncharged ground-state species derived from cinchophen). The differences between the absorption spectra of the various prototropic species derived from cinchophen and cinchoninic acid are apparently due to the presence of the phenyl group in the 2-position. The great extent to which the phenyl group influences the absorption spectra of the prototropic species derived from cinchophen (which show substantial charge-transfer character relative to that of the corresponding species derived from cinchoninic acid) strongly suggests that in the ground and Franck-Condon excited states the phenyl group is coplanar and conjugated with the quinoline ring.

The results in Table 1 show that in concentrated sulphuric acid the absorption spectra of cinchophen and its methyl ester shift towards the red with increasing acid concentration to a considerably greater extent than do the absorption spectra of cinchoninic acid and its methyl ester. However, plots of absorbance *vs.* Hammett acidity at the absorption maxima of these compounds, at $H_0 = -10$ and at $H_0 = -0{\cdot}7$ yield very gradually sloping titration curves. Apparently the red shift is not due to a prototropic process but rather to a solvent effect. That this effect is more pronounced in cinchophen can be rationalized on the basis of the generally greater sensitivity of charge-transfer type spectra to the polarizing influence of solvent[15] and the greater degree of intramolecular charge transfer in the electronic transitions of the 2-phenyl derivative.

Fluorescence spectra and excited state processes

In alkaline solutions the anion derived from cinchoninic acid has a weak violet fluorescence. As the pH is lowered the fluorescence becomes blue with maximum at $2{\cdot}53 \times 10^4\ \text{cm}^{-1}$. The conversion of the violet fluorescence into the blue fluorescence, with decreasing pH, occurs with the same titration characteristics as the absorption spectrum changes in the pH region 7–3. In alkaline solutions the methyl ester of cinchoninic acid fluoresces weakly with maximum at $2{\cdot}39 \times 10^4\ \text{cm}^{-1}$. Since the methyl ester is electronically similar to the neutral molecule (**N**) and fluoresces at a different frequency than does the protonation product of the anion, it can be concluded that the emission at $2{\cdot}53 \times 10^4\ \text{cm}^{-1}$ arises from the excited zwitterion (**Z**). The identity between the fluorimetric and absorptiometric titrations for the interconversion between the anion and zwitterion indicates that the interconversion is static (*i.e.*, equilibrium does not occur during the lifetime of the excited state). That the fluorescences of the zwitterion and the methyl ester occur at lower frequencies than that of the anion indicates that both the carboxylate group and the ring nitrogen atom are more basic and have higher electron densities in the excited state than in the ground state. Because the methyl ester fluoresces at lower frequencies than the zwitterion, the carboxylate group is apparently more basic than the ring nitrogen atom[1] and if prototropic equilibrium was attained during the lifetime of the excited state, phototautomerism of the zwitterion to the neutral species would probably occur. As the pH is lowered to near 0 the fluorescence of both cinchoninic acid and its methyl ester is quenched with ground-state titration characteristics. Apparently, the cations are non-fluorescent and prototropic equilibrium is not attained in the excited state even near pH 0.

In sulphuric acid solutions (from $H_0 = -1$ to $H_0 = -10$) of cinchoninic acid and its methyl ester, an intense blue-green fluorescence appears at $H_0 = -1$, rises to a maximum near $H_0 = -5$ and is quenched sigmoidally with further increase in sulphuric acid concentration (Fig. 3). At $H_0 = -10$ a weak yellow-green fluorescence is observed. These titration phenomena suggest that two prototropic processes are occurring in the lowest excited singlet state in the region from $H_0 = -1$ to $H_0 = -10$ since no ground-state prototropic processes were detected absorptiometrically in this region of acidity. That two protonations occur between $H_0 = -1$ and $H_0 = -10$ is somewhat perplexing since the excited singly-protonated cations of cinchoninic acid and its methyl ester are the species present at the lower end of the Hammett acidity region and only the carboxyl (or carbomethoxy) group is sufficiently basic in the excited state to become protonated. It was considered that protonation might also occur at a carbon atom in the aromatic ring but this would withdraw a pair of electrons and reduce the aromaticity of the π-electronic system, a process that should result in a substantial shift towards the blue

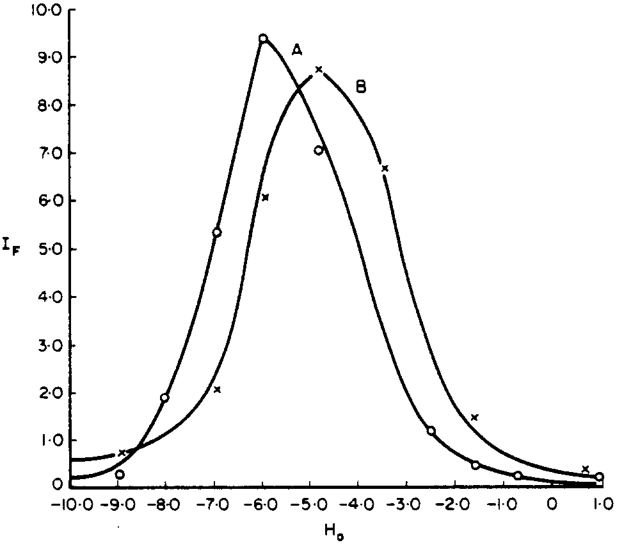
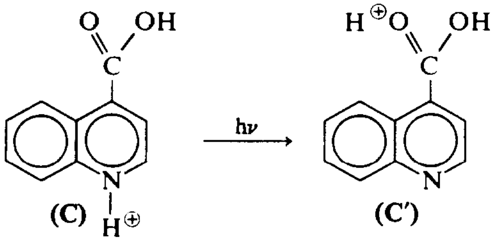


Fig. 3. Fluorimetric titrations in sulphuric acid media of *A*, cinchoninic acid, *B*, methylcinchoninate.

or complete quenching of the fluorescence with increasing acidity. Since this was not observed this possibility was dismissed. An alternative explanation of the unusual fluorimetric titration behaviour of cinchoninic acid and its methyl ester is as follows. If the carboxyl group were more basic than the ring nitrogen atom of cinchoninic acid in the excited state, the singly-charged cation, protonated at the ring nitrogen atom, which is formed in the ground state, would be expected to phototautomerize biprotonically to the cation protonated at the carboxyl group, during the lifetime of the excited state (Scheme 3).

Scheme 3



(C) (C′)

This process would entail excitation of (C) to the lowest excited singlet state followed by protonation at the carboxyl group and very rapid dissociation from the ring nitrogen atom. Fluorescence would then occur from C′. Thermodynamically this process should be independent of solution acidity because there is no net gain or loss of protons. However, the short lifetime of C in the excited state, as evidenced by the lack of fluorescence from this species, precludes the rate-determining protonation at the carboxyl group in dilute acid before the cation returns to the ground state in a radiationless transfer. As the acidity of the medium is increased, protonation of the carboxyl group and hence phototautomerism of C to C′ becomes more probable so that the titration curve in the region from $H_0 = -1$ to $H_0 = -5$ represents the kinetics rather than the thermodynamics of the phototautomerism. The blue-green fluorescence in sulphuric acid is thus believed to originate from the singly-charged cation C′, protonated at the carboxyl group. At higher acidities protonation of the ring nitrogen atom of C′ becomes thermodynamically feasible so that the titration curve in the region from $H_0 = -5$ to $H_0 = -10$ represents the conversion of C′ into the doubly-protonated cation in the excited state. Because the ring nitrogen atom is more basic in the excited state than in the ground state the fluorescence of the doubly-charged cation occurs at lower frequencies than that of the singly-charged cation.

The fluorescences of cinchophen and its methyl ester and their acidity dependences are similar to those of cinchoninic acid and its methyl ester. That the fluorescences of the prototropic species derived from cinchophen and its methyl ester are very close to those of the corresponding species derived from cinchoninic acid and its methyl ester suggests that the 2-phenyl groups in the former molecules are not conjugated with the quinoline rings in the thermally relaxed excited states. Thus excitation of cinchophen appears to be followed by a rotation of the phenyl ring out of plane with the quinoline ring, a process which is probably precipitated by the transfer of charge from the homocyclic ring of quinoline into the heterocyclic ring, upon excitation, thereby repelling, π-electronic charge back into the phenyl group and destroying the conjugation of the phenyl group with the quinoline ring.

The intense blue-green fluorescences of cinchoninic acid and cinchophen in sulphuric acid solutions appear to be the only emissions observed which are of sufficient intensity for sensitive quantitative analysis of these compounds. However, owing to the great sensitivities of the quantum yields of these fluorescences to acidity, great care must be exercised in controlling the Hammett acidities of standard and unknown solutions.

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Zusammenfassung—Die Abhängigkeit der Absorptions- und Fluoreszenzspektren von Cinchoninsäure (Chinolin-4-carbonsäure), Atophan (2-Phenylchinolin-4-carbonsäure) und ihrer Methylester vom pH bzw. der Hammett'schen Aciditätsfunktion wurde untersucht. Die im Grundzustand überwiegend vorliegenden ungeladenen Spezies, die sich von den freien Säuren ableiten, sind Zwitterionen. Prototrope Gleichgewichte sind zu langsam, um bei Wasserstoffionenkonzentrationen, wie sie durch die pH-Skala dargestellt werden, bei der Desaktivierung des angeregten Zustandes mit der Fluoreszenz konkurrieren zu können. Mit der Protonierung einhergehende Fluoreszenzverschiebungen zeigen jedoch, daß im angeregten Zustand die Carboxylgruppe basischer ist als das Stickstoffatom im Ring. Im Bereich der Hammett'schen Aciditätsfunktion machen die einfach geladenen Kationen aller untersuchten Verbindungen im niedrigsten angeregten Singlettzustand eine Phototautomerie durch. Die Geschwindigkeit dieses Vorgangs hängt von der Acidität ab. In sehr·konzentriert schwefelsauren Lösungen werden im angeregten, jedoch nicht im Grundzustand zweifach geladene Kationen gebildet. Die intensiven Emissionen dieser Verbindungen in mäßig konzentrierter Schwefelsäure könnten zur quantitativen Analyse geeignet sein, wenn man die Acidität der Lösung sehr sorgfältig einstellt.

Résumé—On a étudié les relations entre le pH et l'acidité de Hammett et les spectres d'absorption et de fluorescence de l'acide cinchoninique (acide quinoléine 4-carboxylique), du cinchophène (acide 2-phénylquinoléine 4-carboxylique) et de leurs esters méthyliques. Les espèces à l'état fondamental non chargées dérivées des acides libres qui prédominent sont des zwitterions. Les équilibres prototropiques sont trop lents pour entrer en compétition avec la fluorescence pour la désactivation de l'état excité aux concentrations en ion hydrogène représentées par l'échelle de pH. Toutefois, des changements de fluorescence accompagnant la protonation indiquent que le groupe carboxyle est plus basique que l'atome d'azote cyclique à l'état excité. Dans le domaine d'acidité de Hammett les cations à une seule charge de tous les composés étudiés subissent un phototautomérisme à l'état singulet excité le plus bas. La vitesse de ce processus dépend de l'acidité. Dans des solutions très concentrées en acide sulfurique, il se forme des cations doublement chargés à l'état excité mais non à l'état fondamental. Les émissions intenses de ces composés en acide sulfurique modérément concentré peuvent convenir à l'analyse quantitative si l'acidité de la solution est contrôlée avec grand soin.

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BESTIMMUNG ^{35}S-MARKIERTER POLYTHIONATE NACH HOCHSPANNUNGSIONOPHORETISCHER TRENNUNG

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Zusammenfassung—Die Aktivitätsmessung ^{35}S-markierter Polythionate auf Pherogrammen erfolgt einmal nach Elution und Überführung in $Ba^{35}SO_4$ mit einem Geiger-Müller-Endfensterzählrohr oder direkt auf dem Trägermaterial durch Flüssigszintillation. Beide Meßmethoden werden mit einander verglichen. Die Zählausbeute beträgt für die $BaSO_4$-Methode 0,25% und für die der Flüssigszintillationsmethode 55%. Bei letzterer tritt jedoch eine Substanzabhängigkeit der Zählausbeute auf.

Für die Untersuchung von Gemischen verschiedener Polythionate hat sich als Trennmethode die Hochspannungspapierionophorese bewährt.[1-4] Die anschließende Bestimmung kann u.a. nach Abbau zu $S_2O_3^{2-}$ coulometrisch vorgenommen werden.[5]

Durch den Einsatz ^{35}S-markierter Ausgangsverbindungen läßt sich der Nachweis der einzelnen Zonen sehr empfindlich gestalten. Außerdem sind die Zonen des Sulfits und des Sulfats noch leicht auf den Pherogrammen zu erkennen.[1-4] Auch die Bestimmung der Schwefelverbindungen kann dann über eine Messung der Aktivität erfolgen. Hierzu werden in der vorliegenden Arbeit zwei Wege eingeschlagen.

ELUTION DER ZONEN UND BESTIMMUNG ALS $Ba^{35}SO_4$

Die Lage der ionophoretisch getrennten Schwefelverbindungen auf dem Pherogramm ergibt sich aus der aufgenommenen Aktivitätsverteilungskurve.

Die einzelnen Zonen werden ausgeschnitten und in ein Gemisch von 1 ml konz. Ammoniak, 1 ml Perhydrol und 25 ml 0,04*M* Natriumsulfat-Lösung gegeben. Der Zusatz an inaktivem Na_2SO_4 dient zur Erzielung einer unendlichen Schichtdicke an $Ba^{35}SO_4$. Nach einer Stunde verkocht man das überschüssige H_2O_2, gibt 100 ml H_2O hinzu und nimmt die Papierstücke vorsichtig aus der Lösung heraus. Ein anschließendes zweimaliges Eluieren mit je 30 ml warmen Wasser reicht zur vollständigen Entfernung von eventuell am Papier adsorbiertem SO_4^{2-} aus. Die vereinigten Eluate werden auf 150 ml eingedampft. Die Fällung erfolgt dann bei pH 2 durch tropfenweise Zugabe von 12 ml 0,1*M* $BaCl_2$-Lösung in der Siedehitze.

Bei 120 durchgeführten Elutionen schwanken die Auswaagen der einzelnen Proben nur zwischen 237 mg und 240 mg. Der Sollwert von 233 mg wird um durchschnittlich 6 mg überschritten. Dies ist durch die Verwendung des schwefelsäurehaltigen pH-3 Grundelektrolyten bedingt. Die Substanzmenge der Schwefelverbindungen in den Zonen ist jeweils $<0,1$ mg und beeinflußt die Auswaage nicht.

Für die Messung müssen die $BaSO_4$-Niederschläge in Aluminiumschälchen überführt werden, wobei vor allem auf eine über die gesamte Fläche gleichmäßige Schicht zu achten ist. Außerdem darf die Oberfläche keine Risse oder Blasen aufweisen. Bewährt

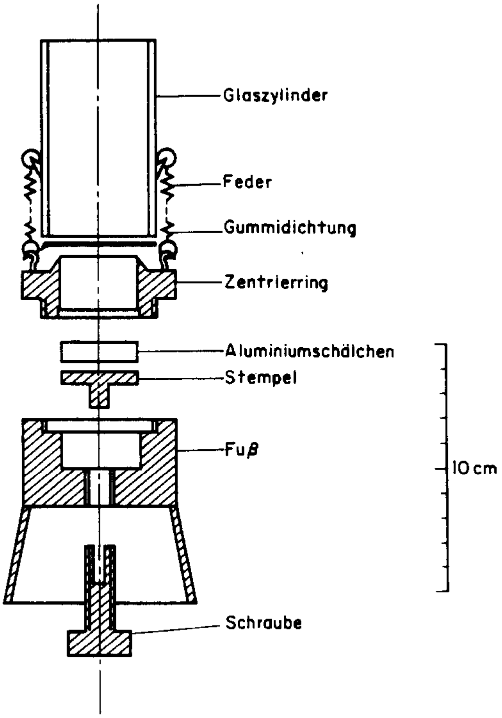

Abb. 1. Anordnung zur Sedimentation von $Ba^{35}SO_4$-Niederschlägen.

hat sich die Sedimentation aus einer Suspension sehr feiner Teilchen. Die hierzu entwickelte Anordnung zeigt Abb. 1. Sie besteht aus einem Glaszylinder, an den vier Glashaken angeschmolzen sind. Vier Federn pressen den unten plangeschliffenen Zylinder gegen den Zentrierring. Das vorher gewogene Aluminiumschälchen wird auf den Stempel im Fuß der Anordnung gelegt und mit der Schraube gegen den Zentrierring gedrückt. Der Innendurchmesser der Bohrung im Zentrierring ist gleich dem

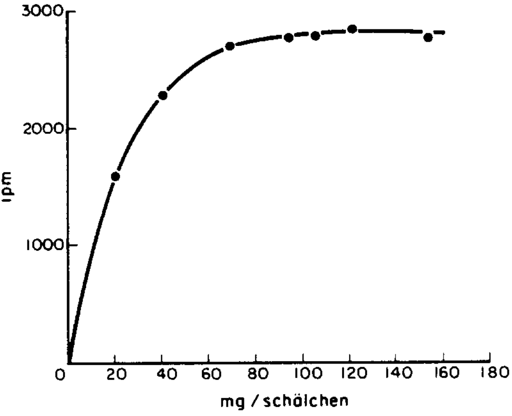

Abb. 2. Nettoimpulsrate für ^{35}S in Abhängigkeit von der Schichtdicke im Schälchen bei konstanter spezifischer Aktivität.

Innendurchmesser des Aluminumschälchens. Eine Dichtung zwischen Glaszylinder und Zentrierring verhindert das Auslaufen der Lösung.

Das Bariumsulfat wird in einem Achatmörser fein zerrieben und in Äthanol aufgeschwemmt. Die Suspension gießt man in den Glaszylinder und wartet, bis sich alles abgesetzt hat (*ca* 2 h). Anschließend wird der Alkohol vorsichtig mit einer IR-Lampe abgedampft. Um Korrekturen für Selbstabsorptionen und Rückstreuung zu vermeiden, wird bei unendlicher Schichtdicke gemessen (Abb. 2). Sie liegt bei 100 mg $BaSO_4$/Schälchen (= 16,5 mg/cm^2). Die Geometrie der Zählanordnung ist bei allen Messungen konstant. Korrekturen der Meßergebnisse, bedingt durch die Totzeit des Geiger-Müller-Endfensterzählrohrs, entfallen wegen der verhältnismäßig kleinen Impulsraten. Dagegen erfordert die kurze Halbwertszeit des ^{35}S bei Untersuchungen, die sich über einen längeren Zeitraum erstrecken, eine Zerfallskorrektur der Meßergebnisse.

AKTIVITÄTSMESSUNG DIREKT AUF DEM TRÄGERMATERIAL DURCH FLÜSSIGSZINTILLATION

Die direkte Messung trockener Teile der Chromatogramm- bzw. Pherogrammstreifen in einem Szintillator ist eine seit längerer Zeit bekannte und bequeme Methode zur Aktivitätsermittlung vor allem bei ^{14}C-markierten Verbindungen.[6–10]

Zur Messung der ^{35}S-markierten Substanzen werden die getrockneten Pherogramme in 15 x 10 mm Stücke geschnitten. Die Gesamtbreite der Pherogramme beträgt in allen Fällen 30 mm. Jede einzelne Zone setzt sich aus 10–12 Papierstücken zusammen. Die ausgeschnittenen Papierstücke legt man horizontal auf den Boden der Meßgläser und setzt dann 7 ml der Szintillatorlösung zu. Bei diesem Volumen hat man ein Maximum der Zählausbeute (Abb. 3). Die Szintillatorlösung enthält auf 1000 ml Toluol 6,0 g PPO und 0,01 g POPOP. Eine merkliche Löslichkeit der ^{35}S-markierten Substanzen im Szintillator ist nicht zu beobachten.

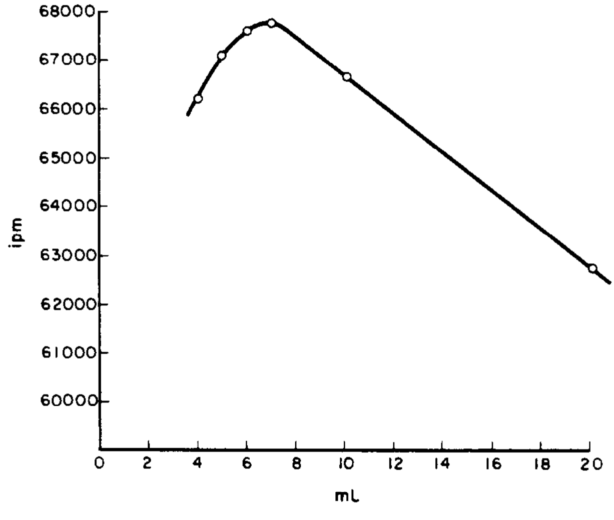

Abb. 3. Abhängigkeit der Nettoimpulsrate von der Menge an Szintillator-Lösung.

Die Messungen selbst erfolgen im Tri-Carb-Spektrometer, Modell 3380 der Fa. Packard Instruments. Der automatische Probenwechsler hat ein Fassungsvermögen von 200 Gläsern. Diese Meßgläser sind standardisiert und bestehen aus einem kaliumarmen Glas. Gemessen wird im fixierten ^{14}C-Kanal. Die im Grundelektrolyten enthaltenen Salze bewirken nur einen vernachlässigbar kleinen Verlust in der Zählausbeute (Tab. 1). Für diese Kontrollmessungen wird eine SO_4^{2-}-Standardlösung eingesetzt, deren radiochemische Konzentration 10,8 μCi/ml beträgt. Die Zählausbeute für ^{35}S-markiertes SO_4^{2-} ergibt sich dann bei Papier als Trägermaterial zu 55%.

Tabelle 1. Nettoimpulsrate in Abhängigkeit des eingesetzten Grundelektrolyten

	Mittelwert aus je 10 Messungen, *ipm*
ohne Grundelektrolyt	65 597
	65 266
	65 626
	64 756
	65 841
	65 676
	$\bar{x}$ = 65 460
Grundelektrolyt pH 7 0,6M $NaCH_3COO$/3,4 . $10^{-3}M$ CH_3COOH	66 408
	66 567
	65 650
	64 748
	65 721
	65 869
	$\bar{x}$ = 65 827
Grundelektrolyt pH 3 0,1M H_2SO_4/1M Glycin	64 185
	65 282
	64 759
	64 382
	64 751
	65 329
	$\bar{x}$ = 64 781

VERGLEICH DER BEIDEN AKTIVITÄTSMESSMETHODEN ANHAND EINES POLYTHIONATGEMISCHES

Die eingesetzte Lösung enthält die Polythionate $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ und $S_6O_6^{2-}$ mit ^{35}S-markierten Sulfonsäuregruppen gleicher spezifischer Aktivität.

Die Konzentrationen betragen: 10,87 mg $S_3O_6^{2-}$/ml, 10,12 mg $S_4O_6^{2-}$/ml, 4,67 mg $S_5O_6^{2-}$/ml und 0,887 mg $S_6O_6^{2-}$/ml. Für den Vergleich werden jeweils zwölf Proben von 1,0; 2,0; 3,0; 4,0; 5,0 μl dieser Polythionatlösung mit der "Agla" Mikrometersyringe auf Ionophoresepapier aufgetragen und getrennt. Nach beendeter Ionophorese nimmt man die Aktivitätsverteilungskurven auf, um die Lage der einzelnen Zonen auf den Pherogrammen festzulegen (Abb. 4). Danach werden die Meßproben nach den oben beschriebenen Vorschriften hergestellt.

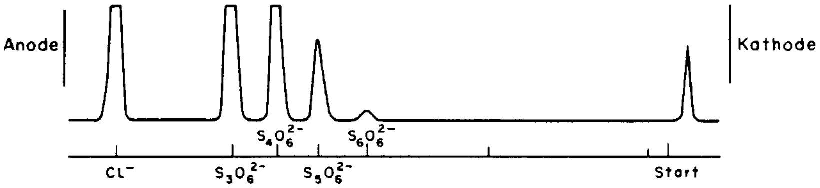

Abb. 4. Typisch Pherogram (Aktivitätsverteilungkurve).

Die Meßzeiten nach Überführung in $Ba^{35}SO_4$ betragen zehnmal vier Minuten, die bei der Messung direkt auf dem Papier zehnmal eine Minute. Tabelle 2 zeigt die Abhängigkeit der Nettoimpulsrate von der Absolutmenge der Ionen nach Überführung in $Ba^{35}SO_4$ und bei direkter Messung auf dem Träger. Die Meßpunkte sind Mittelwerte von jeweils sechs Proben. Impulsrate ist in jedem Falle der aufgetragenen Menge direkt proportional.

Tabelle 2. Abhängigkeit der Nettoimpulsrate von der aufgetragenen Menge der Polythionate

		nach Überführung in $Ba^{35}SO_4$		bei direkter Messung	
Ion	Menge, *µg*	Zählrate, *ipm*	Standardabweichung, *µg*	Zählrate, *ipm*	Standardabweichung, *µg*
$S_3O_6^{2-}$	50	2 500	1,1	618 000	0,5
$S_4O_6^{2-}$	50	2 100	0,8	517 000	0,7
$S_5O_6^{2-}$	20	750	0,4	180 000	0,3
$S_6O_6^{2-}$	5	165	0,2	39 000	0,1

DISKUSSION

Die Messung der Aktivität nach Elution und anschließender Überführung der Schwefelverbindungen in $BaSO_4$ hat den Nachteil der schwierigen und zeitraubenden Meßprobenvorbereitung. Für die Elution, Oxydation zu SO_4^{2-} und Sedimentation sind zwei Tage notwendig. Ein weiterer Nachteil ist die geringe Zählausbeute, die bei etwa 0,25% liegt. Dadurch sind Zonen geringerer Substanzkonzentration bei gegebener spezifischer Aktivität nicht mehr meßbar. Die Absolutaktivität einer gerade noch meßbaren Zone beträgt 20 000 Zerfälle/Minute. Der Vorteil dieser Meßmethode aber ist die Unabhängigkeit der Meßergebnisse von der chemischen Zusammensetzung der jeweiligen Schwefelverbindung.

Wesentlich schneller und leichter ist die Messung der Aktivität innerhalb der Zonen direkt auf dem Trägermaterial mittels der Flüssigszintillationsmethode. Die Zählausbeute liegt bei Papier als Trägermaterial bei 55%. Diese Methode besitzt daher eine wesentlich größere Empfindlichkeit.

Vergleicht man aber die Ergebnisse, die für die Polythionate mit den beiden Meßmethoden erhalten werden, so ergeben sich teilweise erhebliche Unterschiede. Bei der direkten Messung tritt eine Substanzabhängigkeit der Zählausbeute auf, wie sie auch bei ^{14}C-markierten Verbindungen bekannt ist.[6] Grund ist die unterschiedliche Absorption der von den Szintillatoren emittierten Photonen durch die einzelnen Polythionate. Dieser Zählverlust muß bei der Auswertung berücksichtigt werden (Tab. 3).

Tabelle 3. Zählausbeute bei der Flüssigszintillationsmessung ^{35}S-markierter Verbindungen

^{35}S-markierte Verbindung	Zählausbeute, %
$S_3O_6^{2-}$	55
$S_4O_6^{2-}$	54
$S_5O_6^{2-}$	53
$S_6O_6^{2-}$	50

Die mit beiden Meßmethoden erhaltenen Substanzmengen liegen im µg-Bereich. Die spezifische Aktivität beträgt etwa $1 \cdot 10^{-2}$ mCi/mMol. Die Substanzmengen können ohne weiteres um den Faktor 1000 verkleinert werden, wenn gleichzeitig die spezifische Aktivität entsprechend erhöht wird. Die spezifischen Aktivitäten der käuflichen Schwefelverbindungen, die eingesetzt werden können, liegen bei 30–40 mCi/mMol.

Grundsätzlich lassen sich beide Methoden zur quantitativen Bestimmung markierter Schwefelverbindungen einsetzen. Bei uniformer Markierung aller Schwefelatome ist die Nettoimpulsrate dem Schwefelgehalt direkt proportional. Mit Eichkurven lassen sich die Absolutmengen einfach ermitteln. Bei genereller Markierung der Schwefelatome der Ausgangsverbindungen ist die Kenntnis des Reaktionsmechanismus notwendig. Außerdem dürfen keine Isotopenaustauschreaktionen auftreten.

Das wesentliche dieser Kombination von Trennung und Aktivitätsmessung liegt aber nicht nur in der Möglichkeit Reaktionsgemische quantitativ zu untersuchen. Vielmehr können mit Hilfe genauer Aktivitätsmessungen Reaktionsmechanismen aufgeklärt und neue Verbindungen nachgewiesen werden.

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Die Untersuchungen würden im Rahmen des Sonderforschungsbereiches 52 „Analytik" durchgeführt.

Summary—The activity of ^{35}S-labelled polythionates has been measured on electropherograms by elution followed by precipitation as Ba^{35}SO$_4$ and end-window GM-tube counting, and directly on the support material by liquid-scintillation counting. The results obtained by the two methods are presented and compared. The count-rate yield is only 0·25% for the first method, but 55% for the second, though this does suffer from a slight dependence on the nature of the ion present.

Résumé—On a mesuré l'activité de polythionates marqués au ^{35}S sur des électrophèrogrammes, par élution suivie de précipitation à l'état Ba^{35}SO$_4$ et comptage par tube GM à fenêtre, et directement sur le matérial-support par comptage par scintillation liquide. On présente et compare les résultats obtenus par les deux méthodes. Le rendement de la cadence de comptage est de 0,25% seulement pour la première méthode, mais de 55% pour la seconde, quoique celle-ci ait l'inconvénient de dépendre légèrement de la nature de l'ion présent.

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EXTRACTION WITH LONG-CHAIN AMINES—VI

SEPARATION OF MANGANESE AS $Mn(CNS)_6^{4-}$ COMPLEX AND ITS COMPLEXOMETRIC DETERMINATION IN CALCAREOUS MATERIAL

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Summary—Manganese is quantitatively extracted into a benzene solution of trioctylmethylammonium chloride from a solution at least 0·25*M* in potassium thiocyanate and at pH 2·5–7. After stripping into dilute ammonia containing triethanolamine (TEA) and hydroxylamine hydrochloride, manganese is determined by EDTA titration. Calcium and magnesium are not extracted even in traces. Iron is co-extracted with manganese and is masked with TEA during the stripping. Aluminium also does not interfere. In the aqueous phase, after the extraction of manganese, calcium or magnesium can be determined by the usual EDTA titration. The method described permits highly selective individual determination of manganese and calcium and/or magnesium in all materials rich in manganese.

In complexometric determination of manganese, calcium and magnesium in materials rich in manganese we encounter some difficulties caused by the relatively low stability constant of the Mn-EDTA complex ($\log K_{MnY} = 13{\cdot}6$). This allows reliable determination of manganese in alkaline medium together with calcium and/or magnesium. Determination in slightly acidic medium (pH 5–6), for example with DCTA and Methylthymol Blue,[1] or with EDTA and Calcein,[2] can be used when very small amounts of calcium and magnesium are present. Masking of calcium with ammonium fluoride[3,4] is limited to a maximum of 10 mg of calcium. On the other hand, manganese in trace amounts (3–4 mg/100 ml) can be masked with triethanolamine (TEA) in strongly alkaline medium,[5] and large amounts up to 80 mg by transforming this intense green Mn–TEA complex into the almost colourless manganese(III) cyanide complex.[6]

In the complete analysis of the mixtures of iron, aluminium, manganese, calcium and magnesium, the known separation methods for iron, aluminium and manganese are used. Manganese can be precipitated in alkaline medium with thioacetamide,[7] or from small volumes with potassium chlorate[8,9] or from acidic solution with ammonium persulphate.[10] In precipitation of manganese we have to allow for small losses of manganese in the filtration, or for some co-precipitation of calcium or magnesium. Separation of iron and aluminium with zinc oxide and then manganese with ammonium persulphate is time-consuming.[11] The extraction methods for manganese described in the literature[12] are suitable mostly for small amounts of manganese and for its colorimetry, but not selective enough for its complexometric determination. Even the extraction of manganese together with heavy metals by extraction as diethyldithiocarbamates into chloroform or ethyl acetate needs large amounts of reagent and solvents.[13,14]

In continuation of our previous work on extraction of some metals as chlorides and iodides into a solution of trioctylmethylammonium chloride (TOMA)[15] we paid attention to the extraction of metals as thiocyanate complexes. We have found that manganese(II) is quantitatively extracted from slightly acidic potassium thiocyanate medium with a chloroform or benzene solution of TOMA, without any extraction of calcium and magnesium. After stripping of manganese into ammonia–triethanolamine solution manganese is determined complexometrically without any interference by iron and aluminium. In the aqueous phase after extraction of manganese, calcium and/or magnesium can be determined by the usual complexometric method. As far as is known, only one method for extraction of a manganese thiocyanate complex (with tributyl phosphate) has been described, by Różycki and Lachowicz.[16] Under the same conditions calcium and magnesium are also almost quantitatively extracted and therefore their method is not suitable for manganese–alkaline earths separation.

EXPERIMENTAL

Reagents

Trioctylmethylammonium chloride solution, 5% in benzene. Prepared by dissolving 50 g of Aliquat 336-S (General Mills Chemical Inc., Kankakee, Illinois, U.S.A) in 1 litre of pure benzene.

Other chemicals used were analytical reagent grade.

EDTA solution, 0·05*M*. Standardized with 0·05*M* lead nitrate with Xylenol Orange as indicator.

Solutions, 0·05*M*, of manganese sulphate, magnesium sulphate and ferric chloride were prepared from proper amounts of the compounds and checked complexometrically.

A 0·05*M* solution of calcium chloride was prepared by dissolving calcium carbonate in sufficient hydrochloric acid, and checked complexometrically.

Indicators used were thymolphthalexone mixture with potassium nitrate 1 : 100 w/w and metalphthalein (cresolphthalexone), 0·1 g, and Naphthol Green B, 0·06 g, mixed with 15 g of potassium nitrate.

Other reagents include 10% solution of triethanolamine (TEA) in water, solid potassium thiocyanate, solid hydroxylamine hydrochloride, and ammonium chloride.

Separation of manganese

Effect of potassium thiocyanate concentration. In 150-ml separatory-funnels 5-ml portions of 0·05*M* manganese sulphate were mixed with 0·25, 0·50, 1·0, 2·0, or 3·5 g of potassium thiocyanate, and diluted to 40 ml with water (final concentrations of potassium thiocyanate were 0·065, 0·13, 0·26, 0·52 and 0·917*M*). The pH was adjusted to about 4 with a few drops of 1*M* sulphuric acid. Each solution was extracted twice with 10 ml of 5% TOMA in benzene with 1 min shaking, each pair of extracts being combined. The aqueous phases were washed with 5–10 ml of pure benzene and the washings added to the appropriate extract. The extracts were then stripped with a mixture of 12·5 ml of ammonia (1 + 1), 12·5 ml of 10% triethanolamine solution and 0·5 g of hydroxylamine hydrochloride. The phases were separated and the organic phase washed with 25 ml of water. The ammonia solution and washings were collected in a 300-ml titration flask (for each extract), diluted to 150–200 ml and after the addition of 0·2 g of ammonium chloride the manganese was determined with 0·05*M* EDTA, with thymolphthalexone as indicator (see Table 1). From these results it was found that at a potassium thiocyanate concentration >0·25*M* the extraction of manganese is quantitative. Excess of thiocyanate does not influence the extraction.

Influence of pH. In a small beaker 5 ml of 0·05*M* manganese solution were diluted to 35 ml with water and 1 g of potassium thiocyanate was added. The pH was adjusted to various values with sulphuric acid (glass electrode). The solution was transferred quantitatively into a 150-ml separatory funnel, and manganese extracted and determined as above. With increasing pH the degree of extraction also increases, being 57% at pH 0·43, 94% at pH 1·2 and at least 99·9% between pH 2·5 and 7.

Dilution and time of extraction. Because during the extraction of manganese equilibration between the thiocyanate and chloride salts of TOMA also takes place, the mutual effect of dilution (concentration of manganese and thiocyanate) and time of shaking was followed. Various volumes containing known concentrations of manganese and thiocyanate were extracted twice with 10 ml of 5% TOMA in benzene for 1, 2, 5 or 10 min and manganese determined as above. The results are summarized in Table 2.

From the table is evident that the minimum time of extraction (shaking) needed is indirectly proportional

and manganese was determined as above. The results are summarized in Table 2.

From the table it is evident that the minimum time of extraction (shaking) needed is indirectly proportional

Table 1. Extraction of manganese. Influence of potassium thiocyanate concentration. Taken, 5 ml of 0·05*M* Mn ≡ 4·96 ml of 0·05*M* EDTA

		Consumption of 0·05*M* EDTA			
KSCN/40 ml, *g*	Molarity of KSCN	After Mn-stripping *ml*		In water phase, *ml*	
0·25	0·06	3·80	3·75	1·14	1·16
0·50	0·12	4·88	4·90	0·07	0·04
1·00	0·25	4·96	4·95	0·03	0·03
2·00	0·5	4·95	4·94	0·03	0·03
3·00	0·9	4·96	4·94	0·03	0·03

Table 2. Dependence of time of shaking on molar concentration of manganese and thiocyanate. (5 ml of 0·05*M* Mn ≡ 4·96 ml of 0·05*M* EDTA)

Volume, *ml*	[KSCN] *M*	[Mn] *mM*	Time of extraction, *min*	Found, *ml* 0·05*M* EDTA	Extraction %
40	0·26	6·2	1	4·96	~100
40	0·26	6·2	2	4·98	~100
80	0·13	3·1	1	4·28	86
80	0·26	3·1	1	4·94	~100
120	0·08	2·1	1	3·02	64
120	0·08	2·1	5	4·96	~100
120	0·26	2·1	1	4·94	~100
160	0·06	1·5	1	2·11	42
160	0·06	1·5	10	4·97	~100
160	0·06	1·5	1	4·95	~100
200	0·05	1·2	1	1·14	23
200	0·05	1·2	10	4·95	~100
200	0·26	1·2	1	4·95	~100

to the concentration of manganese and thiocyanate. For 1–2 min of extraction the lowest concentration of potassium thiocyanate must be again 0·25*M*. At lower concentration—but sufficient for the formation of the Mn(CNS)$_6^{4-}$ complex—the time of extraction must be extended to up to 10 min.

We should mention here that the work was also devoted to the determination of calcium and magnesium after the extraction of manganese. Preliminary experiments have shown that very high amounts of potassium thiocyanate in the aqueous phase after the manganese extraction (more than 2 g of KSCN) disturb the colour change of the indicators in the determination of calcium and magnesium even when the solution is diluted to 500 ml before the titration. It has been found that 1·5 g of potassium thiocyanate might be tolerated for such titrations.

RESULTS AND DISCUSSION

Extraction of manganese with equilibrated TOMA

A few attempts were made to extract manganese directly with TOMA containing thiocyanate. TOMA (5% solution in benzene, 20 ml) was equilibrated with 20 ml of 5*M* potassium thiocyanate by 20 min of shaking. The separated TOMA–SCN solution was divided into two portions which were used for the extraction of 5 ml of 0·05*M* manganese under the same conditions as above. It was found that the normal time of extraction is not sufficient for quantitative recovery of manganese. Further experiments have shown that every extraction must be carried out for at least 5 min. With larger amounts of manganese we can expect that the time of extraction must be prolonged. For this reason we prefer the first method—extraction of manganese from solutions containing sufficient potassium thiocyanate.

Capacity of the extraction

A similar procedure was used for increasing amounts of manganese (10, 15, 20 ml of 0·05*M* solution) with the addition of 1·5 g of potassium thiocyanate. After dilution to 40–60 ml, the manganese was extracted and determined as above. Under these conditions about 32–35 mg of manganese can be quantitatively extracted. Using a 10% solution of TOMA we were able to extract up to 110 mg of manganese with two 25-ml portions of TOMA.

Influence of anions

It has been found that the presence of various salts, such as 1 g of sodium sulphate, sodium chloride, potassium nitrate and ammonium fluoride, in 40 ml of the solution is without effect on the extraction. In the presence of 0·5 and 1·0 g of potassium iodide the recovery of the extraction of manganese was 97 and 90% respectively.

Influence of cations

Iron is co-extracted with manganese and stripped similarly. When triethanolamine with ammonia is used for stripping, iron is masked against EDTA and does not interfere. Cobalt, copper, zinc, *etc.*, if present in the material analysed, accompany manganese through the whole procedure and can be masked with potassium cyanide.

Determination of manganese in the presence of calcium and magnesium

The same procedure was used (40 ml total aqueous volume, pH 4, 1 g of KSCN) for the determination of manganese, double extraction with 10 ml of 5% TOMA and stripping with ammonia as described under *Separation of manganese*). Similar results were obtained in the presence of 10–30 mg of iron. Some results are given in Table 3.

Table 3. Determination of manganese in the presence of calcium and magnesium

Taken			Found
0·05*M* Mn, *ml*	Calcium, *mg*	Magnesium, *mg*	0·05*M* EDTA *ml*
5·03*	—	—	5·05; 5·03; 5·03
5·03	20	—	5·04; 5·02
5·03	—	6	5·03; 5·01
5·03	40	12	5·04; 5·04
5·03	100	30	5·03; 5·01
10·06†	40	12	10·06; 10·03
10·06	100	12	10·05; 10·05
10·06	20	30	10·04; 10·08
3·01$_8$§	40	12	3·01; 3·01
3·01$_8$	100	30	3·03; 3·02

* 13·73 mg Mn.
† 27·47 mg Mn.
§ 8·24 mg Mn.

Determination of manganese and alkaline earths

After the extraction of manganese, calcium and magnesium can be determined complexometrically in the aqueous phase. In some experiments we have observed that after the extraction of manganese from very large volumes containing accordingly large amounts of potassium thiocyanate (more than 1·5 g) the colour change was not too sharp even after dilution of the aqueous phase. For this reason, the original volume for manganese extraction must be limited to 40–60 ml containing about 1 g of potassium thiocyanate. After the double extraction of manganese as described above, the titration of calcium or magnesium, with thymolphthalexone or cresolphthalexone as an indicator (see *Reagents*), gave correct results with reasonably sharp end-points if the solution was diluted to 200 ml. A few results are given in Table 4.

Table 4. Successive determination of manganese and calcium or magnesium

Taken			Found		
0·05*M* Ca, *ml*	0·05*M* Mg, *ml*	0·05*M* Mn, *ml*	0·05*M* Ca, *ml*	0·05*M* Mg, *ml*	0·05*M* Mn, *ml*
3·01	—	5·03	2·95	—	5·04
			3·00		5·02
			3·02		5·02
$5{\cdot}01_5$	—	5·03	5·01	—	5·03
			5·02		5·04
			5·00		5·03
—	3·06	5·03	—	3·07	—
—	5·10	5·03	—	5·07	—

Practical application

The method has been applied to the analysis of one sample of sedimentary manganese ore of carbonaceous-oxide composition, (Czech. standard No. 1-02-001) containing 16·53% Mn, 12·32% CaO and 4·53% MgO.

Because the sample was very resistant to normal dissolution in acids, the following procedure was chosen.

About 1 g of the sample was treated in a Teflon beaker with 10 ml of conc. hydrochloric acid and 20 ml of hydrofluoric acid and evaporated nearly to dryness. Then 20 ml of *aqua regia* were added and evaporated on a sand-bath. During the evaporation 5 ml of 30% hydrogen peroxide were added, three times. To the wet residue 20 ml of hydrochloric acid were added and evaporated again to give a moist residue. The residue was dissolved in 50 ml of water, filtered into a 100-ml volumetric flask and after cooling, diluted to the mark. From this solution 10 ml were taken in a 150-ml separatory-funnel and after the addition of 0·5 g of potassium thiocyanate were extracted twice for 2 min with 10 ml of 5% TOMA in benzene. The remaining water phase was washed with 5 ml of pure benzene, the washings being added to the combined extracts. The benzene solution was stripped with 25 ml of ammonia (1 + 1) containing 5% of triethanolamine and 0·5 g of hydroxylamine hydrochloride. This solution was transferred into a 250-ml titration flask, the organic layer was washed with water (and the washings added to the aqueous phase) and after dilution manganese was titrated with 0·05*M* EDTA, with thymolphthalexone as indicator. The aqueous phase after the extraction of manganese was transferred into a 300-ml titration flask, diluted to 200 ml and after the addition of 0·5 g of hydroxylamine hydrochloride and 10 ml of 10% TEA and ammonia solution the total Ca + Mg was titrated with 0·05*M* EDTA, with Cresolphthalexone-Naphthol Green B mixture as indicator.

For the control another 10 ml of original solution were taken in a 300-ml titration flask, 0·5 g of hydroxylamine hydrochloride 10 ml of 10% TEA solution and 10–30 ml of ammonia solution were added and the sum of Mn + Ca + Mg was determined by EDTA titration, using thymolphthalexone as indicator. Some results are included in Table 5.

Table 5. Determination of manganese in manganese ores

Sample weight in 10 ml, *mg*	0·05*M* EDTA, *ml*					
	Manganese		CaO + MgO		Mn + CaO + MgO	
	Calculated	Found	Calculated	Found	Calculated	Found
96·5		5·85		6·40		
	5·81*	5·82	6·39$_7$*	6·42	12·19*	12·10
		5·83		6·40		
100·0	6·03*	6·06	6·63*	6·63		
		6·05		6·65		
		6·05		6·61		

* Calculated from the declared values 16·53% Mn, 12·32% CaO, 4·53% MgO.

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Zusammenfassung—Mangan wird aus einer Lösung mit mindestens 0·25 M Kaliumthiocyanat und bei pH 2·5–7 quantitativ in eine Benzollösung von Trioktylmethylammoniumchlorid (TOMA) extrahiert. Nach Rückextraktion in Triäthanolamin (TEA) und Hydroxylaminhydrochlorid enthaltenden verdünnten Ammoniak wird Mangan durch EDTA-Titration bestimmt. Calcium und Magnesium werden nicht einmal in Spuren extrahiert. Eisen wird mit Mangan zusammen extrahiert und bei der Rückextraktion mit TEA maskiert. Aluminium stört ebenfalls nicht. Nach der Extraktion von Mangan können Calcium oder Magnesium in der wäßrigen Phase mit der üblichen EDTA-Titration bestimmt werden. Das beschriebene Verfahren erlaubt die hochselektive Einzelbestimmung von Mangan und Calcium und/oder Magnesium in allem manganreichen Material.

Résumé—Le manganèse est extrait quantitativement dans une solution benzénique de chlorure de trioctylméthylammonium (TOMA) à partir d'une solution au moins 0,25 *M* en thiocyanate de potassium et à pH 2,5–7. Après réextraction en ammoniaque diluée contenant de la triéthanolamine (TEA) et du chlorhydrate d'hydroxylamine, on dose le manganèse par titrage à l'EDTA. Le calcium et le magnésium ne sont pas extraits, même à l'état de traces. Le fer est coextrait avec le manganèse et est dissimulé par le TEA lors de la réextraction. L'aluminium n'interfère pas non plus. Dans la phase aqueuse, après l'extraction du manganèse, on peut doser le calcium ou le magnésium par le titrage habituel à l'EDTA. La méthode décrite permet le dosage individuel hautement sélectif du manganèse et du calcium et/ou du magnésium dans tous les produits riches en manganèse.

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EXTRAKTION DER METALLIONEN Cr(III), Fe(III), Co(II), Ni(II), Cu(II) UND Zn(II) MIT GESCHMOLZENEM OXIN UND BESTIMMUNG DER EXTRAHIERTEN METALLE MIT HILFE VON RÖNTGENFLUORESZENZ

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Zusammenfassung—Die Genauigkeit der Röntgenfluoreszenzanalyse bei der Bestimmung einiger Metalle in gepreßten Pillen von Oxin wird diskutiert. Ein Verfahren zur Bestimmung kleiner Metallmengen in Süßwasser und in organischem Material (Zucker) wird beschrieben, wobei das geschmolzene Oxin als Extraktionsmittel dient.

Bei der quantitativen Bestimmung der Elemente mit Hilfe von Röntgenfluoreszenz-Spektrometrie spielt die Homogenität der Probe eine wichtige Rolle. Diese kann am einfachsten dadurch gewährleistet werden, daß man die Probe löst und die Fluoreszenzintensität des zu bestimmenden Elementes A an der Lösung ausmißt.[1,2] Durch die Verdünnung werden auch die Matrixeffekte weitgehend eliminiert, d.h. die Beeinflussung der Fluoreszenzintensität von A durch störende Begleitelemente wird vernachlässigbar klein. Dieselben Vorteile bietet auch die Überführung des zu bestimmenden Elementes A in eine "feste Lösung", wie z.B. in Boraxglas.[3]

Völlige Homogenität kleinster Bereiche kann bei Mischungen aus kristallinen Komponenten nur dann verwirklicht werden, wenn der zu lösende Stoff mit dem "festen Lösungsmittel" (Wirtskristall) Mischkristalle bildet. Gewisse ungeladene Metallkomplexe lösen sich in geschmolzenem Komplexbildner, wie z.B. die Metalloxinate in Oxin. Es ist anzunehmen, daß festes Oxin mit Oxinaten einerseits und verschiedene Oxinate andrerseits Mischkristalle bilden. Jedenfalls kann beim Abkühlen von verdünnten Lösungen der Metalloxinate in geschmolzenem Oxin keine Abscheidung von Oxinat-Kristallen beobachtet werden. Man erhält durch Abschrecken der Schmelze eine homogene Probe, welche sich nach dem Pulverisieren und Pressen für die Messung der Fluoreszenzintensitäten gut eignet. In dieser Arbeit wird nun eine Kombination der Schmelze-Lösung-Extraktion als Anreicherungsmethode und der Röntgenfluoreszenz-Spektrometrie als Analysenmethode beschrieben, wobei das 8-Hydroxychinolin (Oxin, HOX) sowohl als Extraktionsmittel wie auch als Träger für die extrahierten Metalle bei ihrer röntgenspektrometrischen Bestimmung dient.

EXPERIMENTELLER TEIL

Apparatives

Die Fluoreszenzintensitäten wurden unter standardisierten Meßbedingungen[1] mit einem Vakuum-Spektrometer (Philips PW 1540) ermittelt. Für die Aufnahme der Spektren wurde zusätzlich ein automatischer Impulshöhenanalysator (Diskriminator Philips PZ 1370) verwendet, welcher das untere Schwellenpotential entsprechend der reziproken Wellenlänge automatisch einstellt. Die Fensterbreite des Diskriminators bleibt jedoch auf dem eingestellten Wert, welcher folgendermassen bestimmt wurde: man ermittelte die Halbwertsbreite der Impulshöhenverteilungskurve für die mit dem betreffenden Detektor zu messende kürzeste bzw. längste Wellenlänge und benützte deren Summe als Fensterbreite.

Probenpräsentation

In der Röntgenspektrometrie werden üblicherweise solche Proben ausgemessen, deren Oberfläche größer ist als der Querschnitt des primären Strahlenkegels. Der Letztere betrug bei dem verwendeten Apparat *ca.* 3,5 cm^2 und bedingte die Verwendung von großen Pillen mit einem Durchmesser von 40 mm. Die benötigte Oxinmenge betrug mindestens 6 g, was eine große Menge des zu bestimmenden Elements erforderte. Für viele Anwendungen sollte aber die absolute Nachweisgrenze möglichst tief gehalten werden. Darum wurden auch Pillen mit einem Durchmesser von 13 mm auf ihre Anwendbarkeit geprüft. Der Primärstrahl wurde dabei ohne Blenden verwendet, so daß dessen Querschnitt an der Stelle der Probe größer war als die Probenoberfläche. Die Pillen wurden mit Hilfe eines Einsatzes, welcher aus Plexiglas angefertigt wurde und in den käuflichen Probenhalter paßte, in richtiger Position gehalten. Aus 500 mg Oxin ergab sich beim Pressen (mit *ca.* 100 kp/cm^2) eine Pillendicke von *ca.* 2,3 mm, welche noch nicht als "unendliche" Schichtdicke betrachtet werden darf.

Die Eindringtiefe der Primärstrahlung beträgt für reines Oxin 5,4 cm, wenn für eine Wellenlänge von 0,6 Å ($\approx$ AgK_α-Linie), für eine 100fache Abschwächung und für einen Winkel von 45° zwischen dem Lot des primären Strahlenkegels und der Probenoberfläche gerechnet wird. Für die Wellenlänge 2,25 (CrK_α) bzw 1,4 Å (ZnK_α) beträgt die Austrittstiefe 0,17 bzw. 0,65 cm bei einem Winkel von 45° zwischen der Kollimatorachse und der Probenoberfläche und bei 100facher Abschwächung. Die Proben sollten daher möglichst die gleiche Dicke aufweisen.

Herstellung von Eichpillen

Es wurde in einem Rundkolben unter kochendem Wasser während einer Stunde 5 g Oxin und 5 ml der Lösung des betreffenden Metallnitrates, dessen Konzentration durch komplexometrische Titration ermittelt wurde und 0,01*M* betrug, erhitzt. Der Kolben wurde dabei mit einem Schliffaufsatz, der in einer langen, dickwandigen Kapillare endete, verschlossen und so tief ins Wasser getaucht, daß er mindestens 5 cm unter dem Wasserniveau lag. Auf diese Weise konnte der Verlust von Oxin durch Sublimation verhindert werden. Die Kapillare wurde elastisch befestigt, so daß die Dampfstöße im kochenden Wasser ein recht gutes Rühren bewirkten. Nach dem Klarwerden beider Phasen wurde das Wasser am Rotationseindampfer abgedampft. Der Kolbeninhalt wurde schließlich durch nochmaliges Schmelzen und Schwenken homogenisiert, abgeschreckt und pulverisiert. Aus dieser "festen Stammlösung" wurden die Eichpillen verschiedener Konzentrationen durch Verdünnen mit reinem Oxin hergestellt, wobei die Mischung durch Schmelzen und Erhitzen bei 98° homogenisiert wurde.

Zeitlicher Verlauf der Extraktion

Der Anfang der Extraktion wurde so festgelegt, daß man das Oxin (3 bzw. 11 g) und die wäßrige Lösung (100 ml) getrennt auf 98° (Temperatur des siedenden Wassers bei 720 mmHg) erhitzte und erst dann zusammenbrachte. Das Extraktionsgefäß (Zweihalsschliffkolben) wurde während der Extraktion möglichst tief in gut gerührtes Paraffinöl getaucht, welches bei 98° thermostatisch behalten wurde. Das Rühren der wäßrigen Phase mit einem "Vibromischer" wurde in gewissen Zeitabständen kurz unterbrochen, und der wäßrigen Phase eine Probe entnommen, in welcher die Konzentration des nicht extrahierten Metalls nach Ansäuern ($[\mathrm{HNO_3}] = 0{,}1M$) atomabsorptiometrisch bestimmt wurde. Die Extraktionsausbeute $\%E_n$ zu der Zeit der n-ten Probenahme wurde schließlich folgendermassen berechnet:

$$\%E_n = 100 \cdot \left[1 - \frac{[\mathrm{A}]_{\mathrm{w},n}(V_{\mathrm{w}}{}^{\circ} - \sum_n^{n-1} v_n)}{[\mathrm{A}]_{\mathrm{st}} \cdot V_{\mathrm{st}} - \sum_n^{n-1} v_n \cdot [\mathrm{A}]_{\mathrm{w},n}}\right] \tag{6}$$

In dieser Gleichung bedeuten: $[\mathrm{A}]_{\mathrm{w},n}$ die Molarität des Elementes A in der wäßrigen Phase bei der n-ten Probenahme, $V_{\mathrm{w}}{}^{\circ}$ das Anfangsvolumen der wäßrigen Phase, v_n das Volumen der n-ten Probe, $[\mathrm{A}]_{\mathrm{st}}$ bzw. V_{st} die Molarität bzw. das Volumen der Stammlösung, welche zur Herstellung der wäßrigen Phase verwendet wurde.

Ausführung der Extraktion

Es wird 10–20 ml der Probelösung, welche nicht mehr als 0,01 mMole freie Säure, Lauge oder Puffersubstanz enthalten soll, mit 1 g Oxin in einem Rundkolben mit der Kapillare 2–3 Stunden unter kochendem Wasser erhitzt. Nach dem Abkühlen wird die wäßrige Phase mit Hilfe eines Filterstabes abgesaugt. Man wäscht 2–3 mal mit je 10 ml Wasser nach und trocknet die organische Phase am Rotationseindampfer. Das Oxin mit den extrahierten Metallen wird durch Schmelzen und Erhitzen bei *ca.* 100° homogenisiert, im Eiswasser abgeschreckt, pulverisiert und gepreßt.

RESULTATE UND DISKUSSION

Auswertungsverfahren und Reproduzierbarkeit

Die Totalintensität I_A am Maximum der K_α-Linie vom Element A und das Verhältnis V_A dieser Intensität zur Untergrundintensität neben der Linie I_U zeigten eine lineare Abhängigkeit von der Konzentration m_A im untersuchten Konzentrationsbereich von 0,001 bis 0,01 mMole/g (s. Abb. 1). In der Verdünnungsreihe für Kupfer und Zink war die Reproduzierbarkeit bei höherer Konzentration schlechter als im Bereich von (1–6) · 10^{-3} mMole/g. Die K_α-Strahlung von Kupfer und Zink hat eine große Austrittstiefe (s. *Probenpräsentation*), und die meßbare Fluoreszenzintensität weist daher bei der oben beschriebenen Probenpräsentation eine große Abhängigkeit von der Flächenbelegung auf. Bei diesen Versuchen wurde die Probenmenge pro Pille nur auf *ca.* 4% konstant gehalten, was die größere Streuung bei höheren Konzentrationen verursacht haben dürfte. Das Intensitätsverhältnis V_A hängt natürlich weniger stark von der Pillendicke ab, ließ sich demzufolge etwas besser reproduzieren als die Totalintensität I_A und wurde zur Auswertung der Intensitätsmessungen öfters herangezogen. Auswertungsverfahren, welche auf dem Intensitätsverhältnis von Strahlungen vergleichbarer Wellenlänge basieren, sollten auch gewisse langfristige Veränderungen apparativer Faktoren und Absorptionseffekte weitgehend kompensieren.[4]

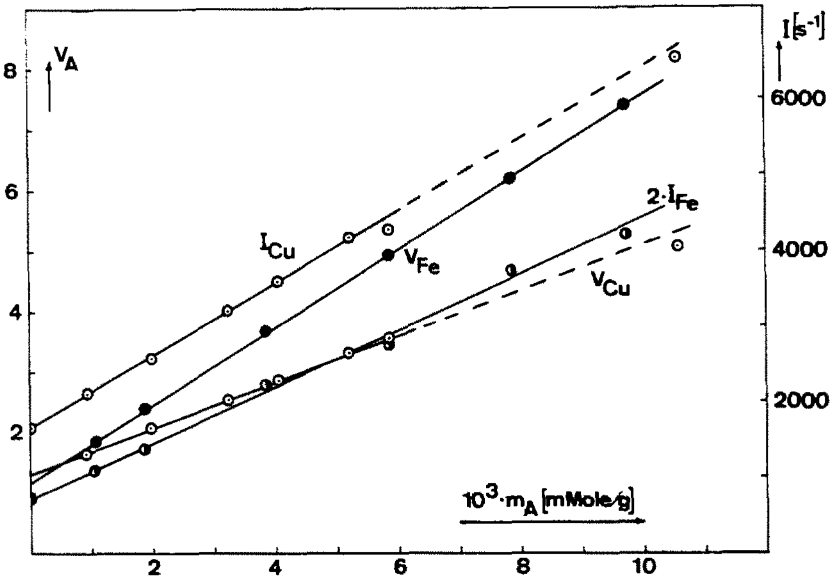

Abb. 1.—Abhängigkeit der Peak-Intensität I_A bzw. des Intensitätsverhältnisses V_A von der Konzentration m_A.

Um die Reproduzierbarkeit der Metallbestimmung in festem Oxin zu ermitteln, wurden je 6 Eichpillen für jedes Metall ausgemessen, wobei sich der Konzentrationsbereich von 0,001 bis 0,01 mMole/g für Eisen, Kobalt und Nickel bzw. von 0,001 bis 0,006 mMole/g für Zink und Kupfer erstreckte. Die folgenden Eichgeraden wurden durch lineare Regression ermittelt:

$$I_A/I_U = V_A = V_A^\circ + k_A \cdot m_A \tag{1}$$

$$I_A = I_A^\circ + K_A \cdot m_A \tag{2}$$

Tabelle 1. Bewertung der Konzentrationsbestimmung nach Gleichung (1)

No.	Größe für A:	Fe	Co	Ni	Cu	Zn
1	$(2\theta)_A$ (Grad)	57,45	52,74	48,61	44,96	41,74
2	$(2\theta)_U$ (Grad)	56,00	51,00	47,50	46,70	40,70
3	k_A (g/mMole)	636,11	570,75	290,07	375,15	376,63
4	$S(k_A)$ (g/mMole)	3,94	9,54	3,42	2,17	5,06
5	$V_A{}^\circ$ —	1,1992	0,9909	0,9642	1,3366	0,9767
6	$S(V_A{}^\circ)$ —	0,0433	0,1084	0,0212	0,0085	0,0194
7	V_{AM} —	4,406	4,006	2,498	2,670	2,284
8	$S(V_{AM})$ —	0,0122	0,0306	0,0111	0,0037	0,0084
9	$10^3 \cdot m_{AM}$ (mMole/g)	5,042	5,283	5,287	3,554	3,471
10	$\varepsilon(m_{AM})$ (%)	1,64	4,37	1,69	1,47	3,00
11	$\varepsilon(m_{AM})_{stat}$ (%)	1,62	1,28	1,23	1,89	1,21
12	$10^3 \cdot m_{NG}$ (mMole/g)	0,272	0,755	0,325	0,121	0,243
13	NG_{abs} (µg)	7,6	22,1	9,5	3,8	7,6

(Oxin-Pillen: Durchmesser = 13 mm, Gewicht = 430 mg (±4%) Messbedingungen[1]: Ag-Röhre, 50 kV, 20 mA, LiF-Kristall, Zeitvorwahl = 100 S., ohne Diskriminator.)

In der Tabelle 1 wurden zusammengestellt: der $(2\theta)_A$-Wert am Maximum der K_α-Linie des betreffenden Metalls für den verwendeten LiF-Kristall, die ausgewählte Untergrundstelle $(2\theta)_U$, die Neigung k_A der Gerade (1) mit ihrer Standardabweichung $S(k_A)$, der Ordinatenabschnitt $V_A{}^\circ$ mit seiner Standardabweichung $S(V_A{}^\circ)$, das mittlere Intensitätsverhältnis V_{AM} mit seiner Standardabweichung $S(V_{AM})$ und die mittlere Konzentration m_{AM}. $V_A{}^\circ$ und $I_A{}^\circ$ können natürlich auch direkt bestimmt werden, da sie mit V_A und I_A für eine A-freie Pille identisch sind. Die direkt bestimmten Werte stimmten im allgemeinen innerhalb der Fehlergrenzen mit den Ordinatenabschnitten überein.

Die Daten der Zeilen 3–9 in Tabelle 1 wurden für die Abschätzung des Fehlers bei der Konzentrationsbestimmung nach Gleichung (1) verwendet. Eine unbekannte Konzentration m_A kann aus Gleichung (1) in Kenntnis von $V_A{}^\circ$ und k_A berechnet werden. Sie ist natürlich mit einem gewissen Fehler behaftet, da einerseits V_A nicht fehlerfrei gemessen werden kann und andrerseits auch der Eichung, d.h. dem $V_A{}^\circ$- und dem k_A-Wert ein gewisser Fehler anhaftet. Nach dem Fehlerfortpflanzungsgesetz beträgt die Standardabweichung von der mittleren Konzentration m_{AM}:

$$S(m_{AM}) = \frac{1}{k_A}\left[S^2(V_{AM}) + S^2(V_A{}^\circ) + \frac{S^2(k_A)}{k_A{}^2}(V_{AM}{}^2 + V_A{}^{\circ 2})\right]^{1/2} \tag{3}$$

Die relative Standardabweichung $\varepsilon(m_{AM})$ der mittleren Konzentration m_{AM} wurde nun berechnet und in der 10. Zeile der Tabelle 1 angegeben. Sie beträgt im Durchschnitt für alle Metalle 2,4% und ist nicht wesentlich höher als der totale statistische Zählfehler.

Um den Letzteren mit Hilfe der Gleichung (3) abzuschätzen, müssen für $S(V_{AM})$, $S(V_A{}^\circ)$ und $S(k_A)$ die theoretischen Werte eingesetzt werden. Die Standardabweichung einer bestimmten Intensität I beträgt theoretisch $(I/T)^{1/2}$, wobei T die Zähldauer bedeutet. Berücksichtigt man noch die Fehlerfortpflanzung, so erhält man für den statistischen Zählfehler der Konzentrationsbestimmung nach Gleichung (1):

$$S(m_{AM})_{stat} = \frac{1}{k_A} \cdot \left|\frac{V_{AM}(V_{AM}+1) + V_A{}^\circ(V_A{}^\circ + 1)}{T \cdot I_U{}^\circ}\left(1 + \frac{V_{AM}{}^2 + V_A{}^{\circ 2}}{k_A{}^2 \cdot m_{AM}{}^2}\right)\right|^{1/2} \tag{4}$$

Diese Gleichung ist für die Zeitvorwahl-Meßtechnik abgeleitet worden und $I_U{}^0$ bezeichnet darin die Untergrundintensität für die reine Oxinpille. Der relative statistische Fehler $100 \cdot S(m_{AM})_{stat}/m_{AM}$ wurde nun für eine Meßzeit von 100 S. berechnet und in der 11. Zeile der Tabelle 1 angegeben. Für alle fünf Metalle betrug das Verhältnis des totalen Fehlers $\varepsilon(m_{AM})$ zu dem statistischen Zählfehler $\varepsilon(m_{AM})_{stat}$ im Durchschnitt 1,8, welches gewöhnlich auch bei der Analyse von Lösungen gefunden wird und somit auf eine gute Homogenität der Proben hindeutet. Der Totalfehler dürfte sich daher hauptsächlich aus dem statistischen Zählfehler und aus Fehlern, welche durch kurzfristige Apparateschwankungen verursacht werden, zusammensetzen.

Ersetzt man in Gleichung (3) V_{AM} durch $V_A{}^0$ und $S(V_{AM})$ durch $S(V_A{}^0)$, so erhält man Gleichung (5), welche zur Abschätzung der Nachweisgrenze dient:

$$m_{A,\,NG} = \frac{t(\%,\, N)}{k_A}\left[2 \cdot S^2(V_A{}^0) + 2 \cdot V_A{}^{02} \cdot S^2(k_A)/k_A{}^2\right]^{1/2} \tag{5}$$

$t(\%,\, N)$ ist ein statistischer Faktor[7] und hängt von der gewünschten Sicherheit sowie von der Zahl der Meßpunkte ab, welche für die Ermittlung von $S(V_A{}^0)$ und $S(k_A)$ benützt wurden. Die Nachweisgrenze wurde nun für 95%ige statistische Sicherheit berechnet, und in der 12. Zeile der Tabelle 1 angegeben. Multipliziert man diese Werte mit dem Gewicht einer Pille (0,5 g) und mit dem Atomgewicht des betreffenden Metalls, so erhält man die absolute Nachweisgrenze. Diese ist in der letzten Zeile der Tabelle 1 angegeben und beträgt für die 5 Metalle im Durchschnitt 10 μg.

Die statistische Prüfung des Auswertungsverfahrens nach Gleichung (2) führte zu ähnlichen Resultaten, welche daher nicht weiter diskutiert werden. In der Tabelle 2 sind lediglich die Fluoreszenzintensitäten für kilogrammolare "feste Lösungen" im Oxin den molaren Fluoreszenzintensitäten wäßriger Lösungen gegenübergestellt. Ein Vergleich beider Größen ist zulässig, weil sie mit dem gleichen Spektrometer unter standardisierten Meßbedingungen[1] ermittelt wurden.

Tabelle 2. Fluoreszenzintensität von kilogrammolaren Lösungen einiger Metalle in festem Oxin und im Wasser (K_A in s^{-1}.kg.mol^{-1})

	Cr	Fe	Co	Ni	Cu	Zn
$10^{-5} \cdot K_A$ (Oxin, 13)*	0,608	1,83	2,47	3,34	4,84	6.46
$10^{-5} \cdot K_A$ (Oxin, 40)	1,29	3,55	4,74	6,11	8.58	11,6
$10^{-5} \cdot K_A$ (H_2O, 32)	0,794	3,16	5,89	4,78	8,92	12,9

* (Die Zahlen in der Klammer geben den Durchmesser der Probe in mm an. Der Durchmesser des primären Strahlenkegels betrug an der Probenoberfläche *ca.* 20 mm)

Die K_A-Werte für ein bestimmtes Metall A sind ungefähr gleich in Wasser und in Oxin, wenn die Probenoberfläche größer als der Querschnitt des primären Strahlenkegels ist. Theoretisch ist dies für homogene Lösungen mit ungefähr gleichen Massenabsorptionskoeffizienten zu erwarten. Der zweifache Verlust an Empfindlichkeit wird bei der Verwendung von kleinen anstelle der großen Pillen durch die zwölfmal kleinere Probenmenge mehr als aufgewogen.

Extraktion der Metallionen mit geschmolzenem Oxin

Die Extraktion von Metallionen kann entweder mit einer Lösung des Oxins in einem mit Wasser nicht mischbaren Lösungsmittel (gewöhnlich Chloroform) bei Zimmertemperatur oder mit geschmolzenem Oxin bei 80–100° ausgeführt werden.[8] Bei der "normalen" Extraktion kann die gemeinsame Phasengrenze viel größer gehalten werden als bei der "Schmelzextraktion", was eine größere Transportgeschwindigkeit zwischen den beiden Phasen ermöglicht. Die erstgenannte Technik wird daher meistens vorgezogen, wenn die Bildungsgeschwindigkeit des extrahierbaren Komplexes groß ist. Erfolgt die Bildung des Oxinates sehr langsam (z.B. für $Cr(OX)_3$), so ist die Schmelzextraktion wegen der höheren Temperatur und wegen der großen Oxinkonzentration in der wäßrigen Phase die bessere Methode.

Nach Umland[8] liegt die Verteilung des Metalls zwischen der wäßrigen Lösung und dem geschmolzenen Oxin–ausser bei Alkalimetallen–stets weit auf der Seite der Oxinphase, wodurch das Oxin zu einem universellen Extraktionsmittel für die meisten Metalle wird. Die Schmelzextraktion wurde bereits erfolgreich angewandt in Kombination mit Spektrophotometrie[5,8] und Spektroskopie.[6] Die Anwendung der Schmelzextraktion in

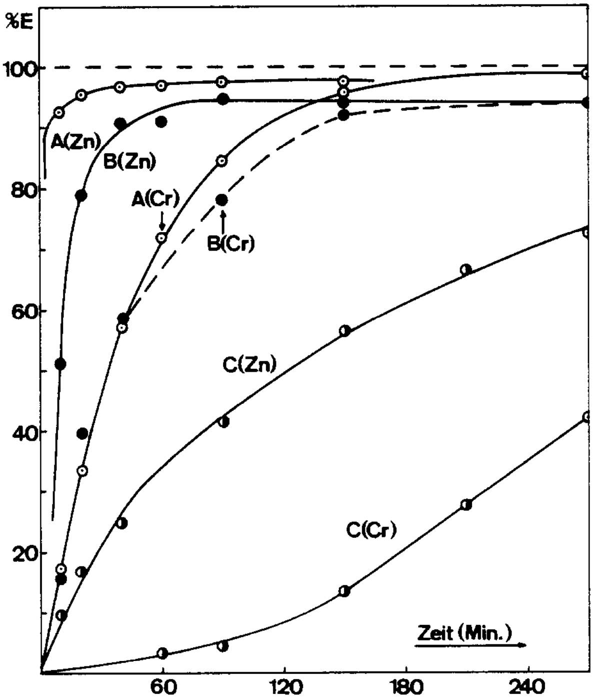

Abb. 2.—Zeitlicher Ablauf der Extraktion von Cr(III) und Zn(II) mit geschmolzenem Oxin bei 98° C.

Anfängliche Zusammensetzung der wäßrigen Phase: $[ZnX^-] = [CrX] = 1 \cdot 10^{-4} M$, $[Na_2HX] = 2 \cdot 10^{-3} M$, wobei X^{3-} das Anion der Nitrilotriessigsäure, welche zur Verhinderung des Ausfalls von $Zn(OX)_2 \cdot 2H_2O$ diente, bedeutet.

A: $V/V_0 = 11$, wäßrige Phase mit "Vibromischer" gerührt
B: $V/V_0 = 53$, wäßrige Phase mit "Vibromischer" gerührt
C: $V/V_0 = 53$, nicht gerührt

Verbindung mit Röntgenfluoreszenz-Spektrometrie als Meßmethode sollte die selektive und genaue Bestimmung der meisten Metalle ermöglichen.

Damit die Extraktion genügend schnell erfolgt und die Extraktionsausbeute möglichst hoch ist, sollte das Volumenverhältnis V/V_0 der wäßrigen zu der organischen Phase nicht zu groß sein ($V/V_0 < 50$). Den Einfluß von V/V_0 auf die Geschwindigkeit der Extraktion von Cr(III) und Zn(II) zeigt Abb. 2, in welcher die Extraktionsausbeute ($\% E$) in Abhängigkeit der Extraktionsdauer aufgetragen ist. Bekanntlich verhalten sich diese Metalle kinetisch sehr verschieden. Während das Zn(II) rasche Ligandaustauschreaktionen eingeht, bildet das Cr(III) robuste Komplexe. Dementsprechend ist die Bildungsgeschwindigkeit von $Cr(OX)_3$ für die Extraktionsgeschwindigkeit sogar bei 98° maßgebend, was dadurch gezeigt wird, daß in beiden Versuchen A ($V/V_0 = 11$) und B ($V/V_0 = 53$) zum Erreichen eines konstanten Extraktionsgrades ungefähr die gleiche Zeit benötigt wird. Da sich das Zinkoxinat praktisch momentan bildet, können die Kurven *A* (Zn) und *B* (Zn) zur Beurteilung des Einflusses von V/V_0 auf die Schnelligkeit der Extraktion dienen. Eine konstante Extraktionsausbeute wird bei dem größeren Volumenverhältnis V/V_0 offensichtlich langsamer erreicht, was mit der Verkleinerung der Transportgeschwindigkeit über die Phasengrenze mit zunehmendem V/V_0 zu erklären ist. In beiden Versuchen A und B wurde die wäßrige Phase mit einem "Vibromischer" so stark gerührt, daß sich die Phasen noch nicht vermischten. Ein zu starkes Rühren, welches die Verteilung des geschmolzenen Oxins in der wäßrigen Phase bewirkt hätte, wurde vermieden, damit ein eindeutiger Zusammenhang zwischen dem Volumenverhältnis und der Größe der gemeinsamen Phasengrenze, welche die Geschwindigkeit der Extraktion hauptsächlich bestimmt, bestehen bleibt.

Beim Versuch C wurde auf das Rühren verzichtet, was eine sehr langsame Einstellung des Gleichgewichtes bewirkte. Zudem zeigten Zn(II) und Cr(III) eindeutig verschiedenes Verhalten. Die Extraktion von Cr(III) setzte nach einer gewissen "Induktionsperiode" ein, welche verstreichen muß, damit die Konzentration des Oxins in der wäßrigen Phase genügend ansteigt.

Anwendungsmöglichkeiten

Bestimmung der Metallionen in Süß wasser. Da das Volumenverhältnis V/V_0 möglichst klein sein muß, können die Metallionen aus solchen wäßrigen Proben, deren Abdampfrückstand relativ klein ist, gut angereichert werden. Diese Proben können entweder ohne Ausfall von festen Stoffen vorkonzentriert werden, oder der Rückstand kann in einer kleinen Menge eines Lösungsmittels gelöst werden. Zink und Eisen konnten z.B. in Zürcher Trinkwasser bei einer 550fachen Anreicherung bestimmt werden (s. Abb. 3). Diese bestand hier aus der 100fachen Vorkonzentrterung im Rotationseindampfer und aus der 55fachen Anreicherung bei der Extraktion.

Bestimmung der Metalle in organischem Material. Die Spurenelemente werden aus der Asche mit Säure herausgelöst, und die Metallionen aus der neutralisierten Lösung mit geschmolzenem Oxin extrahiert. Wie die Abb. 4 zeigt, liefern 128 g Kristallzucker (gewöhnliche Handelsware) durch Veraschen und Extraktion mit 1 g Oxin eine Pille mit gut meßbaren Fluoreszenzintensitäten für die K_α-Linien der Elemente Eisen, Kupfer und Zink.

Der Eidg. Stiftung zur Förderung Schweizerischer Volkswirtschaft durch wissenschaftliche Forschung danken wir für finanzielle Unterstützung.

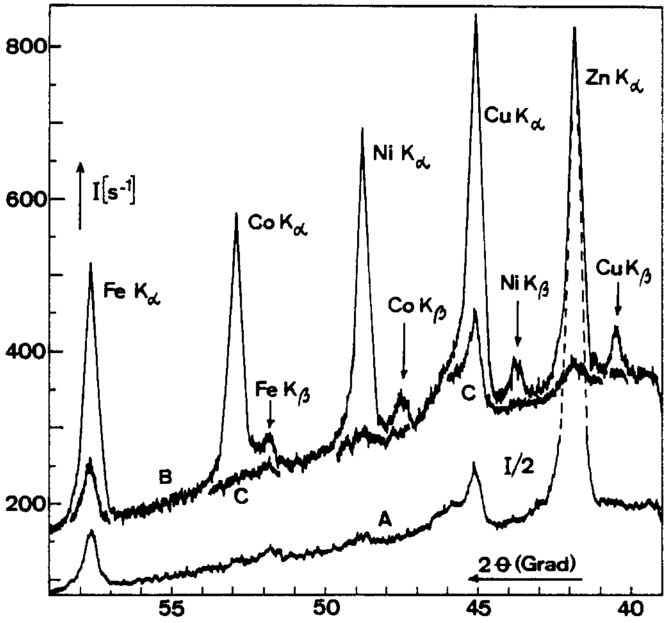

Abb. 3.—Spektren von Oxinpillen.

(*A*) Pille aus der Oxinphase, in welcher Metallspuren aus Zürcher Leitungswasser 550fach angereichert wurden. (Die Intensitäten entsprechen 0,05 mg Fe bzw. 0,72 mg Zn pro Liter Wasser).

(*B*) Eichpille mit je 0,002 mMole Metall pro g Schmelze.

(*C*) Reines Oxin.

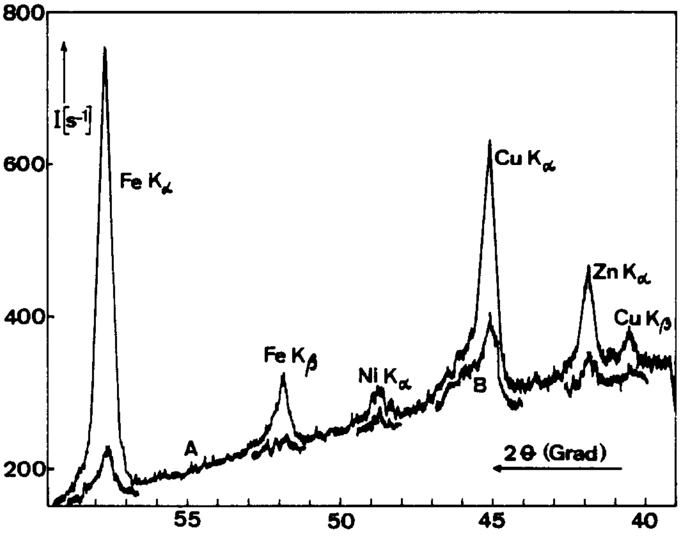

Abb. 4.—(*A*) Spekrum einer Oxinphase, in welcher Metallspuren aus 128 g Kristallzucker angereichert wurden.
Die Intensitäten entsprechen den folgenden Metallgehalten in Zucker (ppm): Fe (1,24), Cu (0,40), Zn (0,18).

(*B*) Spektrum des zur Extraktion verwendeten Oxins.

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Summary—The accuracy of the determination by X-ray fluorescence spectrometry of a number of metals in pressed tablets of oxine has been investigated. A procedure is described which has been used for the determination of trace metals in fresh water and in sugar, in which molten oxine is used as the extractant.

Résumé—On a étudié la précision de la détermination par spectrométrie de fluorescence aux rayons X d'un certain nombre de métaux dans des pastilles comprimées d'oxine. On décrit une technique qui a été utilisée pour le dosage de métaux à l'état de traces dans l'eau douce et dans le sucre, dans laquelle l'oxine fondue est utilisée comme agent d'extraction.

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IRON(II)-CHLORAMINE-T REACTION

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Summary—When a large excess of the oxidant is used in the iron(II)-chloramine-T reaction at pH 2·56–5·6 the amount of oxidant consumed is well above the stoichiometric amount required to oxidize iron(II) to iron(III). This has been attributed to the formation and subsequent behaviour of free radicals during the reaction. The formation of free radicals has been experimentally demonstrated. They apparently dimerize to give products of the type R–NCl–NCl–R (R = $CH_3C_6H_4SO_2$), which are further oxidized by chloramine-T. The dimerized species liberate iodine very slowly from acidified potassium iodide. This explanation satisfactorily accounts for the observed extent and rate of destruction of excess of chloramine-T in presence of small amounts of Fe(II) or bromide at pH 2·65–4·70. The storage of chloramine-T in metal containers might cause extensive destruction of the oxidant by a similar free radical mechanism and should be avoided.

Chloramine-T ($CH_3C_6H_4SO_2NClNa.3H_2O$) is generally used as an oxidizing agent in strongly acid[1] medium but recently its utility in alkaline[2] and weakly acid[3] media has been reported. This oxidant is of particular interest for the study of reaction mechanisms as it furnishes different types of oxidants such as monochloramine-T ($CH_3C_6H_4SO_2NHCl$), dichloramine-T ($CH_3C_6H_4SO_2NCl_2$) and the anion ($CH_3C_6H_4SO_2NCl^-$), depending on the pH of the medium; chlorine[4] is also produced in strongly acid medium in presence of large amount of chloride ions. It is reported[5] that monochloramine-T disproportionates according to equation (1) fairly rapidly in the pH range 2·65–5·6 and fastest at pH 4·7.

$$2CH_3C_6H_4SO_2NHCl \longrightarrow CH_3C_6H_4SO_2NCl_2 + CH_3C_6H_4SO_2NH_2 \qquad (1)$$

During this disproportionation, a minor side-reaction leads to slight but significant destruction of chloramine-T by combination of the $CH_3C_6H_4SO_2NCl$ free radicals.[4]

Earlier work on the oxidation of iron(II) with chloramine-T has been concerned only with determination of iron(II). Poethke and Wolf[6] reported that iron(II) can be determined by adding excess of chloramine-T in presence of 10% hydrochloric acid, then reducing the surplus chloramine-T with excess of arsenite, the excess being back-titrated with chloramine-T, with *p*-ethoxychrysoidine or Brilliant Carmoisine as indicator. Bishop and Jennings[7] confirmed this. The oxidation of iron(II) by chloramine-T is of trivial analytical interest, as far better methods are already available. We undertook a study of the oxidation with a view to finding whether the results would help in explaining the rapid deterioration of chloramine-T stored in metal containers. Interesting results were obtained in the oxidation of iron(II) with chloramine-T in the pH range 2·65–4·7 and are mechanistically and analytically significant.

EXPERIMENTAL

Reagents

Ferrous sulphate solutions, 0·05*M* and 0·1*M*, were standardized with dichromate. Ferrous ammonium sulphate could not be used as the ammonium ion[2] would react with chloramine-T, producing chlorine as one of the products, which would interfere in the Fe(II)-chloramine-T reaction.

Chloramine-T solution, 0·05*M*, was standardized iodometrically.

Sodium thiosulphate solution, 0·05*M*, was standardized against dichromate.

Stock buffer solutions were prepared from acetic acid and sodium acetate for the pH range 2·65–4·7 and from potassium hydrogen phthalate for pH 4·0.

Analytical-grade reagents or reagents of known purity were used.

Procedure

To 20 ml of 0·05*M* ferrous sulphate 20 ml of 2*N* hydrochloric or sulphuric acid or a buffer in the pH range 2·65–5·6 were added and the reaction mixture was diluted to 80 ml in a stoppered iodine-flask. To this, 100–500% excess of chloramine-T solution was added and the contents were let stand for a definite time. Then 5 g of potassium fluoride were added to complex ferric iron, followed by 15 ml of 10% potassium iodide solution and if necessary 20 ml of 2*N* sulphuric acid, and the iodine liberated was titrated with thiosulphate, with starch as indicator. Similar experiments were done without the ferrous sulphate. The difference in the titration values of blank and test gives the amount of chloramine-T used. In some cases excess of chloramine-T was taken in the conical flask, the pH was adjusted and iron(II) solution was added from the burette.

The free radical nature of the iron(II)-chloramine-T reaction at pH 4·7 was demonstrated as follows. To 20 ml of 0·05*M* chloramine-T solution, 40 ml of distilled water and 20 ml of acetic acid–acetate buffer (pH 4·7) were added and the solution was deaerated for 1 hour by bubbling pure nitrogen gas through it. Then 5 ml of 0·1*M* ferrous sulphate solution and 1 ml of methyl methacrylate monomer (deaerated for 1 hr) were added, and the flask was stopped and set aside in the dark for 1 hr. The mixture was then diluted to 400 ml to dissolve the dichloramine-T. It was found that there was a fairly large amount of polymer (25% yield) formed as a white gummy substance floating on the water surface. A blank experiment without ferrous sulphate gave only traces of polymer.

RESULTS AND DISCUSSION

In 0·2*N* sulphuric acid or hydrochloric acid media, the amount of chloramine-T used was equal to the stoichiometric requirement for the oxidation of iron(II) to iron(III) (Table 1). No complications arose in these media. This is in agreement with earlier reports.

Table 1. Oxidation of ferrous sulphate with chloramine-T in strongly acid medium at 25–30°C.
(Chloramine-T added, 2·181 meq. Acid, 20 ml of 1*N*. Total volume 100 ml)

Order of adding reagents	$FeSO_4$ taken, *mmole*	Standing time, *min*	CAT consumed, *meq*
CAT—H_2SO_4—Fe(II)	0·9268	5	0·9234
	0·8124	5	0·8120
	0·6530	5	0·6520
	0·9268	30	0·9240
	0·8124	30	0·8120
	0·6530	30	0·6522
Fe(II)—H_2SO_4—CAT	0·9268	5	0·9245
	0·6530	5	0·6521
	0·9268	30	0·9250
	0·6530	30	0·6520
CAT—HCl—Fe(II)	0·9268	5	0·9250
	0·6530	5	0·6520
	0·9268	30	0·9250
	0·6530	30	0·6521
Fe(II)—HCl—CAT	0·9268	5	0·9251
	0·6530	5	0·6520
	0·9268	30	0·9250
	0·6530	30	0·6520

However, the behaviour of excess of chloramine-T towards iron(II) in the pH range 2·65–4·7 (Table 2) had unusual features: (*i*) the amount of chloramine-T consumed far exceeded that required for oxidation of iron(II) to iron(III); (*ii*) this consumption of chloramine-T increased with the duration of keeping of the mixture of iron(II) and chloramine-T; (*iii*) this consumption of chloramine-T was greatest at pH 4·7 and particularly when the iron(II) was added to the chloramine-T solution. It is significant that iron(II) was completely oxidized within a minute after addition of excess of chloramine-T in all the media tested. This was demonstrated by mixing the reagents and within a minute adding excess of arsenite to destroy any remaining chloramine-T, acidifying the mixture with 20 ml of 4*N* sulphuric acid, and titrating any iron(II) with vanadate, using diphenylamine as indicator. None was found.

It was also found that ferric iron and *p*-toluenesulphonamide have no influence on the stability or the extra consumption of chloramine-T in the iron(II)-chloramine-T reaction at pH 4·7 (Table 3). The large consumption of chloramine-T in the iron(II) reaction at pH 2·65–4·7 is not dependent on the nature of the buffer (Table 2). Chloramine-B ($C_6H_5SO_2NClNa$) behaved similarly to chloramine-T (Table 4) indicating that the methyl group in chloramine-T is not the cause of the overconsumption. However, increasing the ionic strength of the medium at pH 4·7 reduced the overconsumption of oxidant (Table 5). It is generally accepted that formation of free radicals is suppressed in media of high ionic strength. Hence we tested for the formation of free radicals. These observations showed

Table 2. Oxidation of ferrous sulphate with chloramine-T in the pH range 2·65–4·7 at 25–30°C (acetate buffer).

Order of mixing reagents	$FeSO_4$ taken, *mmole*	CAT added, *meq*	Standing time, *min*	CAT consumed, *meq*
CAT—Buffer(pH 2·65)—Fe(II)	0·9268	2·181	5	1·203
	0·6530	2·181	5	1·302
	0·4820	2·181	5	1·420
	0·9268	2·181	30	1·651
	0·4820	2·181	30	1·802
Fe(II)—Buffer(pH 2·65)—CAT	0·9268	2·181	5	1·213
	0·6530	2·181	5	1·450
	0·4820	2·181	5	1·560
	0·9268	2·181	30	1·664
	0·4820	2·181	30	1·812
CAT—Buffer(pH 4·7)—Fe(II)	0·9263	2·181	5	1·807
	0·9550	3·764	30	2·918
	0·9550*	1·882	30	1·757
	0·9550	1·412	30	1·267
	0·2390	1·882	30	1·167
	0·2390*	3·764	30	1·305
	0·9550*	2·010	30	2·005
	0·2390*	1·882	30	1·172
	0·9268	2·181	30	2·124
Fe(II)—Buffer(pH 4·7)—CAT	0·9268	2·181	5	1·736
	0·2390	1·882	5	1·005
	0·9268	2·181	30	2·013
	0·2390	1·882	30	1·100
	0·9268	2·181	30	2·115
	0·2390*	1·882	30	1·102

* Potassium hydrogen phthalate buffer (pH 4·0).

Table 3. Oxidation of ferrous sulphate with Chloramine-T at pH 4·7 in presence of ferric sulphate* and *p*-toluenesulphonamide* at 25–30°C.

Order of adding reagents	$FeSO_4$ taken, *mmole*	CAT added, *meq*	Standing time, *min*	CAT consumed, *meq*
CAT—Buffer(pH 4·7)—Fe(III)—Fe(II)	0·9268	2·181	5	1·808
	0·9550	3·764	5	2·620
	0·2390	1·882	5	0·902
	0·9268	2·181	30	2·124
	0·9550	3·764	30	2·918
	0·2390	1·882	30	1·168
Fe(II)—Buffer(pH 4·7)—Fe(III)—CAT	0·9268	2·181	5	1·740
	0·2390	1·882	5	1·005
	0·9268	2·181	30	2·015
	0·2390	1·882	30	1·105
CAT—Buffer(pH 4·7)—Fe(III)	—	2·181	5	2·178†
	—	2·181	30	2·160†
CAT—Buffer(pH 4·7)—*p*-toluenesulphonamide—Fe(II)	0·9268	2·181	5	1·808
	0·9550	3·764	5	2·620
	0·2390	1·882	5	0·902
	0·9268	2·181	30	2·120
	0·9550	3·764	30	2·916
	0·2390	1·882	30	1·165
CAT—Buffer(pH 4·7)—*p*-toluenesulphonamide	—	2·181	30	2·160†
	—	3·764	30	3·734†

* Ferric sulphate used, 20 ml of 0·05*M* solution; *p*-toluenesulphonamide used, 1 g.

† CAT found. Small difference is due to the intrinsic instability[4] of aqueous Chloramine-T.

Table 4. Oxidation of ferrous sulphate with Chloramine-B in different media and ionic strength at 25–30°C (Chloramine-B added, 1·986 meq; acid, 20 ml of 0·1*N*; buffer added, 20 ml; NaCl or $NaClO_4$ added, 20 ml of 5*M* solution).

Order of adding reagents	$FeSO_4$ taken, *mmole*	Standing time, *min*	CAB consumed, *meq*
CAB—H_2SO_4—Fe(II)	1·133	5	1·129
	0·567	5	0·568
	0·878	5	0·876
	1·133	30	1·134
	0·567	30	0·565
	0·878	30	0·878
CAB—HCl—Fe(II)	1·133	5	1·130
	0·878	5	0·878
	1·133	30	1·130
	0·878	30	0·876
CAB—Buffer(pH 4·7)—Fe(II)	1·133	5	1·445
	0·878	5	1·274
	1·133	30	1·924
	0·878	30	1·969
Fe(II)—Buffer(pH 4·7)—CAB	1·133	5	1·408
	0·878	5	1·221
	1·133	30	1·918
	0·878	30	1·934
CAB—Buffer(pH 4·7)—NaCl—Fe(II)	1·133	5	1·185
	1·133	30	1·380
CAB—Buffer(pH 4·7)—$NaClO_4$—Fe(II)	1·133	5	1·180
	1·133	30	1·362

Table 5. Oxidation of ferrous sulphate with Chloramine-T at pH 4·7* in high ionic strength medium at 25–30°C.
Total volume = 100 ml.

Order of adding reagents	$FeSO_4$ taken, *mmole*	CAT added, *meq*	Standing time, *min*	CAT consumed, *meq*
CAT—Buffer(pH 4·7)—$NaClO_4$—Fe(II)	0·9550	2·023	5	1·129
	0·2390	1·882	5	0·7531
	0·9550	2·023	30	1·127
	0·2390	1·882	30	0·7832
Fe(II)—Buffer(pH 4·7)—$NaClO_4$—CAT	0·9550	2·023	5	0·8692
	0·2390	1·882	5	0·6410
	0·9550	2·023	30	0·8962
	0·2390	1.882	30	0·6520
CAT—Buffer(pH 4·7)—$NaClO_4$	—	1·882	30	1·822†§
	—	1·882	30	1·821†§
CAT—Buffer(pH 4·7)—NaCl—Fe(II)	0·9550	2·351	5	1·232
	0·2390	1·882	5	0·7940
	0·9550	2·351	30	1·432
	0·2390	1·882	30	0·8242
Fe(II)—Buffer(pH 4·7)—NaCl—CAT	0·9550	2·351	5	0·7423
	0·2390	1·882	5	0·6914
	0·9550	2·351	30	1·372
	0·2390	1·882	30	0·7508
CAT—Buffer(pH 4·7)—NaCl	—	1·882	30	1·820†§
	—	1·882	30	1·821†§

* Acetic acid-acetate buffer pH 4·7 used, 20 ml.

† Sodium perchlorate and sodium chloride used, 20 ml of 5*M* solution.

§ CAT found. Small difference is due to instability of Chloramine-T.

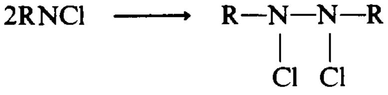
that the overconsumption of chloramine-T is due to the reaction between chloramine-T and the initial products (other than *p*-toluenesulphonamide) formed during the oxidation of iron(II).

In strongly acid medium, the species present initially in large concentrations in aqueous chloramine-T solution is monochloramine-T[5] which would undergo disproportionation slowly. Since no extra consumption of chloramine-T was found when 0·1*N* hydrochloric or sulphuric acid media were used, it was inferred that no side-reaction would take place during oxidation of iron(II) by monochloramine-T. In the pH range 2·65–4·7, the disproportionation of monochloramine-T is very fast, giving rise to dichloramine-T. In these pH ranges, dichloramine-T is the dominant species in the oxidation of the iron(II).

We therefore propose the following explanation for the overconsumption of the oxidant. Dichloramine-T oxidizes iron(II) and gives rise to free radicals

$$RNCl_2 + Fe(II) \longrightarrow RNCl + FeCl^{2+}$$

and if the free radical RNCl were slower than $RNCl_2$ to react with iron(II) then dimerization of the free radical occurs:



$$2RNCl \longrightarrow \underset{\displaystyle Cl}{\underset{|}{R{-}N}}{-}\underset{\displaystyle Cl}{\underset{|}{N{-}R}}$$

(where R = $CH_3C_6H_4SO_2$)

The dimer has very poor oxidation properties towards potassium iodide or iron(II) and moreover can further be oxidized by chloramine-T, which accounts for the continued consumption of chloramine-T after complete oxidation of iron(II) at pH 4·7.

Attempts were made to characterize the nature of the products, other than *p*-toluenesulphonamide, formed during the iron(II)–chloramine-T reaction at pH 4·7, by taking large amounts of iron(II) and chloramine-T. Under these conditions, a yellowish white solid was precipitated. This was separated and dried over phosphorus pentoxide. The solid appeared to be a mixture of substances. Its infrared spectrum revealed bands mostly characteristic of *p*-toluenesulphonamide, but the solid was found to liberate iodine from acidified potassium iodide solution (though very slowly) and it also contained chlorine. There was gradual loss of chlorine content and the weak oxidizing action, on keeping for several days. These observations lead us to assume that the solid consisted, in addition to *p*-toluenesulphonomide, of products of the kind R-NCl-NCl-R, which would be expected to be unstable, to behave as a weak oxidizing agent towards iodine and to be capable of further reaction with chloramine-T.

Similar results have been found by us when small amounts of bromide are used as reducing agent instead of iron(II).

Chloramine-T packed in metal containers has invariably been found to deteriorate very rapidly in its purity and oxidative value. We ascribe this to extensive destruction of the oxidant by free radical formation and dimerization initiated by oxidation of small amounts of metal by the oxidant. This has to be particularly borne in mind during the packing of solid chloramine-T. We would recommend the use of glass or polythene containers for this purpose. The possibility of destruction of chloramine-T by these side-reactions when it is used as an analytical agent in back-titration procedures at pH 2·65–4·7 should be checked during development of the method. These side-reactions will not occur if the free radical RNCl reacts at least as fast as $RNCl_2$ with the oxidizable substrates instead of dimerizing.

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Zusammenfassung—Verwendet man einen großen Überschuß des Oxidationsmittels bei der Reaktion zwischen Eisen(II) und Chloramin-T bei pH 2·56–5·6, dann ist der Verbrauch an Oxidationsmittel erheblich höher, als der für die Oxidation von Eisen(II) zu Eisen(III) benötigten stöchiometrischen Menge entspricht. Dies wurde mit der Bildung und mit Folgeprozessen freier Radikale während der Reaktion begründet. Die Bildung freier Radikale wurde experimentell nachgewiesen. Sie dimerisieren offenbar zu Produkten vom Typ R-NCl-NCl-R ($R = CH_3C_6H_4SO_2$), die von Chloramin-T weiter oxidiert werden. Die dimeren Spezies setzen aus angesäuertem Kaliumjodid sehr langsam Jod frei. Diese Erklärung berücksichtigt die beobachtete Zersetzung von überschüssigem Chloramin-T in Gegenwart kleiner Mengen von Eisen(II) oder Bromid bei pH 2·65–4·70 nach Ausmaß und Geschwindigkeit in befriedigender Weise. Die Aufbewahrung von Chloramin-T in Metallbehältern könnte über einen ähnlichen Radikalmechanismus das Oxidationsmittel in erheblichem Ausmaß zersetzen und sollte daher vermieden werden.

Résumé—Lorsqu'un grand excès de l'oxydant est utilisé dans la réaction fer (II)-chloramine-T à pH 2,56–5,6, la quantité d'oxydant consommée est bien au-dessus de la quantité stoechiométrique nécessaire pour oxyder le fer (II) en fer (III). Ceci a été attribué à la formation et au

comportement ultérieur de radicaux libres durant la réaction. La formation de radicaux libres a été démontrée expérimentalement. Ils se dimérisent apparemment pour donner des produits du type R—NCl—NCl—R ($R=CH_3C_6H_4SO_2$), qui sont plus profondément oxydés par la chloramine-T. L'espèce dimérisée libère très lentement l'iode d'une solution acidifiée d'iodure de potassium. Cette explication rend compte de manière satisfaisante de la grandeur et de la vitesse de destruction observées de l'excès de chloramine-T en présence de petites quantités de Fe (II) ou de bromure à pH 2,65–4,70. Le stockage de la chloramine-T dans des récipients métalliques pourrait causer une forte destruction de l'oxydant par un mécanisme de radical libre semblable et devrait être évité.

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INFRARED MACRO AND SEMIMICRO DETERMINATION OF NITROGEN IN RAW NITROCELLULOSE AND NITROCELLULOSE CONTAINED IN PROPELLANTS

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Summary—The infrared procedure for the determination of nitrogen in raw nitrocellulose has been improved. In the original method 0·31–0·32 g of sample was dissolved in 45 ml of tetrahydrofuran, the solution was weighed, and the infrared peak at 6·0 μm was measured. The calibration curve was prepared by plotting absorbance against mg of nitrogen per g of solution. The method has the disadvantage that the height of the peak is affected by the sample weight. In the improved method the error due to the sample weight is eliminated by using 0·3000 g of sample and diluting to 50 ml in a volumetric flask. The calibration curve is prepared by plotting absorbance against % nitrogen. The method was extended to the semimicro scale by using a 30·0-mg sample and diluting to 5 ml in a volumetric flask. The method has been applied on the macro and semimicro scales to the direct determination of nitrogen in nitrocellulose after a methylene chloride extraction. The amounts of graphite and inorganic salts found in nitrocellulose-base propellants do not interfere, but a correction must be made to refer the results to 0·3000 g of nitrocellulose for the macro method or 30·0 mg of nitrocellulose for the semimicro method. The same calibration curve is used for all procedures.

Levitsky and Norwitz[1] proposed an infrared procedure for the determination of nitrogen in nitrocellulose. In this procedure 0·31–0·32 g of sample was dissolved in 35 ml of tetrahydrofuran in a glass-stoppered Erlenmeyer flask by allowing to stand overnight, the solution was weighed, and the peak at 6·0 μm was measured. The calibration curve was prepared by carrying samples of nitrocellulose of known nitrogen content through the procedure and plotting absorbance *vs.* mg of nitrogen per g of solution.

A "round-robin" group under the chairmanship of Dr. Eugene Burns of Space Technology Laboratories evaluated the procedure and found that it was satisfactory.[2] Dr. Burns showed that the accuracy could be improved somewhat by preparing a calibration curve each day. However, the procedure is not as accurate as the nitrometer method and is designed for rapid control work.

In this procedure there is an error caused by the fact that the calibration curve varies with the sample weight (it is for this reason that 0·31–0·32 g of sample was specified). Clarkson and Robertson[3] stated that this error could be eliminated by correcting all sample weights to a fixed concentration (0·008 g of nitrocellulose per g of solution). Some difficulties have been encountered at times with the method of approach suggested by Clarkson and Robertson; therefore, an investigation was undertaken to develop a more direct method for eliminating the error caused by the sample weight.

Another aspect of the present investigation was to extend the range of the infrared method for the determination of nitrogen in nitrocellulose to the semimicro scale, since there is need for such a method. Elving and McElroy[4] have described a semimicro method for the determination of nitrogen in nitrocellulose by a nitrometer; however, a special apparatus is required. Gardon and Leopold[5] have described a micro spectrophotometric method for the determination of nitrogen in nitrocellulose, using phenoldisulphonic acid, but the conditions for the development of the colour are critical. Roberts[6] described a spectrophotometric method for the determination of nitrogen in nitrocellulose, using diphenylamine; the method is applicable to the micro or semimicro range but is only semiquantitative.

The final aspect of the present paper involved the application of the infrared technique to the direct determination, both on a macro and semimicro scale, of nitrogen in nitrocellulose contained in propellants. The methods that have been previously proposed for the determination of nitrogen in nitrocellulose contained in propellants are troublesome. If the propellant does not contain a significant amount of inorganic material, the determination can be performed by subjecting the propellant to extraction with methylene chloride, ethyl ether, or 70% acetic acid, drying the residue (nitrocellulose), and determining the nitrogen in a weighed portion by titration[7,8] or by use of the nitrometer.[7] If the propellants contain a significant amount of inorganic materials, as is usually the case, the method is subject to an error caused by the fact that these inorganic materials are not extracted by the methylene chloride and are included in the weighed sample of nitrocellulose. For a sample containing 13·00% nitrogen and 1·00% of total inorganic material, the error would be −0·13% total nitrogen. This error can be reduced but not eliminated by dissolution of the nitrocellulose in acetone and precipitation with water.[9]

EXPERIMENTAL

Reagents

Tetrahydrofuran. Store in a constant-temperature room. Keep covered at all times and dispense from a covered container.

Preparation of calibration curve

Air-dry 3 or 4 standard samples of nitrocellulose (with nitrogen content accurately determined by the nitrometer method[7]), then dry them in a vacuum oven (at 20–50 mm Hg pressure) at 65° for 4 hr and cool in a desiccator. Weigh 0·3000 g of the samples into tared 30-ml beakers. Add 35 ml of tetrahydrofuran and immediately cover tightly with aluminium foil which is held in place by rubber bands. Carry along a blank determination. Allow to stand overnight without stirring, in the room (constant temperature) containing the infrared instrument.

After the overnight standing period, stir with a small stirring rod, wash down and remove the stirring rod, transfer to a 50-ml volumetric flask with tetrahydrofuran, dilute to the mark with tetrahydrofuran, stopper, and shake. Work with only one sample at a time from point of stirring to the dilution in the volumetric flask. Rinse and fill a 0·2-mm sodium chloride cell with the solution, using a 1-ml syringe. Obtain the spectrum from 5·80 to 6·05 μm (1724–1653 cm^{-1}) at a speed of 25 cm^{-1} per minute. The gain, response, and resolution settings should be normal. Suppression setting should be zero.

Observe I_A and I (see Fig. 1) and calculate the absorbance from absorbance = $\log (I_A/I)$. Deduct the blank. Plot absorbance against % nitrogen in the nitrocellulose. The calibration curve should be checked ocasionally and should be redrawn if a new lot of tetrahydrofuran is used.

Procedures

Determination of nitrogen in raw nitrocellulose

Macro method. Dissolve 0·3000 g of sample in tetrahydrofuran and measure the intensity of the peak at 6·0 μm as described in the preparation of the calibration curve. Calculate the nitrogen content by referring to the calibration curve.

Semimicro method. Proceed as for the macro method but weigh a 30·0-mg sample in a tared 5-ml beaker (preferably on a semimicro balance), dissolve it in 3 ml of tetrahydrofuran, and dilute to 5 ml in a volumetric flask. Calculate the nitrogen content by referring to the calibration curve.

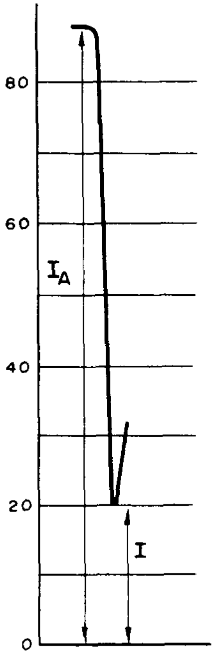

Fig. 1. Spectrum of nitrocellulose in tetrahydrofuran from 5·80 to 6·05 μm.

Determination of nitrogen in nitrocellulose contained in propellants

Macro method. Extract 0·5–5 g of sample of the propellant with methylene chloride in the usual manner, using a Soxhlet extractor.[7] Transfer the residue from the thimble to a weighing dish and dry by heating in a vacuum oven (20–50 mm Hg) at 65° for 2 hr. Calculate the weight of the residue that will contain 0·3000 g of nitrocellulose (NC) as follows.

$$\text{Weight of residue (g) that will contain 0·3000 g of NC} = \frac{30}{100\text{-}A}$$

where A = total per cent of graphite plus inorganic salts (carbonates, nitrates, and sulphates) in the propellant.

Weigh this calculated amount of the residue into a 30-ml beaker, dissolve in tetrahydrofuran, and proceed as described in the macro method for raw nitrocellulose.

Semimicro method. Extract approximately 0·1 g of sample with methylene chloride in the usual manner, using a Soxhlet extractor,[7] and dry the residue. Calculate the weight of residue that will contain 30·0 mg of nitrocellulose, as follows.

$$\text{Weight of residue (mg) that will contain 30·0 mg of NC} = \frac{3000}{100\text{-}A}$$

where A = total per cent of graphite plus inorganic salts (carbonates, nitrates, and sulphates) in the propellant.

Weigh the calculated amount of residue in a tared 5-ml beaker, add 3 ml of tetrahydrofuran, and proceed as described in the semimicro method for raw nitrocellulose.

DISCUSSION AND RESULTS

The sample-weight effect in the original method is eliminated by dissolving 0·3000 g of sample in the tetrahydrofuran in a beaker and diluting to 50 ml in a volumetric flask. The weighing of an exact amount of nitrocellulose is readily performed since the material is very fluffy.

The accurancy of the original method[1] has been further improved by carrying a blank for the tetrahydrofuran through the entire process. This compensates for the small amount of water in the tetrahydrofuran, which shows some absorption at 6·0 μm. The amount of water in commercial tetrahydrofuran is about 0·02%.[10]

As before,[1] it is recommended that transmittance paper rather than absorbance paper be used for recording the peak. The reason for this is that in the region of 20% transmittance, the transmittance paper can be read more accurately than absorbance paper.

As previously stated, the calibration curve in the original method was prepared by plotting absorbance *vs.* mg of nitrogen per g of solution.[1] Analogously, the calibration curve could be prepared in the present method by plotting absorbance *vs.* mg of nitrogen per ml of solution. However, since a constant weight of sample is used, the calibration curve can be prepared by merely plotting absorbance *vs.* per cent of nitrogen in the nitrocellulose.

For the sake of information, an investigation was made to ascertain the extent to which the sample weight affected the calibration curve obtained by plotting absorbance *vs.* mg of nitrogen per ml of solution. For this investigation, curves were plotted for 0·3000 g and 0·2900 g of sample per 50 ml (Fig. 2). It is seen that the weight of sample has a significant effect. The cause of this phenomenon is uncertain.

In establishing the method for nitrogen in nitrocellulose contained in propellants it was first necessary to ascertain whether the results obtained for nitrogen were additive when samples of nitrocellulose of different nitrogen content were mixed together. This is important because nitrocelluloses of different nitrogen content are often blended together to obtain a composite nitrocellulose of required nitrogen content.

To investigate this problem, 0·1500 g of a sample that contained 12·61% nitrogen was mixed with 0·1500 g of a sample that contained 13·47% nitrogen. The results obtained for nitrogen were 13·01, 13·09, and 13·09% with an average result of 13·06%. The latter result does not differ significantly from the theoretical result (13·04%), so it can be concluded that the nitrogen content is additive.

The question of interference from the inorganic materials found in propellents, namely graphite, calcium carbonate, barium carbonate, sodium nitrate, potassium nitrate, sodium

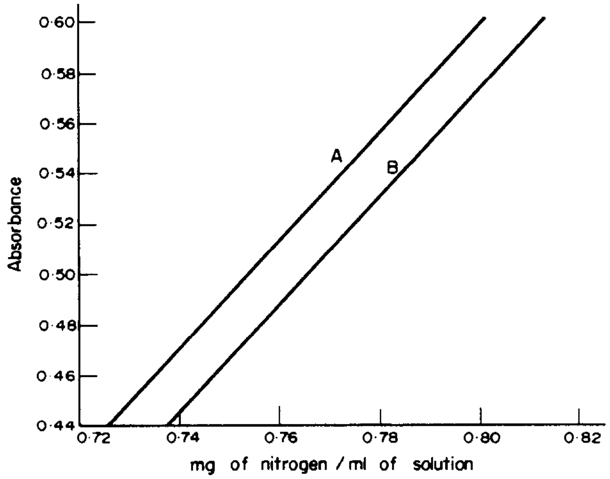

Fig. 2. Effect of amount of nitrocellulose on curve obtained by plotting absorbance *vs.* mg of nitrogen per ml of solution

A. 0·2900 g of nitrocellulose.
B. 0·3000 g of nitrocellulose.

sulphate, and potassium sulphate, was also considered. Experiments were carried out in which 0·0033 g of each of these substances (equivalent to 1·00% on a 0·3000 g sample) was suspended in 50 ml of tetrahydrofuran and the absorbance measured at 6·0 μm. In no case was the absorbance different from the absorbance obtained with tetrahydrofuran.

Aside from the question of the interference by increased absorbance, the problem arose as to how to correct for the weight of the inorganic substances so as to obtain a sample that would contain 0·3000 g or 30·0 mg of nitrocellulose. This problem was solved by using the equations indicated in the procedure.

It was found that the same calibration curve could be used for all methods.

The results obtained for nitrogen in raw nitrocellulose by the macro and semimicro infrared methods on four samples for which nitrogen content had been established by the nitrometer method are shown in Table I. The macro and semimicro infrared results check with the nitrometer results and each other quite well. The average standard

Table 1. Results for nitrogen in raw nitrocellulose by infrared, using macro and semimicro methods

			Nitrogen by infrared, %	
Sample	Nitrogen by nitrometer, %		Macro method	Semimicro method
1	12·58		12·63	
			12·61	
			12·57	
			12·59	
			12·55	
			12·63	
			12·63	
		Ave.	12·60	
		Std. devn.	0·032	
2	13·47		13·40	13.43
			13·51	13·50
			13·49	13·54
			13·43	13·52
			13·41	
			13·48	
			13·52	
		Ave.	13·46	13·50
		Std. devn.	0·049	0·048
3	12·61		12·55	12·57
			12·56	12·57
			12·68	12·64
			12·66	12·62
			12·65	
			12·65	
			12·56	
		Ave.	12·62	12·60
		Std. devn.	0·056	0·036
4	13·16		13·15	13·10
			13·17	13·16
			13·18	13·23
			13·15	13·17
			13·15	
			13·16	
		Ave.	13·16	13·17
		Std. devn.	0·012	0·054

Table 2. Results for nitrogen in nitrocellulose contained in propellants, by macro and semimicro infrared methods

			Nitrogen by infrared, %	
Sample	Specification requirement, %		Macro method	Semimicro method
IMR-4895*	13·10–13·20		13·15	13·15
			13·13	13·14
			13·11	13·13
			13·18	13·09
		Ave.	13·14	13·13
		Std. dev.	0·030	0·026
IMR-4903†	13·10–13·20		13·07	
			13·03	
			13·07	
			13·03	
		Ave.	13·05	
		Std. dev.	0·023	
HPC-1 §	13·15–13·25		13·25	13·21
			13·22	13·18
			13·20	13·14
			13·24	13·22
		Ave.	13·23	13·19
		Std. dev.	0·022	0·031
HPC-14‡	13·15–13·25		13·09	13·20
			13·15	13·19
			13·15	13·20
			13·17	13·18
		Ave.	13·14	13·19
		Std. dev.	0·035	0·010

* Contains 0·26% graphite and 0·48% potassium sulphate.
† Contains 0·40% graphite and 0·59% potassium sulphate.
§ Contains 0·29% graphite and 0·70% potassium sulphate.
‡ Contains 0·28% graphite and 0·74% potassium sulphate.

deviation of the macro infrared method was 0·037% and that of the semimicro method was 0·046%. The average standard deviation of the original method was 0·093%.[1]

The results obtained for nitrogen in nitrocellulose contained in propellants by the macro and semimicro infrared methods are shown in Table 2. There is no accurate method that can be used as a basis of comparison. The macro and semimicro infrared methods check with each other well. The average standard deviation of the macro method was 0·028% while that of the semimicro method was 0·022%. The results for both the semimicro methods are within the specification requirements for nitrogen in nitrocellulose contained in propellants.

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Zusammenfassung—Das Infrarotverfahren zur Bestimmung von Stickstoff in roher Nitrocellulose wurde verbessert. Ursprünglich wurden 0·21–0·32 g Probe in 45 ml Tetrahydrofuran gelöst, die Lösung gewogen und die Infrarotbande bei 6·0 μm gemessen. Die Eichkurve wurde hergestellt durch Auftragen der Extinktion gegen mg Stickstoff pro g Lösung. Das Verfahren hat den Nachteil, daß die Peakhöhe vom Probengewicht abhängt. Bei der verbesserten Methode wird der auf dem Gewicht der Probe beruhende Fehler vermieden, indem 0·3000 g Probe verwendet werden und in einem Meßkolben auf 50 ml verdünnt wird. Die Eichkurve wird hergestellt durch Auftragen der Extinktion gegen % Stickstoff. Das Verfahren wurde durch Verwendung einer 30·0 mg-Probe und Verdünnen im Meßkolben auf 5 ml auf den Halbmikromaßstab ausgedehnt. Das Verfahren wurde im Makro- und Halbmikromaßstab auf die direkte Bestimmung von Stickstoff in Nitrocellulose nach einer Extraktion mit Methylenchlorid angewandt. Die Mengen an Graphit und anorganischen Salzen, die man in Treibmitteln auf Nitrocellulosebasis findet, stören nicht. Eine Korrektur muß angebracht werden, um die Ergebnisse auf 0·3000 g Nitrocellulose für die Makromethode oder auf 30·0 mg Nitrocellulose für die Halbmikromethode zu beziehen. Man verwendet für alle Verfahren die selbe Eichkurve.

Résumé—On a amélioré la technique infra-rouge pour le dosage de l'azote dans la nitrocellulose brute. Dans la méthode originale, on dissolvait 0,31–0,32 g d'échantillon dans 45 ml de tétrahydrofuran, pesait la solution, et mesurait le pic infra-rouge à 6,0 μm. La courbe d'étalonnage était préparée en traçant l'absorbance par rapport au nombre de mg d'azote par g de solution. Le désavantage de la méthode est que la hautur du pic est affectée par le poids d'échantillon. Dans la méthode améliorée l'erreur due au poids d'éhantillon est éliminée en utilisant 0,3000 g d'échantillon et en diluant à 50 ml dans une fiole jaugée. La courbe d'étalonnage est préparée en tracant l'absorbance par rapport au % d'azote. La méthode a été étendue à l'échelle semi-micro en utilisant un échantillon de 30,0 mg et en diluant à 5 ml dans une fiole jaugée. On a appliqué la méthode aux échelles macro et semi-micro au dosage direct de l'azote dans la nitrocellulose après une extraction au chlorure de methylène. Les quantité de graphite et de sels minéraux trouvées dans les agents de propulsion à base de nitrocellulose n'interfèrent pas, mais il faut effectuer une correction pour rapporter les résultats à 0,3000 g de nitrocellulose pour la macrométhode ou 30,0 mg de nitrocellulose pour la semi-microméthode. La même courbe d'étalonnage est utilisée pour toutes les techniques.

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HYDROGEN PEROXIDE FORMATION UPON OXIDATION OF OXALIC ACID IN PRESENCE AND ABSENCE OF OXYGEN AND OF MANGANESE(II)—III

IRON(III) AND COPPER(II) AS RETARDERS*

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Summary—The formation of considerable amounts of hydrogen peroxide upon the slow addition of various oxidizing agents to oxalic acid in dilute sulphuric acid in the presence of oxygen and Mn(II) is greatly retarded in the presence of Fe(III) or Cu(II). With hydrogen peroxide as oxidizing agent and a trace of Fe(II) there is considerable decomposition of peroxide, under a nitrogen atmosphere, after a few hours at 25° in light (from a tungsten lamp), and less decomposition in the dark. This decomposition is decreased by Mn(II) and also when the original mixture contains Fe(III). With oxygen as the oxidizing agent Fe(II) is about 100 times as effective an inhibitor of peroxide formation as Fe(III). With all oxidizing agents used, Cu(II) is some 6–10 times more effective as a retarder than Fe(III). The inhibition is accounted for by the reaction Fe(III) [or Cu(II)] + CO_2^- → Fe(II) [or Cu(I)] + CO_2.

Considerable amounts of hydrogen peroxide are formed upon the slow addition of various oxidizing agents to oxalic acid in dilute sulphuric acid in the presence of oxygen and Mn(II). The oxidizing agents include Mn(VII), Cr(VI), Ce(IV), and the complex Co(III) oxalate,[1] as well as oxygen itself.[2] The initial step appears to be oxidation of Mn(II) to the complex Mn(III)Ox, where Ox denotes oxalate. This is followed by reactions (1)–(3):

$$\mathrm{Mn(III)Ox} \longrightarrow \mathrm{Mn(II)} + CO_2 + \cdot CO_2^- \quad \text{(measurable rate)} \tag{1}$$

$$\cdot CO_2^- + O_2 \longrightarrow \cdot O_2CO_2^- \quad \text{(very fast)} \tag{2}$$

$$\cdot O_2CO_2^- + \mathrm{Mn(II)} + H_2C_2O_4 \longrightarrow \mathrm{Mn(III)Ox} + CO_2 + H_2O_2 \quad \text{(fast)} \tag{3}$$

Reactions (1)–(3) constitute the chain reaction

$$O_2 + H_2C_2O_4 \longrightarrow 2CO_2 + H_2O_2$$

The radical which is formed in reaction (1) may be either $\cdot CO_2^-$ or $\cdot C_2O_4^-$. An approximate theoretical calculation[3] indicates that the latter radical is the more stable, but the two forms do not appear to be distinguishable on the basis of kinetic or spectroscopic evidence.[4] Following the consensus of previous workers we write $\cdot CO_2^-$ in this paper. Also, in this paper, in which all the experiments reported were carried out in 0·1*M* sulphuric acid media, no account is taken of the various protonated or dissociated

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forms of radicals such as $\cdot HCO_2$, $\cdot O_2^-$, and so forth. Many such equilibrium constants are known.[5]

According to Anderson and Hart[6] and many subsequent workers, the radical $\cdot HCO_2$ (*i.e.*, protonated $\cdot CO_2^-$), which is formed in the radiolysis of formic acid, reacts with oxygen according to reaction (2*a*):

$$\cdot HCO_2 + O_2 \longrightarrow \cdot HO_2 + CO_2 \tag{2a}$$

Since $\cdot HO_2$ presumably oxidizes Mn(II) to Mn(III)Ox, the net result in this case is also an induced formation of hydrogen peroxide.

In a study of the oxidation of aqueous solutions of formic acid by X-rays in the presence of Fe^{3+} and/or Cu^{2+}, it was shown[7] that reactions (4*a*) and (4*b*) occur with the formate radical:

$$Fe^{3+} + CO_2^- \longrightarrow Fe^{2+} + CO_2 \tag{4a}$$

$$Cu^{2+} + CO_2^- \longrightarrow Cu^+ + CO_2 \tag{4b}$$

Quite generally with this and other organic radicals, Baxendale and co-workers have found that Cu^{2+} is more reactive than Fe^{3+}, and specifically with the formate radical in $0{\cdot}1N$ sulphuric acid the rate constant for Cu^{2+} is about 6 times as large as that for Fe^{3+}. Therefore both Fe^{3+} and Cu^{2+} may be expected to retard the formation of hydrogen peroxide, the latter more strongly. On the other hand, under our experimental conditions some Fe(III) is present as oxalate complexes, denoted as Fe(III)Ox. These complexes undergo a photochemical decomposition which has been studied intensively (see ref. 4, which gives the earlier literature):

$$\mathrm{Fe(III)Ox} + h\nu \longrightarrow \mathrm{Fe(II)} + CO_2 + \cdot CO_2^- \tag{5}$$

The occurrence of reaction (5) would be expected to promote the formation of hydrogen peroxide. The effects of Fe(III), Fe(II) and Cu(II) on hydrogen peroxide formation on oxidation of oxalic acid in the light and dark are the subject of the present paper.

EXPERIMENTAL

All chemicals were of C. P. quality. The arrangement used for experiments in light (tungsten lamp) and the methods used for determination of the sum of peroxide and oxalic acid have already been described.[1,2] For the determination of hydrogen peroxide in the presence of oxalic acid and Fe(III) or Cu(II), the reaction mixture was made $0{\cdot}3M$ in potassium oxalate and the pH was adjusted to 5·5 by addition of sulphuric acid. The mixture was then made $0{\cdot}01M$ in ammonium molybdate, an excess of potassium iodide was added, and the liberated iodine was titrated with thiosulphate, the end-point being detected either with starch or amperometrically. In the buffered medium (pH 5·5) neither iron(III) nor copper(II) reacts with iodide. In some instances hydrogen peroxide formed was also determined polarographically. The results agreed with those found iodometrically.

RESULTS

The effects of Fe(III) and Cu(II) upon formation of peroxide in the dark are shown in Table 1. In all these experiments it was found that (expressed in equivalents) peroxide formed = oxalic acid disappeared − Mn(VII) added. As expected, Cu(II) is a more powerful retarder than Fe(III). Under the conditions of Table 1, $0{\cdot}01M$ Co(II) had no effect.

The four-hour experiments of Table 1 were repeated with Fe(II) instead of Fe(III). When the equivalent amount of Fe(II) was equal to or greater than the amount of Mn(VII) added, no hydrogen peroxide was formed. No induced oxidation by oxygen occurs as long as there is Fe(II) present. After this has been oxidized by Mn(VII) the

Table 1. Fe(III) and Cu(II) as retarders, 1 equivalent-percent of potassium permanganate as oxidant. Solution $0{\cdot}01M$ in oxalic acid, $0{\cdot}1M$ in H_2SO_4, $0{\cdot}1M$ in $MnSO_4$. Saturated with oxygen at 25°, dark conditions

Time of addition of $KMnO_4$, *hr*	H_2O_2 formed, $10^{-4}M$						
	Fe(III), $10^{-3}M$					Cu(II), $10^{-3}M$	
	0	0·2	0·5	2·0	10·1	0·1	1·0
0·08	6		6		0·1	1·7	0·3
0·5			9				
1	17		12	5	0·1	3·5	1·0
2	25				0·5†		
4	29	23†	18†	6†	0·2†	6·6	1·4
4*	44			17·5†	0·9†	8·5	

* With 5 eq. % of $KMnO_4$ instead of 1%.

† Trace of Fe(II) was detected with 1,10-phenanthroline.

Fe(III) formed acts as if it had been added initially. The same was found true when an amount of Mn(VII) equivalent to the Fe(II) present was added rapidly to the well-stirred reaction mixture. Evidently no oxalic acid reacts with Mn(VII) until all Fe(II) has been oxidized. [It is also possible that the oxidation of Fe(II) is by Mn(III)Ox rather than by Mn(VII), but the net result is the same, that is, the prevention of reaction (1).]

Previously[2] it was found that the decomposition of hydrogen peroxide in dilute sulphuric acid at 25° was either negligible or very slow in the absence and presence of oxalic acid and of Mn(II), both in the dark and in light. Even at 75° the decomposition did not exceed 4% in 3 hr. The addition of a trace of Fe(II) has in some cases a pronounced accelerating effect (Table 2). In the absence of oxalic acid, Mn(II) increases the decomposition. In the presence of oxalic acid and Fe(II) the amount of oxalic acid

Table 2. Effect of $10^{-4}M$ Fe(II) on decomposition of hydrogen peroxide. Solution $2{\cdot}1 \times 10^{-3}M$ in H_2O_2 and $0{\cdot}1M$ in H_2SO_4. In nitrogen atmosphere.

Temp., *C*	$[MnSO_4]$, *M*	$[H_2C_2O_4]$, *M*	H_2O_2 disappearing, %		
			In 1 hr	In 3 hr	
			light	dark	light
25	0	0		0	5
		0·01	21	8	45
		0·1	5*	41	100
	0·01	0	11	6	12
		0·01		3	38
	0·1	0			35
		0·1			33
75	0	0	45†	73	75
		0·01		85	87
		0·1	100§	100	100
	0·01	0		88	85
	0·1	0		100	100

* $10^{-5}M$ Fe(II).

† 40% in the dark.

§ 100% in the dark. 30% in oxygen atmosphere and light.

that disappeared was equimolar with the amount of peroxide that disappeared. Therefore the Fe(II)–peroxide couple under the specified conditions induces the oxidation of oxalic acid. From Table 2 it is clear that Mn(II) retards this induced oxidation at 25°. At 75°, however, there is a substantial decomposition of peroxide which is promoted by Mn(II) and is about the same in the dark as in the light.

Effect of Fe(III). In a mixture which was $10^{-4}M$ in Fe(III) and 2–5 × $10^{-3}M$ in hydrogen peroxide no decomposition occurred in 4 hr in the dark, either in nitrogen or oxygen, in the absence or presence of Mn(II). In light the results were very different (Table 3).

Table 3. Effect of Fe(III) on decomposition of hydrogen peroxide in light. 2·1 × $10^{-3}M$ H_2O_2, 0·1*M* H_2SO_4.

Temp., °*C*	Time, *hr*	[Fe(III)], *M*	[Mn(II)], *M*	[$H_2C_2O_4$], *M*	H_2O_2 disappearing, %	
					N_2 atmosphere	O_2 atmosphere
25	24	0	0·1	0	20	14
	48	0	0·1	0	36	28
	24	10^{-4}	0·1	0	70	45
	48	10^{-4}	0·1	0	100	84
	48	10^{-4}	0	0	0	0
	3	10^{-4}	0	0·01	30	5
	3	10^{-4}	0	0·1	100	5
	3	10^{-4}	0·1	0	36	20
	3	10^{-4}	0·1	0·01	28	
	3	10^{-4}	0·1	0·1	20	
75	0·5	10^{-4}	0	0	25	24
	0·5	10^{-4}	0	0·1	62	8
	1	10^{-4}	0	0	45	46
	1	10^{-4}	0	0·1	100	15
	3	10^{-4}	0	0	76	50
	3	10^{-4}	0·01	0·1		51

In the absence of oxalic acid and Mn(II) there was negligible decomposition at 25° even after 48 hr, whether in a nitrogen or an oxygen atmosphere. In the presence of oxalic acid and Fe(III) complete decomposition occurred in 3 hr at 25° in the absence of Mn(II); the addition of Mn(II) decreased the decomposition.

Oxygen as oxidant. From Table 4 it appears that the slow oxidation of oxalic acid by oxygen in the presence of Mn(II) is retarded by traces of Fe(II) and Fe(III), the former

Table 4. Effects of Fe(II) and Fe(III) upon peroxide formation in the dark, 25°C. Solution 0·01*M* in $H_2C_2O_4$, 0·1*M* in H_2SO_4 and 0·1*M* in Mn(II). Closed system, initially air-saturated.

Time, *hr*	[Fe(II)], $10^{-6}M$	H_2O_2 formed, $10^{-4}M$	[Fe(III)], $10^{-4}M$	H_2O_2 formed, $10^{-4}M$
72	0	10	0	10
	1	6·5	0·5	4·7
	5	0	2	0
120	0	26	0	26
	1	17	0·5	12
	5	0	2	1·4
216	0	44	0	44
	1	36	0·5	34
	5	16	2	9
	50	0	10	0·6

being about 100-fold as effective a retarder as the latter. Table 5 compares Fe(II), Fe(III), and Cu(II) in oxidation by oxygen at 65°. Again, Fe(II) is a much stronger retarder than Fe(III), and Cu(II) also is stronger than Fe(III).

Table 5. Effects of Fe(II), Fe(III), and Cu(II) upon peroxide formation in the dark, 65°C, 4-hr reaction. Composition as in Table 4. Closed system, initially oxygen-saturated.

[Fe(II)], $10^{-6}M$	H_2O_2 formed, $10^{-4}M$	[Fe(III)], $10^{-3}M$	H_2O_2 formed, $10^{-4}M$	[Cu(II)], $10^{-4}M$	H_2O_2 formed, $10^{-4}M$
0	31	0	31	0	31
6	1·8	1	20	0·4	13
8	0·5	10	0	4	3
20	0			10	2

DISCUSSION

The retarding effect of Fe(III) and Cu(II) on formation of peroxide upon addition of Mn(VII), Table 1, is accounted for by the competition of reaction (4) with (2). The Fe(II) or Cu(I) formed in reaction (4) is oxidized at once by the slowly-added Mn(VII). As already mentioned, the results of Baxendale and Smithies[7] indicate that the rate constant of (4*b*) may be about six times that of (4*a*). In agreement with this expectation, by graphical interpolation of the data in Table 1, Cu(II) is found to be 5–10 times as effective a retarder as Fe(III) at the same concentration.

The results of Table 3 can be interpreted in the following way. The Haber-Weiss mechanism for the reaction between hydrogen peroxide and Fe(II), as modified by Baxendale and colleagues,[8] involves the reactions:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH \tag{6}$$

$$\cdot OH + H_2O_2 \longrightarrow \cdot HO_2 + H_2O \tag{7}$$

$$\cdot HO_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + O_2 \tag{8}$$

$$Fe^{2+} + \cdot OH \longrightarrow Fe^{3+} + OH^- \tag{9}$$

Under our conditions (Table 2) there is hardly any decomposition in the absence of oxalic acid in the presence of $10^{-4}M$ Fe(II) after 3 hr in the dark at 25°, but there is a noticeable decomposition in the light, which is accelerated by Mn(II). The effect of light is accounted for by reaction (10):

$$\text{Fe(III)} + H_2O_2 + h\nu \longrightarrow Fe^{2+} + H^+ + \cdot HO_2 \quad \text{(slow)} \tag{10}$$

In addition to (6) reactions (11) and (12) occur in the presence of Mn(II):

$$\text{Mn(II)} + \cdot OH \longrightarrow \text{Mn(III)} + OH^- \tag{11}$$

$$\text{Mn(II)} + H_2O_2 \longrightarrow \text{Mn(III)} + OH^- + \cdot OH \tag{12}$$

At 75°, however, there is little if any difference in the results in light and in the dark, and the decomposition of peroxide is pronounced after 3 hr. Even with only $10^{-5}M$ Fe(II) there is noticeable decomposition. Also at 75° Mn(II) promotes the decomposition.

In the presence of oxalic acid (Table 2) the decomposition of peroxide is enhanced in the dark and more so in the light. The initiating reaction appears to be (13):

$$Fe^{2+} + H_2O_2 + H_2C_2O_4 \longrightarrow Fe(III)Ox + H^+ + H_2O + \cdot OH \qquad (13)$$

followed by (14) and (15) which constitute a chain:

$$\cdot OH + H_2C_2O_4 \longrightarrow H_2O + H^+ + CO_2 + \cdot CO_2^- \qquad (14)$$

$$\cdot CO_2^- + H_2O_2 \longrightarrow CO_2 + OH^- + \cdot OH \qquad (15)$$

In light there is an additional contribution from reaction (5). Mn(II) decreases the decomposition of peroxide in the presence of oxalic acid, both in the dark and in light, because of reaction (16),

$$\cdot OH + Mn(II) + H_2C_2O_4 \longrightarrow Mn(III)Ox + H_2O + H^+ \qquad (16)$$

followed by (1), (2) and (3) which regenerate peroxide, to compensate for its destruction in (7) and (8).

In a mixture containing initially Fe(III) and hydrogen peroxide (Table 3), no decomposition of peroxide occurred at 25° after 3 hr in *nitrogen*, but there was considerable decomposition in the additional presence of 0·01M oxalic acid and complete decomposition with 0·1M oxalic acid. The decomposition in nitrogen and in light, accompanied by an equimolar disappearance of oxalic acid, is accounted for by reactions (5), (15), (14), and (9). The retarding effect of Mn(II) is the same as explained above.

It is especially interesting (Table 3) that oxygen in light almost completely prevents the induced oxidation of oxalic acid in the absence of Mn(II) (*e.g.*, after 3 hr at 25°, 100% in nitrogen, 5% in oxygen). Apparently the $\cdot CO_2^-$ formed in reaction (5) reacts very rapidly with oxygen (reaction 2), followed by reaction (17)

$$\cdot O_2CO_2^- + Fe(III) \longrightarrow Fe^{2+} + CO_2 + O_2 \qquad (17)$$

and reaction (6).

Finally, with oxygen as oxidizing agent (Tables 4 and 5) Fe(II) is about 100 times as effective an inhibitor of peroxide formation as Fe(III). Considering the results at 65°, the initiating reaction appears to be

$$O_2 + Mn(II) + H_2C_2O_4 \longrightarrow Mn(III)Ox + \cdot HO_2 + H^+ \quad \text{(slow)} \qquad (18)$$

The Mn(III)Ox thus formed reacts rapidly with Fe^{2+} and hence reaction (1) does not occur. The relatively much weaker inhibiting effects of Cu(II) and Fe(III) are explained (as in respect to Table 1) by reactions (4*b*) and (4*a*).

The inhibiting effect of Fe(III) and Cu(II) has been made use of in the time-honoured method of determination of active oxygen in manganese dioxide by digestion with an excess of oxalic acid in about 4N sulphuric acid and titration of the remaining oxalic acid. The method gives high results, but the error can be largely eliminated[9] when iron(III) or copper(II) are present during the digestion. From the results in this and the preceding papers, it is evident that the error arises from an induced oxidation of oxalic acid by oxygen, in the presence of Mn(II) formed during the digestion, to hydrogen peroxide, which in turn decomposes before the titration with permanganate. It is also evident that the presence of Cu(II) or Fe(III) should largely prevent this error, as has been found experimentally.

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Zusammenfassung—Die Bildung erheblicher Mengen Wasserstoffperoxid bei der langsamen Zugabe verschiedener Oxidationsmittel zu Oxalsäure in verdünnter Schwefelsäure in Gegenwart von Sauerstoff und Mangan(II) wird in Gegenwart von Fe(III) oder Cu(II) stark verlangsamt. Mit Wasserstoffperoxid als Oxidationsmittel und einer Spur Fe(II) zerfällt unter Stickstoffatmosphäre nach ein paar Stunden bei 25° im Licht (von einer Wolframlampe) eine beträchtliche Menge Peroxid, im Dunkeln weniger. Die Zersetzung wird von Mn(II) verlangsamt, ebenso, wenn die Ausgangsmischung Fe(III) enthält. Mit Sauerstoff als Oxidationsmittel inhibiert Fe(II) die Peroxidbildung etwa 100-mal effektiver als Fe(III). Bei allen verwendeten Oxidationsmitteln ist Cu(II) als Verlangsamer 6–10-mal wirksamer als Fe(III). Man kann die Inhibitorwirkung durch die Reaktion Fe(III) [oder Cu(II)] + CO_2^- → Fe(II) [oder Cu(I)] + CO_2 erklären.

Résumé—La formation de quantités considérables d'eau oxygénée par l'addition lente de divers agents d'oxydation à l'acide oxalique en acide sulfurique dilué en la présence d'oxygène et de Mn(II) est fortement retardée en la présence de Fe(III) ou Cu(II). Avec l'eau oxygénée comme agent oxydant et une trace de Fe(II), il y a une décomposition considérable de peroxyde, sous une atmosphère d'azote, après quelques heures à 25° à la lumière (d'une lampe au tungstène), et une moindre décomposition à l'obscurité. La décomposition est diminuée par Mn(II) et aussi lorsque le mélange initial contient Fe(III). Avec l'oxygène comme agent oxydant, Fe(II) est un inhibiteur de formation de peroxyde environ 100 fois plus efficace que Fe(III). Avec tous les agents d'oxydation utilisés, Cu(II) est quelques 6–10 fois plus efficace comme retardateur que Fe(III). L'inhibition est expliquée par la réaction Fe(III) [ou Cu(II)] + CO_2^- → Fe(II) [ou Cu(I)] + CO_2.

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LOGARITHMIC DIAGRAMS AND GRAN-CURVES AS AN AID IN POTENTIOMETRIC TITRATIONS IN COMPLEXOMETRY

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Summary—A detailed exposition is given of the use of logarithmic diagrams and Gran plots to construct titration curves and to determine accurately the equivalence point in potentiometric complexometric titrations.

Gran-curves are being used more frequently for the evaluation of the results of potentiometric titrations. In acid-base titrations, no special problems arise when Gran-functions are used, but with complexometric titrations it is sometimes difficult to decide whether Gran-curves can be used. In some cases only one part of the titration curves can be utilized in the evaluation, but logarithmic diagrams are often valuable for handling these problems. Two different questions are of particular interest:

(*a*) how can a titration curve be constructed when the concentrations and the stability constants are known and

(*b*) how can the equivalence volume be calculated when an unknown sample is being titrated?

TITRATION CURVES

Titrations where [M] or pM can be measured

Johansson and Wänninen[1] have shown that logarithmic diagrams are a convenient means of surveying the conditions of a complexometric titration. First, consider a titration of the type $M + Y = MY$, the equilibrium equation being $[MY] = K_{MY}[M][Y]$. All quantities may be conditional.[2] A logarithmic diagram for a complexometric equilibrium is constructed in the following way. In a diagram with pY along the horizontal axis and log C (C denoting concentration) along the vertical axis, a system point ($\log K_{MY}$, $\log C_M$) is marked (point S in Fig. 1). C_M denotes the concentration of the metal ion at the start of the titration. From this point, four lines are drawn, two parallel to the pY-axis, the other two having slopes $+1$ and -1 respectively. The lines are connected in pairs according to the figure.

The point of intersection between the curved parts lies 0·3 (= log 2) logarithmic units below the system point. Finally, a line with slope -1 is drawn with the origin as the starting point. The three graphs in Fig. 1 represent the species M, MY and Y, and show the logarithm of the concentration of each of these species at a certain value of pY. The diagram then is fully analogous to an acid-base diagram, with the exception that no line representing OH^- is needed. A comprehensive survey of logarithmic diagrams has been made by Sillén.[3] During the titration, the total concentration of Y increases, *i.e.*, pY

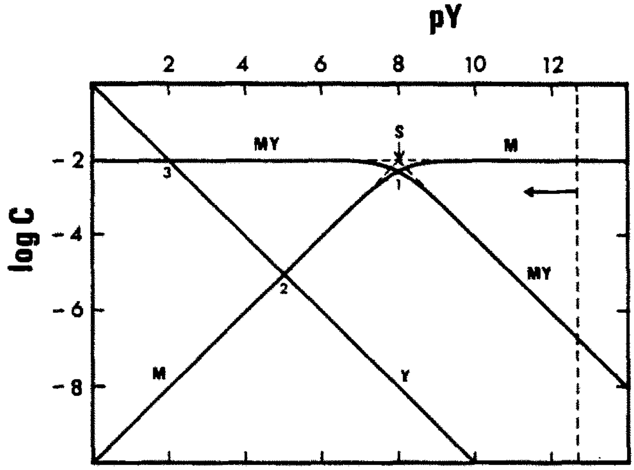

Fig. 1. Logarithmic diagram of log C as a function of pY. The total concentration is $10^{-2}M$ and log K_{MY} is 8·0.

Table 1. Values of pM corresponding to different values of the titration ratio a, the number of moles of titrant added per mole of metal ion, for the calculation of titration curves

a	pM	a	pM
0	$-\log C_{\mathrm{M}}$	1·01	$\log K_{\mathrm{MY}} - 2{\cdot}00$
0·1	$-\log C_{\mathrm{M}} + 0{\cdot}05$	1·02	$\log K_{\mathrm{MY}} - 1{\cdot}70$
0·2	$-\log C_{\mathrm{M}} + 0{\cdot}10$	1·03	$\log K_{\mathrm{MY}} - 1{\cdot}52$
0·3	$-\log C_{\mathrm{M}} + 0{\cdot}15$	1·04	$\log K_{\mathrm{MY}} - 1{\cdot}40$
0·4	$-\log C_{\mathrm{M}} + 0{\cdot}22$	1·05	$\log K_{\mathrm{MY}} - 1{\cdot}30$
0·5	$-\log C_{\mathrm{M}} + 0{\cdot}30$	1·06	$\log K_{\mathrm{MY}} - 1{\cdot}22$
0·6	$-\log C_{\mathrm{M}} + 0{\cdot}40$	1·07	$\log K_{\mathrm{MY}} - 1{\cdot}15$
0·7	$-\log C_{\mathrm{M}} + 0{\cdot}52$	1·08	$\log K_{\mathrm{MY}} - 1{\cdot}10$
0·8	$-\log C_{\mathrm{M}} + 0{\cdot}70$	1·09	$\log K_{\mathrm{MY}} - 1{\cdot}05$
0·9	$-\log C_{\mathrm{M}} + 1{\cdot}00$	1·10	$\log K_{\mathrm{MY}} - 1{\cdot}00$
0·91	$-\log C_{\mathrm{M}} + 1{\cdot}05$	1·20	$\log K_{\mathrm{MY}} - 0{\cdot}70$
0·92	$-\log C_{\mathrm{M}} + 1{\cdot}10$	1·30	$\log K_{\mathrm{MY}} - 0{\cdot}52$
0·93	$-\log C_{\mathrm{M}} + 1{\cdot}15$	1·40	$\log K_{\mathrm{MY}} - 0{\cdot}40$
0·94	$-\log C_{\mathrm{M}} + 1{\cdot}22$	1·50	$\log K_{\mathrm{MY}} - 0{\cdot}30$
0·95	$-\log C_{\mathrm{M}} + 1{\cdot}30$	1·60	$\log K_{\mathrm{MY}} - 0{\cdot}22$
0·96	$-\log C_{\mathrm{M}} + 1{\cdot}40$	1·70	$\log K_{\mathrm{MY}} - 0{\cdot}15$
0·97	$-\log C_{\mathrm{M}} + 1{\cdot}52$	1·80	$\log K_{\mathrm{MY}} - 0{\cdot}10$
0·98	$-\log C_{\mathrm{M}} + 1{\cdot}70$	1·90	$\log K_{\mathrm{MY}} - 0{\cdot}05$
0·99	$-\log C_{\mathrm{M}} + 2{\cdot}00$	2·00	$\log K_{\mathrm{MY}} - 0{\cdot}00$
1·00	$(\log K_{\mathrm{MY}} - \log C_{\mathrm{M}})/2$	2·00	$\log K_{\mathrm{MY}}$

Dilution was disregarded when the values of Table 1 were calculated, but if it is desired to take it into account, the term $\log(ar + 1)$ where r is the ratio of the molarities of the titrand and the titrant, should be added to pM.

decreases and hence *the vertical line representing the system moves from right to left in the diagram.*

The diagram in Fig. 1 was constructed assuming the original concentration of M to be $10^{-2}M$ and the stability constant of MY to be 10^8.

From the diagram it can be seen for instance that pM = 2 at the start of the titration (no addition of Y). At the point where half the metal has been titrated (i.e. [M] = [MY], point no. 1) the pM value is 2.3. At the equivalence point (point no. 2), the conditions should be the same as in a $10^{-2}M$ solution of MY in water. Part of the MY is then dissociated into M and Y, the concentrations of these species being equal. It can also directly be seen that the larger the value of the stability constant of the complex, the smaller is [M]. The diagram shows that at the equivalence point, pM = 5 [*i.e.*, (8 + 2)/2]. At point no. 3, where [MY] and [Y] are equal, the amount of Y added is, all told, double the amount of M, and pM = log *K*.

Hence when the titration begins, $pM = -\log C_M$ and when twice the amount of titrant required to reach the equivalence point has been added, $pM = \log K_{MY}$. The values of pM between these extreme values are easily calculated but can also be taken from Table 1.

It is, however, easy to read more points from logarithmic diagrams and not only equivalence points, half-titration points etc. It is possible to introduce a scale *a* (the degree of titration) in the diagram and read the pM values directly. The following table gives values of pY corresponding to values of *a*.

Table 2. Values of pY corresponding to different values of the titration ratio *a*

a	pY	*a*	pY
0·01	$\log K_{MY} + 2{\cdot}00$	0·99	$\log K_{MY} - 2{\cdot}00$
0·10	$\log K_{MY} + 0{\cdot}95$	1·00	$(\log K_{MY} - \log C_M)/2$
0·25	$\log K_{MY} + 0{\cdot}48$	1·01	$2{\cdot}00 - \log C_M$
0·50	$\log K_{MY}$	1·10	$1{\cdot}00 - \log C_M$
0·75	$\log K_{MY} - 0{\cdot}48$	1·50	$0{\cdot}30 - \log C_M$
0·90	$\log K_{MY} - 0{\cdot}95$	2·00	$-\log C_M$

See also Fig. 2 which illustrates the titration of a metal ion with a complexing agent Y to form a complex MY with stability constant equal to 10^8.

Titrations where pM cannot be measured

Indirect electrodes. It is not always possible to follow the course of a titration with an electrode having a potential that is directly proportional to [M]. Frequently, an indicator electrode is used, that consists of Hg^{2+}/Hg or Ag^+/Ag and requires addition of HgY or AgY to the titrated solution before the start of the titration. The titration curves that are obtained in such titrations can have different shapes. The problem has been treated by various authors.[4–13] In this case, logarithmic diagrams provide a convenient guide to the appearance of the titration curves.

The following assumptions are made. A metal ion M with total concentration C_M is titrated with a complexing agent Y. An indicator ion is added in the form of AY. The total concentration of A is denoted by C_A. The (conditional) stability constants are K_{MY} and K_{AY}, respectively.

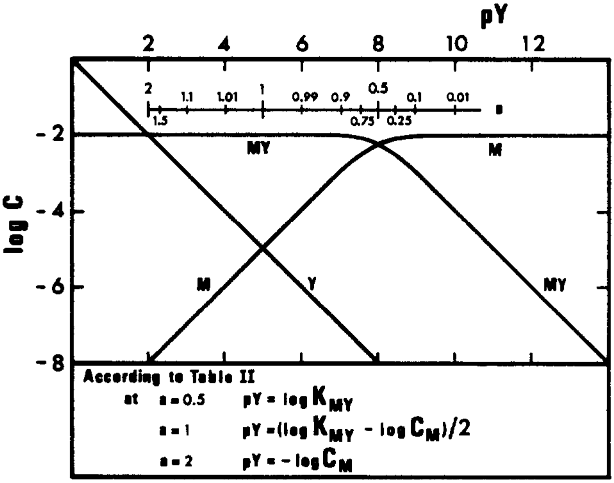

Fig. 2. Logarithmic diagram for the titration of a metal ion M with a complexing agent Y. $K_{MY} = 10^8$; $C_M = 0{\cdot}01M$. A scale for $a = C_Y/C_M$ is introduced in the diagram.

It is possible to distinguish three cases.

1. $K_{AY} = K_{MY}$

This case is demonstrated in Figs. 3 and 4. When the solutions are mixed before the titration ($a = 0$), the reaction M + AY = MY + A takes place. This means that [A] and [MY] are then equal, corresponding to point no. 1 in Fig. 3. It is also clear from this diagram that the graph representing M is parallel to the graph representing A over its entire course. In a logarithmic diagram, this means that pA − pM is constant, which implies that [A] = constant × [M]. It is easy to construct a conventional titration curve with the aid of the logarithmic diagram and the scale for $a = C_Y/C_M$. Figure 4 shows the titration curve pA = $f(a)$. The figure also contains a scale showing the variations of pM as a function of a.

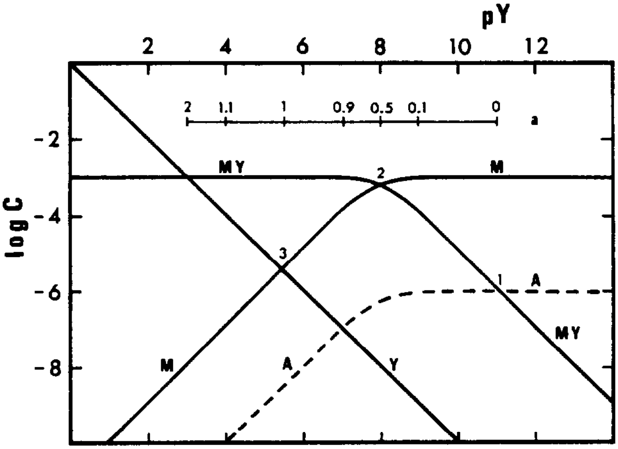

Fig. 3. Logarithmic diagram of log C as a function of pY. C_M is $10^{-3}M$ and C_A is $10^{-6}M$. Log K_{AY} = log K_{MY} = 8.

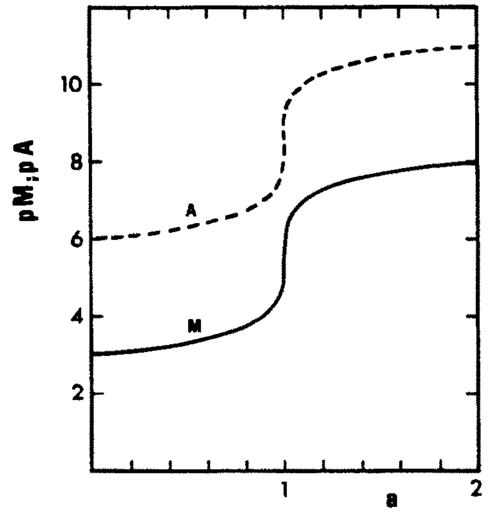

Fig. 4. Titration curve of pM and pA as a function of the degree of titration *a*. This curve is constructed from the logarithmic diagram in Fig. 3. $K_{MY} = K_{MA}$.

Of course, it is a rare coincidence when K_{AY} and K_{MY} happen to be equal in a titration. However, considering that we are dealing with conditional constants, it is clearly possible to adjust the conditions so as to make the values of the constants equal. As an example, let us take titration of zinc ion with EDTA using an Hg^{2+}/Hg electrode at pH = 4·5. The acetate complexes of the zinc and mercuric ions differ considerably in their stabilities and $K_{Zn'Y'}$ and $K_{Hg'Y'}$ can be adjusted to equal magnitudes by proper choice of the concentration of acetate ion. It is also possible to adjust the magnitude of $K_{Hg'Y'}$ by varying the concentration of chloride ion.

2. $K_{AY} < K_{MY}$

Figure 5 illustrates how such a titration is treated. At the start ($a = 0$), [MY] = [A],

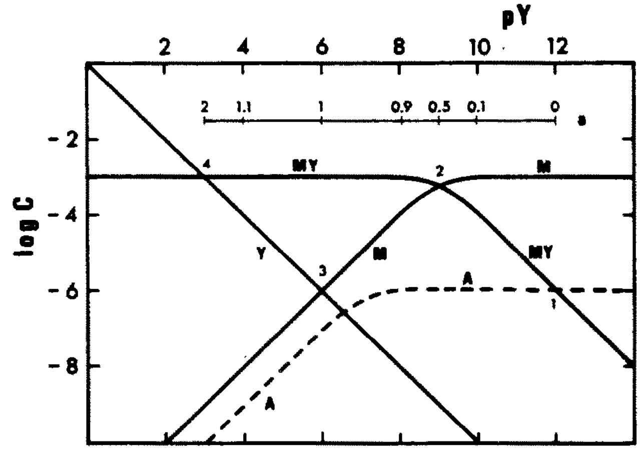

Fig. 5. Logarithmic diagram of log *C* as a function of pY. C_M is $10^{-3}M$ and C_A is $10^{-6}M$; log $K_{MY} = 9$ and log $K_{MA} = 7$.

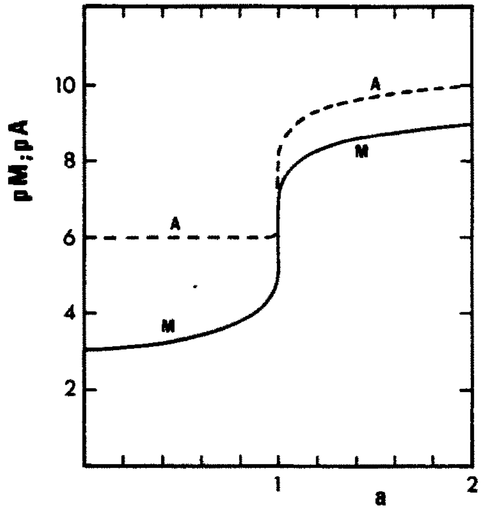

Fig. 6. Titration curve of pM and pA as a function of the degree of titration a. This curve is constructed from the logarithmic diagram in Fig. 5. K_{MY} is greater than K_{AY}.

i.e., pA = 6. When [M] = [MY], *i.e.*, $a = 0{\cdot}5$, (on a line parallel to the C-axis and through point no. 2), pA still equals 6. At the equivalence point, point no. 3, where [M] = [Y] (strictly [Y] = [M] + [A]), pA = 7. After the equivalence point, the lines representing A and M run parallel and pA and pM differ by a constant amount, in this case 1·0. Along an ordinate drawn through point no. 4 ($a = 2$), pA is found to be 10 and pM = 9.

Figure 6 is a titration curve in which pA is plotted as a function of a. The equivalence volume may be calculated in the same way as if pM were measured. However, only values recorded after the equivalence point has been passed can be used in the calculation of the equivalence volume.

3. $K_{AY} > K_{MY}$

Figure 7 is a graph of log C *vs.* pY. By the reasoning used above, we arrive at the following values, which can be read from the diagram.

a :	0 ,	0·1,	0·25,	0·5,	0·75,	0·9,	1·0,	1·5,	2·0
pA:	6·1,	7·5,	8·1,	8·5,	9·0,	9·5,	11·0,	13·2,	13·5

The curves in Fig. 8 plot pA and pM as a function of a. The courses of the pA and pM curves are parallel from a point slightly before the equivalence point. Only data after the equivalence point can be used to calculate the equivalence volume.

Ion-selective electrodes. Even though an electrode fully specific for the ionic species which is to be determined is not always available, it is often possible to use an ion-selective electrode to follow the course of a potentiometric titration. There are several types of both anion and cation electrodes available. As there are at present no good electrodes that respond to EDTA activity, we shall discuss only cation, *i.e.*, metal ion, electrodes.

The responses of all cation electrodes are influenced by other ionic species present in the solution titrated. The potential of the electrode is determined not only by the activity of the ion to be determined but also by the activities of the other ions present.

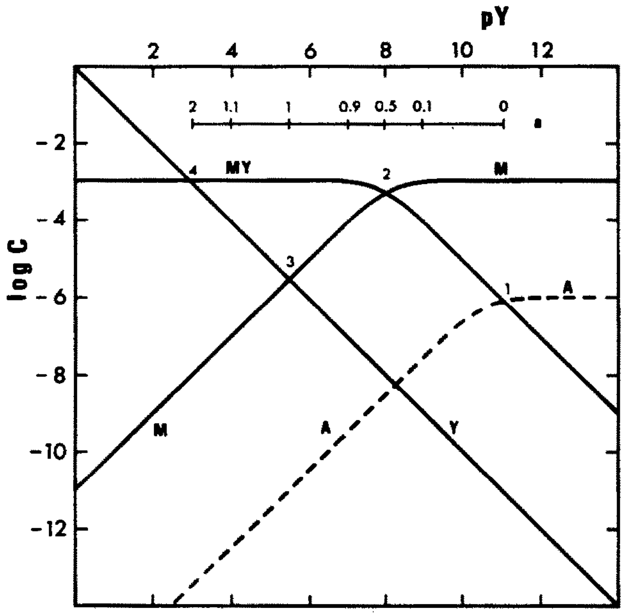

Fig. 7. Logarithmic diagram of log C as a function of pY. The figure is based upon the following values: log $K_{AY} = 10{\cdot}5$, log $K_{MY} = 8$, $C_M = 10^{-3}M$ and $C_A = 10^{-6}M$.

It is therefore customary to include an appropriate correction factor in the Nernst equation and according to Eisenman[14] write

$$E_C = E_C{}^0 + \frac{RT}{nF}\ln([M^{n+}] + \sum_i K_i[M_i{}^{z_i}]^{n/z_i})$$

where $[M_i]$, z_i and K_i are the concentrations, charges and selectivity coefficients of the interfering ionic species. If, for the sake of simplicity, we assume that $n = z_i$ and that the effects of the interfering species can be expressed by a single term, we may write

$$E_C = E_C{}^0 + \frac{Q}{n}\log([M^{n+}] + K_i[M_i{}^{n+}]) \tag{2}$$

where $Q = (RT \ln 10)/F$.

A value of the selectivity coefficient K_i less than unity means that the electrode is more sensitive to changes in the concentration of M than to changes in the concentrations of M_i, and, *vice versa* if $K_i > 1$. If K_i is large in value, the concentration of M_i must be low, in order that its influence will not be too great. During a titration the concentration of M decreases, whereas the concentration of the interfering ion remains constant. The interference of the latter ion may thus finally be so great that the electrode is no longer able to follow the changes in the concentration of M. The result is the same as if the concentration of M were larger than it actually is. It is possible to deduce readily from a logarithmic diagram how great the influence of an interfering ion will be (Fig. 9).

If $K_i[M_i] = 10^{-3}$, the apparent concentration of M is 10% too high even at the beginning of the titration. If $K_i[M_i] = 10^{-5}$, [M] and $K_i[M_i]$ will be equal at the equivalence point and hence [M] will be apparently twice the true value. Values of [M] at values of $a = C_Y/C_M$

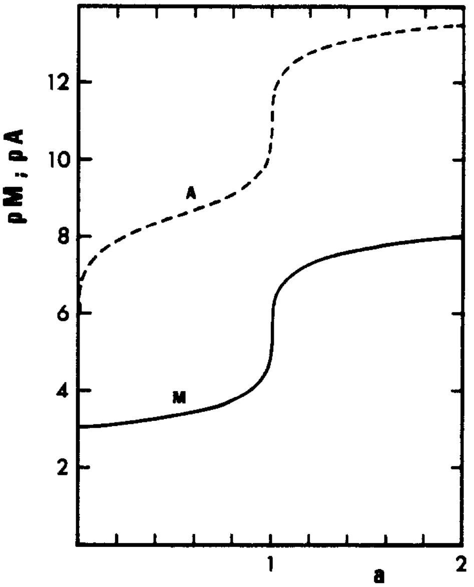

Fig. 8. Titration curve of pM and pA as functions of the degree of titration *a*. This curve is constructed from the logarithmic diagram in Fig. 7. K_{AY} is greater than K_{MY}

greater than 0·9 should not be included when calculating the equivalence volume. The interference will then be at most 1%.

The forms of titration curves in different cases can be easily deduced from logarithmic diagrams. Values of pM read from Fig. 9 are plotted in Fig. 10 against $a = C_Y/C_M$ for the case where $K_i[M_i]$ is equal to 10^{-5}.

CALCULATION OF EQUIVALENCE VOLUMES

The reverse problem, calculation of the equivalence volume from a number of corresponding volume–pM (or e.m.f.) values or from a titration curve can be solved in an analogous manner to that employed by Johansson[14] for acid–base titrations.

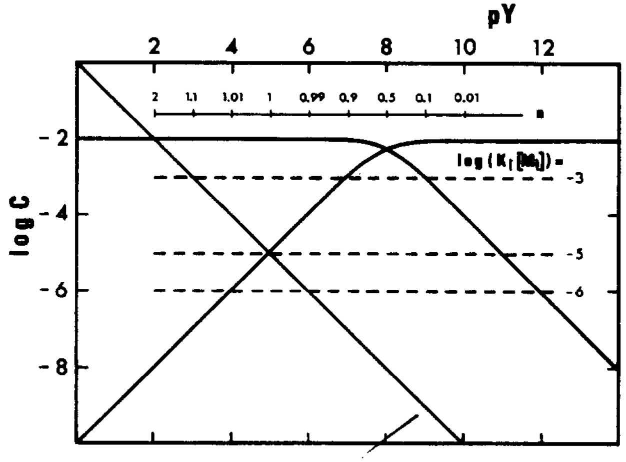

Fig. 9. Logarithmic diagram for the titration of a metal ion M with a complexing agent Y in the presence of an interfering metal ion M_i when $K_i \cdot (M_i)$ has the values 10^{-3}, 10^{-5} and 10^{-6}. $K_{MY} = 10^8$ and $C_M = 0{\cdot}01M$.

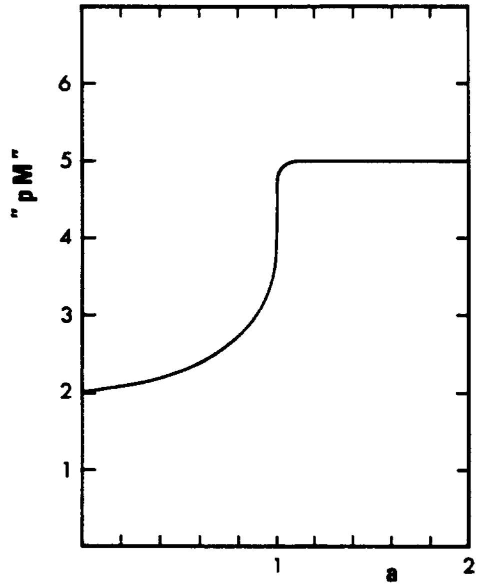

Fig. 10. Titration of a $10^{-2}M$ metal ion (M) in solution containing an interfering metal ion M_i with a complexing agent Y when K_{MY} is 10^8 and $K_i \cdot (M_i)$ is 10^{-5}.

V_0 ml of a $C_M{}^0$ molar metal ion solution are titrated with V ml of a $C_Y{}^0$ molar solution of a complexing agent Y. Only a 1 : 1 complex with stability constant K_{MY} is assumed to be formed by the metal ion and the complexing agent.

The following equations are valid.

$$M + Y \rightleftharpoons MY \tag{3}$$

$$C_M = [MY] + [M] \tag{4}$$

$$C_Y = [MY] + [Y] \tag{5}$$

$$K_{MY} = [MY]/([M][Y]) \tag{6}$$

$$C_M = V_0 \cdot C_M{}^0/(V_0 + V) \tag{7}$$

$$C_Y = V \cdot C_Y{}^0/(V_0 + V) \tag{8}$$

$$V_e \cdot C_Y{}^0 = V_0 \cdot C_M{}^0 \tag{9}$$

V_e denotes the equivalence volume, the volume of titrant added up to the equivalence point. C_M and C_Y are the total concentrations of the metal ion and the complexing agent when V ml of the titrant have been added. By combining equation (8) with equations (4), (5), (7) and (9), we obtain

$$V \cdot C_Y{}^0 = V_e \cdot C_Y{}^0 - (V_0 + V)([M] - [Y]) \tag{10}$$

[Y] is negligible in comparison with [M] before the equivalence point. Equation (10) then assumes the form

$$V_e - V = \frac{(V_0 + V)}{C_Y{}^0} \cdot [M] \tag{11}$$

Thus if $f_1(V) = (V_0 + V)[\mathrm{M}]$ is plotted against V ml, a straight line is obtained, which intersects the V-axis at $V = V_e$.

After the equivalence point, [Y] dominates in equation (10). By combination of equations (4) and (6) with (7), we get

$$[\mathrm{Y}] = \frac{1}{K_{\mathrm{MY}}[\mathrm{M}]}\left(\frac{V_0 \cdot C_{\mathrm{M}}{}^0}{(V_0 + V)} - [\mathrm{M}]\right) \tag{12}$$

[M] in the parentheses in equation (12) is negligible. By substituting equation (12) for [Y] in equation (10), we obtain

$$V - V_e = \frac{V_0 \cdot C_{\mathrm{M}}{}^0}{K_{\mathrm{MY}} \cdot C_{\mathrm{Y}}{}^0 \cdot [\mathrm{M}]} \tag{13}$$

A straight line will result when $f_2(\mathrm{V}) = 1/[\mathrm{M}]$ is plotted as a function of V. The point of intersection of the straight line with the V-axis is the equivalence volume V_e and the slope is $V_0 \cdot C_{\mathrm{M}}{}^0/K_{\mathrm{MY}}C_{\mathrm{Y}}{}^0$. (Note that $1/[\mathrm{M}]$ is not multiplied by $(V_0 + V)$ as is the conventional Gran procedure.) Equations (11) and (13) are consequently suitable for determining equivalence volumes either graphically or with a computer. The data obtained before and after the equivalence point should be kept apart. It is, however, possible to combine equations (10) and (12) to give

$$V \cdot C_{\mathrm{Y}}{}^0 = V_0 C_{\mathrm{M}}{}^0 - (V_0 + V)[\mathrm{M}] + \frac{V_0 - C_{\mathrm{M}}{}^0}{K_{\mathrm{MY}}[\mathrm{M}]} - \frac{(V_0 + V)}{K_{\mathrm{MY}}} \tag{14}$$

which, in turn yields

$$V_e - V = \frac{(V_0 + V)[\mathrm{M}]}{C_{\mathrm{Y}}{}^0} - \frac{V}{1 + K_{\mathrm{MY}}[\mathrm{M}]} \tag{15}$$

Equation (15) makes it possible to use all the titration data simultaneously. However, knowledge of an approximate value of the stability constant K_{MY} is required.

In equations (11) and (13) it is necessary that values of [M] be known. These can be calculated in the usual way by using the Nernst equation.

$$E_C = E_C^0 + \frac{\mathrm{RT}}{nF} \cdot \ln[\mathrm{M}] \tag{16}$$

where $E_C{}^0 = E_{\mathrm{M}}{}^0 + E_{\mathrm{ref}} + \frac{\mathrm{RT}}{nF} \ln \gamma_{\mathrm{M}} +$ junction potentials. $E_{\mathrm{M}}{}^0$ is the normal potential, E_{ref} the potential of the reference electrode and γ_{M} the activity coefficient of the ion M^{n+}.

$E_C{}^0$ is hence a conditional quantity that remains constant only as long as the junction potentials and the activity coefficient remain constant. Therefore it is important that the ionic strength should be constant during the titration.

According to equation (16)

$$[\mathrm{M}] = 10^{(E_C - E_C{}^0)n/Q} \tag{17}$$

where $Q = (RT \ln 10)/F$.

We consequently arrive at the conclusion that when calculating the equivalence volume it is suitable to plot before the equivalence point

$$f_1(V) = (V_0 + V)[\mathrm{M}] = (V_0 + V) \cdot 10^{(E_\mathrm{C} - E_\mathrm{C}^0)n/Q} \tag{18}$$

as a function of V, and after the equivalence point

$$f_2(V) = 1/[\mathrm{M}] = 10^{(E_\mathrm{C}^0 - E_\mathrm{C})n/Q} \tag{19}$$

as a function of V, both plots giving straight lines that intersect the V-axis at the equivalence point.

When an indicator ion, A, is used, [M] in these equations can be replaced by [A], on the condition that [A] = const.[M]. Equations (18) and (19) then remain unchanged.

Ordinarily it is only possible to use data obtained after the equivalence point.

Even when ion-selective electrodes are used in potentiometric titrations, it sometimes happens that only part of the titration curve can be used for purposes of evaluation, (usually the first part). In all these cases, logarithmic diagrams provide the answer to the question as to which part of the titration curve should be used.

Example

As an illustration to the usefulness of the method, an example will be treated in detail.

A solution prepared by mixing 5 ml of 0·05*M* copper sulphate, 50 ml of 0·1*M* sodium acetate–acetic acid buffer of pH 4·6 and 45 ml of water, was titrated with 0·05*M* EDTA. Mercuric ion, added in the form of its complex with EDTA, (HgY), was used as indicator ion. This solution can be prepared by dissolving mercuric oxide in 0·01*M* EDTA. HgY should be added to give a relatively high concentration, *e.g.*, 1% of the concentration of the copper ion. In this way, the signal will be more stable and less sensitive to external interference. In the case in question, 0·25 ml of 0·01*M* HgY was added. As indicator electrode, an amalgamated silver rod was used, and the reference electrode was an Orion model 90-02 double-junction reference electrode.

The following stability constant values are valid for the reactions that determine the shape of the titration curve:

$[\mathrm{HY}] = 10^{10\cdot3}[\mathrm{H}][\mathrm{Y}]$

$[\mathrm{H_2Y}] = 10^{16\cdot6}[\mathrm{H}]^2[\mathrm{Y}]$

$[\mathrm{CuY}] = 10^{18\cdot8}[\mathrm{Cu}][\mathrm{Y}]$

$[\mathrm{CuHY}] = 10^{3\cdot0}[\mathrm{H}][\mathrm{CuY}]$

$[\mathrm{Cu(OH)Y}] = 10^{2\cdot5}[\mathrm{OH}][\mathrm{CuY}]$

$[\mathrm{CuAc}] = 10^{1\cdot7}[\mathrm{Cu}][\mathrm{Ac}]$

$[\mathrm{CuAc_2}] = 10^{2\cdot7}[\mathrm{Cu}][\mathrm{Ac}]^2$

$[\mathrm{CuAc_3}] = 10^{3\cdot1}[\mathrm{Cu}][\mathrm{Ac}]^3$

$[\mathrm{CuAc_4}] = 10^{2\cdot9}[\mathrm{Cu}][\mathrm{Ac}]^4$

$[\mathrm{CuOH}] = 10^{6\cdot0}[\mathrm{Cu}][\mathrm{OH}]$

$[\mathrm{H_3Y}] = 10^{19\cdot3}[\mathrm{H}]^3[\mathrm{Y}]$

$[\mathrm{H_4Y}] = 10^{21\cdot4}[\mathrm{H}]^4[\mathrm{Y}]$

$[\mathrm{HgY}] = 10^{21\cdot8}[\mathrm{Hg}][\mathrm{Y}]$

$[\mathrm{HgHY}] = 10^{3\cdot1}[\mathrm{H}][\mathrm{HgY}]$

$[\mathrm{Hg(OH)Y}] = 10^{4\cdot9}[\mathrm{OH}][\mathrm{HgY}]$

$[\mathrm{HgAc}] = 10^{7\cdot2}[\mathrm{Hg}][\mathrm{Ac}]$

$[\mathrm{HgAc_2}] = 10^{8\cdot4}[\mathrm{Hg}][\mathrm{Ac}]^2$

$[\mathrm{HgOH}] = 10^{10\cdot3}[\mathrm{Hg}][\mathrm{OH}]$

$[\mathrm{Hg(OH)_2}] = 10^{21\cdot7}[\mathrm{Hg}][\mathrm{OH}]^2$

Using Ringbom's procedure, the following conditional constants are calculated.

$$\log K_{\mathrm{Cu'Y'}} = 11{\cdot}0 \quad \text{and} \quad \log K_{\mathrm{Hg'Y'}} = 8{\cdot}7$$

Figure 11 shows a plot of E_{Hg} as a function of the volume of added titrant as recorded with a Metrohm Potentiograph Model E 336 A. As can be seen from the figure, the potential jump is asymmetrical. Therefore, it is difficult to determine the location of the equivalence point in the usual way by differentiation of the curve. It is, however, easy to determine the equivalence volume by plotting 1/[Hg] as a function of the added volume of titrant.

The following data were obtained in a similar titration where the e.m.f. values were measured with an Orion Model 801 digital voltmeter. The temperature was 22°. Values of 1/[Hg] were calculated from equation (19) in the form

$$1/[\mathrm{Hg}] = 10^{(E^0 - E)/29\cdot28} \tag{20}$$

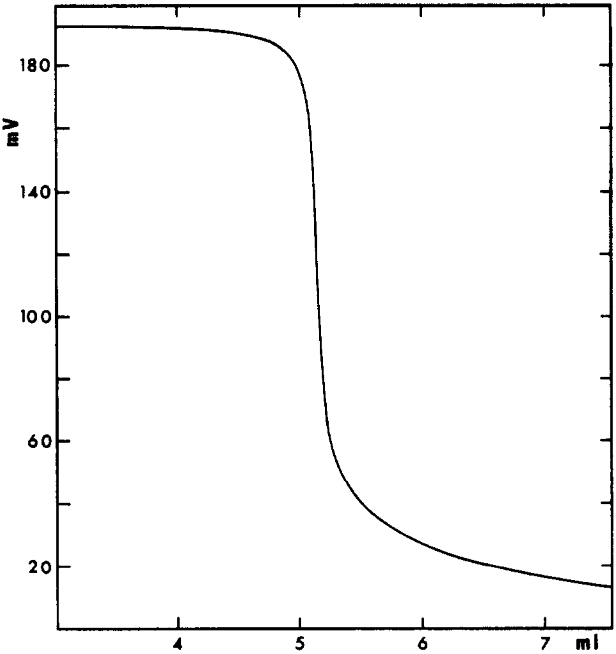

Fig. 11. Experimental curve of E (mV) *vs.* V (ml) from a titration of 100 ml of 0·0025*M* copper sulphate with 0·05*M* EDTA. 0·25 ml of 0·01*M* HgY is added (pH = 4·6). An arbitrary zero-point is chosen for the mV-scale.

E^0, which includes the normal potential, the potential of the reference electrode, the activity factors and junction potentials, may be unknown, in which case an arbitrary value may be inserted in its place. When this is done, the calculation does not yield 1/[Hg], but a constant divided by [Hg]. In the example given, E^0 was taken to be 200 mV.

V, ml	*E, mV*	(200 − *E*)/29·28	constant/[Hg]
5·0	295·0		0
5·5	159·7	1·376	2·38
6·0	148·8	1·748	5·60
6·5	142·9	1·950	8·91
7·0	138·9	2·087	12·22
7·5	135·9	2·189	15·45
8·0	133·5	2·271	18·66
8·5	131.5	2·339	21·83
9·0	129·8	2·398	25·01

A plot of constant/[Hg] against V gives a straight line which intersects the V-axis to give the equivalence volume V_e = 5·11 ml; the theoretical value is V_e = 5·12 ml.

The shape of the titration curve agrees well with that of a curve constructed from a logarithmic diagram (Fig. 12). At the start of the titration, pHg is constant and equals 4·6. This means that pHg = 10·3 since log α_{Hg} = 5·7.

Just before the equivalence point, pHg′ begins to increase and at the equivalence point, pHg′ = 6·8 (or pHg = 12·5). After the equivalence point (point 1, where [Y′] = [Hg′] + [Cu′]), the lines plotting pHg′ and pCu′ run parallel.

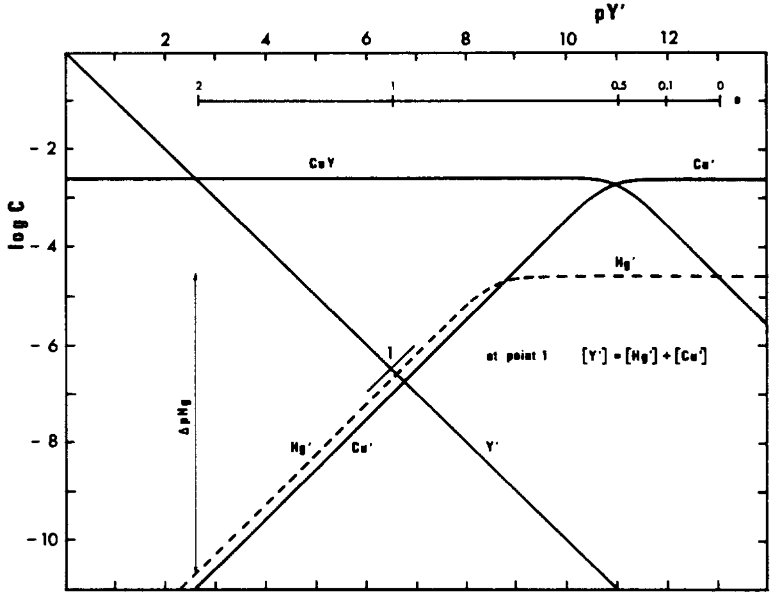

Fig. 12. Logarithmic diagram for the titration of copper ion with EDTA in the presence of mercuric ion (the indicator ion). $K_{\mathrm{Cu'Y'}} = 10^{11 \cdot 0}$; $K_{\mathrm{Hg'Y'}} = 10^{8 \cdot 7}$; $C_{\mathrm{Cu}} = 10^{-2 \cdot 6} M$; $C_{\mathrm{Hg}} = 10^{-4 \cdot 6} M$.

The pHg' of the solution increases by 2·2 units from the start of the titration to the equivalence point. This is equivalent to 64 mV. The potential jump during the titration until twice the equivalence volume of titrant has been added is 6·2 × 29·3 mV = 181·7 mV (at $a = 2$, pHg' = 10·8 and consequently ΔpHg = 10·8 − 4·6 = 6·2). The experimentally found value was 183 mV.

A calculation of a similar titration curve with the aid of a computer and the Haltafall program (by Sillén *et al.*[16]) is described by Dyrssen *et al.*[17]

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Zusammenfassung—Die Verwendung von logarithmischen Diagrammen und Gran-Kurven zur Konstruktion von Titrierburven und zur genauen Bestimmung des Äquivalenzpunktes bei potentiometrischen komplexometrischen Titrationen wird ausführlich geschildert.

Résumé—On donne un exposé détaillé de l'emploi de diagrammes logarithmiques et de tracés de Gran pour construire les courbes de titrages et pour déterminer avec précision le point d'équivalence dans les titrages complexométriques potentiométriques.

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PREPARATION AND INFRARED SPECTRA OF PALLADIUM DERIVATIVES OF SOME ORGANOPHOSPHORUS INSECTICIDES

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Summary—The preparation of palladium complexes of phosphorodithioate (Guthion, Ethyl Guthion, Imidan, and Cidial) and phosphorothioate (Fenthion) insecticides is described. The Pd : pesticide ratios in the derivatives are *ca.* 1 : 1 for the phosphorodithioates and 2 : 1 in the case of Fenthion. The infrared spectra of the derivatives are compared with those of the parent insecticides. Palladium complexation of phosphorodithioates results in a lowering of the P—S frequencies by 60–75 cm^{-1} and also produces changes in the P-O-C region. Milligram quantities of Thimet, Trithion, and Cidial on thin-layer chromatograms were reacted *in situ* with sodium tetrachloropalladate(II). The infrared spectra of the compounds recovered from the plate depended greatly on the Pd : pesticide ratio on the spot, and the analytical significance of these results is discussed.

Palladium(II) chloride has been widely employed as a qualitative detection reagent for organophosphorus insecticides on thin-layer chromatograms since its initial use by Baumler and Rippstein[1] in 1961. The reagent is somewhat selective in that it does not react with organophosphates which contain no sulphur.[2] Blinn[3,4] has studied the separation of Thimet and its metabolites by thin-layer chromatography (TLC) and has described the use of palladium(II) chloride as a detection reagent before removal of the compounds from the plate and identification by infrared spectroscopy. Recently it was shown that the sensitivity of palladium detection methods can be markedly increased by combining palladium(II) chloride with a fluorescent metallochromic indicator such as Calcein or Calcein Blue; the resulting sprays have been used for quantitative *in situ* fluorimetry of nanogram quantities of phosphorodithioate insecticides.[5]

Despite the widespread use of palladium-containing spray reagents, no studies have been made of the interaction between palladium and the insecticides nor have the complexes been prepared other than as spots on TLC plates. Since the effect of palladium complexation on the infrared spectra of these pesticides is of analytical importance, this work was carried out in order to compare the spectra of the derivatives with those of the parent compounds.

EXPERIMENTAL

Reagents

Palladium. Sodium tetrachloropalladate(II) and 5% palladium(II) chloride solution in hydrochloric acid were used as sources of palladium.

Pesticides (≥95% *purity*). These were obtained from the manufacturers listed by Kenaga and Allison.[6]

All other chemicals were analytical reagent quality.

Apparatus

Infrared spectrometers. Perkin-Elmer models 237B and 521. Samples were run in chloroform or as KBr discs.

Thermogravimetry

A Fisher Differential Thermalyzer equipped with a Model 120 TGA Accessory and a Cahn Electrobalance was used.

Preparation and analysis of palladium derivatives of pesticides

Pesticides (0·5–2 g) were dissolved in the minimum volume of ethanol–water (3 : 1–5 : 1, v/v) and a sub-stoichiometric quantity of palladium as sodium tetrachloropalladate(II) or palladium(II) chloride was added as a solution in the same solvent. The derivatives of Guthion, Ethyl Guthion, Imidan and Cidial were formed immediately as fine yellow-orange precipitates which were washed with ethanol, air-dried overnight at room temperature, and finally vacuum-dried at 80° over phosphorus pentoxide. The Fenthion product was an oil which solidified after cooling for several hours in an ice–salt mixture. The solid was finely ground, washed with ethanol, and dried as above; m.p. 117–120°. All these derivatives were formed in good yield (85–103%). Attempts to prepare palladium derivatives of Thimet and Trithion resulted in oil formation and the complexes of these two pesticides were not studied further except as recovered from TLC plates. No suitable recrystallization solvent could be found for the derivatives, but samples of Pd-Guthion and Pd-Cidial were "recrystallized" by dissolving the solids in chloroform and reprecipitating by adding carbon tetrachloride or petroleum ether respectively. The palladium analyses of products so obtained were no different from those of the original solids. Pd–Guthion, Pd–Ethyl Guthion, and Pd–Imidan were soluble in chloroform and insoluble in water, alcohols, acetone, carbon tetrachloride and hydrocarbon solvents. Pd–Cidial and Pd–Fenthion were soluble in carbon tetrachloride, acetone, and toluene as well as in chloroform.

The palladium derivatives were checked for the presence of free pesticides by thin-layer chromatography. A chloroform solution of the complex was spotted along with suitable standards of the pesticide on a 0·25-mm silica gel N TLC plate. The plate was developed in 3 : 1 hexane–acetone; the complex remained at the origin while the free pesticide migrated ($R_f = 0{\cdot}3$–$0{\cdot}5$). The developed chromatogram was sprayed with palladium–Calcein reagent[5] and the quantity of free pesticide was determined by *in situ* fluorimetry.

Palladium was determined gravimetrically as the iodide[7] after wet oxidation of the organic matter with a nitric–sulphuric acid mixture.

Recovery of pesticides and palladium derivatives from TLC plates

Pesticides (1–3 mg) in chloroform were spotted onto acetone-washed TLC plates (0·5 mm, 1 : 1 silica gels N and G). Sodium tetrachloropalladate(II) in ethanol–water was spotted on top of the pesticides and the plates were allowed to stand overnight to ensure complete reaction.[3,5] The spots were scraped from the plate and the compounds were extracted and incorporated into 200-mg KBr discs by Blinn's procedure.[3]

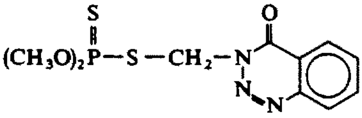
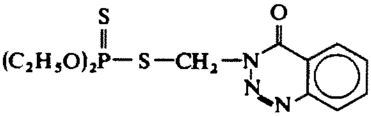
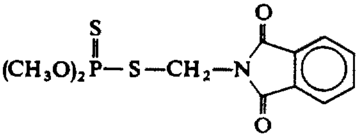
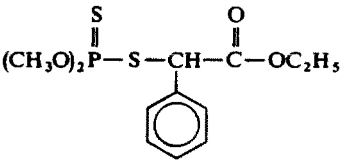
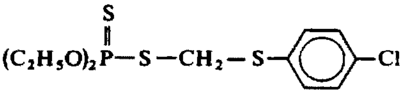
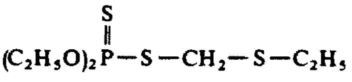
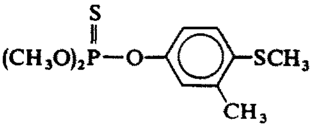
RESULTS AND DISCUSSION

General observations

When solutions of the phosphorodithioate pesticides (Table 1) and sodium tetrachloropalladate(II), each having a pH of 3·5–5, are mixed the product precipitates and the pH of the supernatant liquid falls to ≥ 1·5, indicating the release of protons during the reaction. This pH change was not observed in the case of Fenthion, a phosphorothioate insecticide (Table 1). Qualitative tests for chloride after sodium decomposition of the complexes were positive for Pd–Fenthion but negative for the Pd–phosphorodithioate derivatives. The chloride contents of Pd–Guthion and Pd–Imidan as determined by X-ray fluorescence were 0·7 and 0·2% respectively. Less than 0·5% of free pesticide was found in the palladium derivatives of the phosphorodithioate insecticides by TLC; the Fenthion complex decomposed during chromatography.

Pd-Fenthion was the only complex to have a distinct melting point. The other solids turned brown and finally black without melting on heating in air to above *ca.* 140°. Samples of Pd–Guthion, Pd–Ethyl Guthion, and Pd–Imidan which have been air-dried at room temperature undergo small weight losses when heated in air (Fig. 1). These losses occur within 15 min of heating at 80–90°, after which the weight remains constant over at least a 12-hr period, and are ascribed to loss of solvent which was not removed

Table 1. Pesticides used in this study

Pesticide	Chemical name	Structure
Guthion	*O*,*O*-dimethyl-*S*-4-oxo-1,2,3-benzotriazin-3-(4*H*)-ylmethyl phosphorodithioate	
Ethyl Guthion	*O*,*O*-diethyl-*S*-4-oxo-1,2,3-benzotriazin-3-(4*H*)-ylmethyl phosphorodithioate	
Imidan	*O*,*O*-dimethyl-*S*-phthalimidomethyl phosphorodithioate	
Cidial	ethyl mercaptophenylacetate *O*,*O*-dimethyl phosphorodithioate	
Trithion	*S*-[(*p*-chlorophenylthio)methyl] *O*,*O*-diethyl phosphorodithioate	
Thimet	*O*,*O*-diethyl-*S*-(ethylthio)methyl phosphorodithioate	 $(C_2H_5O)_2\overset{S}{\overset{\|}{P}}-S-CH_2-S-C_2H_5$
Fenthion	*O*,*O*-dimethyl-*O*-(4-methylthio)-*m*-tolyl) phosphorothioate	

by air-drying the derivatives at room temperature. However, the infrared spectra of these phosphorodithioate derivatives show broad bands in the 3300–3600 cm^{-1} region (Figs. 2, 3, and 5 respectively) even for samples which have been vacuum-dried at 80° for up to 18 hr, suggesting that these products also contain firmly bound solvent (or possibly hydroxyl groups) which is not easily removed.

The palladium content of the derivatives was reproducible and independent of the Pd : pesticide ratio in the reaction mixture as long as an excess of pesticide was used (Table 2). Mixtures containing excess of palladium produced dark brown precipitates with varying palladium contents. These products were not studied further. The palladium analyses indicate a Pd : pesticide stoichiometry of *ca.* 1 : 1 for the phosphorodithioate pesticides and 2 : 1 in the case of Fenthion. If this is generally true for phosphorothioates it would help explain why these pesticides are less sensitive to fluorigenic palladium–Calcein sprays.[5] The agreement of the other elemental analyses (Table 3) with the theoretical is only fair, however, and therefore little can be said at this time about the mechanism of the

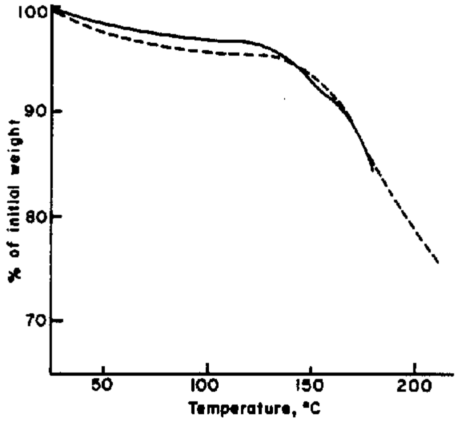


Fig. 1. TGA of Pd–Guthion and Pd–Imidan, 10–14-mg samples.
——— Pd–Guthion, heating rate 23°/hr
------ Pd–Imidan, heating rate 10°/hr

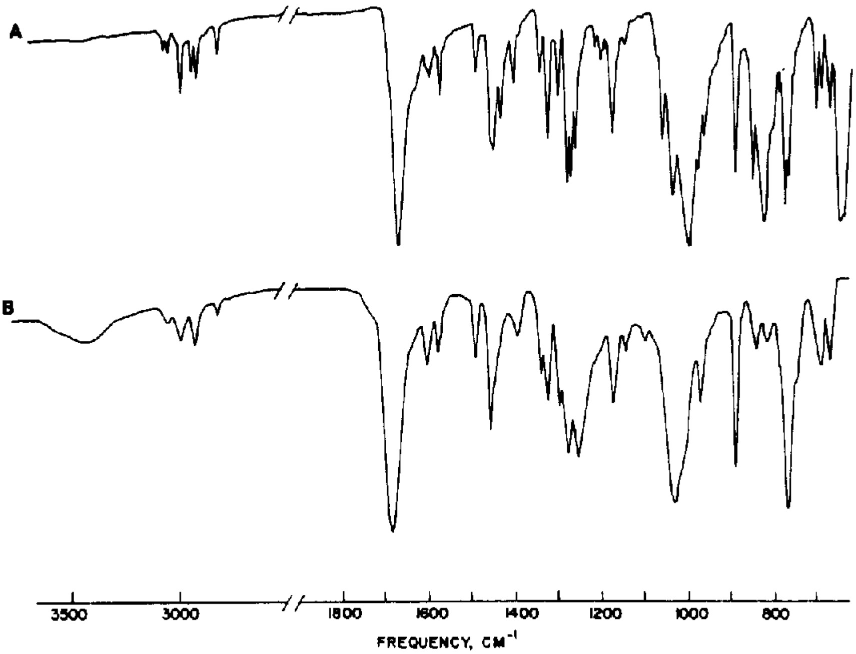


Fig. 2. Infrared spectra of Guthion (*A*) and its palladium derivative (*B*), KBr discs.

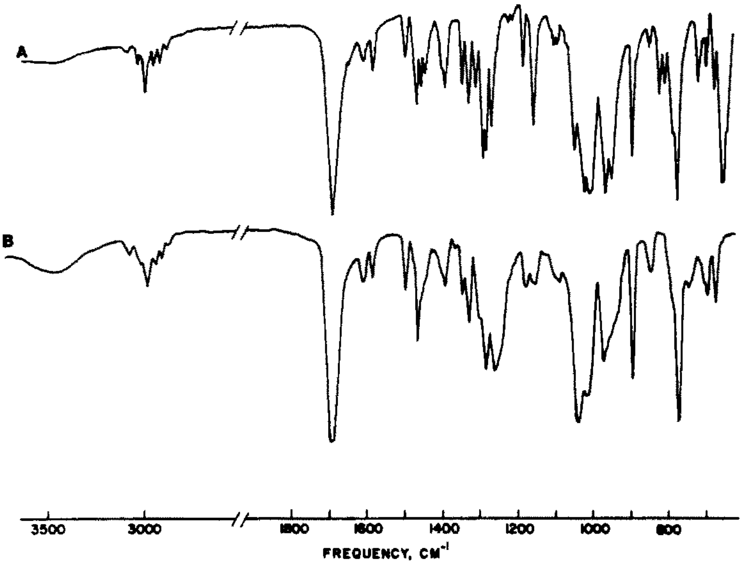


Fig. 3. Infrared spectra of Ethyl Guthion (*A*) and its palladium derivative (*B*), KBr discs.

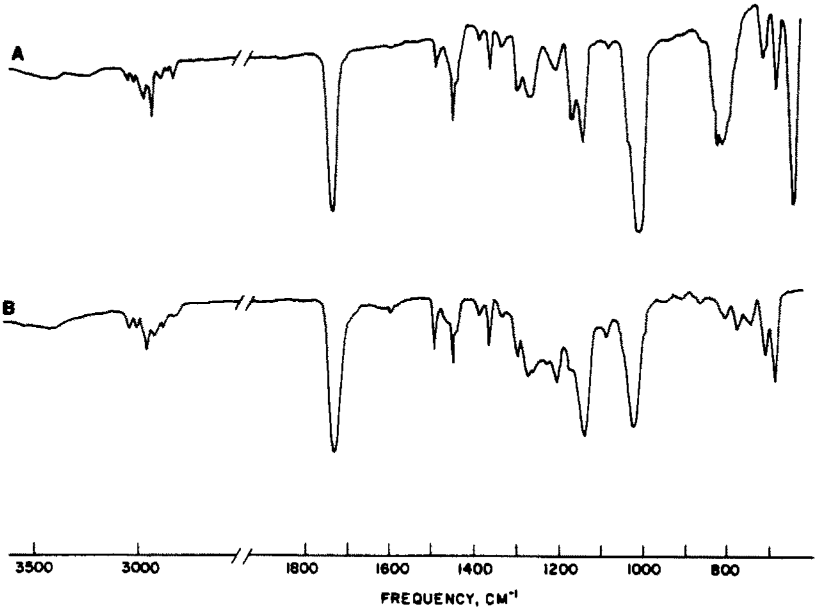


Fig. 4. Infrared spectra of Cidial (*A*) and its palladium derivative (*B*), KBr discs.

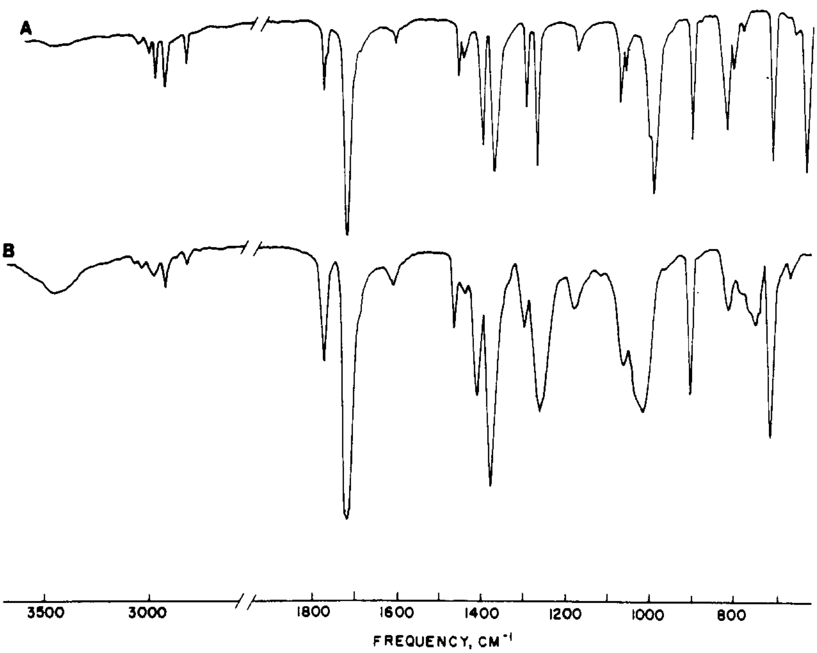


Fig. 5. Infrared spectra of Imidan (*A*) and its palladium derivative (*B*), KBr discs.

Table 2. Palladium analysis of derivatives

Pesticide	Pd : pesticide in reaction mixture	Pd found, range, %	Pd, theoretical, %			
			Pd(pest)	$Pd(pest)_2$	$Pd(pest)(H_2O)_2$	$Pd(pest)_2Cl_2$
Guthion	0·50–0·71 (4)*	23·1–23·3	25·1	14·4	23·3	
Ethyl Guthion	0·12–0·70 (2)	22·2–22·5	23·6	13·4	21·8	
Imidan	0·66 (1)	23·5	25·1	14·4	23·2	
Cidial	0·30–0·57 (2)	22·2–22·7	24·9	14·2	23·0	
Fenthion	0·10–0·47 (3)	13·2–13·8	27·7	16·1		14·5

* Number of preparations.

Table 3. Analysis of palladium–pesticide derivatives

Compound	Calculated, %*				Found, %			
	C	H	N	S	C	H	N	S
Pd–Guthion	28·4	2·9	9·9	15·1	29·8	2·8	11·3	15·4
Pd–Ethyl Guthion	31·9	3·6	9·3		33·2	3·0	11·6	
Pd–Imidan	31·2	2·9	3·3	15·1	32·8	2·8	3·7	13·9

* For 1 : 1 stoichiometry.

pesticide interaction. Although the Fenthion derivative may be a simple adduct of palladium(II) chloride, this is certainly not true for the phosphorodithioate complexes since they contain only traces of chloride. Furthermore the release of protons during the reaction indicates an interaction more complex than adduct formation.

Neutral organophosphorus esters have been shown to react with metal chlorides and bromides in relatively anhydrous systems by a dealkylation mechanism.[8] The corresponding metal derivatives (possibly polymeric[9]) are halide-free and alkyl halides are released during the reaction. Such interactions have been recently reviewed[10] and are common for phosphates, phosphonates, and their thiophosphoryl analogues. Pistschimuka[11] synthesized several metal complexes of phosphorodithioate esters almost 60 years ago, but little work has since been done on these compounds. Further work will be required to determine whether a dealkylation mechanism is operative in the present system. If so, it does not necessarily occur *via* the release of alkyl halides since the reactions take place even if palladium(II) nitrate is used instead of palladium(II) chloride.

Infrared spectra

The spectra of the pesticides and their palladium derivatives are compared in Figs. 2–9. Pesticides containing carbonyl groups show strong C=O bands in the 1600–1800 cm^{-1} region. Measurements in chloroform (Cidial and Guthion) indicate approximately equal carbonyl intensities for the free pesticide and its palladium derivative.

Considerable controversy exists concerning the P=S vibration. Chittenden and Thomas[12] have collected data on many compounds and have assigned two bands which appear to be connected with this group. For compounds having the general structure (RO)(R′O)(R″S)P=S (R-groups alkyl) the band I and band II frequency limits are 790–833 cm^{-1} and 645–663 cm^{-1} respectively. For (RO)(R′O)(R″O)P=S the ranges are 800–844 cm^{-1} and 602–662 cm^{-1}. It is not known which frequency corresponds to the true P=S band. Some authors[13,14] assign band II to $\nu_{P=S}$, but Bellamy[15] has reviewed the subject and has cautiously suggested that the evidence favours band I as the P=S stretching frequency. The relative intensities of the bands are reported[12] to vary considerably with the substituent groups on the phosphorus. From published spectra of organophosphorus insecticides[16,17] band II is generally strong in phosphorodithioates and less intense in phosphorothioates.

Palladium complexation of phosphorodithioate pesticides produces significant changes in the P=S bands. Band I appears to be lowered in frequency by 60–75 cm^{-1} and reduced in intensity. The band I intensity of the phosphorodithioates studied is greater for the $(CH_3O)_2(RS)P{=}S$ pesticides than those having $(C_2H_5O)_2(RS)P{=}S$ structures (*cf.* Guthion and Ethyl Guthion, Figs. 2 and 3), and the changes in this frequency are therefore more noticeable for the former group of pesticides. The far-infrared spectra of Pd–Imidan (Fig. 7), Pd–Guthion, and Pd–Ethyl Guthion indicate that band II is also lowered in frequency by 60–75 cm^{-1} and is thus shifted out of the sodium chloride region covered by most infrared instruments. These shifts are larger than the reported[18] $\Delta\nu_{P=S} = 47\ cm^{-1}$ for the triphenylphosphine sulphide adduct of palladium(II) chloride. Palladium complexation also produces changes in the P–O–C region (995–1050 cm^{-1}) which must remain unexplained until more is known about the mechanism of derivative formation.

According to Blinn[3] the use of palladium(II) chloride as a detection reagent for Thimet on TLC plates does not interfere with the infrared spectrum of the recovered pesticide.

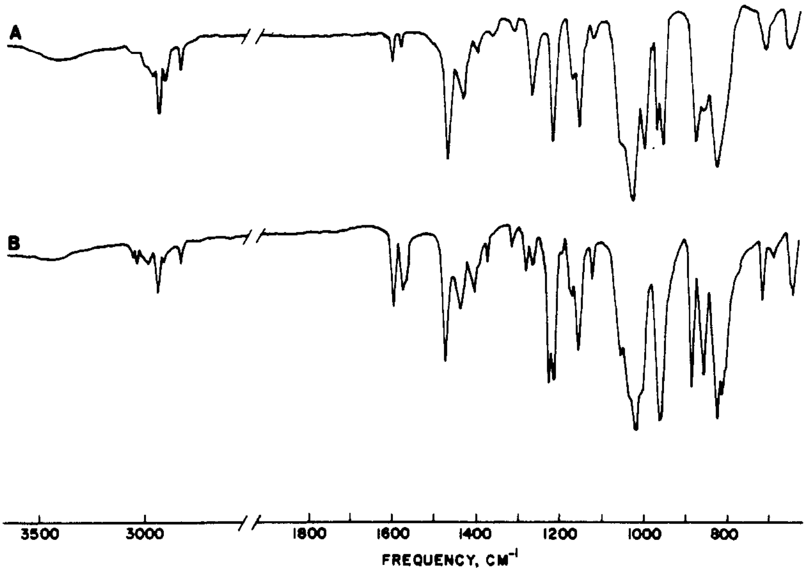


Fig. 6. Infrared spectra of Fenthion (*A*) and its palladium derivative (*B*), KBr discs.

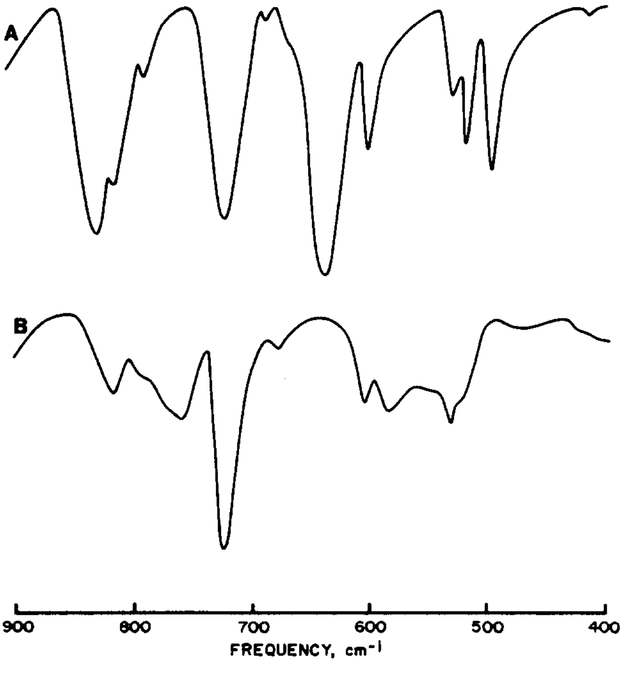


Fig. 7. Far-infrared spectra of (*A*) Imidan and (*B*) Pd–Imidan.

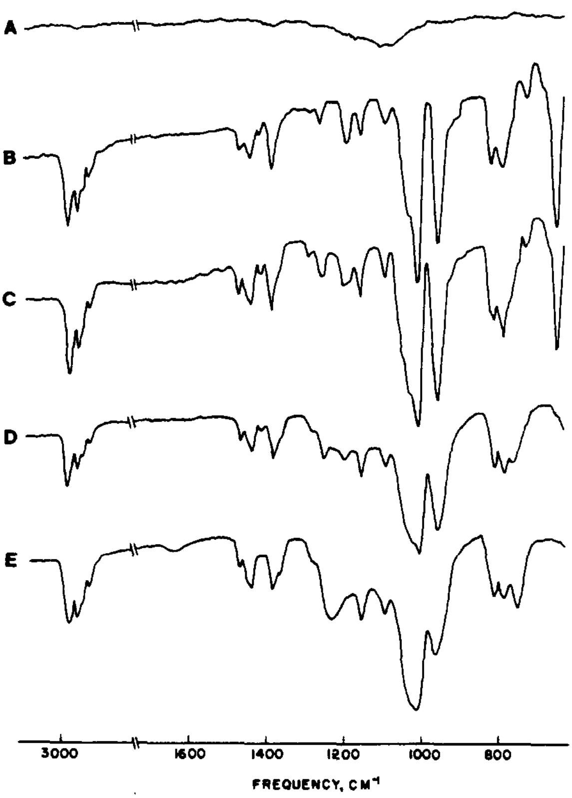


Fig. 8. Effect of varying quantities of palladium on the infrared spectra of Thimet spots recovered from TLC plates
(*A*) blank, extract of unspotted silica gel, (*B–E*) mole ratio of Pd : Thimet = 0·0, 0·5, 1·0, and 1·5 respectively.

In our work Thimet, Trithion, and Cidial spots on TLC plates were reacted with 0–1·5 times the equivalent molar quantity of sodium tetrachloropalladate(II). The infrared spectra of the compounds recovered from the Thimet and Trithion plates are shown in Figs. 8 and 9; similar results were obtained with Cidial. The spectra show differences which depend on the ratio of palladium to pesticide on the spot; in particular, the P=S peak at 625–660 cm^{-1} shows a decrease in intensity due to the palladium–pesticide reaction. This frequency is of analytical importance since it has been recommended that the oxidation of phosphorodithioate pesticides be followed by its disappearance.[16]

CONCLUSION

Although palladium(II) chloride is useful for locating organophosphorus pesticides on TLC plates before their identification by infrared spectroscopy, it should be realized that the spectra of the complexes differ from those of the parent compounds. Indiscriminate use of the reagent could lead to interpretative errors, particularly when microgram quantities of the pesticide are involved. Palladium derivatives of phosphorodithioate esters represent a new group of metal–organophosphorus complexes and a further study of the mechanism of this interaction in aqueous systems would be interesting.

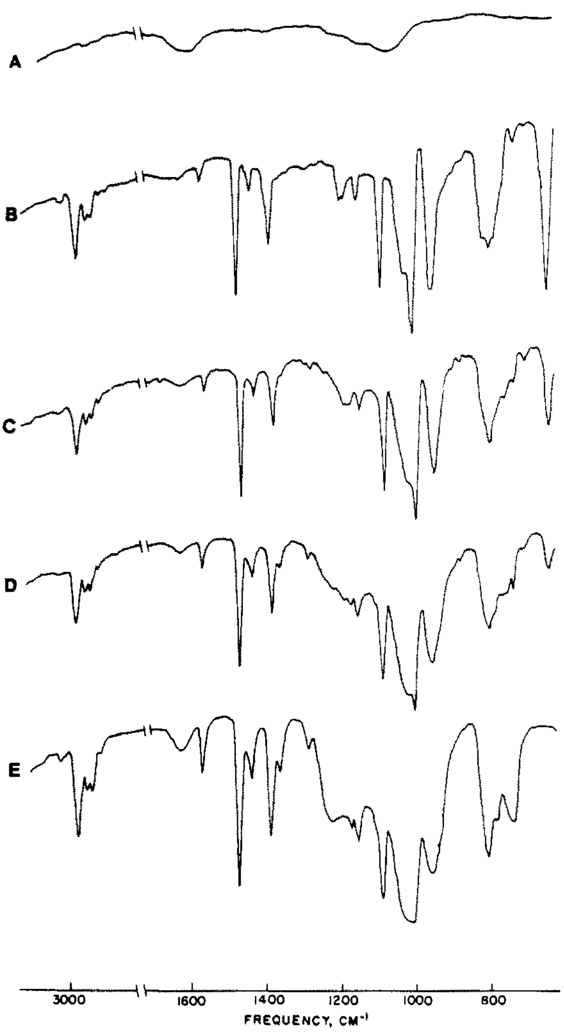


Fig. 9. Effect of varying quantities of palladium on the infrared spectra of Trithion spots recovered from TLC plates.

(*A*) blank, 12 μmole of Na_2PdCl_4 extracted from silica gel, (*B–E*) mole ratio of Pd : Trithion = 0·0, 0·5, 1·0, and 1·5 respectively.

Acknowledgements—This work was supported by grants from the Department of the Environment and the National Research Council of Canada. The authors wish to thank Sandoz Corp. for performing elemental analyses.

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Zusammenfassung—Die Herstellung der Palladiumkomplexe von Insektiziden vom Dithiophosphorsäureestertyp (Gusathion, Gusathion A, Imidan und Cidial) und vom Thiophosphorsäureestertyp (Baytex) wird beschrieben. Die Verhältnisse Pd:Pestizid in den Derivaten sind etwa 1 : 1 für die Dithiophosphorsäureester und 2 : 1 bei Baytex. Die Infrarotspektren der Derivate werden mit denen des zugrunde liegenden Insektizids verglichen. Die Komplexbildung der Dithiophosphorsäureester mit Palladium bewirkt eine Erniedrigung der P-S-Frequenzen um 60–75 cm^{-1} und ruft auch Veränderungen im P-O-C-Bereich hervor. Milligrammengen Thimet, Trithion und Cidial wurden auf Dünnschichtchromatogrammen in situ mit Natriumtetrachloropalladat(II) umgesetzt. Die Infrarotspektren der von der Platte abgelosten Verbindungen hängen stark vom Verhältnis Pd : Pestizid im Fleck ab. Die analytische Bedeutung dieser Ergebnisse wird diskutiert.

Résumé—On décrit la préparation de complexes palladiés d'insecticides phosphorodithioates (Guthion, Ethyl Guthion, Imidan et Cidial) et phosphorothioate (Fenthion). Les rapports Pd : pesticide dans les dérivés sont d'environ 1 : 1 pout les phosphorodithioates et 2 : 1 dans le cas du Fenthion. On compare les spectres infra-rouges des dérivés à ceux de l'insecticide apparenté. La complexation au palladium des phosphorodithioates a pour résultat un abaissement des fréquences P=S de 60–75 cm^{-1} et produit aussi des changements dans la région P–O–C. On a fait réagir *in situ* des quantités de l'ordre du milligramme de Thimet, Trithion et Cidial sur chromatogrammes en couche mince avec le tétrachloropalladate de sodium (II). Les spectres infra-rouges des composés récupérés de la plaque dépendent grandement du rapport Pd : pesticide sur la tache, et l'on discute de la signification analytique de ces résultats.

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A NEW METHOD FOR THE ISOLATION OF METHYLMERCURY FROM BIOLOGICAL TISSUES AND ITS DETERMINATION AT THE PARTS-PER-MILLIARD LEVEL BY GAS CHROMATOGRAPHY

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Summary—A new method has been developed for the isolation of methylmercury from biological tissue. It is based on the volatilization of methylmercury cyanide formed in the reaction of methylmercury in the tissue with hydrocyanic acid released in the interaction of potassium hexacyanoferrate(II) with sulphuric acid at elevated temperature. The methylmercury cyanide released is captured on cysteine paper in a microdiffusion cell. The isolated methylmercury is set free with hydrochloric acid, extracted into benzene and determined by gas chromatography. A special closed micro-extractor is used for the final extraction into benzene for samples containing the lowest levels of methylmercury. The method can be used for a wide range of samples and concentrations (including background levels). The simplicity of the method makes it suitable for routine application.

The method at present used in most laboratories for the isolation of methylmercury was originally devised by Gage[1] and later modified and developed into a gas-chromatographic procedure by Westöo.[2,3,4] For most biological tissues the extraction has to be carried out in two stages; the original homogenized tissue is first acidified and extracted with a relatively large volume of the solvent, followed by stripping of methylmercury from the benzene phase into an aqueous solution of cysteine and re-extraction, after acidification, into a smaller volume of organic solvent. A few μl of this solution are then injected into the gas-chromatographic column for quantitative evaluation with an electron-capture detector. In the literature, an emission spectrometric detector using helium plasma has also been described.[5]

The early stages of this extraction and purification procedure require relatively large amounts of sample as well as large volumes of solvents, particularly if the expected concentration of methylmercury is in the ppM range (parts per milliard).

Sumino[6] substituted glutathione for cysteine in the purification stage and Newsome[7] hydrobromic acid for hydrochloric acid. Methylmercury bromide (as does the iodide or cyanide) shows the same gas-chromatographic behaviour as the chloride. These modifications did not solve the essential problems associated with this method.

Two main difficulties which may arise during the separation of methylmercury are the following: the formation of emulsions which are very persistent with certain types of samples, and volatility of methylmercury, which may result in losses during repeated equilibrations unless great care is taken in all stages involving extractions and transfers.

Obviously the organic extracts cannot be concentrated by evaporation of the solvent. Other less volatile organomercurials do not present difficulties in extraction separations as they can be concentrated by evaporation of the solvent.

In the present work the formation and volatility of methylmercury cyanide have been successfully exploited for its selective isolation from biological tissue. This approach is a continuation of our philosophy of utilizing the volatility of mercury and its compounds in its determination, *e.g.*, by selective trapping in a neutron-activation method.[8]

Preliminary work on the separation of methylmercury by use of the volatilization principle was based on the distribution of methylmercury chloride between the acidified tissue and toluene, kept separately in the two compartments of a diffusion cell.[9] Later it was modified by the much more selective and efficient isolations of methylmercury cyanide and its binding on paper impregnated with cysteine.

Sulphuric acid of appropriate concentration releases hydrocyanic acid from potassium hexacyanoferrate(II) at elevated temperatures according to the reaction

$$2K_4[\bar{Fe}(CN)_6] + 3H_2SO_4 = 6\ HCN + 3K_2SO_4 + K_2Fe[Fe(CN)_6]$$

Too high a concentration of sulphuric acid as well as higher temperatures favour the production of carbon monoxide and have to be avoided.

In the presence of biological tissue containing methylmercury, hydrocyanic acid reacts to give volatile methylmercury cyanide. Sulphuric acid provides not only the necessary hydrogen ions for setting free hydrocyanic acid but also reduces the amount of water vapour, thus preventing the decomposition of cysteine and helping further in the homogenization of the sample.

Depending upon the amount of methylmercury in the sample, the cysteine paper is extracted with hydrochloric acid either in a test-tube or in a specially designed micro-extractor described later.

EXPERIMENTAL

The various parameters, including the temperature, time of diffusion and optimum amounts of hexacyanoferrate, sulphuric acid and cysteine, were investigated systematically. Cysteine was applied on filter paper as a buffered solution.

Reagents

Potassium hexacyanoferrate(II), saturated solution.

Sulphuric acid, (1 + 1).

Hydrochloric acid, 12*M* and 5*M*.

Benzene, p.a.

Cysteine solution. For the analysis of muscle tissue this was prepared by dissolving 20 mg of cysteine hydrochloride in 1 ml of 5% sodium pyrophosphate solution. For other tissues, particularly liver, kidney and blood, a 3% pyrophosphate solution containing potassium citrate (40%) or sodium acetate trihydrate (10%) must be used.

Methylmercury dicyandiamide, stock solution.

Apparatus

Gas chromatograph, Pye Series 104.

Electron-capture detector, ^{63}Ni radioactive source.

Column, 1/4 in. × 5 ft.

Solid support. Diatomite "C," AW, 100–120 mesh.

Liquid phase. Phenyldiethanolamine succinate, (trade names PDEAS or HIEFF-10B) 4% or polyethyleneglycol succinate (PEGS), 5%.

Standard glass Conway dishes with thick plate-glass covers, or, for amounts of sample over 1 g, the diffusion cell shown in Fig. 1.

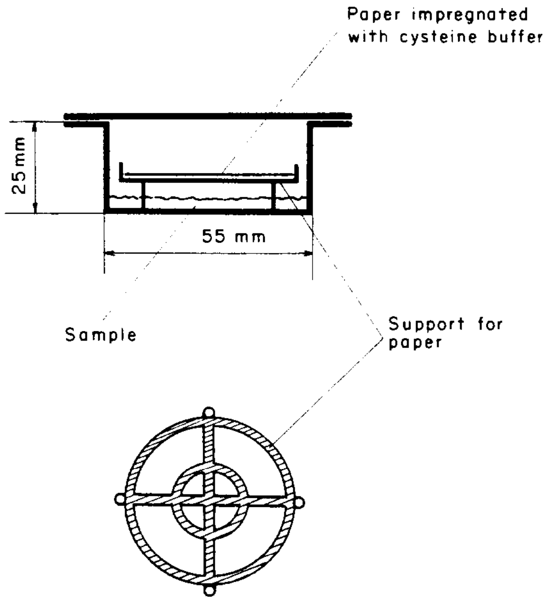

Fig. 1. Diffusion cell for the isolation of methylmercury from larger samples (> 1 g) of biological tissue.

Centrifuge tubes, 5-ml with ground-glass stoppers.
Micro-extractors (see below).
Filter paper, Schleicher and Schüll, No. 589[3].

Chromatography conditions

Column temperature 170°.
Injector temperature 200°.
Detector temperature 200°.
Carrier gas N_2, flow-rate 100 ml/min.
Voltage adjusted according to the amount of methylmercury measured.

Method

For methylmercury concentrations higher than 30 ng/g the procedure is as follows. Homogenized tissue in quantities up to 1 g is placed in the inner compartment of the Conway cell. A saturated solution of potassium hexacyanoferrate(II) is added (0·25 ml) and the contents mixed. A ring of filter paper to fit the outer compartment is placed in the cell, the paper ring having previously been impregnated with 0·1 ml of cysteine reagent and dried. Finally 0·5 ml of sulphuric acid is added to the tissue. After mixing of the reaction mixture, the cell is closed with a circular plate-glass cover.

The amount of sulphuric acid and potassium hexacyanoferrate(II) is increased for samples over 1 g and a special diffusion cell, as shown in Fig. 1, is substituted for the Conway cell.

The glass cover is fixed on the cell with a rubber sleeve. The reaction between cysteine and methylmercury is rapid, so there is no need to seal the cell hermetically. Care must be taken, however, that cells are kept in darkness and that the filter paper is processed immediately after it has been taken out of the cell.

The cell is placed in the thermostat at 75° for 14 hr. After this time the cell is cooled, and the filter paper ring is removed with tweezers, dropped into a 5-ml centrifuge tube and completely moistened with 0·25 ml of 5*M* hydrochloric acid. Following the addition of 1 ml of benzene, the tube is closed with a ground-glass stopper and shaken for 10 min. The filter paper is removed and the sample centrifuged. Aliquots of 5 μl of benzene phase are injected into the gas chromatographic column.

The overall performance of the isolation of methylmercury was tested by using different standard solutions. A stock solution was prepared from a 1·5% solution of a commercial preparation of "Panogen" (methylmercury dicyandiamide) by diluting it with water to give a concentration of 6 μg of methylmercury per ml. Aliquots of this solution (0·1 ml) were acidified with an equal volume of 5*M* hydrochloric acid and extracted with

10 ml of benzene. After centrifuging, the organic phase was removed and further diluted with the solvent to give a set of solutions for the calibration curve, covering the range between 0·1 and 2 ng for 5 μl of the solution injected into the gas chromatograph.

Micromethod

For the determination of methylmercury in organic material a further increase in sensitivity appeared to be possible by a modification of the extraction procedure.

Since a significant increase in the quantity of sample is not practicable, only a reduction in the amount of solvent could come into consideration. In the method above, the volume of solvent (1 ml) is two hundred times the amount actually needed for a determination. In practice it can be reduced by a factor of at least ten (to 0·1 ml). For this reason, a micro-extractor was designed. At the same time, a reduction of the surface of the cysteine paper was required. Evaporation of methylmercury chloride should be prevented during the extraction, and therefore the extraction should proceed essentially in a closed system.

The present version of a micro-extractor is shown in Fig. 2. Volatilization and binding of methylmercury is carried out in Conway cells as described above. Octagonal filter papers (Fig. 3) of somewhat smaller dimensions (3 mm width) are used and the volume of cysteine solution is reduced to 0·07 ml. After the end of the reaction, the filter paper is cut into 16 sections as indicated by the dotted lines in Fig. 3. The strips of paper are combined in a bundle and pushed into the wider end *B* of the capillary extractor. A minimum amount (0·075 ml) of concentrated hydrochloric acid is introduced with a pipette (Fig. 2) directly on to the paper, and the extractor is assembled. Through the opening at *A*, 0·15 ml of benzene is introduced in such a way as to form a column occupying the whole diameter of the capillary. Immediately after, a 1-ml syringe with glass piston is attached to the capillary (polyethylene tubing is recommended but rubber should not be used) and the solvent column is driven forwards and backwards through the paper bundle for 4 min. The paper should not be packed too tightly, in order to provide for thorough contact during the passage of the solvent. Finally the solvent is pushed through the vertical capillary section into the conical reservoir. Normally there is no need to dry the benzene phase; exceptionally, if this phase is turbid, a small plug of filter paper previously held in hydrochloric acid vapour is plugged into the upper part of the capillary just ahead of the outlet to the reservoir. During extraction the reservoir is closed with the ground-glass stopper. Aliquots of the collected solvent are then withdrawn into a microsyringe for gas-chromatographic determination of the extracted methylmercury; 5 μl of the solvent are normally used. It is important to clean the diffusion cell, in particular the outer

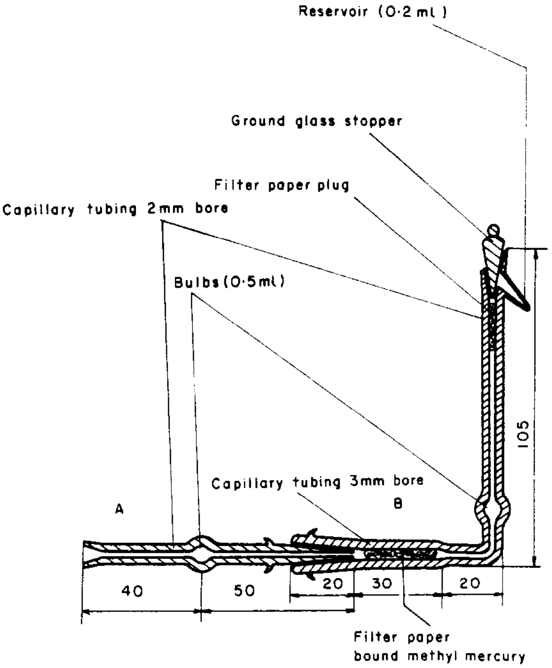

Fig. 2. Micro-extractor.

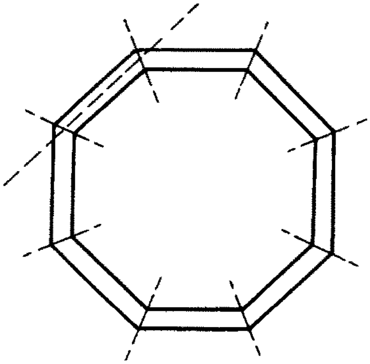

Fig. 3. Octagonal filter paper, impregnated with cysteine buffer, to fit the diffusion cell. Before the extraction paper is cut into sixteen strips along the dotted lines.

compartment, very thoroughly. The micro-extractor is rinsed after use with demineralized water, methanol and benzene. It is recommended that the diffusion procedure and the opening of the diffusion cells be carried out in a well-ventilated laboratory, owing to the presence of some hydrocyanic acid.

DISCUSSION

Preliminary experiments and investigation showed that yields of methylmercury in the procedures above could be influenced by the binding of methylmercury cyanide on the cysteine paper being incomplete because of (*a*) decomposition of cysteine, (*b*) the limit capacity of the cysteine buffer, and (*c*) unsuitable conditions during the diffusion.

(*a*) According to Warburg[10] and Sakuma,[11] cysteine is readily oxidized in the presence of traces of metals such as iron, manganese, copper *etc.* Warburg[12] found that the oxidation by iron and manganese is prevented by the addition of pyrophosphate. Therefore pyrophosphate is added as one of the components of all buffers used. The stability is further improved by carrying out the diffusion in darkness and by using a concentration of sulphuric acid large enough to keep the vapour pressure of water low. As a consequence the filter paper remains dry during the diffusion period.

(*b*) The capacity of the cysteine buffer could be exceeded, in particular when samples contain higher concentrations of halides. This becomes noticeable when two different aliquots of the same sample are taken for analysis; the results with the larger aliquots are lower. Therefore a combined buffer, as described under reagents, is used when analysing larger samples (up to 1 g) of liver, blood, brain *etc.* However, in the analysis of fresh-water fish muscle sodium pyrophosphate alone is sufficient even when samples as large as 2 g are taken. If the inner compartment is covered with an additional filter paper disc impregnated with lead acetate, volatile compounds, including thio-compounds, are removed without affecting the recovery of methylmercury; the lead salt also acts as a buffering component for hydrochloric or hydrobromic acids. The yield remains high and constant.

(*c*) At lower temperatures impractically long diffusion periods would be required; higher temperatures on the other hand enhance the oxidation of cysteine and possibly of hydrocyanic acid. Yields were highest at a temperature of 75°. It is also essential that the ground-glass joints of the micro-extractor fit perfectly in order to prevent the escape of volatile methylmercury during the extraction.

The recovery of methylmercury could be lowered as a result of incomplete extraction from the cysteine paper.

Experiments with labelled methylmercury (^{203}Hg) have shown that the extraction depends on the amount of available cysteine. When 10% cysteine solution was used (0·10 ml in the macro or 0·07 ml in the micro version) recoveries from a single extraction with benzene were between 50 and 70%. When the concentration of cysteine was varied between 1 and 3%, the same volume being used, the yield was constantly over 90% in both the micro and macro procedures.

Westöo[3] has shown that from the equilibria between methylmercury chloride (CH_3HgCl) and cysteine-bound methylmercury (CH_3HgSR) it follows that their ratio is higher at higher concentrations of hydrogen and chloride ions and low concentrations of cysteine (RSH):

$$\frac{[CH_3HgCl]}{[CH_3HgSR]} = \frac{[Cl^-][H^+]K}{[RSH]}$$

where K combines the equilibrium constants for the dissociation of methylmercury chloride, cysteine, and methylmercury–cysteine complex.

The overall reproducibility as a function of the amount of sample taken was determined by analysing fish muscle containing three different concentrations of methylmercury. The samples were prepared by homogenizing 50 g of fish muscle (a young trout) obtained from a fish-breeding station to avoid the high levels of methylmercury usually found in samples from natural environments. A larger number of aliquots was taken for checking the performance of the micro method than in the method normally used. The concentration of methylmercury in the original sample, 39 ng/g, was such as to enable comparative results to be obtained for the macro as well as the micro method. These results are shown in Fig. 4. To check the performance of the method at higher levels, "Panogen" stock solution was added to two aliquots of this sample in amounts to give 85 ng/g and 285 ng/g respectively. The yields were also satisfactory, with no dependence on sample weight.

Also analysed were samples of human blood, and organs collected from an autopsy. In the range investigated, recoveries do not depend on the quantity taken for analysis. It is clear, however, that when very small amounts of sample are used there is a wider

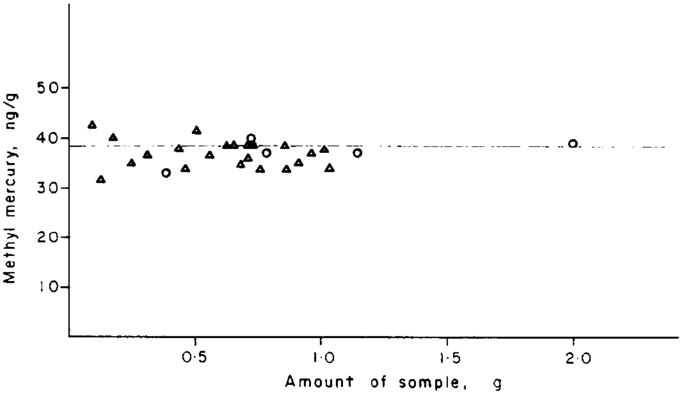

Fig. 4. Recovery of methylmercury from biological tissue as a function of the amount of sample. △ Micromethod, ○ Macromethod. Dotted line indicates the expected value based on precise determination of total Hg and on the assumption that it is all in the methyl form.

spread of results. The relative standard deviations were 5 and 7% respectively for the macro and micro method.

The other two types of sample (liver and blood) appear to contain volatile substances which reduce the recoveries if sodium pyrophosphate alone is used as the buffer for cysteine. This is probably due to the low buffering capacity. However, if the internal compartment containing the sample is covered with filter paper previously impregnated with a concentrated solution of lead acetate and dried, quantitative recoveries are obtained with pyrophosphate as well as with all other buffers tested. The amounts of sample used in these experiments were from 530 to 866 mg and were again without influence on the recovery of methylmercury.

Concentrations of inorganic mercury in amounts up to 20 ppm have no effect on the results obtained for methylmercury in blood and in liver samples. In the presence of milligram quantities of mercury(II) chloride, however, methylmercury appears to form in liver and blood and results are accordingly much above the actual content of CH_3Hg^+. This was not the case when mercury(II) chloride or cyanide was added to fish muscle.

RESULTS

The method has been successfully applied to a wide variety of plant, autopsy and animal samples with concentrations of methylmercury varying between 1 ng/g and a few μg/g.

As an illustration, results are presented in Table 1, giving methylmercury to total mercury ratios (calculated as Hg), in muscle and liver respectively, for three groups of trout caught at different sampling points along the river Idrijca which is contaminated with depleted mercury-ore sediments. Results indicate that although the total mercury

Table 1. Total and methylmercury concentrations in μg/g in fish muscle and liver from the River Idrijca at Idrija, Stopnik and Most na Soči (April–June 1971)

Sampling point	No.	Sample (fish) weight, *g*	Age, *years*	Muscle CH_3Hg^+	Muscle Total Hg^+	Muscle Ratio $[CH_3Hg^+]/[Hg]$	Liver CH_3Hg^+	Liver Total Hg	Liver Ratio $[CH_3Hg^+]/[Hg]$
A	1	—	—	0·16	4·9	0·03	0·6	77·4	0·01
	2	—	—	0·52	2·6	0·20	1·9	28·7	0·07
	3	—	—	0·70	2·7	0·25	0·8	49·2	0·02
	4	—	—	0·73	2·9	0·25	1·7	46·2	0·04
	5	—	—	0·29	6·5	0·045	0·6	118·8	0·005
B	6	240	4	0·90	0·99	0·91	1·63	10·0	0·16
	7	196	4	0·43	0·59	0·72	0·93	16·4	0·06
	8	270	5	0·51	0·66	0·77	1·12	11·9	0·09
	9	124	—	1·08	1·24	0·87	2·35	31·3	0·08
	10	120	3	0·92	1·12	0·82	1·84	15·8	0·12
	11	120	3	0·76	0·87	0·87	1·91	19·2	0·09
	12	520	4	0·60	0·52	1·13	1·16	5·13	0·23
C	13	500	4	0·64	0·66	0·97	0·59	5·55	0·11
	14	210	3	0·43	0·39	1·10	0·44	2·73	0·16
	15	275	4	0·26	0·30	0·86	0·28	3·41	0·08
	16	165	3	0·45	0·51	0·88	1·07	6·18	0·17
	17	95	2	0·33	0·35	0·93	—	2·36	—

Sampling point A: (Marof) at source of inorganic mercury contamination.
Sampling point B: (Stopnik) 20 km downstream from the source.
Sampling point C: (Most na Soči) 35 km downstream from the source.

content decreases with distance downstream its proportion in the methyl form increases. The equilibria possibly involved in interpreting these results are not yet fully understood; nevertheless, they clearly show the methylation of inorganic mercury in this aquatic system as well as its longer biological half-life in fish.

Table 2 shows the concentrations of methylmercury in a selection of samples, including the hair of persons from varying occupations.

Table 2. Methylmercury and total mercury concentrations in human hair and some aquatic organisms

Sample	CH_3Hg^+ (*ng/g*)	Hg total (*μg/g*)
Hair (1) (chemical technician)	175	0·504
Hair (2) (dentist)	210	2·11
Hair (3) (male)	61	0·159
Hair (4) (female)	140	0·357
Hair (5) (female)	120	0·177
Beard	80	0·514
Algae (dry weight)	44	25·0
Trichoptera	27	10·8
Ephemeroptera	107	13·7

The chromatograms obtained by following this method are in general very clear and do not present any problems in the evaluation of results. An exception is hair, where numerous other peaks are occasionally observed. Overlapping can occur when some other liquid phases are used, but using phenyldiethanolamine succinate in the column results in very good resolution and provides for satisfactory evaluation of the methylmercury peaks. Up to twenty determinations were made by one technician daily during this investigation with one column and the simple inexpensive apparatus described above. It is clear that the scale of operation could easily be expanded to allow large number of serial analyses on a routine basis.

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Zusammenfassung—Ein neues Verfahren zur Isolierung von Methylquecksilber aus biologischem Gewebe wurde ausgearbeitet. Es beruht auf der Verflüchtigung von Methylquecksilbercyanid, das sich im Gewebe aus Methylquecksilber und Blausäure bildet, die ihrerseits durch die Reaktion von Kaliumhexacyanoferrat(II) mit Schwefelsäure bei erhöhter Temperatur freigesetzt wird. Das ausgetriebene Methylquecksilbercyanid wird in einer Mikrodiffusionszelle auf Cysteinpapier aufgefangen. Das isolierte Methylquecksilber wird mit Salzsäure freigesetzt, in Benzol extrahiert und gaschromatographisch bestimmt. Bei Proben, die geringsten Mengen an Methylquecksilber enthalten, wird für die abschließende Extraktion in Benzol ein besonderer geschlossener Mikro-Extraktor verwendet. Das Verfahren kann für viele verschiedenartige Proben und für weite Konzentrationsbereiche (einschließlich des Untergrundes) verwendet werden. Die Einfachheit der Methode macht sie für die routinemäßige Anwendung geeignet.

Résumé—On a élaboré une nouvelle méthode pour l'isolement du méthylmercure de tissus biologiques. Elle est basée sur la volatilisation du cyanure de méthylmercure formé dans la réaction du méthylmercure dans le tissu avec l'acide cyanhydrique dégagé dans l'interaction de l'hexacyanoferrate(II) de potassium avec l'acide sulfurique à température élevée. Le cyanure de méthylmercure dégagé est fixé sur un papier à la cystéine dans une cellule de microdiffusion. Le méthylmercure isolé est libéré par l'acide chlorhydrique, extrait en benzène et dosé par chromatographie en phase gazeuse. On utilise un microextracteur clos spécial pour l'extraction finale en benzène pour les échantillons ayant les plus faibles teneurs en méthylmercure. On peut utiliser la méthode pour un large éventail d'échantillons et de concentrations (y compris les teneurs de base). La simplicité de la méthode la rend convenable pour l'application de routine.

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SHORT COMMUNICATIONS

IDENTIFICATION DE SUBMICROQUANTITES D'IONS IODURE

(*Reçu le* 17 *février* 1972. *Accepté le* 5 *juin* 1972)

La reaction iode-amidon, mise souvent à profit pour l'identification de faibles quantités d'iode, de l'ordre de 0,1 μg, n'est plus utilisable pour la recherche de traces.

Selon nos essais, l'ion iodure, oxydé par le chlore en IO_3^- fournit, par action d'iodure de potassium en milieu acide, un anion I_3^- révélé par le nitron avec lequel il forme un triiodure coloré.

$$I^- \xrightarrow[H_2O]{Cl_2} IO_3^- \xrightarrow[H^+]{I^-} I_3^- \xrightarrow{\text{Nitron}} NtI_3$$

En pratique, sur du papier pour chromatographie (Whatman 3 convient bien) on dépose à l'aide d'un tube capillaire en verre (fig. 1) 0,01 ml de solution étudiée par fractions de 0,002 ml et, à 2 cm du premier dépôt, on dépose de même de l'eau bidistillée. Le papier est alors placé dans les vapeurs de chlore, audessus d'eau saturée de chlore par exemple puis séché à l'air chaud. A l'emplacement des deux dépôts, on dépose à l'aide d'un capillaire 0,003 ml de solution préparée extemporanément à 20 pour cent d'iodure de potassium. Après séchage à température ordinaire et à l'abri de la lumière, on dépose 0,004 ml de solution 0,2*N* d'acide sulfurique. Il apparaît, si la réaction est positive, un anneau jaune à brun. Après 3 à 4 min, un anneau semblable apparaît dans le témoin, dû à l'oxydation à l'air du réactif.

Fig. 1.

La réaction permet à la limite de déceler 0,01 ng d'iode à l'état d'iodure soit une concentration de $1/64 \cdot 10^7$.

La présence des ions Cl^-, Br^-, SO_4^{2-}, PO_4^{3-} et CO_3^{2-} n'apporte pas de gêne. La réaction n'est pas applicable en présence d'oxydants tels les ions ferriques. Ceux-ci peuvent être éliminés au préalable par précipitation à l'état d'hydroxydes.

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Résumé—Une stilliréaction, fondée sur la formation de triiodure de nitron (NtI_3) coloré en jaune brun permet de déceler 0,01 μg de I^- ($1/64.10^7$).

Summary—A spot-test, based on the formation of yellow-brown nitron tri-iodide permits detection of 0·01 ng of iodide (limit of dilution 1 in 64×10^7).

Zusammenfassung—Eine Tüpfelprobe, die auf der Bildung von gelbbraunem Nitron-Trijodid beruht, erlaubt den Nachweis von 0·01 ng Jodid (Verdünnungsgrenze 1 in $64 . 10^6$).

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ATOMABSORPTIONSSPEKTRALPHOTOMETRISCHE BESTIMMUNG VON ZINK IN GALLIUMARSENID UND GALLIUMALUMINIUMARSENID

(*Eingegangen am* 3. *Mai* 1972, *Angenommen am* 6. *Juni* 1972)

ZUR KONTROLLE des Gehaltes von Zinkverunreinigungen und zur Ermittlung von Zinkdotierungskonzentrationen in $A^{III}B^{V}$-Materialien wurde von uns eine atomabsorptionsspektralphotometrische Bestimmungsmethode ausgearbeitet.

Die Atomabsorptionsspektralphotometrie ist—wie zahlreiche Veröffentlichungen zeigen[1,2]—auf Grund ihrer Selektivität und Empfindlichkeit für die Spurenbestimmung von Zink gut geeignet. Bei der Erarbeitung des Bestimmungsverfahrens wurde berücksichtigt, daß die zu untersuchenden Materialien ein Gewicht von nur einigen Milligramm haben. Diese Bedingung erfordert eine spezielle Arbeitsmethode, die kein Anreicherungsverfahren benötigt und trotzdem eine hohe Empfindlichkeit besitzt.[3]

EXPERIMENTELLER TEIL

Apparatives

Verwendet wurde ein Eigenbau-Atomabsorptionsspektralphotometer, welches aus folgenden Teilen bestand:
Spiegelmonochromator SPM 1 mit Quarzprisma (VEB C. Zeiss, Jena)
Sekundärelektronenvervielfacher M 12 FQS 52 A (VEB C. Zeiss, Jena)
Kompensationsbandschreiber G_1B_1 (VEB C. Zeiss, Jena)
Hochspannungsversorgungsgerät für SEV (PGH Statron, Fürstenwalde)
Vorkammerringspaltzerstäuber (Eigenbau)
gekühlter Schlitzbrenner (l = 120 mm) (Eigenbau)
Hohlkathodenlampe (Kathodenmaterial: Messing; Neondruck 4 mm Hg-Säule) (Eigenbau)

Als optimale Bedingungen ergaben sich für die Zinkbestimmung: Wellenlänge 213,8 nm, Lampenstrom 5 mA, Spaltbreite 100 um, Acetylen: 44 l./h, Luft: 3 at, 56 l./h, Zusatzluft: 170 l./h, Lösungsverbrauch: 2 ml/min.

Da nur geringe Probemengen vorhanden waren, wurden der Ringspaltzerstäuber und die Gaszusammensetzung unter dem Gesichtspunkt eines möglichst geringen Lösungsmittelverbrauchs optimiert. Der Strahlendurchgang durch die Flamme lag 6 mm oberhalb der Brenneroberfläche.

Reagenzien

Standard-Zinklösung: 1 g Zink(II)-sulfat *p.a.* pro Liter
Standard-Galliumlösung: 2,5 g Gallium (99,999%) pro 100 ml
Standard-Arsenlösung: 3,5 g Arsentrioxid *p.a.* pro 100 ml
Salzsäure pA
Salpetersäure pA

Bestimmungsvorschrift

Das zu untersuchende Galliumarsenid bzw. Galliumaluminiumarsenid (*ca.* 5–20 mg) wurde mit einem Gemisch aus konzentrierter Salz- und Salpetersäure (1 : 1) aufgelöst. Nach vorsichtigem Eindampfen des Säuregemisches wurde der Rückstand sofort in 1 ml 1*M* Salzsäure aufgenommen. Diese Lösung wurde direkt zerstäubt. Die gemessenen Extinktionen wurden mit Hilfe einer Eichkurve in Konzentrationen umgerechnet. Zur Erhöhung der Genauigkeit empfiehlt es sich, den arithmetischen Mittelwert von 3 Extinktionsmessungen für die Konzentrationsbestimmung zu verwenden.

ERGEBNISSE

Säureeinfluß

Die Eichkurve einer Zinksulfatlösung in 1*M* Salzsäure verlief etwas steiler als die der wäßrigen Lösung ohne Säuregehalt. Dieser Effekt findet seine Erklärung darin, daß durch die Anwesenheit der Salzsäure die Hydrolyse der Zinksalze in der Flamme zurückgedrängt wird und außerdem das in der Flamme entstehende Zinkchlorid leichter und vollständiger verdampft als Zinksulfat bzw. Zinkoxid. Die Änderung der Salzsäurekonzentration zwischen 0,5 und 1,5*M* hatte keinen Einfluß.

Einfluß des Arsenat(V)-ions und des Aluminium(III)-ions

Arsenat(V)- und Aluminiumionen (Aluminiumkonzentration: 0,2 bis 2 mg/ml) beeinflussen die Zinkabsorption nicht.

Einfluß des Gallium(III)-ions

Galliumkonzentrationen zwischen 2,5 und 10 mg/ml rufen eine Blindabsorption in Abhängigkeit von der Galliumkonzentration von 0,01 bis 0,016 Extinktionseinheiten hervor und verursachen somit eine Parallelverschiebung der Eichkurve.

Die Lösungen, die in 1 ml 1*M* Salzsäure zwischen 5 und 20 mg unterschiedlich zusammengesetzter Matrixsubstanz enthielten, beeinflußten ebenfalls die Zinkabsorptionswerte. Es ergaben sich Parallelverschiebungen der Eichkurven in Abhängigkeit der in den Lösungen enthaltenen Galliumkonzentration. Die Größe der Verschiebung entsprach der Blindabsorption der zinkfreien Galliumlösung (s. Tabelle 1).

Tabelle 1. Abhängigkeit der Absorption bei 213,8 nm von der Matrixsubstanz

Zink Konzentration, *ppm*	Zusatz in 1*M* HCl, *ppm*	Extinktion
0	0	0
0	5000 GaAs	0,01
0	10000 GaAs	0,013
0	20000 GaAs	0,015
0,8	0	0,089
0,8	5000 GaAs	0,101
0,8	10000 GaAs	0,104
0,8	20000 GaAs	0,107

Aufstellung einer Eichkurve und Genauigkeit des Verfahrens

Zur Aufstellung einer Eichkurve wurden Lösungen hergestellt, die in 1 ml 10 mg Galliumaluminiumarsenid-bzw. Galliumarsenid und unterschiedliche Konzentrationen Zink enthielten. Es wurden jeweils 10 Lösungen eines Zinkkonzentrationswertes untersucht. Die Eichkurve wurde durch Ausgleichsrechnung ermittelt.

Die Nachweisgrenze für das Verfahren wurde zu 0,1 μg/ml nach folgenden Kriterien bestimmt: Blindabsorption plus 3 × Standardabweichung der Blindabsorption. Die Eichkurve ist bis zu einer Zinkkonzentration von 3 μg/ml linear und krümmt sich bei höheren Zinkkonzentrationen zur Abszisse. Die

Tabelle 2. Zinkbestimmung in Galliumarsenid und Galliumaluminiumarsenid

Matrix *mg/ml*	Zink gegeben, *ppm*	Extinktion arithmetisches Mittel aus 3 Messungen	Zink gefunden, *ppm*	Abweichung %
5 GaAs	0,2	0,035	0,18	−10
5 GaAs	0,6	0,086	0,59	− 1,8
5 GaAs	1,0	0,136	1,00	0
5 GaAs	3,0	0,377	2,95	− 0,7
10 GaAs	0,1	0,026	0,10	0
10 GaAs	0,4	0,064	0,42	+ 5
10 GaAs	0,8	0,113	0,80	0
10 GaAs	2,0	0,262	2,01	+ 0,5
20 GaAs	0,2	0,041	0,23	+15
20 GaAs	0,6	0,087	0,60	0
20 GaAs	1,0	0,141	1,03	+ 3
20 GaAs	3,0	0,384	3,03	+ 1
5 $Ga_{0,9}Al_{0,1}As$	0,2	0,036	0,19	− 5
5 $Ga_{0,9}Al_{0,1}As$	1,0	0,134	0,97	− 3
20 $Ga_{0,9}Al_{0,1}As$	0,4	0,066	0,43	+ 7,5
20 $Ga_{0,9}Al_{0,1}As$	2,0	0,263	2,02	+ 1,0

Gesamtstandardabweichung beträgt 5,4 × 10^{-3} Extinktionseinheiten. Das entspricht einem durchschnittlichen Variationskoeffizient von 4,5%. Der Variationskoeffizient an der Nachweisgrenze wurde zu 27% bestimmt.

Die Eichkurve ist verwendbar für die Bestimmung von Zink in Galliumarsenid und Galliumaluminiumarsenid. Die Matrixsubstanz darf in Konzentrationen zwischen 5 und 20 mg/ml in 1*M* Salzsäure vorliegen. Der Matrixeinfluß liegt dann innerhalb der gefundenen Standardabweichung. Die mit Hilfe der Eichkurve erzielten Ergebnisse sind in Tabelle 2 dargestellt.

DISKUSSION

Als Resultat aller durchgeführten Untersuchungen ergab sich, daß die extremen Überschüsse an Matrixelementen (Gewichtsverhältnisse zwischen 1 zu 5000 und 1 zu 200 000 für Zink zu Matrix) die Bestimmung nur unwesentlich beeinflussen.

Zur Klärung der Ursache des geringen Einflusses Gallium enthaltender Lösungen wurde überprüft, ob es sich um Verunreinigungen des benutzten Gallium durch Zink handelt. Zu diesem Zweck überprüften wir die Absorption bei Anwendung einer kontinuierlichen Lichtquelle (Deuteriumlampe). Das Ergebnis ist in Tabelle 3 dargestellt.

Tabelle 3. Absorption des Lichtes einer kontinuierlichen Lichtquelle durch die Flamme

GaAs, *mg/ml*	219 nm	246 nm	213,8 nm
25	0,012	0,013	0,015
20	0,013	0,012	0,013
15	0,010	—	0,007

Vergleicht man die Werte der Tabellen 1 und 3 miteinander, so stellt man fest, daß der größere Teil der Blindabsorption unspezifisch ist und somit durch Lichtstreuung und molekulare Absorption hervorgerufen wird. Die Ursache kann die Bildung von festen Galliumoxid-Teilchen in der Flamme sein, die wegen ihrer Größe und ihres hohen Siedepunktes (größer als 2000°) nicht vollständig verdampfen.

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Zusammenfassung—Es wird eine atomabsorptionsspektralphotometrische Bestimmung von Zink in Galliumarsenid und Galliumaluminiumarsenid beschrieben. Die Methode ist anwendbar für Zinkmengen zwischen 0,1 und 3 μg in 5–20 mg Matrix Der Variationskoeffizient beträgt 4,5%. Der Einfluß der Matrixsubstanz auf die Absorption wird beschrieben und diskutiert.

Summary—The determination by atomic-absorption spectroscopy of zinc in gallium arsenide and gallium aluminium arsenide is described. In 5–20 mg of sample, 0·1–3 μg of zinc can be determined. The coefficient of variation is 4·5%. The influence of the matrix is described and discussed.

Résumé—On décrit le dosage par spectroscopie d'absorption atomique du zinc dans l'arséniure de gallium et l'arséniure de gallium et d'aluminium. On peut déterminer 0,1–3 μg de zinc dans 5–20 mg d'échantillon. Le coefficient de variation est de 4,5%. On décrit l'influence de la matrice et en discute.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM WITH 2R-ACID IN THE PRESENCE OF OTHER PLATINUM METALS

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Most chromogenic reagents for osmium are subject to interference from other platinum metals.[1-3] The present paper describes the application of 2-amino-8-naphthol-3,6-disulphonic acid (2R-acid; ANDS), which has already been used for the determination of iron[4] and vanadium[5], for the sensitive and reasonably selective spectrophotometric determination of osmium in the presence of platinum metals.

EXPERIMENTAL

Reagents

ANDS. A stock solution was prepared by dissolving the requisite amount in 1 litre of water.

Osmium tetroxide. One gram was dissolved in a small amount of dilute potassium hydroxide solution and diluted with water to give an alkali concentration of 0·04*M* and an osmium concentration of 0·004*M*. The solution was stored under refrigeration.

Other metal ions. Similar amounts of $RuCl_3$, $RhCl_3$, $IrCl_3$, H_2PtCl_6 and $PdCl_2$ were dissolved directly with water. The metal contents were determined by the usual methods.

Recommended procedure

The sample containing 2–8 μg of osmium is placed in a 25-ml volumetric flask and 10 ml of the stock solution of ANDS are added. The pH of the mixed solution is adjusted to 11·5 by adding a suitable amount of dilute alkali and diluted to the mark with alkali (also at pH 11·5). The solution is heated for 30 min on a water-bath at 90°, and cooled under running water, then the absorbance is measured at 530 nm at room temperature against a distilled water blank. The reagent does not absorb at this wavelength. The osmium content is then read from a standard calibration curve.

The order of addition of the reactants is not significant.

RESULTS AND DISCUSSION

Optimum conditions for reaction

Several samples containing the requisite amounts of osmium were treated by this procedure and the absorbance measured. The standard deviation of readings was 0·002, and the readings remained constant for at least 24 hr.

A green complex is formed between pH 2·5 and 8·0 and a red complex between pH 11·0 and 12·0, but since the green complex is stable for only 2 hr, the red complex was used.

Colour formation at room temperature is very slow; full intensity takes 24 hr to develop. The rate of colour formation increases when the solution is heated on a water-bath at 90°, heating for 30 min being sufficient for maximum colour development. The colour intensity then remains fairly constant even if the solution is kept at 90° for 2 hr.

The absorbance, for a given amount of osmium, attains a constant value when the molar ratio of reagent to metal is 20 : 1.

Optical constants and nature of complex

Beer's law is obeyed over the range 1·5–10 μg of osmium. The molar absorptivity is $1·11 \times 10^4$ $l·mole^{-1}·cm^{-1}$ and the sensitivity of the reaction is 0·2 $\mu g/cm^2$. The optimum range for accurate spectrophotometric determination is 2–8 ppm.

When the solution of the complex was passed through Amberlite IRA-400 ion-exchange resin, the complex was completely adsorbed, with the formation of a red band, thus establishing the anionic nature of the complex.

The absorption spectra of the system containing osmium and ANDS in different stoichiometric ratios show maximum absorbance at 530 nm. The intensity of the colour increases with time but λ_{max} remains unchanged. ANDS does not absorb at this wavelength.

Interferences

Ions which result in a deviation of less than 2% in the determination of 0·2 μg of osmium when present in concentrations of at most $2 \times 10^{-4}M$ are Al(III), Cr(III), Be(II), Cu(II), Li(I), As(III), Sb(III), Cr(VI), Ag(I), Te(IV), Se(IV), Zn(II), W(VI), Ni(II), Mg(II), Mo(VI), La(III), Sc(III), Y(III), Ga(III), In(III), Ru(III), Rh(III), Pd(II), Ir(III) and Pt(IV), and 10 mg of $RuCl_3$ can be tolerated.

Cations which interfere are Fe(III), Th(IV), Zr(IV), Co(II) and V(V). The common anions Cl^-, Br^-, I^- and $No_3{}^-$ do not interfere; oxalate and tartrate interfere.

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Summary—Osmium(VIII) produces two coloured species with λ_{max} 680 nm (green) and 530 nm (red) with excess of 2-amino-8-naphthol-3,6-disulphonic acid in aqueous solution. The green complex is stable between pH 2·5 and 8·0 and the red complex between pH 11·0 and 12·0. The effects of temperature and time, reagent concentration, optimum conditions for the spectrophotometric determination of trace amounts of osmium, and other variables, have been studied at pH 11·5. At this pH, other platinum metals do not interfere. The sensitivity of the colour reaction is 0·2 $\mu g/cm^2$ and the system conforms to Beer's law over a concentration range of 1·5–10 μg of osmium.

Zusammenfassung—Osmium(VIII) bildet mit einem Überschuß von 2-Amino-8-naphthol-3,6-disulfonsäure in wäßriger Lösung zwei farbige Spezies mit λ_{max} 680 nm (grün) und 530 nm (rot). Der grüne Komplex ist zwischen pH 2·5 und 8·0, der rote zwischen pH 11·0 und 12·0 stabil. Der Einfluß von Temperatur, Zeit, Reagenskonzentration, optimalen Bedingungen zur spektrophotometrischen Bestimmung von Osmiumspuren und anderen Variablen wurde bei pH 11·5 untersucht. Bei diesem pH stören andere Platinmetalle nicht. Die Empfindlichkeit der Farbreaktion beträgt 0·2 $\mu g/cm^2$; das System gehorcht dem Beerschen Gesetz bei 1·5–10μg Osmium.

Résumé—L'osmium(VIII) produit deux espèces colorées de λ_{max} 680 nm (vert) et 530 nm (rouge) avec un excès d'acide 2-amino 8-naphtol 3,6-disulfonique en solution aqueuse. Le complexe vert est stable entre pH 2,5 et 8,0 et le complexe rouge entre pH 11,0 et 12,0. Les influences de la température et du temps, la concentration du réactif, les conditions optimales pour le dosage spectrophotométrique de traces d'osmium, et d'autres variables, ont été étudiées à pH 11,5. A ce pH, les autres métaux de la mine du platine n'interfèrent pas. La sensibilité de la réaction colorée est de 0,2 $\mu g/cm^2$ et le système suit la loi de Beer dans le domaine de concentrations, 1,5–10 μg d'osmium.

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RAPID CHELOMETRIC DETERMINATION OF LEAD IN LUBRICATING OILS *VIA* MERCAPTOACETATE EXTRACTION

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In high-pressure lubricating oil, lead naphthenate is often added as an additive, and the lead content must be determined to ascertain the amount of additive present. Both the standard methods given by Institute of Petroleum[1] and ASTM[2] describe the gravimetric method where lead naphthenate is converted into lead sulphate by the "wet ash method" and weighed as such. The method recommended by ASTM has been further modified by dissolution of lead sulphate and electro-disposition of the lead.[3] The latter method has been recommended for the estimation of lead in lubricating greases. These methods are lengthy and tedious, requiring 10–12 hr and hence do not appear suitable for routine analysis.

Methods have been described in which the lead content of such oils is obtained in aqueous solution by acid hydrolysis, and then titrated with EDTA[4,5] with Eriochrome Black T as indicator. The lead has also been extracted by refluxing the oil with glacial acetic acid and benzene, whereby the lead naphthenate is converted into lead acetate, and then precipitated as lead chromate with potassium chromate, an iodometric finish being used.[6,7] These methods also require 1–1½ hour. Spectrographic methods are also in use for the determination of metallic constituents in oils.

A method has now been developed in which lead mercaptoacetate is extracted into aqueous medium by using thioglycollic acid and nitric acid and the lead is finally titrated with EDTA.

EXPERIMENTAL

Procedure

Weigh 5 g of the sample, prepared as in the IP method, into a 50-ml beaker, and dissolve the oil in 15–20 ml of pure benzene and quantitatively transfer the solution into a 250-ml glass-stoppered separating funnel. Add 10 ml of 10% thioglycollic acid solution (freshly prepared) and 5 ml of 5% dilute nitric acid and shake the mixture vigorously for 1 min and allow the layers to separate. Wash the sides of the separating-funnel with distilled water and collect the aqueous extract in a 500-ml conical flask. Repeat the extraction 2 or 3 times. To check that extraction is complete, repeat the process, collect the washings in a separate conical flask, and neutralize the solution with dilute ammonia. If a white precipitate of lead mercaptoacetate does not appear, the extraction may be taken as complete. To the main solution containing the lead extract, add dilute ammonia solution (1 + 1) dropwise until a voluminous white precipitate of lead mercaptoacetate is formed

Table 1.—Determination of lead

	Pb, %w/w	
Sample	By ASTM method[2]	By this method
1	0·76	0·78 0·76
2	1·12	1·13 1·14
3	1·14	1·11 1·12
4	1·10	1·08 1·08
5	0·92	0·94 0·92

and just redissolves in the ammonia. Add 2 drops of ammonia in excess. Add 10 ml of 10% formaldehyde solution and dilute to 100–150 ml with distilled water. Add 30–40 ml of acetate buffer, pH 5 (prepared by mixing 154 of ammonium acetate and 60 ml of glacial acetic acid in 1 litre of distilled water) and 5 or 6 drops of Xylenol Orange indicator (0·5% aqueous solution). Titrate slowly with 0·025*M* EDTA.

RESULTS AND DISCUSSION

Typical results are shown in Table 1 and compared with those obtained by the ASTM method. In the present method zinc and similar bivalent metal ions interfere but are not present except as trace impurities. If necessary they could be masked with 1,10-phenanthroline.[8] The acetate buffer will cause a negative error of about 1% at the lead concentration used,[9] but this error could be eliminated by buffering with hexamine.

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Summary—A rapid complexometric method for the estimation of lead in lubricating oil has been developed. The lead naphthenate present in the oil is extracted with a mixture of dilute thioglycollic acid and nitric acid. The aqueous extract containing lead mercaptoacetate is titrated with EDTA at pH 5 with Xylenol Orange as indicator. The lead content can be determined within 15–20 min.

Zusammenfassung—Ein rasches komplexometrisches Verfahren zur Bestimmung von Blei in Schmierol wurde entwickelt. Das im Öl vorliegende Bleinaphthenat wird mit einem Gemisch von verdünnter Thioglykolsäure und Salpetersäure extrahiert. Der Bleimercaptoacetat enthaltende wäßrige Extrakt wird bei pH 5 mit Xylenolorange als Indikator mit EDTA titriert. Der Bleigehalt kann in 15–20 min bestimmt werden.

Résumé—On a élaboré une méthode complexométrique rapide pour le dosage du plomb dans les huiles de graissage. Le naphténate de plomb présent dans l'huile est extrait par un mélange d'acide thioglycolique et d'acide nitrique dilué. On titre l'extrait aqueux contenant le mercaptoacétate de plomb par l'EDTA à pH 5 avec l'Orangé Xylénol comme indicateur. La teneur en plomb peut être déterminée en 15–20 mn.

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ANALYTICAL DATA

POTENTIOMETRIC DETERMINATION OF STEPWISE STABILITY CONSTANTS OF VANADIUM, MOLYBDENUM AND TUNGSTEN CHELATES FORMED WITH ASPARAGINE AND GLUTAMINE

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The metal chelates of asparagine have been studied earlier by various workers,[1-5] but chelates formed with glutamine have not been investigated so extensively. In earlier publications from this laboratory, the stability constants of some aspartate and glutamate chelates[6] have been reported. Their formation was studied potentiometrically by Irving and Rossotti's[7] method. This paper gives the results of a similar study of some chelates of vanadium, molybdenum and tungsten formed with asparagine and glutamine.

RESULTS AND DISCUSSION

The protonation constants are log K_2^H 8·70, log K_1^H 2·16 for asparagine and log K_1^H 8·91, log K_2^H 2·21 for glutamine.

The formation curves ($\bar{n}$ *vs.* pL) show that $\bar{n}$ approaches a value of 3 for the asparagine and glutamine chelates of V(IV), Mo(VI) and W(VI).

Analysis of the formation curves for the V(IV) chelates show that K_1 and K_2 are very similar, and K_3 quite different. Since $\log K_1 - \log K_2$ is $<0{\cdot}5$, in these cases, K_1 and K_2 cannot be separately computed; instead $\log K_1 \,.\, K_2$ values were obtained from Albert's equation[8]

$$\log K_1 \,.\, K_2 = \log \bar{n} - \log (2 - \bar{n}) - 2 \log [\mathrm{L}]$$

Further since $K_2/K_3 \sim 10^3$, K_3 may be regarded as independent of K_1 and K_2, and its value was computed by the average-value method in the range $2 < \bar{n} < 3$.

Table 1. Stability constants of vanadium(IV), molybdenum(VI) and tungsten(VI) chelates formed with asparagine and glutamine (Temp. 25°C, 0·1M $NaClO_4$ medium).

Metal ion	pH range for $\bar{n}$ calculations	Method	Asparagine			Glutamine		
			log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
V(IV)	3·2–8·0	Interpolation at half-$\bar{n}$ values	7·50	7·10	4·00	7·40	7·00	4.00
		Albert's equation	log $K_1 \,.\, K_2$ 14·50		—	log $K_1 \,.\, K_2$ 14·45		—
		Average-value	—	—	4·04	—	—	4·07
Mo(VI)	2·7–8·5	Interpolation at half-$\bar{n}$ values	8·20	7·18	3·45	8·00	6·80	3·35
		Successive approximation	8·06	7·23	3·45	7·90	6·93	3·35
W(VI)	4–8·5	Interpolation at half-$\bar{n}$ values	6·00	5·00	3·30	5·90	4·35	3·20
		Successive approximation	5·84	5·11	3·30	5·76	5·09	3·20

For Mo(VI) chelates, $K_1/K_2 \sim 10$ and $K_2/K_3 \sim 10^{3\cdot5}$, whereas for W(VI) chelates $K_1/K_2 \sim 10$ and $K_2/K_3 \sim 10^{1\cdot7}$. Therefore in these cases estimated stability constants were obtained by interpolation at half-$\bar{n}$ values and these were further refined by successive approximation.

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Summary—The metal chelates of V(IV), Mo(VI) and W(VI) formed with asparagine and glutamine have been studied potentiometrically. Stepwise stability constants in 0·1*M* sodium perchlorate at 25°C are reported as follows.
Asparagine chelates—log K_1K_2 14·50 and log K_3 4·04 for V, log K_1 8·06, log K_2 7·29 and log K_3 3·45 for Mo, and log K_1 5·84, log K_2 5·11 and log K_3 3·30 for W.
Glutamine chelates—log K_1K_2 14·45, and log K_3 4·07 for V, log K_1 7·90, log K_2 6·93, and log K_3 3·35 for Mo, and log K_1 5·76, log K_2 5·09 and log K_3 3·20 for W.

Zusammenfassung—Die Chelate von V(IV), Mo(VI) und W(VI) mit Asparagin und Glutamin wurden potentiometrisch untersucht. Es werden folgende stufenweise Stabilitätskonstanten in 0·1*M* Natriumperchlorat bei 25°C mitgeteilt:
Mit Asparagin. log K_1K_2 14·50, log K_3 4·04 für V, log K_1 8·06, log K_2 7·29, log K_3 3·45 für Mo, log K_1 5·84, log K_2 5·11, log K_3 3·30 für W.
Mit Glutamin. log K_1K_2 14·45, log K_3 4·07 für V, log K_1 7·90, log K_2 6·93, log K_3 3·35 für Mo, log K_1 5·76, log K_2 5·09, log K_3 3·20 für W.

Résumé—On a étudié potentiométriquement les chélates métalliques de V (IV), Mo (VI) et W (VI) formés avec l'asparagine et la glutamine. Les constantes de stabilité étagées en perchlorate de sodium 0,1 M à 25°C sont rapportées comme suit:
Chélates de l'asparagine—log K_1K_2 14,50 et log K_3 4,04 pour V, log K_1 8,06, log K_2 7,29 et log K_3 3,45 pour Mo, et log K_1 5,84, log K_2 5,11 et log K_3 3,30 pour W.
Chélates de la glutamine—log K_1K_2 14,45, et log K_3 4,07 pour V, log K_1 7,90, log K_2 6,93 et log K_3 3,35 pour Mo, et log K_1 5,76, log K_2 5,09 et log K_3 3,20 pour W.

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ANNOTATION

THE ACID STABILITY CONSTANTS OF ALIZARIN FLUORINE BLUE

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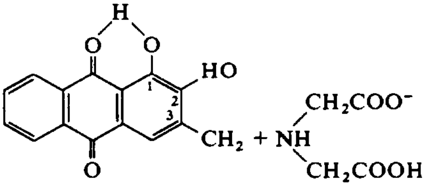
During the past decade since its introduction by Belcher *et al.*,[1] Alizarin Fluorine Blue (alizarin complexan, 3-aminomethylalizarin-*N*,*N*-diacetic acid) has attracted considerable interest from analytical chemists. The reagent provided the analyst with the first positive colour reaction for fluoride ion and has been widely used for the photometric determination of fluoride.[2,3,4] Most work has been done on the ternary complexes formed by the reagent with the rare earth ions and fluoride ion and has been aimed at an improvement of the analytical method. Apart from dissociation constants of the acid and some conditional constants of the ternary complexes, very little is known about the equilibrium data for the reagent and its complexes. In this paper, the stability constants of the protonated species will be discussed and in a forthcoming paper further equilibrium data will be presented.



Alizarin Fluorine Blue

An attempt to determine the dissociation constants of alizarin complexan was made by Laird and Leonard.[5] Quite recently, the dissociation constants have also been determined by Mori *et al.*,[6] whose results differ appreciably from those of Laird and Leonard. Neither of the published sets of constants can explain the absorption spectra of the reagent, however, as will be clear from the following discussion.

Table 1 lists the values of the stability constants for alizarin complexan and two compounds that can be considered the parent compounds of the reagent, iminodiacetic acid (IMDA) and sodium alizarin sulphonate (ARS). The values of both Laird and Leonard, and Mori *et al.* are given for alizarin complexan. The absorption spectra that were recorded by Leonard and West[7] are shown in Fig. 1. (These were found to agree with spectra recorded in connection with the present work).

A glance at the spectra shows that the rise in absorbance at 590 nm for an increase in pH from 12·4 to 13·0 is about 55%. If it is assumed that the increase is due to the dissociation of HL into L and H, the value predicted from the stability constant of Laird and Leonard is only 4·5%. Therefore, the possibility that the value of the stability constant is too low cannot be excluded.

Moreover, if the values of Laird and Leonard were correct, the colour transition at pH = 5·5 that is visible in the spectra would arise from the dissociation of H_4L into H and H_3L. It is, however, reasonable to assume that the colour transitions are associated with changes in the resonance structure of the anthraquinone ring system. In other words, a greater colour effect should follow when one of the phenol groups loses a proton than when one of the carboxyl group hydrogen atoms—or the proton of the imino group—in the side-chain dissociates.

Log $K^{H}_{H_3L}$ = 7·55 (Ringbom's[9] notation is used in this paper) would thus imply that the acidity of one of the carboxyl groups would decrease by as much as five logarithmic units as compared to iminodiacetic acid. Reference to Schwarzenbach *et al.*[10] shows that the order of dissociation of the protons to be expected is as follows.

1. The remaining carboxyl group proton (one is transferred to the imino nitrogen atom during dissolution of the acid).
2. The phenolic proton in position 2.

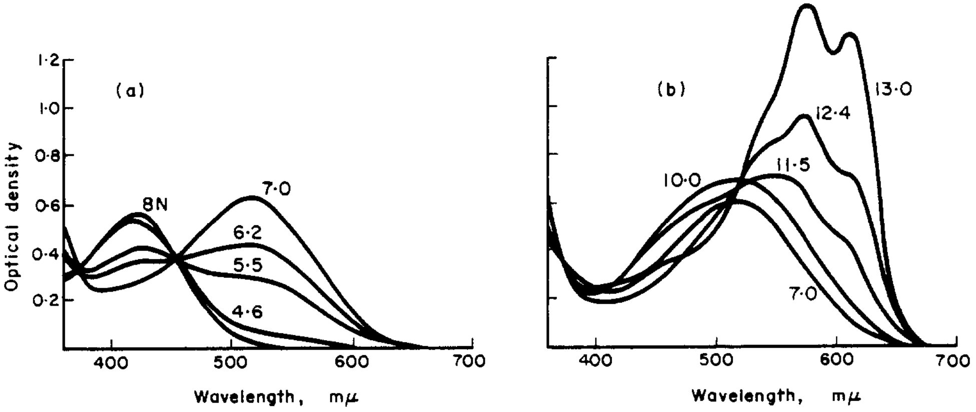


Fig. 1. pH-absorption curves for alizarin complexan (9·63 μg/ml) (from ref. 7 by courtesy of the copyright holders).

Table 1

Reaction		log K Alizarin complexan Ref. 5	 Ref. 6	 IMDA Ref. 8	 ARS Ref. 8
$H + L = HL$	K^{H}_{HL}	11·19	—	9·5	11·0
$H + HL = H_2L$	$K^{H}_{H_2L}$	10·43	10·5	2·3	5·5
$H + H_2L = H_3L$	$K^{H}_{H_3L}$	7·55	6·7	1·8	
$H + H_3L = H_4L$	$K^{H}_{H_4L}$	4.89	3·7		

(L denotes the ligand. For convenience, the signs of charge are omitted. The constants were determined at an ionic strength $\mu = 0{\cdot}1$.)

3. The proton at the imino group.
4. The remaining phenolic proton in position 1.

In comparison with alizarin and methyliminodiacetic acid, the acidity of the first two steps can be expected to increase, whereas the acidity of the last two steps should decrease.

The spectra recorded by Mori *et al.* display a transition back from red to yellow at pH = 8. The yellow colour is said to be stable in the pH range 8–9. Such a change is, however, highly unlikely and some experiments carried out at this laboratory show that the reason must be the use of boric acid as a buffer substance in this pH region. In fact, the colour of the solution will remain yellow throughout the entire pH range up to pH = 12 provided that enough boric acid has been added. It is probable that alizarin complexan is complexed by boric acid (*cf.* the complexation between boric acid and mannitol!). Since the same buffer was used in the electrophoretic experiments, the results should be regarded with caution.

These observations made it clear that further work was justified in order to bring clarity into the apparent confusion. In the following, the results of a potentiometric and spectrophotometric study of the acid stability constants of alizarin complexan will be given.

EXPERIMENTAL

Reagents

Alizarin complexan was purified by suspending 1 g in 50 ml of 0·1*M* sodium hydroxide, filtering the solution and extracting any alizarin with five successive portions of methylene dichloride. The acid was then reprecipitated by dropwise addition of hydrochloric acid whilst stirring the solution, which was kept in an ice-bath. The orange precipitate was collected on a glass filter crucible, washed with ice-water and dried in a vacuum desiccator over solid potassium hydroxide. The purity was checked by alkalimetric titration and by photometric titration with aluminium ion at pH = 4. Two different makes proved to have identical properties.

Hydrochloric acid solution was prepared according to Foulk and Hollingsworth.[11]

Sodium hydroxide solution was prepared according to Sillén[12] and standardized against potassium hydrogen iodate and against the hydrochloric acid solution.

All other reagents were of analytical grade. Redistilled water was used throughout the experiments.

Procedure

A weighed sample of the acid was dissolved in a known amount of sodium hydroxide solution, sufficient to neutralize three of the protons. The test solution was maintained at 25 ± 0·1° by suspending the titration vessel in an oil-filled thermostatically-controlled bath. Additions of titrant were made with pneumatically operated pipettes made by AGA, Lidingö, Sweden. The potentials were measured with a Beckman No. 39301 glass electrode against an Orion No. 90-02-00 double junction reference electrode and read with a digital voltmeter manufactured by Systemteknik (Type S 1016 H), Lidingö, Sweden. The outer sleeve of the reference electrode was filled with the ionic medium. Potassium chloride was used to maintain the ionic strength of the solution at 0·1 or 0·5.

The junction potentials were determined in separate experiments as functions of the acidity and taken into consideration when calculating pH from the measured potential.

The photometric results were handled by a variant of a method described by Sacconi[13] that is to be described later.[14] The results obtained by potentiometric titration were analysed by using the Etitr version of Sillén's computer program Letagropvrid.[15]

The total concentration of alizarin complexan ranged from $10^{-5}M$ to $10^{-4}M$ during the photometric measurements and from $10^{-3}M$ to $10^{-2}M$ in the potentiometric titrations.

RESULTS AND DISCUSSION

The sets of stability constants that give the best fit to the results have been collected in Table 2. It can be seen that the magnitudes of the constants agree well with the ones that can be predicted from the paper by Schwarzenbach *et al.*[10] mentioned earlier. The reaction $H_3L + H_2L = H_5L_2$ was introduced to account for a systematic deviation of the data that was observed when only the first four reactions were assumed to take place. The deviation was reproducible irrespective of any attempts to purify the reagent. By the introduction of the species H_5L_2, the error square sum decreased considerably, indicating a substantially better fit to the data.

Considering the reaction between alizarin complexan and boric acid, a reaction between H_2L and H_3L (containing two hydroxy groups!) does not seem unlikely.

A similar increase in the values of $K^{H}_{H_3L}$ was also observed when photometric results obtained at increasing pH values were used for the calculation of the stability constant. The change was much smaller than for the

Table 2. Stability constants of the reactions of alizarin complexan with protons.

Reaction	log $K \pm 3\sigma$ Ionic strength = 0·1	0·5
$H + L \rightarrow HL$	11·98 ± 0·03	12·10 ± 0·03
$H + HL \rightarrow H_2L$	10·07 ± 0·03	9·81 ± 0·03
$H + H_2L \rightarrow H_3L$	5·54 ± 0·05	5·47 ± 0·05
$H + H_3L \rightarrow H_4L$	2·40 ± 0·05	2·54 ± 0·07
$H + H_4L \rightarrow H_5L$		
$H_3L + H_2L \rightarrow H_5L_2$	2·2 ± 0·2	2·2 ± 0·2

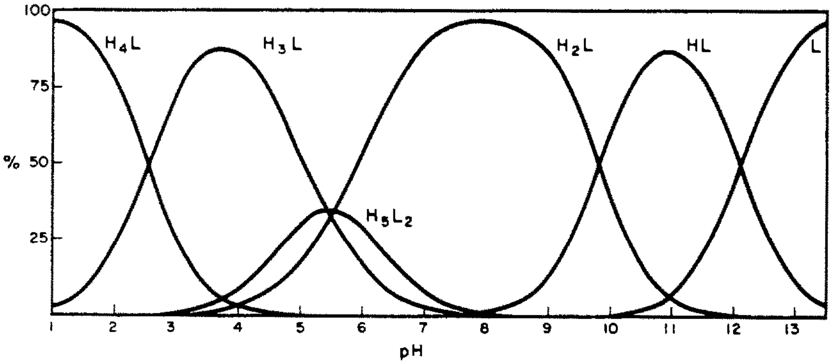


Fig. 2. Distribution diagram showing the proportion of alizarin complexan present in each ionized form at different pH values. Total concentration of alizarin complexan, $C_L = 0{\cdot}01M$.

potentiometrically obtained results, which is to be expected if it is due to formation of the H_5L_2 species, the overall concentration of the reagent being much less in the photometric experiments.

Owing to the uncertainty of glass electrode measurements at high alkalinity, the value of K^{H}_{HL} given in Table 2 was determined photometrically. The potentiometric measurements gave a lower value, $\log K^{H}_{HL} = 11{\cdot}8$ at ionic strength 0·5. The difference between the potentiometrically and the photometrically determined values of $K^{H}_{H_3L}$ was much smaller, the latter being $10^{5\cdot56}$ at 0·1 ionic strength.

If the Debye-Hückel theory is used to account for the effects of the medium, it can be shown that the agreement between the values determined in the different media is very good.

A distribution diagram, showing the proportion of the different ionized forms of alizarin complexan present, as a function of pH, is given in Fig. 2.

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Summary—Two recent attempts to determine the dissociation constants of 3-aminomethylalizarin-*N*,*N*-diacetic acid are discussed and the results compared with values that can be predicted from earlier work on iminodiacetic acid derivatives and from the absorption spectra of the reagent at different pH values. Results of a potentiometric and spectrophotometric study to determine the stability constants of the various protonated species of the reagent in aqueous solution at ionic strengths 0·1 and 0·5 (potassium chloride) are: $\log K^{H}_{HL} = 12{\cdot}1$, $\log K^{H}_{H_2L} = 9{\cdot}81$, $\log K^{H}_{H_3L} = 5{\cdot}47$, $\log K^{H}_{H_4L} = 2{\cdot}54$, and $\log K^{H_2L}_{H_5L_2} = 2{\cdot}2$ at ionic strength 0·5.

Zusammenfassung—Zwei neue Versuche, die Dissoziationskonstanten von 3-Aminomethylalizarin-N,N-diessigsäure zu bestimmen, werden diskutiert und die Ergebnisse mit Werten verglichen, die aus früheren Arbeiten über Iminodiessigsäurederivate und aus den Absorptionsspektren des Reagens bei verschiedenen pH-Werten vorhergesagt werden können. Eine potentiometrische und eine spektrophotometrische Untersuchung der Stabilitätskonstanten der verschiedenen protonierten Spezies des Reagens in wäßriger Lösung bei den Ionenstärken, 0·1 und 0·5 (Kaliumchlorid) ergaben $\log K_{HL}{}^{H} = 12{\cdot}1$, $\log K^{H}_{H_2L} = 9{\cdot}81$, $\log K^{H}_{H_3L} = 5{\cdot}47$, $\log K^{H}_{H_4L} = 2{\cdot}54$ sowie $\log K^{H}_{H_5}{}^{2L}_{L_2} = 2{\cdot}2$ bei der Ionenstärke 0·5.

Résumé—Les deux derniers essais pour déterminer les constantes de dissociation du 3-aminométhylalizarine-N, N-acide diacétique sont discutées et les résultats sont comparés aux valeurs prévues selon les travaux précédents sur les dérivés de l'acide iminodiacétique et des spectres d'absorption du réactif à diverses valeurs de pH. Les résultats d'une étude potentiométrique et spectrophotométrique pour la détermination des constantes de stabilité des divers spécimènes protonés du réactif en solution aqueuse à des solidités ioniques de 0,1 et de 0,5 (chlorure de potassium) sont: $\log K^{H}_{HL} = 12{\cdot}1$, $\log K^{H}_{H2L} = 9{\cdot}81$, $\log K^{H}_{H3L} = 5.47$, $\log k^{H}_{H4L} = 2.54$, et $\log K^{H2L}_{H5L} = 2{,}2$ à une solidité ionique de 0,5.

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TALANTA REVIEW*

USES OF LIQUID ION-EXCHANGERS IN INORGANIC ANALYSIS

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Summary—A review of recent uses of liquid ion-exchangers in inorganic analysis is presented.

Since the publication[1] in *Talanta* in 1964 of the review paper "Recent uses of liquid ion exchangers in inorganic analysis" interest has continued to be shown in this type of reagent. Liquid ion-exchange is a special case of solvent extraction, in that it involves selective transfer of solute between two immiscible phases, the distinction being that whereas solvent extraction involves the formation of a neutral species, whether a chelate, an ion-pair or a non-dissociating compound, liquid ion-exchange refers only to formation of ion-pairs, with special reference to exchange of one ion for another between the aqueous and the organic phase. The degree of transfer, or ion-exchange extraction obtained, is directly proportional to the concentration of the exchanger in the solvent, and distribution coefficients may be obtained similarly to those employed in solvent extraction. Changes in selectivity and in the values for the distribution coefficients of the liquid exchangers are related to changes in pH, temperature, salt concentration, charge on the ions involved, the presence of complexing and competing ions and the organic solvent employed. The behaviour of analogous functional groups in liquid and in resin ion-exchange is similar and it is possible to predict the likely course of a liquid ion-exchange extraction by reference to the literature on ion-exchange resins.

Coleman, Blake and Brown[2] gave a list of liquid ion-exchange materials in *Talanta* in 1962 but ten years later only a few of the materials which they mentioned have been widely used. A useful introduction to the properties and uses of liquid exchangers can be found in the paper by Kunin and Winger[3] published in the same year, and a brief outline was given in the review of 1964 previously cited.[1] The latter paper covered the more important published work up to the middle of 1964 with particular reference to the use of liquid exchangers in the analysis of inorganic materials other than those involving the transuranic elements. The present review covers the period from then until 1972.

LIQUID ANION-EXCHANGERS

Liquid anion-exchangers are based on high molecular weight primary, secondary and tertiary amines, and quaternary ammonium salts. The high molecular weight ensures very

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* For reprints of this Review see Publisher's announcement near the end of this issue.

low solubility in aqueous solutions and high solubility in most water-immiscible organic solvents. Solvents such as aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, high molecular weight alcohols and petroleum distillates are suitable, and amine concentrations of 2–20% are usually employed. While the capacity for the extraction of all anions, present in the form of free acid, increases directly with increase in concentration of the exchanger in the organic phase, a different degree of extraction is exhibited for different anions. When simple anions are involved in formation of a complex anion containing a metal ion, addition of lithium salts of these simple anions will enhance the degree of extraction of the metal ions from solutions having the same total concentration of simple anion (*i.e.*, as lithium salt or free acid), as illustrated in Table 1.

Table 1. Temperature dependence of partition coefficient in the extraction of cobalt from hydrochloric acid solutions by 0·1*M* TOA in benzene[4]
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Temp., °*C*	Partition coefficient	
	8*M* HCl	0·2*M* HCl + 7·8*M* LiCl
20	16·2	31·2
30	11·0	30·5
40	8·21	29·9
50	6·00	29·0

Changing the solvent in which the exchanger is dissolved may affect the degree of extraction for the free acid with the same concentration of exchanger. This effect can be utilized to impart selectivity for the separation of ions, particularly when the ionic charges differ. A list of the most commonly used anion-exchangers is given in the appendix to this paper.

Attention is drawn here to the hazards associated with the use of amines, especially in the undiluted state. It is important that adequate ventilation is provided to prevent any vapours from being inhaled. Precautions should be taken to prevent contact with the eyes or prolonged contact with the skin.

SEPARATIONS WITH ANION-EXCHANGERS

The two most widely employed liquid anion-exchangers, judging from the published literature, are tri-n-octylamine (TOA) and tri-iso-octylamine (TIOA).

Sato[4] studied the extraction of uranium(VI) and cobalt(II) from hydrochloric acid media, with 0·1*M* TOA solution in benzene. Lithium chloride was shown to be an effective salting-out agent in both instances, while increase in temperature reduced the partition coefficient. Table 1 illustrates these two important aspects of liquid ion-exchange very clearly.

In a further paper[5] Sato reported on the extraction of uranium(VI) and cobalt(II) from hydrochloric acid media with a series of cyclohexyl and benzylalkylamines. As expected, the tertiary amines were more effective extractants than the secondary amines, with benzene or chloroform as solvent. The efficiency of the extractions increased with the chain length of the alkyl group and decreased when the alkyl chain was branched. The presence of a benzyl group helped to promote extraction efficiency, and again substituting lithium chloride for the equivalent hydrogen chloride improved the extraction.

Hodara and Balouka[6] employed TOA to extract and separate uranium(VI) from uranium(IV). They used xylene as the solvent and the uranium was present in a mixture of hydrochloric and phosphoric acids. The phosphate complexes the uranium(IV) and prevents its extraction.

Platinum(IV) and tin(II) in hydrochloric acid form an orange complex, which may be extracted by a wide range of liquid anion-exchangers into solvents such as benzene and chloroform, and used for the spectrophotometric determination of platinum.[7] Comparison of the absorption spectra of the Pt–Sn complex in the aqueous and organic phases indicated the presence of the same absorption species in each medium. Irrespective of the amine used the complex showed an absorption maximum at 400 nm. Procedures were described for the determination of platinum in the presence of palladium and rhodium, both of which could interfere. Osmium, iridium and ruthenium probably form complexes but no evidence of extraction was found. Other ions causing no interference were Mo(VI), Co(II), Ni, Fe(III), SO_4^{2-}, NO_3^-, ClO_4^-. TOA as a 0·2*M* solution in benzene pre-equilibrated with 3*M* hydrochloric acid appears to be the best amine to use.

Khattak and Magee also examined the formation of the rhodium(III)–tin(II) complex[8] and its extraction into TOA/benzene before its spectrophotometric determination. The Rh(III) and Sn(II) reaction was carried out in hot 7–11·6*M* hydrochloric acid. Extraction with 0·2*M* TOA in benzene from such highly acidic solutions separates rhodium from the two other metals, platinum and palladium, which form similar complexes. The yellow Rh–Sn complex showed an absorption maximum at 415 nm, suitable for spectrophotometric measurement in the range 0–8 ppm. No interference was encountered from Os, Ru, In, Co(II), Ni, Fe(III), SO_4^{2-}, NO_3^-, ClO_4^-. A third paper[9] described a similar method for the determination of palladium. The extraction of chloro- and bromo-complexes of Ru(III) by a chloroform solution of mono-, di- or tributylamine was examined by Meier *et al.*[10]

The extraction of Pt(IV) and Rh(III) by TOA hydrochloride was reported by Gindin and Ivanova.[11] Extractions with 0·05*M* exchanger in toluene showed decreasing extraction with increasing hydrochloric acid concentration. Separation of the two metals was found to be feasible and suitable procedures were described.

Work on the extraction of platinum-metal nitrites by TOA in toluene was reported by Khan and Morris.[12] Nitrito-complexes of platinum metals are formed when hot neutral or feebly acidic solutions of the chloro-complexes are treated with excess of sodium nitrite. With 0·12*M* TOA hydrochloride in toluene as extractant and at pH 7 the distribution ratios for the platinum metals were Pt 27·8, Pd 15·6, Ru 11·8, Rh 0·0048, Ir 0·0059. The separation of the first three platinum-metals from the last two could obviously be done under the stated conditions. Quantitative back-extraction of platinum, palladium and rhodium was achieved with 1·5*M* perchloric acid.

The extraction of osmium complexes from hydrochloric or hydrobromic acid has been examined by Meier *et al.*[13] It was found that both short- and long-chain amines were suitable extractants. TOA gave over 99·8% extraction. The choice of organic solvent exerted a decisive influence on the degree of extraction obtained.

Gold has been quantitatively determined by employing 1% trioctylmethylammonium chloride in di-isobutyl ketone as extractant. Groenewald[14] used this extraction for gold in ore samples after treating them with *aqua regia*. If the pH of the solution was 0–4 then the relative chloride content was increased to 0·5*M* by addition of sodium chloride. If the pH was 4–10 then cyanide was added to give a concentration of $10^{-2}M$ and sodium chloride to a concentration of 0·1*M*. The presence of the sodium chloride facilitated clarification of the phases after mixing. More than 99·5% of the gold(III) was readily extracted, and measured in the organic phase by atomic absorption. A similar paper by Madigan[15] describes the extraction of gold as $Au(CN)_2^-$ by bis-(1-isobutyl-3,5-dimethylhexyl)amine in kerosene. The gold is back-extracted with 0·1*M* potassium cyanide or sodium carbonate.

McClellan and Benson[16] extracted iron from 2*M* and cobalt from 7·7*M* hydrochloric acid with 5% TOA in carbon tetrachloride. Two extractions were necessary to extract 98% of each metal. The metals were back-extracted for spectrophotometric determination in the aqueous phase.

Using methyldioctylamine, MDOA, in chloroform, Bullock and Tuck[17] examined the extraction of the anionic mercuric compounds formed with sulphate, selenate and oxalate. The 0·4*M* chloroform solution of MDOA was first equilibrated with the appropriate dilute acid solution and then the mercury compounds were extracted, their initial concentration being approximately $10^{-3}M$. Extraction of the sulphato-complex decreased rapidly with increasing sulphuric acid concentration; use of sodium sulphate in place of some of the sulphuric acid effected only a minor improvement. A similar trend was shown by the extraction from selenic acid. However, extraction from oxalic acid solutions increased rapidly with increase in oxalate concentrations above 0·2*M*.

Studies of the extraction of niobium and tantalum oxalato-complexes by TOA, TDA (tri-n-decylamine) and TDDA (tri-n-dodecylamine) in carbon tetrachloride were made by Djordjević *et al.*[18] All three exchangers behaved the same. For quantitative extraction in one pass with 3% exchanger solution from 0·2*M* oxalate solution, for both metals the sulphuric acid concentration needs to be below 0·5*M*. A similar paper by Abdel-Gawad *et al.*[19] reported the extraction of niobium from oxalic, citric and acetic acid solutions.

Sato and Watanabe[20] examined the extraction of zirconium by tricaprylethylammonium chloride ("Aliquat-336") in benzene from hydrochloric acid. Extraction increased rapidly with hydrochloric acid concentration above 6*M*. A study of the effect of the organic solvent showed that benzene was not particularly suitable for the extraction of Zr, and that chlorobenzene, dichlorobenzene or nitrobenzene were much superior. A later paper by the same authors[21] examined the use of a number of high molecular weight amines for extraction of zirconium from hydrochloric acid media.

Alimarin *et al.*[22] separated niobium(V) from titanium(IV) with a 0·2*M* solution of TOA in carbon tetrachloride. A single extraction of niobium from 8·5*M* hydrochloric acid was about 97% complete.

Ishibashi *et al.*[23] determined zirconium spectrophotometrically after extraction of the Zr–Alizarin Red S chelate into a toluene solution of TOA. The zirconium was first reacted with Alizarin Red S, then the solution was adjusted to pH 1 with hydrochloric acid, and allowed to stand for an hour. The zirconium complex was then extracted with 0·1*M* TOA in toluene, which had been previously equilibrated with 1*M* chloroacetic acid. On shaking the organic layer with an acetate buffer at pH 4·1 a polymeric chelate was formed which had an absorption maximum at 538 nm. Molybdate and tungstate were the major interfering ions.

A systematic study by Ivanov *et al.*[24] of the extraction of niobium from hydrochloric acid media by amines dissolved in carbon tetrachloride or chloroform, showed that the amine salt, not the amine, was the extractant. Hydrochloric acid concentrations above 7*M* were found to be necessary to form the extractable niobium species—$NbOCl_5^{2-}$.

By employing Aliquat-336 in xylene, Moore[25] formulated an improved method for the separation of actinide–lanthanide elements from plutonium waste solutions. These elements are readily extracted from relatively dilute aluminium nitrate–nitric acid solution by Aliquat-336 in the nitrate form. They are stripped with dilute mineral acids such as hydrochloric.

In another paper,[26] Moore described the use of Aliquat-336 in the thiocyanate form to separate the actinide–lanthanide elements from each other. The tervalent actinides were preferentially extracted by a xylene solution of the exchanger, and the addition of dilute acids, such as sulphuric, markedly improved the separation factors obtained.

Moore[27] has suggested that the actinide and lanthanide elements could be separated by extraction with anion-exchangers from solutions containing organic acids or EDTA. Most metal ions form amine-extractable anionic complexes with citric, oxalic and tartaric acids. Since these acids prevent hydrolysis of metal ions over a wide pH range there is no need to use acid solutions for extraction when they are present and this could widen the scope of extraction by amines.

Factors affecting the efficiency of the extraction of gallium from thiocyanate solution by TOA were investigated by Mikheev *et al.*[28] The best conditions are pH about 2 and 0·2–8·0*M* thiocyanate.

The extraction of gallium and indium from hydrochloric, hydrobromic and hydriodic acids by 1% "Adogen 364" in toluene was described by Sherif *et al.*[29] Gallium was 100% extracted from 3–10*M* hydrochloric acid, but indium showed maximum extraction (80%) from the 6*M* acid and much less from the 0–4*M* and 8–10*M* acid. Gallium extraction was maximum from hydrobromic acid >2*M* in concentration, but indium extraction did not start at acid concentrations <3*M* and was maximum from >5*M* acid. Indium was 100% extracted from hydriodic acid >0·5*M*, but gallium was not extracted at acid concentrations below 1·5*M*, 100% extraction not being achieved unless the acid was >5*M*.

Alian[30] used trilaurylamine (TLA) in xylene to extract protactinium, iron, mercury, silver, zinc, cobalt and selenium from hydrobromic or perchloric acid. It was found that increasing the hydrobromic acid concentration increased the degree of extraction for all the metals except silver and mercury, while increasing the TLA concentration gave corresponding increases in extraction. Corresponding experiments for the perchloric acid media showed extraction of Pa, Fe(III) and Se(IV) increasing and of Hg(II) decreasing. No extraction occurred at all for Co and Zn and very little for Ag.

The determination of microgram amounts of vanadium can be very difficult because of its variable oxidation state. Patrovský[31] based a photometric method on reaction of vanadium(IV) to form a catechol complex in which co-ordinately bound water could be replaced with tributylamine (TBA). The new complex was extractable into chloroform and was suitable for spectrophotometric measurement at 595 nm. The colour was stable for at least 60 min and other elements such as Ti and Mo which gave yellow complexes did not interfere with the measurement of the blue vanadium complex.

A comprehensive study of the extraction of zinc and nickel with aromatic tertiary amines was presented in a paper by Gagliardi and Wieland.[32] Twenty-four amines were tried as 0.5% solutions in chloroform and extractions were made from 0·5–5*N* hydrochloric, nitric and sulphuric acid media. Some effective extractants for zinc were discovered, but the nickel was partially or completely masked by most of the amines.

A 0·25*M* solution of TOA in xylene was found to be a suitable extractant for fluorosilicic acid, H_2SiF_6, from aqueous hydrofluoric acid media up to 1*M*.[33] Over 99·5% extraction was achieved and separation was complete from other elements which did not form anionic fluoro-complexes under the conditions employed. Niobium and tantalum were also extracted but could be separated by prior extraction from solution of higher hydrofluoric acid concentration; the solutions could then be diluted to 1*M* acidity and the H_2SiF_6 extracted.

Concentrations of cadmium down to 10 ppm were determined by Vasyutinskii *et al*[34] with 2% TBA in dichlorethane by extraction from a solution about 0·4*M* in hydrobromic acid. A dithizone solution in dichloroethane was added to the organic phase which was then washed with sodium hydroxide/sodium potassium tartrate solution, and filtered. The absorbance of the Cd-complex with dithizone in the organic phase was measured at 529 nm. No interference was encountered from Ni, Co, Cr, Cu, Zn, Mg, Fe, Mn and Al.

Using TOA to extract iron(III) citrate complexes into chloroform, Pyatnitskii and Tabenskaya[35] found extraction maximal at pH 1·8–2·6. A citric acid concentration of 0·02–0·8*M* in the aqueous phase gave conditions suitable for extraction by a 0·03*M* TOA solution. It was observed that alkali metal chlorides and nitrates inhibited the extraction and would completely suppress it if present above a concentration of 0·025*M*.

Angelova and Diocheva[36] extracted rhenium and molybdenum with dialkylbenzylmethylammonium salts, employing a mixed organic reagent consisting of 69% kerosene, 30% xylene, 7% isopentanol and 1% of the substituted ammonium salt. For Re(VII) a substituted ammonium chloride gave the best extraction but the Mo(VI) extraction was unaffected by the nature of the anion in the extractant. The two metals could be separated by using an aqueous solution at around pH 10, the distribution coefficient for Re(VII) then being 1000 times that for Mo(VI).

Shimizu[37] found suitable conditions for the extraction of scandium, thorium, zirconium and uranium from 0·1*M* sulphuric acid–0·01*M* ammonium sulphate medium with a 10% solution of "Amberlite LA-2" in xylene. No extraction was found for Al, Cd, Co, Cu, Ga, Hg, Mn, Ni, Y and the rare-earth metals, but Fe(III), In, and V(IV) showed partial extraction. Scandium and thorium could be back-extracted into the aqueous phase with 1*M* sulphuric acid. Zirconium and uranium(VI) could be back-extracted with 5*M* hydrochloric acid and 10% sodium carbonate solution respectively.

Marchenko and Voronina[38] extracted antimony(V) quantitatively from 7–10*M* hydrochloric acid with 2% TBA solution in chloroform, and separated it from chromium. The antimony was back-extracted with sodium potassium tartrate in aqueous ammonia solution.

Shevchuck and Shripnik[39] extracted aluminium as AlF_6^{3-} from an aqueous phase at pH 4–6 with 0·1*M* dodecylamine solution in chloroform.

Hofer[40] employed 10% Amberlite LA-2 solution in chloroform for separating traces of tin in nickel by extraction from 6*M* hydrochloric acid.

It was shown by Yagnyatinskaya and Nazarenko[41] that a TBA solution in chloroform would extract niobium from hydrochloric acid solution containing excess of catechol, extraction being maximal at pH 4·5 or at 1·5–3*M* acid concentration. The yellow Nb complex showed maximum absorption around 330–360 nm. Of many ions examined only Ti and oxalate were found to have any effect on the extraction. A procedure for the determination of small amounts of niobium in ores was described. Preliminary separation of thorium and uranium from each other and from interfering substances is often required before their determination. It was indicated by Cospito and Rigali[42] that the two well-known extraction systems—uranium from sulphuric acid by tertiary amines and thorium from nitrate media by quaternary ammonium salts—could be combined to achieve these separations. The uranium was first extracted by 3% TCA (tricaprylamine) in xylene from 0·05–0·2*M* sulphuric acid. The phases were separated and the uranium back-extracted with 0·5*M* sodium carbonate. The aqueous phase after uranium extraction was made 4*M* in nitric acid and the thorium extracted with 5% Aliquat 336 in xylene. The thorium was easily back-extracted with 3*M* hydrochloric acid.

A study by Florence and Farrar[43] of the extraction of nickel, manganese, chromium and thorium from mixed hydrochloric acid/lithium chloride solution, showed that high chloride but low free acid concentration greatly improved the degree of extraction. A further big improvement could be achieved if the extraction was made from methanolic lithium chloride rather than aqueous solutions. This was attributed to lower water activities in both phases when methanol was used as solvent. The authors suggested that elements such as aluminium and beryllium, which form only weak halide complexes, could be extracted by use of concentrated lithium halide solutions, selectivity being achieved by control of the halide concentration and free acidity.

Intensely coloured complexes of Xylenol Orange with traces of certain metals may be extracted by anion-exchangers from solutions at pH 0–3. This fact was utilized by Přibil and Veselý[44] who employed Aliquat-336 in chloroform for these extractions from mineral acid solutions. It was shown that it was possible to detect small amounts of gallium in indium and *vice versa*, and titanium or zirconium in thorium. The authors considered that the reactions could be made the basis for suitable spectrophotometric procedures.

Later Přibil and Adam[45] described a spectrophotometric method for the determination of molybdenum, employing mercaptoacetic acid. Sufficient 1*M* solution of the reagent was added to form complexes with all the molybdenum, iron, chromium and vanadium present, plus 0·5 ml in excess, the solution was neutralized, 5 ml of anhydrous acetic acid were added, and the molybdenum complex was extracted into 5% TOA in chloroform. The absorbance was measured at 370 nm and only the less common ions Bi, Hg and W interfered.

Yotsuyangi *et al.*[46] employed 4-(2-pyridylazo)resorcinol, PAR, as spectrophotometric reagent for Fe(II), Co, Ni and V(V). The complexes, formed in buffered neutral or weakly basic media in the presence of EDTA, were extracted with a chloroform solution of benzyldimethyltetradecylammonium chloride. For iron the solution was buffered to pH 10 with sodium borate and sodium hydroxide. The absorption was maximum at 522 nm and the molar absorptivity (ε) was $4{\cdot}00 \times 10^4$ l.mole^{-1}.cm^{-1}. For cobalt the pH used was 8·3, (borate–phosphate buffer), λ_{max} was 520 nm and ε $5{\cdot}9 \times 10^4$, for nickel, pH 9·3 (borate buffer), λ_{max} 505 nm and ε $7{\cdot}65 \times 10^4$, and for vanadium, pH 6·8 (phosphate buffer), λ_{max} 560 nm and ε $4{\cdot}30 \times 10^4$. For the determination of cadmium in nuclear-grade Zircaloy-2, Ghersini and Mariottini[47] employed an ion-exchange extraction from hydrochloric acid solution with 0·1*M* TOA in cyclohexane, previously equilibrated with hydrochloric acid. The cadmium was back-extracted with 2*M* sulphuric acid.

Ko[48] used a 20% TOA solution in xylene to extract plutonium, to an extent >99%, and this allowed concentration of tantalum, titanium, tungsten and zirconium, present in low concentration, before their determination spectrographically .

A recent paper by Ueno and Saito[49] suggested that extractions could be made with anion-exchangers from solutions of various metal ions in ammonium carbonate or sulphate media. Trioctylmethylammonium chloride (TOMA-Cl) was employed as exchanger as a 10% solution in toluene. The metal ions were added as radiotracers to 0·1–2*M* ammonium carbonate or sulphate solutions. In general, extraction was not critically dependent on ammonium sulphate concentration but did tend to decrease if the latter was >1*M*. Extraction decreased as the ammonium carbonate concentration increased.

SEPARATIONS WITH CATION-EXCHANGERS

The major part of the work on liquid cation-exchange has involved di-(2-ethylhexyl)orthophosphoric acid (HDEHP).

Sato[50] employed this reagent in kerosene in concentrations 0·005–0·1*M* to extract zirconium from hydrochloric acid solutions. The distribution ratio ($[\mathrm{Zr}]_{\mathrm{org}}/[\mathrm{Zr}]_{\mathrm{aq}}$) decreased as the acidity of the aqueous layer increased up to 2*M*, and then increased steeply above this acidity. This variation was interpreted as follows: "at low aqueous acidity zirconium is extracted by a cation-exchange reaction in which hydrogen [*sic*: hydrogen ion is meant] is liberated, while at high aqueous acidity the extraction is by a solvating reaction similar to that shown by non-ionic reagents such as tributyl phosphate." It was also shown that the partition coefficient for zirconium increased with temperature, which is contrary to the effect found for uranium(VI) and thorium(IV) but analogous to that for zirconium in nitric acid.

Extraction of sodium and strontium by HDEHP was investigated by McDowell and Coleman,[51] with benzene as solvent and the metals present as nitrates of the radioisotopes ^{85}Sr and ^{24}Na. With dilute solutions containing only sufficient $\mathrm{Na^+}$ or $\mathrm{Sr^{2+}}$ to satisfy 25% or less of the available ion-exchange capacity of the HDEHP, the extractions could be expressed as

$$\mathrm{Na^+ + 2(HA)_2 \rightleftharpoons NaA\cdot 3HA + H^+}$$
$$\mathrm{Sr^{2+} + 3(HA)_2 \rightleftharpoons SrA_2\cdot 4HA + 2H^+}$$

With increasing loading the simple salts corresponding to NaA and $\mathrm{SrA_2}$ were formed, with increasing polymerization and water extraction according to the generalized overall reaction

$$x\mathrm{Na^+} + \frac{x}{2}\mathrm{(HA)_2} + z\mathrm{H_2O} \rightleftharpoons \mathrm{(NaA)}_x z\mathrm{H_2O} + x\mathrm{H^+}$$

Separation of rare earths,[52] in particular praseodymium and neodymium, by means of HDEHP was examined by Goto and Smutz. The reagent was employed as a 1*M* solution in "AMSCO 125-82" (American Mineral Spirit Co.); no indication was given of just what this solvent is, which is unfortunate as it reduces the value of the work to other investigators. Perchlorate, chloride, nitrate and chloride/nitrate systems were investigated.

The determination of radiostrontium from a mixed fission product matrix containing isotopes of cerium, praseodymum, caesium, ruthenium, rhodium, zirconium, niobium and yttrium was described by Johnson.[53] The rare earths and yttrium were preferentially extracted into 1·5*M* HDEHP in toluene from dilute nitric acid media, before extraction of the strontium into isobutyl methyl ketone (IBMK) containing thenoyltrifluoroacetone.

For the separation and determination of thallium(III) Levin and Rodina[54] employed HDEHP. Extraction could be made from perchloric, hydrochloric or sulphuric acid media containing bromine; back-extraction employing 70% ammonium acetate solution at pH about 7 separated thallium from any amount of Mg, Zn, Cd, Cu(II), Hg(II), Fe(III), Ga, In, Al, Bi, As(V), Cr(VI) and Mn(VII). The determination of thallium was completed by titration of the extract with EDTA, after heating to 90° and adjusting to pH 4, with Xylenol Orange as indicator. In a previous paper[55] the recommendation was to back-extract the thallium into hydrochloric acid or sodium chloride solution. The EDTA titration was then carried out in an aqueous ammonia solution, containing chloroacetic acid, at pH 3–3·2.

Using HDEHP in kerosene, Csovary *et al.*[56] extracted scandium from 1*M* perchloric acid solution. Extraction was quantitative in the presence of chloride, nitrate or sulphate ions but phosphate, fluoride or oxalate ions reduced the degree of extraction.

The concentration of trace impurities by use of mixed cation-exchangers was described by Goryushina and Biryukova.[57] From 0·5*M* nitric acid solution, a mixed exchanger system of 2-ethylhexyl dihydrogen phosphate and bis-(2-ethylhexyl) hydrogen phosphate in carbon tetrachloride was shown to extract macro amounts of gallium, indium, thallium, bismuth or antimony. Impurities down to a level of 0·01 ppm, such as Cr(III), Mn, Co(II), Ni, Cu(II), Zn, Cd, As, Se and Te, remained in the aqueous phase, permitting their concentration by a factor of 50 or more.

A similar concentration process was outlined by Yudelevich *et al.*[58] for the analysis of high purity indium. The indium was extracted by *M* HDEHP in heptane from a 2*M* nitric acid solution of the alloy. Impurities were determined in the aqueous phase, recoveries being satisfactory except for bismuth and beryllium, when only 70–80% was obtained.

The extraction of macro amounts of indium with HDEHP in heptane from sulphuric or nitric acid solutions was described by Levin *et al.*[59] The indium was back-extracted into sulphuric or hydrochloric acid, excess of EDTA was added and the solution was back-titrated at pH 5 with zinc acetate, with Xylenol Orange as indicator.

Photometric determination of molybdenum as thiocyanate, after separation as Mo(VI), has been suggested by Kletenick *et al.*[60] The extraction was made from 2*M* hydrochloric or nitric acid solution with a benzene solution of HDEHP, the metal being back-extracted with 0·1*M* hydrogen peroxide in 2*M* hydrochloric acid, before its reaction with the thiocyanate.

An unusual type of extraction employing HDEHP was described by Kletenick and Bykhovskaya.[61] They found that the fluoride ion could be extracted by HDEHP, previously reacted with metals such as zirconium, thallium, titanium and quadrivalent tin, in hexane, carbon tetrachloride or benzene. Extraction varied with the nature of the solvent and was greatest when the metal attached to the exchanger was quadrivalent. In mineral acid solution Zr/HDEHP was the preferred extractant. The fluoride was back-extracted into the aqueous phase with TBP plus acetone and sodium hydroxide, before its determination by some suitable spectrophotometric method.

Extraction of iron(III) from hydrochloric acid solutions with HDEHP was described by Cerrai and Ghersini.[62] The iron was extracted from acid chloride solution that had a final chloride content <3·8*M*, an iron content between 0·04 and 6·0 μg/ml, and was 0·1*M* with respect to hydrochloric acid; an equal volume of 0·5*M* HDEHP in cyclohexane was used. An aliquot of the organic phase was transferred to a calibrated flask and the iron reduced with ascorbic acid in 95% ethanol. Bathophenanthroline and pyridine were added and the absorbance of the coloured solution was measured at 533 nm. Increasing the volume ratio of aqueous to organic phase up to 100 : 1 enabled extremely small amounts of iron to be determined with reasonable precision.

Extraction of small amounts of zinc from perchloric acid media by aliphatic carboxylic acids was investigated by Schweitzer and Clifford.[63] Zinc as radiotracer ^{65}Zn was extracted from 0·1*M* sodium perchlorate media adjusted to various pH values by the addition of sodium hydroxide or perchloric acid as appropriate. Solvents employed included benzene, chloroform and 4-methyl-2-pentanone.

Employing high molecular weight carboxylic acids, De and Roy[64] made a systematic study of the extraction of transition metals. The carboxylic acids used were (1) "Versatic-9", a mixture of highly branched saturated aliphatic acids containing nine carbon atoms, and (2) "SRS-100", a 1 : 1 mixture of highly branched, predominantly tertiary, acids containing fifteen carbon atoms and neutral oil. These were employed in benzene solution and the metal ions Fe(III), Co(II), Ni, Mn(II) and Cu(II) were in sulphate media. Optimum pH values for quantitative extractions were established as: iron 3·15, cobalt 8·12, nickel 8·3, manganese 7·95 and copper 6·15 for SRS-100. With Versatic 9, the pH for nickel was 7·5, for manganese 7·05, and for the others virtually the same as with SRS-100. The effect of changing the organic solvent was tabulated and some separations of transition metals outlined. The order of extraction of metal ions with carboxylic acids is the order of the relative stabilities of the metal carboxylates so an exchange or displacement reaction is possible between metal carboxylates in the solvent and a more acidic metal in the aqueous phase. For example, this exchange could occur between metal pairs such as Fe(III)/Cu(II) or Fe(III)/Co(II) *etc.* if the aqueous phase is at optimum acidity for iron, pH 3·2.

CHROMATOGRAPHIC USES OF LIQUID ION-EXCHANGERS

Chromatographic separations employing both anion- and cation-exchangers have been widely reported. The materials used to support the exchangers include silica gel, kieselguhr, polyethylene, polyglycol, cellulose *etc.*

A review of the uses of the liquid ion-exchangers TOA and HDEHP on inert supports was provided by Cerrai[65] in 1964 and supplements the information given in the previously mentioned review.[1]

Chromatographic separations with anion-exchangers. Brinkman *et al.*[66] examined the use of primary, secondary and tertiary amines in thin-layer chromatography with silica gel as support. The three amines chosen were "Primene JM-T", "Amberlite LA-1" and "Alamine-336" as representatives of each class and also as weakly, moderately and strongly absorbing anion-exchangers. Over fifty ions were examined, as the chlorides, in solutions containing from 2 to 12 mg/ml and eluted with hydrochloric acid. For silver, lead and thallium the nitrates were employed. A complete description of the apparatus and a brief outline of the identification tests applied was given and R_F values for each ion for the three amines and the silica gel without exchanger, at various hydrochloric acid concentrations, were presented graphically. To illustrate the practical uses of their experimental results the authors have given a number of useful separations which could be made, *e.g.*, (1) for the four elements Ni, Co, Mn, Zn, encountered in the $(NH_4)_2S$ group of the classical separation system; (2) Al, In, Ga: (3) As(III), Sb(III), Bi; (4) SeO_3^{2-} from TeO_3^{2-}.

The same workers[67] investigated the nature of some of the anionic chloro-complexes of cations present in the organic phase for the same three amines and for the quaternary ammonium salt Adogen 464, in reversed phase chromatography. The metals involved were copper(II), cobalt(II), manganese(II), zinc and iron(III). Irrespective of the class of exchanger, the concentration of the chloride ion in the aqueous phase or the use of hydrochloric acid or lithium chloride as the source of Cl^-, the sole metal-containing species in the organic phase were found to be $CoCl_4^{2-}$, $CuCl_4^{2-}$, $MnCl_4^{2-}$ and $FeCl_4^-$.

Brinkman and de Vries[68] have applied thin-layer chromatography to the separation of 25 metal ions from sulphuric acid and sulphate salt systems, using silica gel impregnated with the same three amines, Primene JM-T, Amberlite LA-2, Alamine-336 and also with the quaternary ammonium salt Aliquat-336, each being equilibrated with sulphuric acid before being applied to the silica gel. The metal ions were applied as 2–10 mg/ml solutions of their sulphates, and the eluents sulphuric acid, lithium sulphate or ammonium sulphate were used in a range of concentrations. High R_F values were recorded for those cations—13 out of the 25 tested—which do not form sulphato-complexes. With the remaining ions, increasing R_F values were obtained as the sulphuric acid concentration was increased but the R_F values decreased with increase in sulphate salt concentration, whether lithium or ammonium. This was taken to indicate a shift in the $SO_4^{2-} \rightleftharpoons HSO_4^-$ equilibrium with the introduction of extra hydrogen or sulphate ions into the eluent. Few analytically useful separations could be formulated for cations which have low or medium R_F values in sulphate media.

Employing Amberlite LA-2 in the thiocyanate form, Graham and Carr[69] extended the investigations of Brinkman *et al.*[70] who used silica gel as the support media. Graham and Carr employed cellulose as support and examined 68 metal ions, using 0·1–7·0*M* ammonium thiocyanate as eluent. Most of the metal ions either moved with the solvent front or were strongly complexed and remained at the point of application. Useful R_F values were obtained for VO(II), Ni, Tl, Pb, Bi, Ag, Cu(II), Cd and Mn(II), and these last five ions were studied further for the effects of the degree of impregnation of the stationary phase with the exchanger.[71] Manganese(II) ions migrated at all concentrations of ammonium thiocyanate from 0·1 to 7·0*M*; silver ions migrated at eluent concentrations >0·5*M* and moved with the solvent front with eluent >5*M*. Copper(II) ions migrated with $[SCN^-] > 1M$, and cadmium and bismuth ions at >2*M* thiocyanate, the R_F values increasing regularly as the concentration of the thiocyanate increased. Increasing the exchanger loading of the cellulose caused a decrease in the R_F values for the metals studied, with 4*M* ammonium thiocyanate as eluent.

Graham *et al.*[72] reported on the use of thin-layer chromatography with Primene JM-T on cellulose, using hydrochloric acid eluents. By variation of the concentration of the impregnating amine over the range 0·1–0·7*M* the R_F values of some of the metal ions were changed significantly. A linear relationship was established between the logarithm of the concentration of the impregnant solution up to 0·5*M* and the R_M values. The R_M value is given by

$$R_M = \log_{10}\left(\frac{1}{R_F} - 1\right)$$

Separations which were shown to be possible in the primene JM-T hydrochloride/hydrochloric acid systems included the following.

1. Be, Mg and alkaline earths, in 8–9*M* acid.
2. Zn and Fe(III) from Ti(II), VO(II), Cr(III), Mn(II), Co(II), Ni, Cu(II), with Zn migrating with 1*M* acid (R_F 0·56) and Fe stationary with acid >8*M*, the remaining

elements having R_F values between 0·7 and 0·9 for 6–9*M* acid and R_F values around 1·0 for acid <5*M*.

3. Al, Ga, In and Tl, separated in the acid range 6–9*M*.
4. Sn(II), Sn(IV) and Pb(II) separated over the whole acid range 1–9*M*.
5. Sb(III) separated from Bi over the range 1–9*M*.

A similar dependence of R_F and amine concentration was reported by Brinkman *et al.*[73] who used various amines on silica gel and 7*M* hydrochloric acid as eluting agent. Typical results obtained are shown in Table 2 for Cu, Co, Bi and Zn with Amberlite LA-1. The authors considered that a 1 : 1 mixture of Amberlite LA-1 and TIOA could provide a useful mixture for separation of some metal chloro-complexes. Experiments showed that this was the case; the amine mixture gave R_F values intermediate between those found for the separate components. The amines could be classified according to adsorption strength in hydrochloric acid media as follows.

Table 2. Dependence of R_F values and migration rate of eluent on molarity of amine HCl solution (Amberlite LA-1 was used as liquid ion-exchanger and approx. 7*M* HCl as the eluting agent)[73]
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	R_F value at amine concentration shown			
Ion	0·05*M*	0·10*M*	0·15*M*	0·25*M*
Cu	0·79	0·64	0·45	0·30
Co	0·76	0·62	0·46	0·23
Bi	0·89	0·72	0·58	0·38
Zn	0·32	0·17	0·11	0·02
Length of run, *mm*	35	32	26	20
Time, *min*	10	10	10	20

TIOA > Adogen 364 ~ Adogen 368 ~ Alamine 336 ~ tetrahexylammonium
~ TNOA > Aliquat 336 ~ Adogen 464 > Hyamine 1622 > Amberlite LA-1
~ Amberlite LA-2 > Hyamine 2389 > Primene JM-T

Graham *et al.*[74] examined the quantitative determination of zinc after thin-layer chromatography on cellulose impregnated with Primene JM-T. 2-(Pyridylazo)-2-napththol (PAN) was employed as chromogenic reagent to locate the zinc spots, with hydrochloric acid as eluent. The Joyce-Loebl "Chromoscan" recording and integrating densitometer with thin-layer attachment was employed in the reflectance mode and the spots scanned 25 times, the mean of the integrator counts being taken. An error of about 5% was achieved at the 1-μg level of zinc; the greatest source of error in the procedure was associated with the application of the PAN solution to the chromatographic layer. The spots themselves showed no significant fading after more than 30 min. The same authors[75] compared the results obtained by densitometric measurement with those from removal of the chromatographic spot and subsequent spectrophotometric measurement with PAN as chromogenic agent. The two methods gave similar degrees of accuracy but the densitometric method was very much quicker.

Pierce and Henry[76] have used TIOA as an anion-exchanger in partition chromatography. The exchanger was deposited on poly-(vinyl chloride/vinyl acetate) copolymer, available commerically as "CORVIC R51/83." Distribution ratios were obtained for the

CORVIC/TIOA, by using batch extraction with 1 g of solid and 20 ml of aqueous phase, and the separations were made on columns 180 mm long × 6 mm diameter, radiotracers being used to follow the elution. Schemes for chromatographic separations were designed from the distribution ratios, at different hydrochloric acid concentrations, obtained in the batch extractions. Useful separations included (1), As, Ge and In, employing 8·6*M* hydrochloric acid for As elution, 1·05*M* hydrochloric acid for Ge and water for In; (2) Mn, Co, Cu, Zn, employing 5·89*M* hydrochloric acid for Mn, 3·09*M* hydrochloric acid for Co, 0·55*M* hydrochloric acid for Cu and water for Zn.

Using columns of TOA on polytrifluorochloroethylene ("KEL-F") as inert support[77] Espoñal and Marafuschi determined tungsten in stainless steel. Radioactive tracers were employed and the ions added to the column in hydrochloric acid solution. Chromium was easily eluted with 10*M* hydrochloric acid, then tungsten was eluted with 7*M* hydrochloric acid + 1*M* hydrofluoric acid. Cobalt moved down the column only very slowly while iron remained firmly held at the top. Although the method was intended for stainless-steel analysis no mention was made of the part played by nickel.

Przeszlakowski[78] employed various liquid anion-exchangers in the thiocyanate form to develop chromatograms of metal ions on paper impregnated with ammonium thiocyanate. Interesting changes in R_F values occurred for silver, mercury(II), palladium, gallium, molybdenum(IV), antimony(III), titanium(IV), manganese(II), zinc, cadmium, bismuth, indium, iron(III), uranium(IV), and cobalt(II) with changes in the concentration of ammonium thiocyanate on the paper, and changes in the solvent in which the exchangers were dissolved.

In the system Aliquat-336–hydrochloric acid[79] Stronski reported the separation of the radioisotopes ^{51}Cr, ^{185}W, ^{99}Mo, ^{54}Mn, ^{65}Zn, ^{60}Co, ^{59}Fe, ^{182}Ta, ^{186}Re, ^{234}Th, ^{233}Pa and ^{235}U. A column of KEL-F was treated with 0·1*M* Aliquat-336 and the ions successfully eluted with various concentrations of hydrochloric acid. The same worker[80] reported on the separation of In, Cd, Sn, Te and Sb, using Amberlite LA-2 on silica gel and eluting with various concentrations of hydrochloric acid.

Employing Aliquat-336 on a column of "Plaskon" (a trifluorochloroethylene polymer), Huff[81] studied the separation of americium, yttrium and the rare earths in the thiocyanate system. Gradient elution with ammonium thiocyanate from 2 to 0·3*M* achieved only partial separation of 1-mg quantities of rare earths on a 15-cm column, breakthrough of the next metal in the series occurring before the previous metal was completely eluted. Owing to this cross-contamination no clear-cut separations of rare-earth elements was possible.

Ruthenium in aqueous nitric acid solutions forms a series of nitrosylruthenium compounds of general formula $RuNO(NO_3)_x(OH)_y(H_2O)_z$ where x, y and z vary from 0 to 5, and the co-ordination number is 6. The relative concentration of the different species is affected by acid concentration, solution age and temperature. Hallaba *et al.*[82] extracted these nitrato complexes, using various tertiary amines, and showed that extraction decreased with increasing nitric acid concentration and increased with amine concentration. High concentrations of aluminium and sodium nitrates did not greatly influence the degree of extraction obtained. The organic solvent employed had no significant effect on the extraction pattern for ruthenium but there were changes in the values of the distribution ratios.

Leene *et al.*[83] described the preparation of trialkylamine oxide by the action of aqueous hydrogen peroxide on the tertiary amine Alamine 336-S. A 0·1*M* solution of this oxide in chloroform was equilibrated with 2*M* hydrochloric acid. The solution was mixed with silica gel and the slurry was coated onto microscope slides. With 0·1–11*M* hydrochloric acid or 0·1–9·5*M* lithium chloride in 0·5*M* hydrochloric acid as eluent, the R_F values of thirty cations were determined. Comparison was made with the R_F values obtained with trioctylarsine oxide prepared and used in a similar fashion.

The separation of niobium and titanium in microgram amounts and in all ratios from 1 : 100 to 100 : 1 was described by Alimarin *et al.*[84] The separation was made on a column of PTFE granules coated with 0·5*M* TOA, with various concentrations of hydrochloric acid as eluent.

Chromatographic separations with cation-exchangers. The use of liquid cation-exchangers for chromatographic separations has been restricted almost entirely to di-(2-ethlhexyl)orthophosphoric acid (HDEHP). Raaen[85] used HDEHP in thin-layer chromatography on polytetrafluoroethylene ("Fluoroglide 200 TWO 218," from Chemplast Inc., N.J., U.S.A.) Thin films of the PTFE were prepared and dried on "Mylar" polyester film (Kensington Scientific Corp., U.S.A.), then 1 μl of solution, containing the radiosotope under investigation dissolved in nitric acid, was placed on the start and allowed to dry. Each chromatogram was developed with 5 ml of 0·5*M* HDEHP in IBMK, about 1 hr being required, and the films were dried. The chromatograms obtained were placed in contact with X-ray film for 2 or 3 days and the films then developed. The autoradiograms, produced for 31 metal ions, gave pictures which naturally were the reverse of the usual type of chromatogram, since those ions most strongly complexed by the exchanger moved with the solvent front while uncomplexed ions remained at the origin. Numerous separations were shown to be possible under the conditions selected. It is possible that still further useful separations could be evolved by use of an alternative solvent and slight changes in acidity of the layer of PTFE.

Pierce and Flint[86] employed HDEHP in conjunction with silica gel and granulated poly(vinyl chloride) (CORVIC D55/3, I.C.I. Ltd.) for thin-layer chromatography. Separations of mixtures of rare earths, of strontium and yttrium, and of nickel, copper, silver, zinc and iron, were shown to be satisfactory with hydrochloric acid as eluent. A similar study by Herrmann[87] used HDEHP on silica gel, with 1*M* hydrochloric acid, to separate europium and gadolinium.

The separation of fission products from uranium(VI) is a complex problem. Tomazic and Siekierski[88] employed HDEHP on a support of kieselguhr (ratio 1 : 10) to achieve a useful degree of separation. Uranium reacts strongly with HDEHP even in highly acidic solutions and was retained on a column of reagent and kieselguhr quite well when other metal ions were eluted with nitric acid. A sample was prepared in 0·1*M* nitric acid containing caesium, strontium, barium, lanthanum, cerium(III), europium, terbium, yttrium, zirconium and a quantity of uranium equivalent to 50% of the ion capacity of the chromatographic column. The caesium, strontium and barium were eluted with 0·5*M* nitric acid as one group, followed after a short break by lanthanium and cerium. When the concentration of acid was increased to 5*M*, europium, lead and yttrium were eluted. Finally the column was treated with concentrated hydrochloric acid, and the uranium was eluted and the zirconium remained on the column.

Employing paper treated with HDEHP Cerrai and Ghersini[89] examined 67 cations in the hydrochloric acid system. The chromatographic paper used was Whatman No. 1. (CRL/1 type), spots with a volume of 0·05 ml were applied (containing approx. 1×10^{-7} equivalents of the cation concerned) and elutions made with hydrochloric acid at concentrations between 1×10^{-4} and $10M$. The results obtained showed good agreement with the literature on liquid/liquid extraction, the R_F value of any ion being related to the extraction coefficient E_a of the same ion in the analogous liquid/liquid system by the well-known relationship

$$\log\left(\frac{1}{R_F} - 1\right) = \log E_a + \log k$$

where k is a constant depending on the chromatographic conditions. A discussion of the behaviour of the 67 ions examined was included and separations which might be useful in analysis were suggested.

Cerrai and Ghersini[90] examined the separation of the alkali and alkaline earth metals, using Whatman paper No. 1, CRL/1 type, treated with HDEHP. The metal ions were placed on the paper as chlorides and eluted with various concentrations of acetic acid from 0·1 to $3M$. A number of potential separations were found including Ca/Sr, Mg/Ba/Ca, Mg/Ca, Na/Ca/Sr, Cs/Sr, Cs/Ca/Sr.

A comparison of the cation-exchangers HDEHP and H_2EHP (2-ethylhexyldihydrogen phosphate) on Whatman No. 1 paper, for the separation of metal ions, was made by Lyle and Nair.[91] When the chromatograms were developed with hydrochloric acid those employing H_2EHP were found to be inferior to those employing HDEHP for similar metals such as lanthanides. Good separations were obtained with either ester for Fe(III) and Co(II), and HDEHP-impregnated paper could be used to separate Au(III) and Pt(IV). Table 3 shows how the separation factors for iron and cobalt were found to vary with the eluent concentration for the two exchangers.

Table 3 R_F values and separation factors for iron(III) and cobalt(II)[91]
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	HDEHP			H_2MEHP		
[HCl], M	R_F(Fe)	R_F(Co)	Sepn. factor	R_F(Fe)	R_F(Co)	Sepn. factor
0·10	0·0	0·84	—	—	—	—
2.0	0·0	0·98	—	0·0	0·97	—
4·0	0·11	0·90	8·2	0·08	0·86	11
6·0	0·64	0·90	1·4	0·33	0·83	2·5
8·0	0·03	0·87	29	0·67	0·86	1·3

Conditions for the separation of calcium, strontium and barium on silica columns loaded to 13% with HDEHP, were reported by Jaskolska.[92] Up to 0·3 mg of total metal ions was absorbed on the column and selective eluents were employed—barium was eluted with $0{\cdot}5M$ sodium nitrate at pH 3·2, strontium with $0{\cdot}5M$ sodium nitrate at pH 2·0, then calcium with $0{\cdot}5M$ sodium nitrate at pH 0·8, the pH being adjusted with nitric acid.

An investigation by Mikhailichenko and Pimenova[93] into the use of HDEHP on columns of silica gel for the separation of the rare-earth metals has been reported. Radioactive tracers ^{153}Gd, ^{160}Tb, ^{159}Dy, ^{166}Ho, ^{169}Er, ^{170}Tm, and ^{90}Y were applied to the column in $0{\cdot}1M$ hydrochloric or nitric acid. Selective elution was attempted, employing various concentrations of hydrochloric and nitric acids, but only the pairs Dy–Y and Tb–Y showed satisfactory separation, with 2·6*M* nitric acid at 40°.

In two papers, Cerrai and Ghersini[94,95] demonstrated the separation of aluminium, gallium, indium, thallium, iron(III), nickel and cobalt(II), using paper impregnated with HDEHP. Changes of R_F values with 0·1–10*M* hydrochloric acid and different concentrations of HDEHP showed some useful separations were possible. Combining their results with other published work[96,97] the authors considered the following combinations of elements could be separated satisfactorily: Be/Fe/Al/Sr with 7·5*M* hydrochloric acid; Ti/Ga/Fe/Tl/U/Ba/Ca/Ni with 8*M* hydrochloric acid; Zr/Fe/Y/In/Ni with 2*M* hydrochloric acid; Ti/Fe/Tl/U/Ba/Sr with 8*M* hydrochloric acid; Ga/Fe/Ba/Mn with 7*M* hydrochloric acid; Y/Ga with 1·5 or 7*M* hydrochloric acid.

MISCELLANEOUS

For the determination of gallium in the presence of aluminium, Levin and Balakireva[98] used the mixed solvents H_2EHP and TBP (tributyl phosphate). From a sulphuric or hydrobromic acid solution, at pH 4–5, gallium and aluminium were extracted with 2*N* H_2EHP (2-ethylhexyl dihydrogen phosphate) in heptane, any ferric iron present being previously reduced with ascorbic acid. The extract was washed twice with perchloric acid then once with water. Aluminium was removed from the organic phase by mixing with an equal volume of TBP and washing with 7*N* sulphuric or hydrobromic acid. To recover the gallium the organic phase was treated twice with 4*N* sulphuric acid. The determination of the gallium was completed by adding an excess of 0·01*M* EDTA, heating to 70°, neutralizing to Congo Red with ammonia solution, buffering to pH 5 with acetate buffer and titrating excess of EDTA with 0·01*M* zinc nitrate with Xylenol Orange as indicator.

A similar technique using a mixed extractant was described by Watanabe.[99] The extractant was a mixture of both cation- and anion-exchangers in carbon tetrachloride. Various concentrations of HDEHP up to 15% with 0·5 or 5·0% Primene JM-T were employed. Thorium, iron(III), zinc, lanthanum, indium and cerium(III) could be extracted from 0·01–0·1*N* sulphuric acid media. The effects of changes in ligand and acid concentration were given and an explanation of the results was proposed.

Blasius and Finkenauer[100] described the preparation of an azo dye by coupling diazotized anthranilic acid and 4-dodecylphenol. This dye was then employed as a liquid ion-exchanger, as its ammonium salt dissolved in carbon tetrachloride, chloroform, benzene or trichlorobenzene, to extract cations. Separation coefficients for calcium, strontium, beryllium and aluminium were reported and a method given for the quantitative separation of strontium from concentrated alkali metal salt solution.

The use of HDEHP as stationary phase in gas chromatography was outlined by Ilie *et al.*[101] A solution of HDEHP in diethyl ether was used to treat silaned "Chromosorb W" (0·18–0·25 mm particle size), the product being stirred at room temperature until all the ether had evaporated, leaving a product containing 15% of the exchanger. The Chromosorb was then made into columns (3 m × 6 mm) and used in the chromatographic study of various organic compounds vaporized at 150°. Hydrogen was used as carrier gas and the columns were operated at 70°, 90° and 110°. Satisfactory separations were achieved for benzene and cyclohexane, for C_1–C_4 alcohols and C_3 and C_4 ketones, and also for various chlorinated derivatives of methane and ethane.

For the determination of long-chain quaternary ammonium salts, Olcina and Palomino[102] suggested the use of Methyl Red. The complex of the quaternary ammonium salt with Methyl Red in 0·1M sodium carbonate was extractable into a 19 : 1 benzene–octanol mixture. The colour was developed either with aqueous ammonia-ethanol mixture followed by spectrophotometric measurement at 400 nm or with dilute hydrochloric acid–ethanol mixture, measurement then being at 510 nm.

For the determination of iron(III) by complexometric titration with EDTA, with thiocyanate as indicator, Fujimoto *et al.*[103] recommended the addition of an amine to improve the end-point. The ferric iron solution was buffered to pH. 2·8, a small quantity of ammonium thiocyanate solution was added, followed by 1 ml of 10% Amberlite LA-1 in carbon tetrachloride. The solution was then titrated slowly with 0·01M EDTA, with vigorous shaking and heating to 60° near the end-point, which is indicated by a sharp change in colour from red to pale yellow.

A use of liquid ion-exchangers which is of recent origin is in the preparation of ion-selective electrodes, such as those available from Corning, Orion or Beckman. For example, in the case of nitrate ions the Corning exchanger contains tridodecylhexadecylammonium nitrate in n-octyl *o*-nitrophenyl ether as the liquid ion-exchanger. Employing this Corning exchanger, Davies *et al.*[104] described the preparation of nitrate ion-exchange membranes. The exchanger (0·42 g) was added to a solution of 0·177 g of PVC in 6 ml of tetrahydrofuran. The solution was poured into a glass ring (33 mm i.d) resting on a glass plate and the organic solvent was allowed to evaporate to give a master membrane, which was then cut by means of a cork borer into discs of 6 mm diameter, suitable for inserting into the electrode. A similar nitrate-sensitive electrode was prepared by Coetzee and Freiser,[105] employing a 10% solution of methyltrioctanoylammonium nitrate in decanol as exchanger. Moody *et al.*[106] described the preparation of a calcium-selective electrode by incorporating a calcium liquid ion-exchanger in a membrane based on PVC and later reported that for a functional membrane a minimum of 20% PVC was found to be necessary. A recent publication by Moody and Thomas[107] devotes an entire chapter to the subject of liquid ion-exchanger electrodes and is a useful background for further work on this subject.

THEORY ASSOCIATED WITH LIQUID ION-EXCHANGE

It was noted in the 1964 review[1] that two of the major obstacles to the advance of liquid ion-exchange techniques were the lack of knowledge of the basic principles involved and adequate means of assessing the relative "strengths" of the exchangers. Some eight years later the theory of liquid ion-exchange has advanced considerably, due to many workers. Probably the largest contribution has been made by the Department of Inorganic and Structural Chemistry at the University of Leeds, England. Workers under Professor H. M. N. H. Irving have published a number of papers covering extractions of particular ions from various media, or of various ions from particular media, with an excellent breakdown of the factors involved. In a paper in 1965, Irving and Damodaran[108] examined the determination of perchlorate in the presence of other halogen acids by means of a coloured liquid anion-exchanger. The coloured exchanger was a quaternary erdmannate obtained by shaking a solution of tetrahexylammonium iodide in 1 : 4 IBMK–xylene solution with an aqueous solution of Erdmann's salt, $[NH_4]^+[Co(NH_3)_2(NO_2)_4]^-$. The coloured liquid ion-exchanger had a molar absorbtivity of approximately 10^4 $l.mole^{-1}.cm^{-1}$, and on equilibration with an aqueous solution containing perchlorate ions the coloured erdmannate ion was displaced and there was a corresponding decrease in the absorbance of the organic phase. Methods for the calculation of the equilibrium constant for this reaction were outlined from the measurements of the absorbances of the aqueous and organic phases and the relevant molar absorbtivities.

Two papers by Irving and Nabilsi[109] in 1968 examined the extraction of cupric and cuprous copper by a solution of quaternary n-hexylammonium chloride in ethylene dichloride. Increasing the concentration of chloride ions in the aqueous phase increased the degree of extraction of copper(II) but decreased that of copper(I). Irving and Damodaran[110] extracted silver from hydrochloric acid solutions, using tri-n-hexylammonium and tetra-n-hexylammonium chloride in 1,2-dichloroethane. Silver was added as radioactive tracer, with a half-life of 274 days, and measurements of activity in aqueous and organic phases enabled conclusions to be drawn about the anionic complexes formed by silver in hydrochloric acid. As was the case with copper(I) the univalent ion Ag^+ showed a decrease in extraction as the chloride concentration was increased.

Conflicting results by other workers on the extraction of indium induced Irving and Damodaran[111] to examine the extraction of indium from aqueous solutions of halogen acids and thiocyanates. It was shown InI_4^- was extracted in preference to $InBr_4^-$, and $InBr_4^-$ in preference to $InCl_4^-$. This is the reverse of the stability of these complex ions. The course of the extraction curve was found to be governed by the activity of the halide ions and it was noted that the plots for extraction from hydrochloric acid, lithium chloride and sodium chloride media could be superimposed. The nature of the ions present in both halogen acid and thiocyanate media was elucidated.

Irving and Damodaran[112] noted the tendency for the tetracyano complexes of zinc $[Zn(CN)_4^{2-}]$, cadmium $[Cd(CN)_4^{2-}]$ and mercury $[Hg(CN_4)^{2-}]$ to be extracted by tetrahexylammonium salts in IBMK. This was examined further for the extraction of mercury(II), when it was found that the anions $Hg(CN)_4^{2-}$ and $Hg(CN)_3^-$ were extracted, the latter species probably being solvated. Further work by the same workers[113] covered the complex cyanides of gold, nickel, palladium, platinum, copper and iron. The extraction constants for these metals were discussed in terms of the size and stereochemistry of the complex anions. Desreux[114] has examined the question of the association of water with long-chain alkylammonium salts such as TLA–HCl, TLMA–SCN (trilaurylmethylammonium thiocyanate) and TLMA–Cl. The infrared and n.m.r. spectra were recorded for the carbon tetrachloride solvent before and after shaking with an aqueous phase, and Karl Fischer titration was used to obtain the water content of the solvent. The results showed that trilaurylmethylammonium thiocyanate was monohydrated in the organic solvent whereas the trilaurylmethylammonium chloride was present in the form of several polyhydrated species.

The distribution of lithium chloride and lithium bromide between aqueous lithium chloride solutions and a benzene solution of Aliquat-336 was studied by Scibona *et al.*[115] Thermodynamic relations were derived for lithium chloride distribution between the two phases, and a thermodynamic equation was derived for the dependence of the observed distribution coefficient of lithium bromide on activity coefficients and concentrations. Explanation was offered for the deviation of the observed distribution coefficient from a simple mass-action law. Using TOA,[116] Sato studied the distribution equilibria of nitric, hydrochloric, perchloric, sulphuric and phosphoric acids between aqueous solutions and benzene solutions of the exchanger. Infrared and partition results indicated that the extraction of the acids was governed by the formation of the monoamine salts of monobasic acids and of the mono- di- (and tri-) amino salts of di- (and tri-) basic acids.

The extraction of chromium(III) from aqueous EDTA (H_4Y) solutions with tetra-n-hexylammonium chloride in dichloroethane was examined by Irving and Al Jarrah.[117] Maximum extraction occurred at pH 4·7. Only the violet complex $CrY(H_2O)^-$ was extracted as the ion-pair $[NR_4]^+[CrY(H_2O)]^-$ (where R = n-hexyl) over the pH range 3·6–6·0. The neutral species $CrHY(H_2O)$ and the two anionic species $CrY(OH)^{2-}$ and $CrY(OH)_2^{3-}$ were not extractable.

A very useful paper by Eubanks,[118] draws attention to limitations which must be imposed on the use of amines, owing to degradation reactions occurring. Available evidence indicated that the amines were frequently degraded by the process chemicals used. Amine reactions were initiated either photochemically or radiolytically and the reaction path usually involved initial reaction of a methylene hydrogen on the carbon atom α to the nitrogen. Tables included showed the radiolysis products for a number of amines and references were given for work which had been reported on air-oxidation of amines, their reactions with the organic solvents most commonly employed, and with reagents such as nitric and nitrous acids.

PRESENT AND FUTURE PROSPECTS FOR LIQUID ION-EXCHANGE

It is 24 years since Smith and Page[119] introduced the technique of liquid ion-exchange. Very little work was done with this analytical technique, except in the field of the transuranic elements, until the early 1960's, despite its obvious possible advantages. This may have been due to the revival of interest in solvent extraction, employing the readily available chelating agents, and the introduction of the synthetic-resin exchangers which took place around the same period. During the last ten years or so it has been realized that liquid ion-exchange has much to offer the analyst—providing as it does both the speed of separation associated with solvent extraction and the selectivity offered by ion-exchange under appropriate conditions. "Where does liquid ion exchange go from here?" is not an easy question to answer. That it will continue to be used increasingly for liquid/liquid extractions and for chromatographic separations is certain. Extractions with mixed exchangers, such as two anion-exchangers[73] or one cation- and one anion-exchanger,[99] or a neutral co-reagent and an exchanger,[98] may open up new possibilities. The use of these exchangers in gas chromatography[101] could be a pointer to further applications. Certainly, the increasing use being made of the organic phase directly, without back-extraction, increases the attractiveness of liquid ion-exchange, and its incorporation as a separation stage in inorganic analysis will become commonplace.

The recent introduction of ion-selective electrodes containing liquid ion-exchangers, or incorporating membranes prepared from exchangers evaporated onto inert supports such as PVC or Bakelite[104–107] has opened up new fields of application, the likely limits of which cannot yet be seen.

APPENDIX

Commonly used anion-exchangers

Adogen 364, a tri-n-alkylamine with 27 carbon atoms on average, consists principally of octyl (60%) and decyl (33%) chains. It contains minimally 95% tertiary amine In the yellow turbid liquid a waxy deposit may form on standing. Average m.w 380

Adogen 368, a pale yellow tri-n-alkylamine, of which the alkyl groups consist principally of octyl (40%), decyl (25%) and dodecyl (30%) chains, has a minimal tertiary amine content of 95%. Average m w 430.

Adogen 464, a methyltri-n-alkylammonium chloride with a yellow-brown colour, has a minimal quaternary ammonium salt content of 92% Average m.w 431.

Alamine-336, a pale yellow liquid ("tricaprylamine") is a tertiary amine with three straight-chain alkyl groups, mainly octyl and decyl. The number of carbon atoms totals 26–32 and the average m w. of the tertiary amine content (min. 90%, typical 95%) is 392.

Aliquat-336, a yellow viscous liquid, obtainable as the chloride, is a methyltri-n-alkylammonium salt ("methyltricaprylammonium chloride") with 27–33 carbon atoms on average. The alkyl groups mainly consist of octyl and decyl chains, and the average m.w. is 475

Amberlite LA-1. A fairly viscous yellow liquid (viscosity at 25° is 72 cp) is an *N*-dodecenyltrialkylmethylamine. The unsaturated amine contains 24–27 carbon atoms and has an average m.w. of 372.

Amberlite LA-2, a yellow liquid with a viscosity of 18 cp at 25°, is a saturated secondary amine, *N*-lauryltrialkylmethylamine, with an average m.w of 374.

Primene JM-T is a yellow primary trialkylmethylamine with 18–24 carbon atoms and an average m w of 311.

Tribenzylamine, TBA, is a white crystalline solid of m.w. 287 (>99% pure).

Tri-iso-octylamine, TIOA, a nearly colourless liquid, has m.w. 353. It contains a mixture of dimethylhexyl, methylheptyl, *etc.* chains, principally 3,5-, 4,5-, and 3,4-dimethylhexyl.

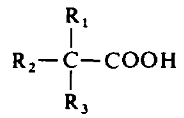
Tri-n-octylamine, TOA, is a colourless liquid of m.w 353.

Commonly used cation-exchangers

Di-(2-ethylhexyl) phosphoric acid (D2EHPA, DEHPA or HDEHP). A dialkylorthophosphoric acid, the exchanger is supplied as a commercial grade and needs purification before use in analysis The method described in *U.S.A. At. Energy Comm. Rept.* ORNL 3548 (1964) is recommended. The monoacidic liquid, after purification, has a sp gr. of 0·97 and m.w. 322. It is the hydrogen atom of the -OH group which undergoes exchange with an equivalent cation.

Dinonylnaphthalene sulphonic acid (DNS). This is a mixture of isomers resulting from the sulphonation of dinonylnaphthalene, which itself is prepared by controlled alkylation of naphthalene with nonene, and is usually supplied by the manufacturers as a 45–50% solution in n-heptane. It is the hydrogen atom of the $-SO_3H$ group which undergoes exchange, as with the sulphonated-resin exchangers.

Versatic 911. A mixture of saturated tertiary monocarboxylic acids of C_9, C_{10} and C_{11} chain length, manufactured from C_9–C_{11} olefines. The structure of Versatic 911 may be represented by



$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{C}}-COOH$$

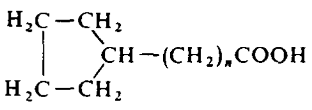
and at least one of the R groups is always methyl. The particular structure of the material distinguishes it from the common straight-chain fatty acids of similar molecular weight. The average m.w. of the water-white Versatic 911 is 175, and the sp.gr. 0·92. The extraction of the metal ion proceeds in a manner analogous to the overall reaction for the cation-exchange resins:

$$R{\cdot}COOH + XCl \longrightarrow R{\cdot}COOX + HCl$$

Excessive contact with the skin should be avoided.

Naphthenic Acids N.A 180 and N.A 230

These acids have the general formula



It will be seen from this formula that they are saturated monocyclic carboxylic acids, the carbon ring being almost invariably five-membered. The two most common naphthenic acids are designated N.A 180 and N A. 230, these numbers representing the acid value in terms of mg of KOH required to neutralize 1 g of the material. They are both clear, bright liquids of sp.gr. 0·98 and contain 8–12% w/w of neutral oil.

Naphthenic acids are not highly toxic, and provided any affected parts of the skin are washed well with soap and water, any slight skin irritation caused by exposure to these acids is not unduly dangerous.

Some manufacturers of these ion exchangers are as follows,

The Adogens	Archer-Daniels-Midland Co, Minneapolis, Minn. U S A

The Amberlites and Primene JM-T	Rohm and Haas Co , Philadelphia, Pa. U.S.A.
Alamine and Aliquat	General Mills Inc., Kankakee, Ill. U.S.A
The remaining anion-exchangers	Available from a number of the general suppliers of laboratory chemicals
Di-(2-ethylhexyl) phosphoric acid	Available from a number of sources, including. Van Waters and Rogers Co. Inc., Seattle, Wash U.S.A Virginia Carolina Chemical Corp., Richmond, U.S.A Union Carbide Chemicals Corp., 270 Park Avenue, New York, N Y 10017, U.S.A. Koch-Light Laboratories Ltd., Colnbrook, Bucks., England
Dinonylnaphthalene sulphonic acid	R T Vanderbilt Co. Inc., 230 Park Avenue, New York, N Y. 10017, U.S.A.
or	King Organic Chemicals Inc., 415 Lexington Ave., New York, N.Y. 10017, U.S.A
Versatic and Naphthenic acids	Shell Co. Ltd., London, ENGLAND.

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Zusammenfassung—Es wird eine Übersicht über neuere Anwendungen flüssiger Ionenaustauscher in der anorganischen Analyse gegeben

Résumé—On présente une revue sur les emplois récents des échangeurs d'ions liquides en analyse minérale

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THE KINETICS OF OXIDATION OF SELENOSEMICARBAZIDE BY OXYGEN IN THE PRESENCE OF CUPRIC IONS

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Summary—In acidic medium selenosemicarbazide undergoes oxidation by oxygen, dissolved in water, in the presence of copper(II) as a catalyst The oxidation product exhibits an activating effect The kinetics of the reaction have been investigated and the kinetic equations deduced both for small and high concentrations of the oxidation product The constants involved in the kinetic equations deduced have been calculated. The proposed mechanism of the reaction agrees with the experimental results. The oxidation product is supposed to be the bis-selenosemicarbazidinium cation The postulation of formation of this cation is based on the electronic structure and reactivity of selenosemicarbazide. The reaction can be used for copper determination

Crystalline selenosemicarbazide–copper(II) complexes have been reported.[1] In the course of our study of the formation of such complexes in aqueous solutions, we have found that the yellow solution containing selenosemicarbazide–copper(II) in acidic medium is decolorized on standing. The decrease in the absorbance has been found to be due to disappearance of selenosemicarbazide (SSC). The reaction rate depends on the concentrations of copper, acid and oxygen, dissolved in water. The copper acts as a catalyst and the oxygen concentration decreases with time. The conclusion drawn is that SSC undergoes a catalytic oxidation by oxygen, dissolved in water, in the presence of copper(II).

It has been found that other metal ions either do not catalyse this reaction at all or have much lower catalytic activities. Therefore this reaction can be used to develop a rather sensitive and selective kinetic method for copper determination.

EXPERIMENTAL

Reagents

SSC was prepared by the method reported by Huls and Renson.[2] The purity was checked by means of the melting point

Copper solutions were prepared from analytically pure cupric nitrate and standardized electrolytically.

Chemically pure perchloric acid was used for the acidic medium, because it has no absorption in the ultraviolet region, has little tendency for complexation or ion-association and does not oxidize SSC in the absence of cupric ions or/and oxygen

Procedure

Absorbances were measured at 262 nm, the wavelength of maximum absorption by SSC in strongly acidic medium, and at 364 nm, near the absorption maximum of the SSC–Cu(II) complex (350 nm)

Reaction rates were determined by graphical differentiation of the absorbance *vs* time curves

RESULTS AND DISCUSSION

Figure 1 shows a typical absorbance–time curve, which is similar to the curves of autocatalytic reactions. Therefore we have reason to suppose that the reaction product activates the catalyst, and the following dependence is to be examined

$$\frac{dC_X}{dt} = f(C_{SSC}, [H^+], [O_2], C_{Cu}, C_X)\cdot F, \tag{1}$$

where C represents the total concentration of the species indicated by suffix, the equilibrium concentrations are in square brackets, X is the oxidation product, and F is the activity factor.

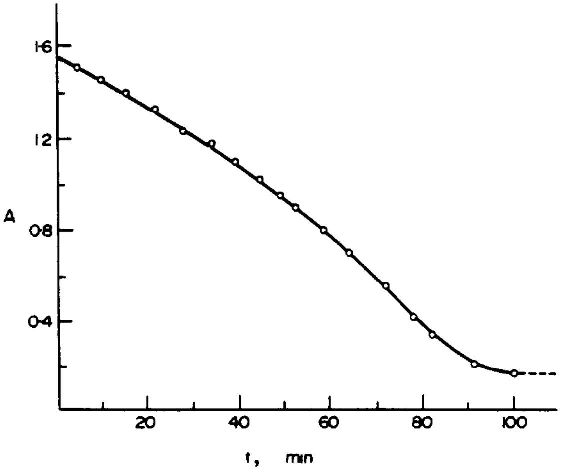


Fig. 1. The change of absorbance with time

λ 262 nm, $l = 1$ cm, $C^0_{SSC} = 2 \times 10^{-4}M$,
$C_{Cu} = 1 \times 10^{-5}M$, $C_{HClO_4} = 0.64M$.

In order to find the reaction-rate dependence on the SSC concentration, curves similar to that given in Fig. 1 were obtained at constant initial concentrations of all reaction components except SSC, the initial concentration of which was varied. All the curves appear identical, and this fact allows us to conclude that the rate is independent of C_{SSC}. This statement is, however, valid only in the presence of an excess of SSC relative to copper. That is why all the calculations have been made with large $C_{SSC} : C_{Cu}$ ratios.

Similarly at constant concentration of all the reaction components except copper the absorbance–time curves were measured to find the reaction order with respect to C_{Cu}. Constancy of $[H^+]$ and $[O_2]$ was achieved by using a large excess. The reaction rates were compared at equal ΔA values (ΔA = change in absorbance from the beginning of the reaction) to ensure constancy of C_X. The reaction appeared to be first-order with respect to copper.

To determine the reaction-rate dependence on the acidity and the concentration of X, we varied $[H^+]$ and plotted $-dA/dt$, which is proportional to the reaction rate dC_X/dt, against ΔA, which is similarly proportional to the reaction product concentration. The variation of the oxygen concentration in the course of reaction was neglected because this variation, as will be seen later, is insignificant. These plots, given in Fig. 2a, show

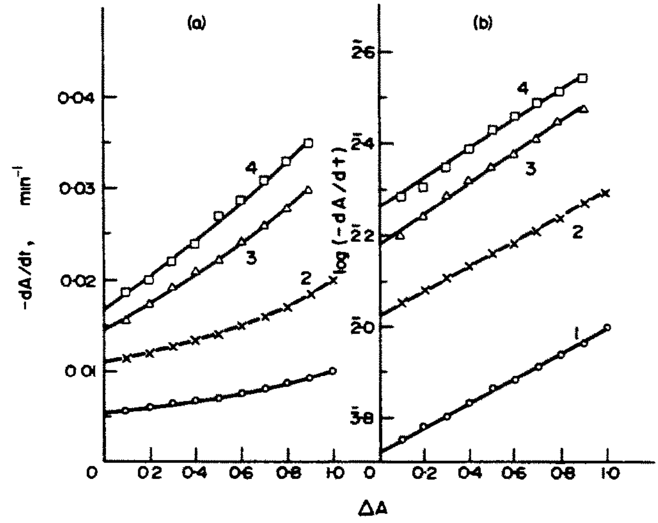


Fig. 2. Plot of the rate of absorbance change (*a*) and the logarithm of this rate (*b*) against the absorbance change from the beginning of the reaction ($\Delta A = A_0 - A$).

λ 262 nm, $l = 1$ cm, $C^0_{SSC} = 2 \times 10^{-4} M$, $C_{Cu} = 1 \times 10^{-5} M$,
$C_{HClO_4} = 0.32M$(1), $0{\cdot}64M$ (2), $0{\cdot}96M$ (3), $1{\cdot}28M$ (4)

that the higher the ΔA values the more the deviation of these curves from a straight line. A plot of the logarithm of the rate against ΔA (Fig. 2b) gives a set of parallel straight lines, with some deviations due to errors arising from graphical differentiation. It can therefore be accepted that the reaction rate depends exponentially on C_X.

To find the dependence of the reaction rate on $[H^+]$, the rate of absorbance change was plotted against $[H^+]$ at various constant ΔA values. It is clear from Fig. 3 that this dependence is linear, and the reaction is first-order with respect to $[H^+]$. Deviations at higher $[H^+]$ values may be attributed to salt effects and therefore related to the activity factor F. The kinetic equation may now be written as

$$\frac{dC_X}{dt} = K_1([O_2]) \cdot [H^+] \cdot C_{Cu} \cdot \exp(K_2 C_X) \cdot F \qquad (2)$$

This equation, however, appears to be valid only at not too high C_X values. Figure 4 shows the absorbance change when C_{SSC} and C_{Cu} are ten times the values used earlier. The curve assymptotically approaches the final value of A. Subsequent saturation of the solution with oxygen, by shaking it with air, leads to complete oxidation of SSC. So the decrease in the reaction rate is due to the dissolved oxygen being used up. After the lapse of some time from the beginning of the reaction the curve exhibits no dependence on the reaction product concentration. Probably, when C_X becomes sufficiently high, the reaction step in which the oxidation product X participates no longer determines the reaction rate and the step in which the oxygen participates becomes rate-determining. Then the kinetic equation may be written as

$$\frac{dC_X}{dt} = K \cdot [H^+] \cdot [O_2]^p \cdot C_{Cu} \cdot F \qquad (3)$$

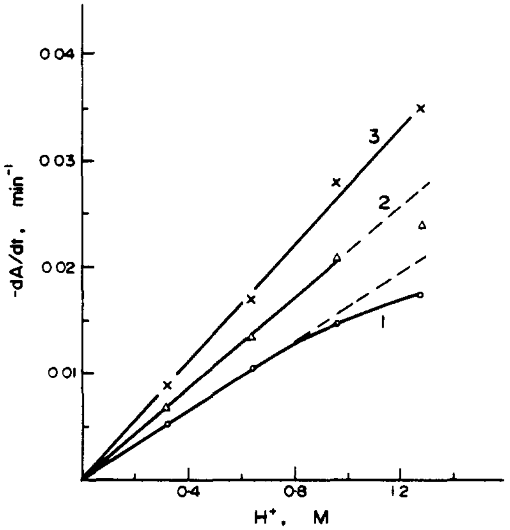


Fig. 3. Plot of the reaction rate against the hydrogen ion concentration at constant values of $\Delta A = A_0 - A$.

$\Delta A = 0$(1), 0·4 (2), 0·8 (3).

The curve in Fig. 4 allows us to find the reaction order p with respect to the oxygen concentration. Let the total reaction equation be

$$m\text{SSC} + q\text{O}_2 \longrightarrow n\text{X} \tag{4}$$

then the oxygen concentration at every instant of time is equal to

$$[\text{O}_2] = [\text{O}_2]_0 - \frac{q}{m}(C^0_{\text{SSC}} - C_{\text{SSC}}) \tag{5}$$

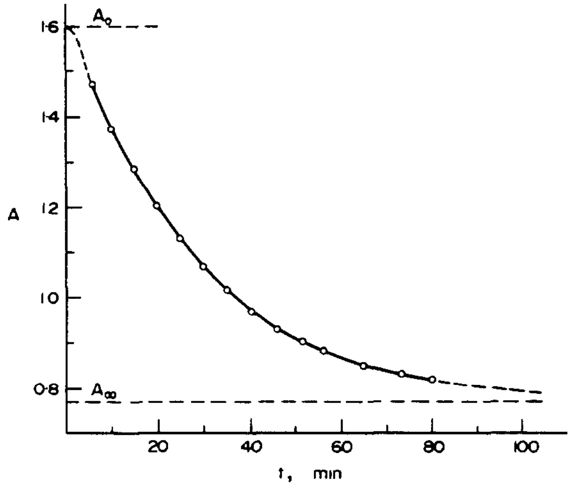


Fig. 4. The change of absorbance with time.
λ 262 nm, $l = 0·1$ cm, $C^0_{\text{SSC}} = 2 \times 10^{-3}M$,
$C_{\text{Cu}} = 1 \times 10^{-4}M$, $C_{\text{HClO}_4} = 1·6M$

where $[O_2]_0$ and C^0_{SSC} are initial concentrations. The reaction obviously stops when $[O_2]$ falls to zero and, hence, equation (5) leads to

$$[O_2]_0 = \frac{q}{m}(C^0_{SSC} - C^{\infty}_{SSC}) \tag{6}$$

where C^{∞} indicates the final concentration. Equations (5) and (6) give

$$[O_2] = \frac{q}{m}(C_{SSC} - C^{\infty}_{SSC}) \tag{7}$$

By substituting this value in equation (3) we obtain

$$\frac{dC_X}{dt} = K \cdot [H^+] \cdot \left(\frac{q}{m}\right)^p \cdot (C_{SSC} - C^{\infty}_{SSC})^p \cdot C_{Cu} \cdot F$$

Assuming $[H^+]$, C_{Cu} and F to be constant and using absorbances instead of concentrations, we obtain

$$-\frac{dA}{dt} = \text{const} \cdot (A - A_{\infty})^p$$

The plot of $-dA/dt$ against $(A - A_{\infty})$ is given in Fig. 5. At low values of $(A - A_{\infty})$, corresponding to lower $[O_2]$ and higher C_X values, the plot shows a linear dependence. The higher $[O_2]$ and lower C_X values give deviation from the straight line. This may be due to the influence of the slower step in which the oxidation product participates. So the reaction is first-order with respect to oxygen concentration, and equations (2) and (3) can be rewritten as

$$\frac{dC_X}{dt} = K_1[H^+][O_2]C_{Cu} \cdot \exp(K_2 C_X) \cdot F \tag{8}$$

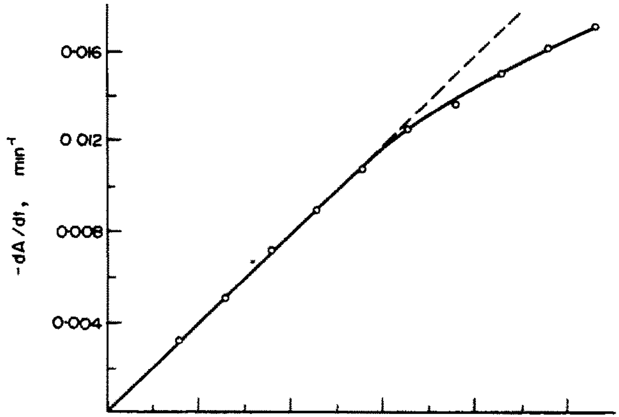


Fig 5 Plot of the reaction rate against the concentration of oxygen. λ 262 nm, $l = 0.1$ cm, $C^0_{SSC} = 2 \times 10^{-3} M$, $C_{Cu} = 1 \times 10^{-4} M$, $C_{HClO_4} = 1.6 M$.

and

$$\frac{dC_X}{dt} = K_3[H^+][O_2]C_{Cu}\cdot F \tag{9}$$

Equation (8) holds good for low values of C_X and equation (9) for high values of C_X.

The results enable us to determine the constants involved in equations (8) and (9). By using absorbances and assuming that m molecules of SSC yield n molecules of X, we obtain from (8)

$$-\frac{dA}{dt} = \frac{m}{n}\left(\varepsilon_{SSC} - \frac{n}{m}\varepsilon_X\right)l\cdot K_1[H^+][O_2]C_{Cu}\exp\left\{\frac{\frac{n}{m}K_2}{\left(\varepsilon_{SSC} - \frac{n}{m}\varepsilon_X\right)l}\cdot \Delta A\right\}\cdot F \tag{10}$$

where ε_{SSC} and ε_X are the molar absorptivities of SSC and X respectively at the wavelength employed and l is the pathlength. The value of $n\varepsilon_X/m$ can be easily found from the final absorbance of the reaction mixture: $A_\infty = n\varepsilon_X C^0_{SSC}\,l/m$. At the wavelength 262 nm $\varepsilon^{262}_{SSC} = 8{\cdot}0\times 10^3$ and $n\varepsilon^{262}_X/m = 0{\cdot}8\times 10^3$l. mole^{-1}. cm^{-1}.

The oxygen concentration can be estimated from the solubility in water,[3] approximately $2{\cdot}8\times 10^{-4}M$.

The value of K_1 is now easily determined from the slope of the straight line corresponding to $\Delta A = 0$ in Fig. 3 (assuming $F = 1$). By use of equation (10) an approximate value of $K_1 \sim 830$ n/m l^2. mole^{-2}. min^{-1} is obtained.

The value of K_2 in equation (8) can be estimated from the slope of the straight lines in Fig. 2*b* (after changing to natural logarithms). The approximate value of K_2 is $5{\cdot}0\times 10^3$ m/n l. mole^{-1}.

The value of the constant K_3 in (9) can be obtained by using Figs. 4 and 5. It can be seen from Fig. 4 that $A_0 - A_\infty = 0{\cdot}83$. This corresponds to the SSC concentration decreasing by $C^0_{SSC} - C^\infty_{SSC} = (A - A_\infty)/(\varepsilon_{SSC} - n\varepsilon_X/m)l \sim 1{\cdot}15\times 10^{-3}M$.

Dividing this quantity by the initial concentration of oxygen, $[O_2]_0 \sim 2{\cdot}8\times 10^{-4}M$, the number of SSC molecules oxidized by one oxygen molecule is obtained, *viz.* 4. Now according to (7)

$$[O_2] = \tfrac{1}{4}(C_{SSC} - C^\infty_{SSC}),$$

so (9) (using absorbances) transforms to

$$-\frac{dA}{dt} = \frac{1}{4}\cdot\frac{m}{n}\cdot K_3\cdot[H^+]\cdot(A - A_\infty)\cdot C_{Cu}\cdot F$$

Now from the straight part of the curve in Fig. 5 an approximate value of K_3 (corresponding to $1{\cdot}6M$ perchloric acid) is obtained: $K_3\cdot F \sim 1{\cdot}0\times 10^3$ n/m l^2. mole^{-2}. min^{-1}.

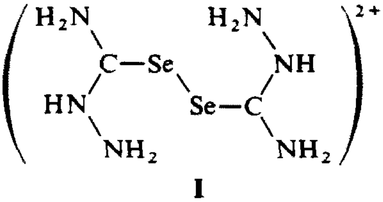
REACTION MECHANISM

In order to establish the stoichiometry of the copper(II) complex with SSC in solution the isomolar series method was used. The measurements were carried out in neutral medium (where the oxidation process does not take place) at 364 nm. Only the complex corresponding to the molar ratio Cu(II) : SSC = 1 : 2 was observed. On account of this and the composition of the complex in the crystalline state,[1] and by analogy with thiosemicarbazide–copper(II) in solution,[4] we believe that the $Cu(SSC)_2^{2+}$ complex species exists in solution. By passage of the solution through a column containing a cation-exchange resin the complex was confirmed to be positively charged.

The spectrum of the complex undergoes no change in strongly acidic medium, which shows that also under redox reaction conditions copper exists as the same species $Cu(SSC)_2^{2+}$. The absorbance measurements at 364 nm during the course of the reaction indicate that the concentration of the complex does not change up to the point of inflexion on the curve for change of the absorbance measured at 262 nm. This means that the complexation equilibrium does not shift during the course of the reaction (till there is an excess of SSC), and this is possible only if the copper is almost completely used in complex formation.

It has been mentioned earlier that the reaction rate is independent of the SSC concentration and is proportional to the total concentration of copper. In view of these conclusions it may be said that it is only the $Cu(SSC)_2^{2+}$ complex species which is responsible for the reaction, and the free SSC molecules do not participate directly in the redox reaction.

So far as the SSC oxidation product is concerned, it has been shown in the previous section that one oxygen molecule is used for oxidation of 4 SSC molecules. In other words every SSC molecule loses only one electron. The SSC molecule which has lost one electron has an unpaired electron left. The boundary electron density distribution corresponding to the highest occupied molecular orbital of the SSC molecule now represents the electron spin density distribution on an SSC molecule which has lost one electron (Fig 6). The diagram shows that the spin density is almost completely concentrated on the selenium atom. This must lead to a high probability for linking of two such molecules together through the selenium atoms, resulting in the formation of the bis-selenosemicarbazidinium cation (BSSC, I)



I

A similar cation is also formed during the oxidation of selenourea by hydrogen peroxide in acidic medium.[5]

Figure 6 also gives the charge distribution in an SSC molecule which has lost one electron. It can be proposed that in BSSC the charge distribution should be almost the same. The diagram demonstrates that the positive charge is mainly concentrated on the carbon and selenium atoms, but not on the nitrogen atoms as might have been thought. The same thing should hold true for the cation resulting from selenourea oxidation.[5]

The BSSC formation must be accompanied by disappearance of the SSC absorption band, related to the negative charge-transfer from selenium to carbon and the loosening of the C=Se bond, which is observed during the course of the reaction.

Thus we believe that BSSC is the SSC oxidation product. Then the catalytic effect of copper becomes clear. First, the cupric ion serves as a matrix on which two properly

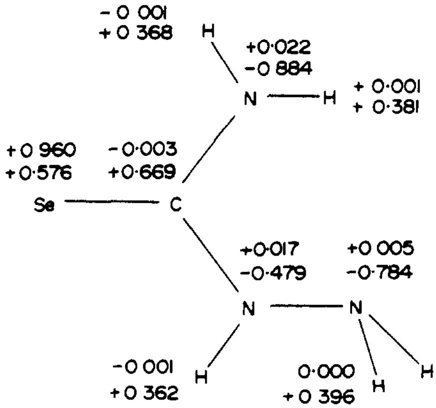
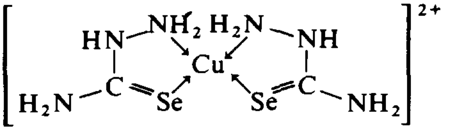


Fig. 6. The diagram of electron spin density distribution (upper figures) and effective charge distribution (lower figures) in an SSC molecule which has lost one electron. The calculations were carried out by Hoffmann's method

arranged adjacent SSC molecules (in a rather stable square planar complex with SSC ligands, which seem to be in a *cis*-arrangement, II), get a chance to lose two electrons simultaneously (each SSC ligand losing an electron) and to link together through the selenium atoms. Secondly, the copper, complexes of which are often able to co-ordinate molecular oxygen, serves as medium for electron-transfer from SSC to oxygen. It is obvious that the need for the metal ion to serve in the two capacities makes the reaction rather selective with respect to copper as a catalyst.



II

Taking into account the arguments above we can advance a mechanism for the SSC oxidation. First, complex formation is achieved and the corresponding equilibrium obtained very rapidly:

$$Cu^{2+} + 2SSC \rightleftharpoons Cu(SSC)_2^{2+} \tag{11}$$

The next step seems to be the formation of the activated complex by an oxygen molecule and hydrogen ion adding to $Cu(SSC)_2^{2+}$:

$$Cu(SSC)_2^{2+} + O_2 + H^+ \rightleftharpoons Cu(SSC)_2(O_2H)^{3+} \tag{12}$$

Such a suggestion is favoured by the kinetic data given in the previous section. The activated complex is unstable and easily decomposes into BSSC and a peroxide complex $Cu(O_2H)^+$:

$$Cu(SSC)_2(O_2H)^{3+} \longrightarrow BSSC^{2+} + Cu(O_2H)^+ \tag{13}$$

After this the activation effect of the oxidation product is initiated. It is difficult to say anything precise about this activation mechanism. However, it can be supposed that the reaction product together with the first activated complex $Cu(SSC)_2(O_2H)^{3+}$ yields in a few steps some additional superactivated complexes. Each of them easily decomposes in the same manner as in reaction (13):

$$\begin{aligned} \mathrm{Cu(SSC)_2(O_2H)^{3+} + BSSC^{2+}} &\rightleftharpoons \mathrm{Cu(SSC)_2(O_2H)^{3+}, BSSC^{2+}} \\ \mathrm{Cu(SSC)_2(O_2H)^{3+}, BSSC^{2+} + BSSC^{2+}} &\rightleftharpoons \mathrm{Cu(SSC)_2(O_2H)^{3+}, 2BSSC^{2+}} \qquad (14) \\ \ldots\ldots & \end{aligned}$$

$$\begin{aligned} \mathrm{Cu(SSC)_2(O_2H)^{3+}, BSSC^{2+}} &\longrightarrow \mathrm{Cu(O_2H)^+ + 2BSSC^{2+}} \\ \mathrm{Cu(SSC)_2(O_2H)^{3+}, 2BSSC^{2+}} &\longrightarrow \mathrm{Cu(O_2H)^+ + 3BSSC^{2+}} \qquad (15) \\ \ldots\ldots & \end{aligned}$$

The number of steps in (14) is difficult to define. However, taking into account that the plots of the reaction rate against C_X, given in Fig. 2*a*, deviate from straight lines towards higher rates with increase in C_X, it can be stated that the number of steps in (14) is more than one.

The peroxide ion $\mathrm{Cu(O_2H)^+}$ can dissociate into the $\mathrm{(O_2H)^-}$ anion which afterwards forms a hydrogen peroxide molecule. In this case it is assumed that hydrogen peroxide subsequently oxidizes two additional SSC molecules. Hydrogen peroxide has been found to oxidize SSC rather rapidly even in the absence of copper ions. If such an assumption is accepted, then this reaction step will not affect the reaction rate, because it succeeds reactions (13) and (14) and is not rate-determining.

However, it is more likely that the $\mathrm{Cu(O_2H)^+}$ ion co-ordinates two SSC molecules

$$\mathrm{Cu(O_2H)^+ + H^+ + 2SSC} \rightleftharpoons \mathrm{Cu(SSC)_2(H_2O_2)^{2+}} \qquad (16)$$

yielding a new activated complex which subsequently decomposes:

$$\mathrm{Cu(SSC)_2(H_2O_2)^{2+}} \longrightarrow \mathrm{BSSC^{2+} + Cu^{2+} + 2OH^-} \qquad (17a)$$

$$\mathrm{Cu(SSC)_2(H_2O_2)^{2+} + H^+} \longrightarrow \mathrm{BSSC^{2+} + Cu^{2+} + OH^- + H_2O} \qquad (17b)$$

$$\mathrm{Cu(SSC)_2(H_2O_2)^{2+} + 2H^+} \longrightarrow \mathrm{BSSC^{2+} + Cu^{2+} + 2H_2O} \qquad (17c)$$

Then the copper ions evolved participate in reaction (11) and the whole cycle is repeated. It will be seen that the type of the kinetic equation is independent of the type of reaction (17), because the reactions (13) and (17) are irreversible.

To deduce the kinetic equation corresponding to the proposed reaction mechanism, we employed a graph method.[6] The constancy of the $\mathrm{Cu(SSC)_2^{2+}}$ concentration enabled us to use the approximation of stationary concentrations. Figure 7 represents

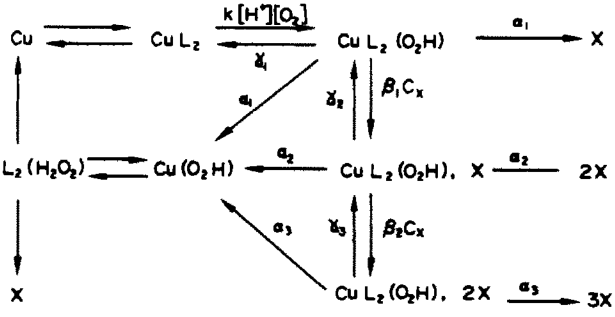


Fig 7 Mechanism of the catalytic oxidation of SSC

$\mathrm{L = SSC, X = BSSC^{2+}}$

graphically the sequence of reactions (11)-(12)-(13)-(14)-(15)-(16)-(17*a*)-(11) with only two steps in (14).

The total reaction rate is given by Mason's equation:[6]

$$\frac{dC_X}{dt} = \frac{\sum_i \det(i) \cdot V_i}{\sum_i \det(i)} \cdot C_{Cu} \tag{18}$$

where det(*i*) is the determinant of the *i*th apex and V_i is the rate of reaction-product formation in the *i*th apex.

Under the conditions of our investigation, as soon as practically all the copper exists as the $Cu(SSC)_2^{2+}$ complex species, we can neglect all the determinants in the denominator of equation (18) except $\det\{Cu(SSC)_2^{2+}\}$ and obtain a simpler equation

$$\frac{dC_X}{dt} = \frac{\sum_i \det(i) \cdot V_i}{\det\{Cu(SSC)_2^{2+}\}} \cdot C_{Cu}. \tag{19}$$

After calculating all the determinants from Fig. 7 and putting them in Eq. (19) and after some transformations we obtain finally

$$\frac{dC_X}{dt} = \frac{2k[H^+][O_2]C_{Cu}(\mathbf{A} + \mathbf{B} \cdot C_X + \mathbf{D} \cdot C_X{}^2)}{\mathbf{E} + \mathbf{F} \cdot C_X + \mathbf{D} \cdot C_X{}^2} \tag{20}$$

where

$$\mathbf{A} = a_1(1 + a_2 + a_3 + a_2 a_3)$$
$$\mathbf{B} = b_1 a_2(1 + a_3) + a_1 b_2 a_3$$
$$\mathbf{D} = b_1 b_2 a_3$$
$$\mathbf{E} = 1 + a_1 + a_2 + a_3 + a_1 a_2 + a_1 a_3 + a_2 a_3 + a_1 a_2 a_3$$
$$\mathbf{F} = b_1 a_2(1 + a_3) + b_2 a_3(1 + a_1)$$
$$a_i = \frac{\alpha_i}{\gamma_i},\ b_i = \frac{\beta_i}{\gamma_i}$$

and k, α, β and γ are the rate constants, indicated in Fig. 7.

Let us analyse equation (20) at low and high values of the reaction product concentration C_X. It is evident that at small C_X values the terms containing C_X in the denominator of (20) can be neglected. Then the equation reduces to

$$\frac{dC_X}{dt} = \frac{2k\mathbf{A}}{\mathbf{E}} \cdot [H^+][O_2]C_{Cu}\left(1 + \frac{\mathbf{B}}{\mathbf{A}} C_X + \frac{\mathbf{D}}{\mathbf{A}} C_X{}^2\right) \tag{21}$$

If we suppose that the magnitude of the constant **D** approaches $\mathbf{B}^2/2\mathbf{A}$, then the expression in parentheses in (21) represents the first three terms of the expansion of $\exp(K \cdot C_X)$, where $K = \mathbf{B}/\mathbf{A}$. Then good agreement with the empirical equation (8) is achieved.

At higher values of C_X the term containing the highest power of C_X, $\mathbf{D} \cdot C_X{}^2$, predominates both in the numerator and in the denominator of (20). Therefore, in this boundary case equation (20) reduces to

$$\frac{dC_X}{dt} = 2k[H^+][O_2]C_{Cu} \tag{22}$$

which corresponds perfectly to the empirical kinetic equation (9).

Thus the proposed reaction mechanism leads to good agreement with experiment. However, this mechanism has certain shortcomings. In some steps it requires the interaction of several highly-charged species. This must lead to a strong dependence of the reaction rate on the ionic strength of the solution, but the results we have obtained indicate that the activity factor *F* is rather constant over a wide range of ionic strengths (from ~0·3 to ~1·0) and seems to be near unity. Only when the ionic strength exceeds unity does *F* begin to decrease rapidly, resulting in a negative salt effect.

In order to bring these facts into agreement with the proposed mechanism it can be supposed that some of the (positively) charged species take part in the reaction as neutral ion-association complexes with the perchlorate anions present, so that in each step not more than one charged species participates simultaneously. From recent publications it is seen that there is a reasonable probability that such complexes exist.

The kinetic method for copper determination will be described separately.

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Zusammenfassung—Selenosemicarbazid erleidet in saurem Medium in Gegenwart von Kupfer(II) als Katalysator Oxidation durch im Wasser gelosten Sauerstoff. Das Oxidationsprodukt zeigt einen aktivierenden Effekt Die Kinetik der Reaktion wurde untersucht, für kleine und große Konzentrationen des Oxidationsprodukts wurden kinetische Gleichungen abgeleitet. Die Konstanten in den abgeleiteten kinetischen Gleichungen wurden berechnet. Der vorgeschlagene Reaktionsmechanismus stimmt mit den experimentellen Ergebnissen überein. Es wird vermutet, daß das Reaktionsprodukt das Bis-selenosemicarbazidinium-Kation ist. Die Annahme der Bildung dieses Kations beruht auf der elektronischen Struktur und Reaktivitat von Selenosemicarbazid Die Reaktion kann zur Kupferbestimmung verwendet werden.

Résumé—En milieu acide, le sélénosemicarbazide subit l'oxydation par l'oxygène dissous dans l'eau, en la présence de cuivre (II) comme catalyseur Le produit d'oxydation présente un effet activateur On a étudié la cinétique de la réaction et déduit les équations cinétiques pour les concentrations aussi bien faibles qu'élevées du produit d'oxydation On a calculé les constantes impliquées dans les équations cinétiques déduites Le méchanisme proposé pour la réaction est en accord avec les résultats expérimentaux. On suppose que le produit d'oxydation est le cation bis-sélénosemicarbazidinium L'hypothèse de formation de ce cation est basée sur la structure électronique et la réactivité du sélénosemicarbazide On peut utiliser la réaction pour le dosage du cuivre

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SPECTROPHOTOMETRIC PROCEDURE USING RHODAMINE B FOR DETERMINATION OF SUBMICROGRAM QUANTITIES OF ANTIMONY IN ROCKS*

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Summary—A spectrophotometric procedure using Rhodamine B is given for the determination of antimony in mineralized rocks after its separation as stibine A study of the Rhodamine B reaction points to the importance of the order of addition of reagents in enhancing sensitivity and increasing the stability of the system The tolerance of some 26 elements is established for the overall procedure Although the limit of determination is approximately 0·5 ppm Sb in a 0 2-g sample, the procedure is intended primarily for screening samples containing more than 1 ppm Sb. In pure solutions 0 1 μg of antimony can be determined with a relative standard deviation of 25%. For >0·2 μg of antimony a relative standard deviation of 15% or less can be expected

Geochemical studies of the antimony content of rocks require accurate and reasonably rapid methods for the determination of antimony at the submicrogram level. Although neutron-activation methods are sufficiently sensitive,[1,2] they require expensive instrumentation. Emission spectrographic procedures require preconcentration to attain the required sensitivity and to ensure representative sampling.[3,4] Atomic-absorption spectrophotometric procedures have been applied to the determination of antimony but at present are not sensitive enough for most rock samples.[5–8] Higher sensitivity may be obtained for antimony by atomic-fluorescence[9] and atomic-absorption methods using high-temperature flameless volatilization techniques.[10] However, these methods are not as yet directly applicable to geological materials.

Optical spectrophotometric procedures for the determination of antimony involving Rhodamine B have been widely investigated[11–21] and found to have considerable sensitivity but to suffer interference from gold, gallium, silver and thallium and from iron when present in moderate amounts. However, the procedures have been of limited use at the submicrogram level owing to lack of precision. Triphenylmethane dyes offer rather better sensitivity but are subject to more interferences.[22]

This paper investigates the conditions that will permit the rapid and reasonably precise determination of submicrogram quantities of antimony in rocks. These conditions include the sample decomposition, the stibine generation, its absorption into mercuric chloride, the antimony oxidation and the benzene extraction of a Rhodamine B chloroantimonate. The variation in the absorbance of the Rhodamine B–chloroantimonate product with the order of reagent addition is shown. This method is applied to the determination of antimony in two standard rock samples previously analysed by radiochemical techniques.

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* Publication authorized by the Director, U S Geological Survey

EXPERIMENTAL

Reagents

Tartaric acid solution, 10% *w/v*

Zinc shot (low in antimony content)

Cadmium sulphate solution, 5% *w/v*

Mercuric chloride–hydrochloric acid solution, Mercuric chloride 0·5% *w/v* in 6*M* hydrochloric acid

Ceric sulphate solution, 0·2*M*. Dissolve 10·6 g of tetrasulphatoceric acid, $H_4Ce(SO_4)_4$, in 80 ml of water, add 5·56 ml of sulphuric acid (1 + 1) and dilute to 100 ml.

Rhodamine B solution, 0·2% *w/v*

Rhodamine B-hydroxylamine hydrochloride solution A 0·1% *w/v* Rhodamine B and 1% w/v hydroxylamine hydrochloride solution. Prepare daily

Standard antimony solution, 100 *μg/ml* Dissolve 0·274 g of potassium antimonyl tartrate hemihydrate in 1 litre of 2·5% v/v sulphuric acid. Prepare other standards by appropriate dilution Dilute solutions should not be used if more than a week old

Apparatus

Hydride generator. An arsine generator, described by the Committee on Analytical Reagents,[23] has been modified as shown in Fig. 1 The absorber of the arsine generator has been replaced with a delivery tube, 14 cm long, which is bent at right angles so that it leads directly into a 60-ml separatory funnel

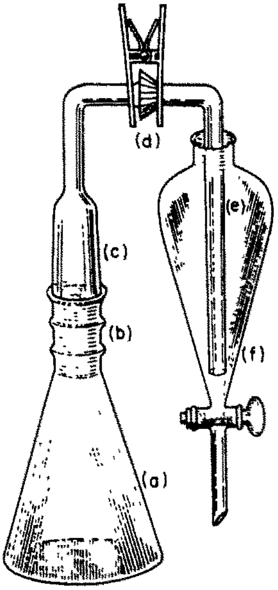

Fig 1. Hydride generator *a*, 125-ml generator flask, *b*, standard taper (24/40), *c*, scrubber, *d*, ball socket joint (12/3), *e*, delivery tube, *f*, 60-ml separatory funnel

Procedure

Fuse 1·5 g of potassium pyrosulphate in a quartz or Vycor crucible until the moisture is removed Add 0·200 g of sample and fuse for 10–15 mins Add 14 ml of water and 1 ml of tartaric acid solution to the crucible and dissolve the melt by heating on a steam-bath Transfer the resulting solution to the hydride generator flask Wash the crucible with approximately 4 ml of water followed by 40 ml of sulphuric acid (1 + 1). Transfer the washings to the generator flask and add 1 ml of cadmium sulphate solution Cover, and bring the resulting solution to a boil Cool the flask to 20–25°

Add 15 g of zinc shot to the generator flask and quickly connect the scrubber/delivery-tube assembly to the generator and insert the delivery tube into the separatory funnel containing 20 ml of the mercuric chloride-hydrochloric acid solution After 2 hr, remove the delivery tube from the separatory funnel and discard the contents of the generator flask Add 10·0 ml of benzene to the separatory funnel, followed by

0.5 ml of cerium(IV) solution, and shake for 1 min. Add 10 ml of the Rhodamine B-hydroxylamine hydrochloride solution and shake for 1 min. After the phases have separated, drain and discard the aqueous layer. Wash the benzene phase by shaking with 10 ml of 4*M* hydrochloric acid for 1 min and discard the aqueous phase. Repeat the washing.

Drain the organic phase into a small glass beaker and transfer it into a 15-ml centrifuge tube, holding back the aqueous droplets in the beaker. Centrifuge for 2 min and then measure the absorbance at 550 nm *vs* benzene, using 5-cm cells. If the absorbance is greater than 0·6, use 1-cm cells.

Prepare two standard curves, one for 0–1·0 μg and the other for 1–10 μg of antimony. Generate stibine from flasks containing 1.5 g of potassium pyrosulphate, collect it in mercuric chloride solution and then proceed as for samples.

DISCUSSION

Conditions for the generation and collection of stibine

In preliminary work on the separation of antimony by the generation of stibine, amalgamated zinc was reacted with 9*M* hydrochloric acid according to the recommendations of Zaikovsky.[24] This system was abandoned in favour of the simpler system described by Dal Cortivo *et al*[25] in which stibine is formed by the reaction of a sulphuric acid solution of cadium sulphate with 20-mesh zinc, these concentrations being approximately the same as those prescribed in this paper. The reaction between the acid and the 20-mesh zinc proved to be very rapid, especially if such elements as iron were present. Amalgamation of the 20-mesh zinc resulted in essentially no reaction with the acid solution. Substitution of zinc shot proved to be very satisfactory.

Also investigated were the effects of varying the concentrations of the acid and the cadmium sulphate, the amount of the zinc, the temperature of the reaction medium, and the solution volume. With cadmium sulphate fixed at 100 and 500 mg in a 55-ml volume, the concentration of the sulphuric acid was increased from 3 to 8*M*, in increments of 1 mole/l. The reaction rate between the acid and the zinc shot decreased with increasing sulphuric acid concentration and was excessively slow with $>7M$ sulphuric acid. Slightly higher concentrations of sulphuric acid were tolerated at the higher cadmium sulphate level. The recovery of 10 μg of antimony increased from 80% at 3*M* acid to approximately 100% between 5 and 7*M* acid. With 8*M* sulphuric acid recovery decreased to 20% owing to the negligible reaction during the reaction period of 1 hr.

The concentration of the cadmium sulphate was varied from 0 to 1·5 g in a 55-ml volume with little change in antimony recoveries. With 6*M* sulphuric acid and 15 g of zinc shot, the recovery of 10 μg of antimony increased from 82% in the absence of cadmium sulphate to approximately 100% with 25 mg or more of cadmium sulphate.

A 15-g amount of zinc shot was found to be sufficient for the reaction period with some margin of surplus. Ideally the amount of zinc that dissolves should be the same for all samples and standards. However, the presence of Co, Fe, Ge, Ni and Pt accelerates the reaction rate between the acid and the zinc, whereas Bi, Hg and Tl decrease the rate. For this reason the purity of the zinc is of extreme importance especially if submicrogram quantities of antimony are to be determined.

The effect of the temperature of the solution in the hydride generator flask on the recovery of 10 μg of antimony was investigated by both cooling and heating the solution either before the zinc addition or during some part of the reaction period. A greater tolerance for some metals, *e.g.*, iron, is obtained when the reaction flask is cooled, whereas for others, *e.g.*, copper, heating of the reaction medium proves favourable. It is difficult to predict the best conditions for a given sample but, generally, for rock samples best results can be expected if the solution is at 20–25° before the addition of zinc.

Because of the variation in reaction rate from sample to sample, a 2-hr period for stibine generation is recommended.

Increasing the volume of the acid solution did decrease the interference of certain elements but at the same time decreased the recovery of antimony, probably because of the correspondingly greater amount of stibine dissolved.

Webster and Fairhall[11] found that 20 ml of 6% mercuric chloride solution in $6M$ hydrochloric acid effectively absorbed 100 ml of gas containing 200 ppm of stibine, at a flow-rate of approximately 4 l./min. Because the procedure presented in this paper is designed for antimony at levels not to exceed 10 μg in a 0·2-g sample, the concentration of the mercuric chloride may be decreased. Stibine corresponding to 30 μg of antimony was generated and passed into 20 ml of $6M$ hydrochloric acid containing 0, 50, 100, 200, 400 or 600 mg of mercuric chloride. The antimony recovery was 0% in the absence of mercuric chloride and approximately 100% in the presence of 50–600 mg of mercuric chloride. A 100-mg mercuric chloride level was arbitrarily adopted.

Effect of the hydrochloric acid concentration on the oxidation and the benzene extraction

Antimony is oxidized to the quinquevalent state by cerium(IV) in $6M$ hydrochloric acid.[12] However, the benzene extraction of the Rhodamine B chloroantimonate at this acidity gave low antimony recoveries. Increasing the hydrochloric acid concentration to $8M$ resulted in even lower recoveries. Neumann and Ramette[26] found that hydrogen ion accelerates the hydrolysis of the hexachloroantimonate ion. Ramette and Sandell[17] report that in $6M$ hydrochloric acid at 25° the rate of hydrolysis of the hexachloroantimonate ion is about 1%/min. As the hydrolysis product does not react with Rhodamine B it is imperative to add the reagent soon after oxidation, and to time the interval if it is more than a fraction of a minute. These investigators found it advantageous to carry out the extraction at a lower acidity than $6M$ because the extraction is more complete and the rate of hydrolysis is less. Acidities below $3M$ hydrochloric acid are not recommended because benzene extracts a colourless lactone of the dye, which on standing is converted into a coloured species.

Experiments have confirmed that good results are obtained by oxidizing antimony in $6M$ hydrochloric acid and then diluting to $4M$ hydrochloric acid for the benzene extraction of the Rhodamine B chloroantimonate.

Effect of the cerium (IV), hydroxylamine hydrochloride and Rhodamine B concentrations

Initial experiments showed that increasing the amount of $0{\cdot}1M$ cerium(IV) from 0·5 to 1·0 ml increased the sensitivity of the procedure. Additional oxidant resulted in no substantial increase in sensitivity and necessitated additional hydroxylamine hydrochloride. The amounts of the hydroxylamine hydrochloride and of the Rhodamine B are not critical but they must be sufficient to destroy the excess of oxidant and to react with the antimony. A combination of 100 mg of hydroxylamine hydrochloride and 10 mg of Rhodamine B is satisfactory.

Variation of the absorption spectrum of Rhodamine B chloroantimonate with order of reagent addition

According to several authors,[11,14,16,18] the recommended order of reagent addition is: cerium(IV), hydroxylamine hydrochloride for the destruction of excess of oxidant, Rhodamine B, and finally benzene as the extractant. The recommended wavelength for the absorbance measurements is 565 nm.

Antimony was oxidized in 25 ml of 6*M* hydrochloric acid by 1 ml of 0·1*M* cerium(IV), the excess of oxidant was destroyed with a few drops of 1% hydroxylamine hydrochloride solution, 5 ml of 0·2% Rhodamine B solution were added and the Rhodamine B chloroantimonate was extracted into 10 ml of benzene. A plot of the absorbance of the benzene phase (*vs.* pure benzene) between 450 and 600 nm showed peaks at 565 and 520 nm, the 565 nm peak being the larger. The absorbance of the 565 nm peak decreased by 15% in 1 hr. After 24 hr the peak at 565 nm had decreased by approximately 40% while the one at 520 nm had increased and was the greater of the two.

With conditions that more nearly approximate those recommended in this paper, the variations of the spectra with the order of reagent addition, and also with the omission of hydroxylamine hydrochloride, were investigated further. In each case the amount of antimony was the same. The concentrations of hydrochloric acid, mercuric chloride, cerium(IV), and wash solution were those used in the prescribed procedure. The amount of hydroxylamine hydrochloride, when used, was 0·5 ml of 1% solution (Figs. 2*A* and *C*), with the exception of the final case (Fig. 2*F*) in which the conditions were those recommended in this paper. One minute of shaking followed each reagent addition.

Figure 2 shows the spectra which are obtained immediately after the benzene extraction (followed by its two washings). In Figs. 2*A* and *C* a second spectrum is shown which was obtained after 24 hr. For the other cases the spectra remained essentially unchanged. The

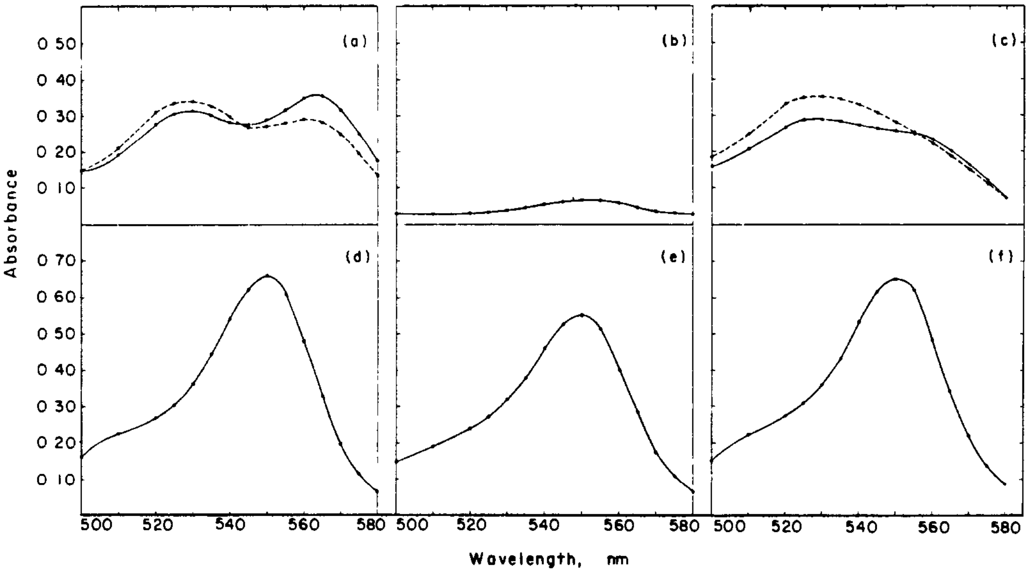

Fig 2. Variation of the absorption spectrum of Rhodamine B chloroantimonate with the order of reagent addition.

A. Ce(IV), NH_2OH HCl, Rhodamine B, benzene
B Ce(IV), Rhodamine, B, benzene
C Ce(IV), benzene, $NH_2OH \cdot HCl$, Rhodamine B
D Ce(IV), benzene, Rhodamine B
E Benzene, Ce(IV), Rhodamine B
F Benzene. Ce(IV). mixed Rhodamine B-$NH_2OH \cdot HCl$ solution (method of this report).
—— Immediate absorbance
---- Absorbance after 24 hr

blanks in all cases were negligible in the 400–600 nm range and remained so after 24 hr. Figure 2*A* illustrates the spectrum obtained after the conventional order of reagent addition (oxidant, reductant, dye, and extractant). Figure 2*B* is the spectrum obtained after the conventional order of reagent addition but with the hydroxylamine hydrochloride omitted. The conditions for Fig. 2*C* are similar to those for Fig. 2*A* except that benzene is added after the oxidant and before the hydroxylamine hydrochloride. Figure 2*D* is for the same case as Fig. 2*C*, but with hydroxylamine hydrochloride omitted. For Fig. 2*E* the benzene was added before the oxidant and the hydroxylamine hydrochloride omitted. Most of the dye was destroyed, as indicated by the yellow rather than orange colour of the aqueous phase. The spectrum in Fig. 2*F* results from the conditions recommended in this paper.

Ramette and Sandell[17] found that three dye cations are present which can combine with the chloroantimonate ion to form benzene-extractable products. Although the absorption maximum for none of these is given, the spectra in Fig. 2 suggest two unstable complexes and one of considerable stability with an absorption maximum at 550 nm.

That the antimony was not extracted into the benzene as the hexachloroantimonate ion in the absence of Rhodamine B was ascertained by shaking the benzene phase with Rhodamine B solution after its isolation from the aqueous phase in which the antimony was oxidized. No rhodamine B-chloroantimonate colour was observed.

The foregoing experiments testing the effect of different orders of reagent addition suggest that the simplest procedure is the one in which the timing is critical only after the single step of oxidation rather than after each reagent addition. However, best results are to be expected from use of the same procedure on all samples and standard solutions.

Treatment of the benzene extract

Most of the excess of the Rhodamine B can be stripped from the organic phase by twice shaking the organic phase with 10 ml of 4*M* hydrochloric acid. The benzene phase should be centrifuged after its washing. In earlier work, the benzene extract was filtered through paper to remove moisture but slight variations resulted.

Recovery of ^{125}Sb

A solution containing 2 μg of antimony was spiked with ^{125}Sb to give approximately 10^5 cpm and carried through the procedure. After adjustment of all fractions to a fixed volume, the activity of each fraction was measured and compared with a counting standard. The recovery of the antimony was 77%. Approximately 2% of the antimony remained in the generator flask and another 12% remained in the aqueous phase in the initial extraction. A total of about 5% was found in the two washings of the benzene phase.

Tolerance of the procedure for various elements

The investigation of certain elements as possible interferences was dictated by their reported interference in the stibine generation,[12,27] in the Rhodamine B spectrophotometric procedure for antimony,[11,12] or their common occurrence in rocks.

The tolerance for the elements was established by carrying the elements through the entire procedure. Dilute sulphuric acid solutions of most of the elements being investigated were evaporated to near dryness in Vycor crucibles, or the solids were taken directly as in the case of zinc sulphide and sodium metasilicate, and fused with pyrosulphate both in the presence and absence of antimony. Table 1 gives the results of this investigation.

Al, Ca, Fe, Mg, S and Si are tolerated individually in major quantities; 10 mg or less of Cr, Mn, Mo, Sn, Ti, V, W and Y and 1 mg or less of Au, Cu, and Ga caused negligible interference (Table 1). Approximately 500 μg of arsenic is tolerated. The catalytically active metals, Pt and Ni, are the most troublesome and tend to give reduced antimony recoveries with accelerated reaction rates between the acid and the zinc.

Nickel, owing to its common occurrence and interference, may pose the greatest problem. For more refined work this element should be removed.

Table 1 Tolerance of various elements in the overall procedure

Element	Amount of element added, *μg*	Sb added, *μg*	Sb found, *μg*
Ag	1,000	none	0·00
	100	1·00	0·86
	500	1·00	0·62
	1,000	1·00	0·44
Al	200,000	none	0·00
	200,000	1·00	0·98
As(III)	100	none	0·00
	100	1·00	1·02
	250	none	0·00
	250	1·00	1·14
	500	none	0·00
	500	1·00	0·88
	1,000	none	negative
	1,000	1·00	0·20
	1,000*	none	0·00
	1,000*	1·00	1·08
	1,000*	10·00	9·80
Au	1,000†	none	0·00
	1,000†	1·00	1·00
Bi	1,000§	none	0·00
	20	1·00	1·03
	100	1·00	0·90
	1,000§	1·00	0·36
Ca	50,000‡	none	0·00
	50,000‡	1·00	0·85
Co	1,000	none	0·00
	300	1.00, 1·00	0·86; 1·00
	1,000	1·00	0·71
Cr(III)	10,000	none	0·00
	10,000	1·00	1·10
Cu	10,000	none	0·00
	1,000	1·00	0·98
	5,000	1·00	0·86
	10,000	1·00	0·47
Fe(III)	50,000	none	0·03
	50,000	1·00	1·03
	50,000	3·00	2·73
	100,000	none	0·10
	100,000	1·00; 1.00	0·82; 0·72
Ga	1,000	none	0·00
	1,000	1.00	1.00
Ge	1,000	none	0·00
	50	1·00	1·00
	250	1·00	0·97
	1,000	1·00	0·44

Table 1 Tolerance of various elements in the overall procedure

Element	Amount of element added, μg	Sb added, μg	Sb found, μg
Hg	1,000	none	0·00
	100	1·00	1·03
	500	1·00	0·86
	1,000	1·00	0·67
Mg	200,000	none	0·00
	200,000	1·00	1·05
Mn(II)	10,000	none	0·02
	10,000	1·00	0·97
Mo(VI)	10,000	none	0·00
	10,000	1·00	0·90
Ni	1,000	none	0·00
	25	1·00	1·00
	50	1·00	0·86
	100	1·00	0·85
	200	1·00	0·73
	400	1·00	0·73
	600	1·00	0·52
	800	1·00	0·48
	1,000	1·00	0·47
Pt(IV)	100	none	0·05
	2	1·00, 1·00	1·08; 1·12
	10	1·00, 1·00	0·82; 0·94
	100	1·00	0·40
$S^=$	50,000	none	0·00
	50,000	1·00	0·90
Si	200,000	none	0·00
	200,000	1·00	0·90
Sn	10,000	none	0·00
	10,000	1·00	0·96
Ti	10,000	none	0·15
	10,000	1·00	1·13
Tl	1,000§	none	negative
	10	1·00	1·00
	50	1·00	0·88
	100§	1·00	0·73
	1,000§	1·00	0·13
V(V)	10,000	none	0·00
	10,000	1·00	0·90
W(VI)	10,000	none	0·00
	10,000	1·00	0·91
Y	10,000	none	0·00
	10,000	1·00	0·85

* 1·0 ml of 0·2*M* Ce(IV) used instead of 0·5 ml

† Au is reduced to the metallic state during fusion.

§ Reaction rate excessively slow

‡ Large amount of $CaSO_4$ precipitate.

Interference of arsenic

The procedure yields good antimony recoveries in the presence of approximately 0·5 mg of arsenic. Arsenic formed a golden brown precipitate in the hydrochloric acid solution of the mercuric chloride. The recovery of 1 μg of antimony in the presence of 500 and 1000 μg of arsenic was 88 and 20%, respectively. Increasing the mercuric chloride concentration by a factor of three served only to give poorer antimony recovery. The work was repeated at the 1000-μg level of arsenic in the presence of 1 μg of antimony, but with double the volume of cerium(IV) solution; the recovery of the antimony was 100% with none being found in the blank. Arsenic should be no problem in most rock samples, but should it exist in high concentration, additional oxidant is suggested.

Sample decomposition

Initial work on sample decomposition was conducted on W-1, a U.S. Geological Survey standard diabase rock. Alkaline fusion employing potassium hydroxide alone, potassium hydroxide followed by sodium peroxide, and a mixture of potassium and sodium carbonate, as well as the recommended potassium pyrosulphate, were tried.

The antimony recoveries from samples of W-1 spiked with varying amounts of antimony were essentially zero if the mixed carbonate fusion was used and low and erratic for the potassium hydroxide fusions both in the presence and absence of peroxide. These poor recoveries of antimony following the alkaline fusion were unexpected. Prescott and Johnson[28] state that the antimonates of alkali metals are vapourized or decomposed when ignited in the presence of reducing agents and advise that sodium carbonate fusions be made in the presence of an oxidant. They add that some volatilization may occur since oxidation by fusion is not effected soon enough to prevent some loss of the lower valence compounds by volatilization.

Ward and Lakin[20] found the pyrosulphate fusion of samples to be effective, preparatory to a Rhodamine B procedure for determining antimony in soils and rocks. Potassium pyrosulphate fusions were made on W-1 directly and on W-1 spiked with varying amounts of antimony. Good antimony recoveries were found and therefore all further work involved sample decomposition with this flux. Because the sample decompositions are incomplete, the antimony values represent only a lower limit.

Standard curves

A plot of the absorbance *vs.* the concentration of the antimony conformed to Beer's law from 1 to 10 μg of Sb. The sensitivity according to Sandell's definition was 0·0017 μg/cm^2. Although a detailed examination of the curve at antimony levels below 1 μg showed a non-linear relation the curve is usable for amounts of antimony $\geq 0{\cdot}1$ μg. On six replicate determinations the absorbance of the blank in a 5-cm cell was $0{\cdot}037 \pm 0{\cdot}002_3$.

Test of the procedure

The antimony content of standard rocks G-1 and W-1 was determined on 6 replicate samples of each rock directly and on samples spiked with 1 μg of antimony. The

Table 2 Determination of antimony in a granite, G-1, and a diabase, W-1

Sample	Sb added to 0·200 g sample, *μg*	Sb found and standard deviation, *μg*	Sb, *ppm* This work	Sb, *ppm* Neutron activation[2]
G-1	none	$0{\cdot}078 \pm 0{\cdot}020$	0·39	0·37 ± 0·12*
G-1	1·00	$1{\cdot}09_0 \pm 0{\cdot}055$	0·45	
W-1	none	$0{\cdot}228 \pm 0{\cdot}026$	1·14	1·12 ± 0·18*
W-1	1·00	$1{\cdot}19_4 \pm 0{\cdot}035$	0·97	

* Maximum deviation of the mean

results given in Table 2 are in good agreement with values obtained by neutron activation.

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Zusammenfassung—Zur Bestimmung von Antimon in erzfuhrenden Gesteinen wird ein spektrophotometrisches Verfahren mit Rhodamin B nach Abtrennung als Stibin angegeben Eine Untersuchung der Reaktion mit Rhodamin B weist auf die Wichtigkeit der Reihenfolge der Reagentienzugabe fur die Erhohung der Empfindlichkeit und der Stabilitat des Systems hin Fur das Verfahren insgesamt wird die Anwesenheit von etwa 26 Elementen als tragbar nachgewiesen Obwohl die Nachweisgrenze etwa 0·5 ppm Sb in einer 0 2 g-Probe betragt, ist das Verfahren primar fur die Auswahl von Proben mit uber 1 ppm Sb gedacht In reinen Losungen kann 0·1 μg Antimon mit einer relativen Standardabweichung von 25% bestimmt werden Fur >0 2 μg Antimon kann man eine relative Standardabweichung von 15% oder weniger erwarten

Résumé—On donne une technique spectrophotométrique utilisant la Rhodamine B pour le dosage de l'antimoine dans les roches mineralisees après sa séparation a l'état de stibine Une étude de la réaction de la Rhodamine B montre l'importance de l'ordre d'addition des réactifs sur l'exaltation de sensibilité et l'accroissement de stabilité du système On etablit la tolérance de quelques 26 éléments pour la technique globale Quoique la limite de détermination soit approximativement de 0,5 p p m de Sb dans un échantillon de 0,2 g, la technique est principalement destinée a l'examen d'échantillons contenant plus de 1 p p m de Sb Dans des solutions pures, on peut doser 0,1 μg d'antimoine avec un écart type relatif de 25% Pour >0,2 μg d'antimoine, on peut attendre un écart type relatif de 15% ou moins

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FLUORIMETRIC METHOD FOR THE DETERMINATION OF URANIUM IN NATURAL WATERS

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Summary—A method is described for the fluorimetric determination of uranium in natural waters The limit of detection is 0 3 ppM Ion-exchange is used to preconcentrate the uranium by a factor of 22 and separate it from quenching ions in the sample. The fluorescence is measured in a medium that is 1 35*M* in both sulphuric and phosphoric acids The uranyl ions are excited by radiation of wavelength 280 nm and bandwidth 40 nm. The emitted signal is scanned from 470 to 510 nm After spiking of the sample solution with a small volume of standard uranium solution, the fluorescence signal is scanned again and the uranium content of the sample calculated from the two readings The coefficient of variation is 8·5% for determinations of U in a synthetic water sample having a uranium content of 1·9 ppM Destruction of organic matter in the eluates gives 0 1 ppM detection limit.

In prospecting work, knowledge of the uranium content of natural waters is a valuable guide for selecting regions for detailed investigations. Canadian experience[1,2] shows that the detection limit must be better than a few tenths of 1 ppM (parts per milliard). Any uranium content in excess of 1 ppM is regarded as an anomaly. As Scandinavia is very rich in waters, the number of analyses required each season amounts to several thousands. A simple and rapid method of analysis is therefore needed.

Of the methods in use to determine traces of uranium in water the most common is based upon measuring the fluorescence of the uranyl ion in alkali metal fluoride glass beads.[3,4] Several drawbacks are associated with this method. The fusion requires strictly controlled conditions since the fluorescence yield of the glass beads is highly dependent on their composition, surface characteristics and several fusion parameters, *e.g.*, time, temperature and oxidation-reduction conditions. It is often necessary to dilute the sample or to separate the uranium from the matrix in order to avoid quenching of the fluorescence by other elements in the sample. The fusion complicates the use of addition methods (spiking) for evaluating the uranium content of the sample.

We have chosen a liquid medium for our method. There are the following advantages in using a liquid system: many samples may conveniently be handled simultaneously, the sample solution being analysed can be spiked directly, and effects of quenching ions are more readily studied.

Some kind of preconcentration of the sample as well as separation of the uranium from strongly quenching components is necessary to obtain the required detection limit. Solvent extraction methods were abandoned because even traces of organic compounds quench the fluorescence of the uranyl ion. Ion-exchange in nitric and hydrochloric acid systems, though very useful in separating uranium from other ions,[5] is unacceptable because of quenching. We chose anion-exchange in sulphuric acid medium[6] as being the best separation technique for our purpose. The fluorescence is measured in a solution containing both sulphuric and phosphoric acids.

We shall first describe the concentration process—sorption, washing, elution—and the apparatus. The technique used in the measurement of fluorescence—matrix, spiking and measurement, will then be discussed in some detail and finally some results will be given.

CONCENTRATION AND SEPARATION

Anion-exchange techniques are capable of achieving value lying between 1 and 35,000 for the distribution coefficient (D) of the uranyl ion between a resin phase and an aqueous solution containing sulphuric acid.[7–10] Preliminary experiments indicated that small anion-exchange columns can be used for the separation. We chose to work with Dowex 1-X8 resin, 100–200 mesh, sulphate form, 350 mg of resin being used to make a bed, 8 mm in dia and 8 mm in height. In order to establish the most favourable working conditions it was then necessary to optimize the sorption, washing and elution steps.

Sorption and washing

A 200-ml volume of $0{\cdot}01M$ sulphuric acid containing 1600 μg of U was passed through the column at a flow-rate of 180 ml/hr. The column was then washed with $0{\cdot}01M$ sulphuric acid at the same flow-rate, and successive portions of the effluent were analysed fluorimetrically for uranium. The sorption on the column is better than 99% even after the passage of 1·4 l. of influent. The D value obtained exceeds $1{\cdot}5 \times 10^4$. The sorption of uranium is effective enough to permit the use of large volumes of washing solution, but what will be the smallest volume required to satisfactorily remove the quenching ions?

To find the answer to this question, we used $0{\cdot}01M$ sulphuric acid containing 10 ppm of Na^+, K^+, Mg^{2+}, Ca^{2+}, 5 ppm of Fe^{3+}, 1 ppm of Al^{3+}, 0·5 ppm of Mn^{2+}, 27 ppm of Cl^- and 7 ppm of NO_3^-. This composition corresponds to higher ionic concentrations than are normally found in Swedish ground waters. Then 200 ml of the solution were passed through the ion-exchange column at the flow-rate used in the previous experiment and the column was washed with consecutive 20-ml portions of $0{\cdot}01M$ sulphuric acid. The quenching of the fluorescence of a standard uranium solution by each portion of effluent was then determined. Quenchers were present mainly in the first effluent portions, and the fluorescence yield reached a constant value after the passage of 100 ml of washing solution. It is not possible to remove all quenching by washing. When pure resin was washed with $0{\cdot}01M$ sulphuric acid similar constant fluorescence yields were obtained. These were found to depend on the type of resin, the temperature and the concentration of sulphuric acid in the washing solution. The effect might be due to some organic material being dissolved from the resin by the acid. The constancy and reproducibility suggest that some kind of equilibrium is involved. To allow for exceptional concentrations of quenching ions we finally decided upon using 120 ml of $0{\cdot}01M$ sulphuric acid for washing.

The influence of organic matter in the eluate can be completely eliminated by fuming to dryness with sulphuric acid and hydrogen peroxide.

Elution

Bunney *et al.*[7] determined the distribution coefficient of the uranyl ion between Dowex 2-X8, 200–400 mesh, and $2M$ sulphuric acid and found that the value was

Table 1. Efficiency of elution of uranium by $2M$ sulphuric acid.

Uranium taken, μg	Eluate portion, *ml*	Uranium recovery, %	Cumulative uranium recovery, %
54·4	0 - 1·5	44·0	44·0
	1·5- 3·0	37·6	81·6
	3·0- 4·5	11·8	93·4
	4·5- 6·0	3·8	97·1
	6·0- 7·5	1·5	98·6
	7·5- 9·0	0·7	99·3
	9·0-10·5	0·4	99·7
	10·5-12·0	0·3	100
1·1	0 -1·5	50·2	50·2
	1·5-3·0	29·8	80·0
	3·0-4·5	11·1	91·1
	4·5-6·0	6·3	97·4
	6·0-7·5	2·6	100
	7·5-9·0	0	100

approximately 1. Strelow and Bothma[10] obtained a D value of 2·9 for the same acid, using a Bio-Rad AG1-X8 resin. For Dowex 1-X8 the same magnitude of D may be expected. Consequently a small volume of $2M$ sulphuric acid should suffice to elute the sorbed uranium. Preliminary experiments suggested to 5 ml/hour be a suitable flow-rate for elution. In order to study the elution parameters one ion-exchange column was loaded with 54·4 μg of U and another with 1·1 μg and the columns were washed in the manner described above. We eluted with 1·5-ml portions of $2M$ sulphuric acid at 5 ml/hr flow-rate. The uranium contents of the eluate portions (determined fluorimetrically) are presented in Table 1. It is seen that 6 ml of $2M$ sulphuric acid suffice for the elution of 97% of the added uranium. The estimated D value for uranyl ions between Dowex 1-X8 and $2M$ sulphuric acid is about 5. Complete elution requiring another 4 ml of sulphuric acid will reduce the sensitivity by 30% because of the dilution. It is, however, necessary to wash out the remaining 3% of the uranium with 4 ml of $2M$ sulphuric acid before conditioning the column for reuse.

We tried to elute at higher temperatures in order to reduce tailing but an increase in temperature resulted in increased quenching. We therefore decided to cool the columns with tap water.

APPARATUS

The great number of samples and the high error that could result from contamination made it clear from the beginning that automation of the separation process was needed to maintain reproducible conditions over long working periods. The arrangement is shown in Figs. 1 and 2 and consists of a peristaltic pump system for feeding sample and reagent solutions to ion-exchange columns in a rack. Each rack holds 15 columns. The total ion-exchange cycle, sorption–washing–elution–reconditioning, is completed in about 4 hr. With two operators and two racks, it is possible to handle two distilled water blanks, two synthetic test-water samples and 56 samples in one working day. With 20 working days a month the capacity adds up to 1000 samples per month which is sufficient to meet current demand.

Experience shows that the columns should be reloaded with fresh resin after 10–20 exchange cycles. The reloading is facilitated by the ground-glass fittings separating the ion-exchange chamber from the rest of the column (Fig. 1).

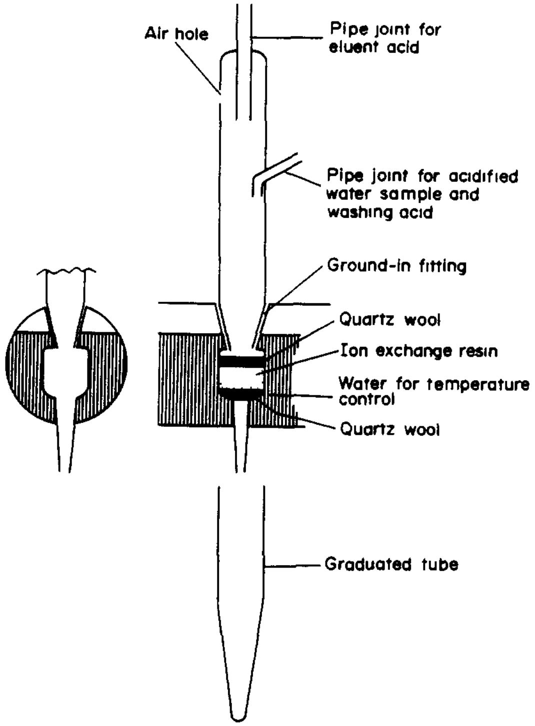

Fig. 1 Ion-exchange apparatus.

The resin is purified by conventional techniques and the smallest particles are removed by decantation. The last steps of the purification are washing with 2*M* and 0·01*M* sulphuric acid and with distilled water. A batch sufficient for several months' work is prepared at one time and stored in air-dry condition.

A Perkin–Elmer Type MPF-2A fluorescence spectrophotometer—equipped with a xenon arc lamp, Osram XBO 150W/1—was used for the measurements.

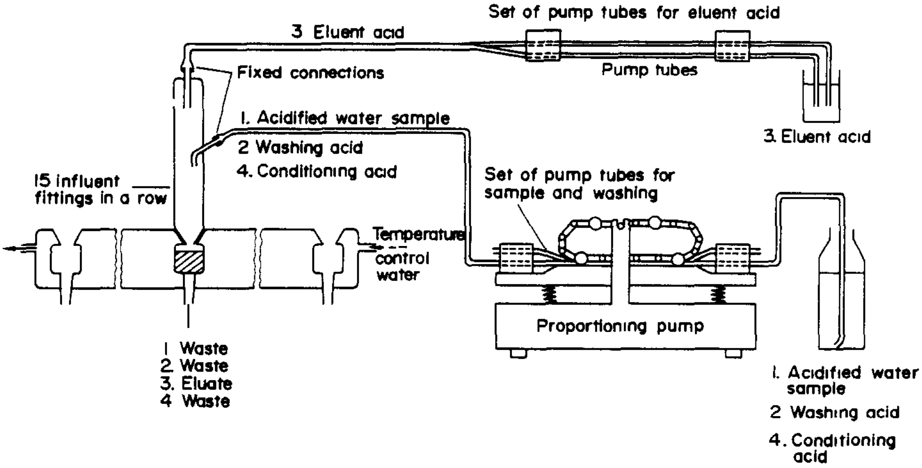

Fig 2. Arrangement of the apparatus. The numbers refer to the different steps of the ion-exchange cycle 1 sorption, 2 washing, 3 elution, 4 conditioning.

MATRIX FOR THE MEASUREMENT OF FLUORESCENCE

Phosphoric acid enhances the fluorescence of a solution containing uranyl ions.[11,12,13] We decided therefore to add phosphoric acid to the eluate. Fairly concentrated phosphoric acid (4*M*) should be used in order to minimize dilution. Maximum fluorescence was found to occur when 3 ml of phosphoric acid were added to 6 ml of the eluate. The enhancement factor is then 2·5 as compared to measurements on the original eluate. Small variations in these acid concentrations are of no importance for the fluorescence intensity. Sulphuric acid quenches the fluorescence in phosphoric acid, in this case by about 15%.

Spiking

Variations in the fluorescence yield can be corrected for by spiking if the fluorescence yield is independent of the uranyl ion concentration. To test if that was true for our system, we determined the fluorescence signals of a series of sample solutions containing quenchers and compared them with signals from solutions containing the same amount of uranium but no quenchers. The quencher concentrations used exceed the upper limit expected to be found in sample solutions after the ion-exchange process. The results summarized in Table 2 show that the fluorescence yields remain reasonably constant throughout the uranium concentration range under test. It is thus possible to spike with a relatively large amount of uranium.

In order to keep the fluorescence yield constant the stock spiking solution, fresh every month, has the same acid composition as the solution being measured. Its uranium concentration is adapted to the range of the uranium contents of the samples so that the two fluorescence signals of the solution are within the range of measurement. The spiking corresponds in our case to 7 ppM of U in a water sample. The volume and concentration of the spiking solution are chosen so as to give satisfactory precision without diluting the sample unduly. As a result of these considerations we add 0·3 ml of a standard solution containing 1500–2000 μg of U per l. to 3·0 ml of the measuring solution.

The regularly decreasing peak heights obtained from successive test samples at fixed measuring parameters are a measure of the condition of the resin beds and indicate when the beds should be exchanged.

Choice of wavelengths and measurement

The excitation spectrum of a uranium solution that is 1.35*M* in both phosphoric and sulphuric acids shows that maximum intensity of the fluorescence occurs when the excitation wavelength is 280 nm. The maximum bandwidth of the instrument gives maximum signal to background ratio.

The fluorescence emission spectrum of the solution displays peaks at 493, 516 and 540 nm. The peak at 493 nm is the most intense and was chosen for use. The peak at 516 nm is less suitable since it is sometimes disturbed.

The background is determined by scanning the emission monochromator through the wavelength range 470–510 nm. This mode of working makes it easy to distinguish between true fluorescence signals and false ones originating from dust particles in the measuring solutions or from electrical disturbances. Small irregularities in the spectrum may be smoothed out and not taken into account, as the intensity of the fluorescence signal is determined from the recorded spectrum. A high uranium content, above 0·1 ppm, in the original sample, gives a more complex spectrum which requires a background scanning through a wider wavelength range, *viz.* 460–540 nm.

Table 2 Dependence of the fluorescence yield on the uranium concentration at different quencher concentrations

Quencher	Quencher concentration, μg/l Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{3+}	Al^{3+}	Mn^{2+}	Cl^-	NO_3^-
Series 1	2500	2500	2500	2500	1250	250	125	6750	1730
Series 2	1250	1250	1250	1250	625	125	62·5	3380	860
Series 3	625	625	625	625	313	62·5	31·3	1680	430
Series 4	313	313	313	313	156	31·3	15·6	840	220

Uranium μg/l	Series 1 Fluorescence intensity* U	Q	Fluorescence yield %	Series 2 Fluorescence intensity* U	Q	Fluorescence yield %	Series 3 Fluorescence intensity* U	Q	Fluorescence yield %	Series 4 Fluorescence intensity* U	Q	Fluorescence yield %
11·0										3·2	2·0	62·5
21·9										5·0	3·0	60·0
32·7										8·8	5·3	60·2
44·4	14·0	2·4	17·2	12·8	4·5	35·6	12·3	6·0	48·8	11·0	6·2	56·3
88·7	33·0	5·3	16·1	29·5	8·8	33·5	26·0	11·3	43·5	26·0	15·6	60·0
133·8	50·4	8·6	17·1	45·0	13·5	30·0	43·8	18·0	41·2	45·5	28·8	63·3
177·4	70·7	11·0	15·5	66·0	18·5	28·0	60·0	27·5	45·8	61·5	38·0	61·7
221·8	86·0	14·0	16·3	80·0	22·6	28·2	71·5	33·0	46·2	74·0	45·5	60·8
Mean value			16·4			31·1			45·1			60·0
Standard deviation			0·7			2·3			2·9			2·1
Coefficient of variation, %			4·3			10·6			6·1			3·5

* *U* denotes solutions without quenchers
Q denotes solutions with quenchers
Intensity expressed in arbitrary units

The following formula gives the uranium content of the sample in ppM:

$$\frac{h_1 V_2 k}{h_2(V_1 + V_2) - h_1 V_1} \cdot \frac{V_e}{V_p}$$

where

V_1 = volume of unspiked solution in the quartz cell (ml)
V_2 = volume of added spiking solution (ml)
V_p = volume of influent sample (ml)
V_e = volume of eluate after phosphoric acid addition (ml)
h_1 = peak height of fluorescence signal above background (mm)
h_2 = peak height of fluorescence signal above background after spiking (mm)
k = concentration of U (μg/l.) in spiking solution

A small desk computer with programming facility is used to calculate the uranium content of the sample.

PROCEDURE

Add 1 ml of 2*M* sulphuric acid to 200 ml of sample, shake for 10 min and filter through a 1·2 μm cellulose nitrate filter. Pass the acidified sample through a conditioned ion-exchange column at a rate of 180 ml/hr. Wash the column with 120 ml of 0·01*M* sulphuric acid solution at the same rate and elute the uranyl ions with 6 ml of 2*M* sulphuric acid at a rate of 5 ml/hr. Add to this eluate 3·0 ml of 4*M* phosphoric acid and scan the fluorescence signal of 3·0 ml of this solution through the range 470–510 nm. Add 0·3 ml of the spiking solution directly to the sample solution in the quartz cell and scan again through the same wavelength range. Use the peak heights at 493 nm to calculate the uranium content of the sample.

To recondition the column, elute with a further 4 ml of 2*M* sulphuric acid and wash with 60 ml of 0·01*M* sulphuric acid. Discard the resin after 10–20 cycles.

For samples containing organic matter, fume the eluate overnight to dryness with 1·5 ml of 30% hydrogen peroxide in a perfectly clean teflon beaker (45 mm in dia). This leaves a black stain. Make sure that no sulphuric acid is left in the beaker. Leach with 10 ml of 0·8*M* phosphoric acid and 0·01*M* sulphuric acid while the beaker is still hot. After leaching (complete in about 30 min), add sufficient water to cover the bottom of the beaker and transfer to graduated tubes. Make up to 6 ml and proceed with the measurement as before, the spiking solution now being 1·33*M* in phosphoric acid and 0·0167*M* in sulphuric acid.

RESULTS

Table 3. Analysis of a synthetic water sample containing 1·87 ppM of uranium

Sample No.	Volume of eluate + 3·0 ml of 4*M* H_3PO_4, *ml*	Sample peak, *mm*	Spiked peak, *mm*	Calculated U conc., *ppM*
1	9·3	7·4	26·0	1·93
2	9·2	7·4	27·1	1·81
3	9·3	8·2	30·2	1·81
4	9·3	8·0	27·3	2·01
5	9·4	7·3	27·8	1·75
6	9·2	7·4	26·5	1·86
7	9·3	8·2	28·9	1·92
8	9·2	9·0	27·5	2·32
9	9·0	6·8	25·0	1·76
10	9·0	8·2	27·2	2·02
11	9·1	7·7	27·3	1·88
12	9·2	7·3	27·3	1·76
13	9·2	6·7	25·6	1·71
14	9·0	6·6	23·2	1·87
15	9·1	6·8	26·1	1·68
				Mean 1·87

Table 3 lists the results of 15 determinations of uranium in a synthetic water sample, a fresh ion-exchange column being used for each determination. The water sample contained 1·87 ppm of U, 10 ppm of Na^+, K^+, Ca^{2+}, 5 ppm of Al^{3+}, Mg^{2+}, 2·5 ppm of Fe^{3+}, 0·5 ppm of Mn^{2+}, Zn^{2+} and 41 ppm of Cl^-. The coefficient of variation was 8·6%. In routine work, every 30th sample is a test water sample. The coefficient of variation of 140 samples run over a period of 14 weeks was 10%.

Several factors affect the limit of detection for a given enrichment factor. The most important are the fluorescence yield of the sample solution being tested, the quality and state of the optical parts and the light source and the reproducibility of the peak height determination. If the solution contains only uranium and no quenchers, the detectable signal corresponds to 0·1 ppM of U, assuming that the smallest peak height that can be measured is 1 mm. The apparent uranium contents were less than 0·3 ppM in 97·5% of the 281 blanks analysed over a period of 28 weeks.

Samples very low in uranium or high in organic matter should be analysed according to the modified procedure given above, since quenching and increased background level otherwise combine to decrease sensitivity. The detection limit in routine work is then improved to 0·1 ppM for a 200 ml sample.

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Zusammenfassung—Eine Vorschrift zur fluorimetrischen Bestimmung von Uran in naturlichen Wassern wird angegeben. Die Nachweisgrenze betragt 0·3 ppM. Zur Voranreicherung des Urans um einen Faktor 22 und zur Abtrennung von fluoreszenzloschenden Ionen in der Probe wird ein Ionenaustauschschritt verwendet. Die Fluoresenz wird in einem Medium, das je 1 35 M Schwefelsaure und Phosphorsaure enthalt, gemessen Die Uranylionen werden durch Strahlung der Wellenlange 280 nm mit der Bandbreite 40 nm angeregt Das emittierte Signal wird von 470 bis 510 nm aufgenommen Nach Zugabe einer kleinen Menge Standard-Uranlosung zur Probenlosung wird das Fluoreszenzsignal nochmals aufgenommen und der Urangehalt der Probe aus den beiden Ablesungen berechnet Bei der Bestimmung von Uran in einer synthetischen Wasserprobe mit einem Urangehalt von 1 9 ppM betragt der Variationskoeffizient 8 5%.

Résumé—On décrit une méthode pour le dosage fluorimétrique de l'uranium dans les eaux naturelles La limite de détection est de 0,3 p p M On utilise l'échange d'ions pour préconcentrer l'uranium par un facteur 22 et le separer des ions inhibiteurs dans l'échantillon. On mesure la fluorescence dans un milieu qui est 1,35 *M* tant en acide sulfurique qu'en acide phosphorique. Les ions uranyle sont excités par la radiation de longueur d'onde 280 nm et largeur de bande 40 nm. Le signal émis est examiné de 470 a 510 nm Après addition rapide à la solution d'échantillon d'un petit volume de solution étalon d'uranium, le signal de fluorescence est examiné de nouveau et al teneur en uranium de l'échantillon est calculée a partir des deux lectures Le coefficient de variation est de 8,5% pour le dosage de l'U dans un échantillon synthétique d'eau ayant une teneur en uranium de 1,9 p p M.

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DETERMINATION OF THE OPTIMUM WORKING RANGE FROM A CALIBRATION CURVE FOR COLORIMETRIC ANALYSIS WITH AN "AUTOANALYZER"

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Summary—A study has been made of the types and distribution of errors in determining the optimum working range from a calibration curve for automated analysis Three error equations are derived for the fitting of a linear, quadratic or cubic curve, involving a thorough statistical analysis of the data The errors from a set of silica and alumina standards, requiring a quadratic and cubic fit respectively, compare favourably with replicate analyses of standard rocks done on a previous occasion

In the past, various authors[1-4] have made a study of the optimum working range for non-differential spectrophotometric analysis. Calculations were based either on the well-known equation

$$\frac{dc}{c} = \frac{0{\cdot}4343\,dT}{10^{-A}A}$$

when Beer's law was obeyed, or on a Ringbom–Ayres plot when it was not. However, Gridgeman[5] first pointed out the importance of the distribution of errors and the need to apply a statistical theory of errors, and Crawford[6] showed the ways in which errors could vary with transmission. Erdey *et al.*[7] proposed a method for error calculations which took into consideration the error due to fitting a straight-line curve. As all previous work in this field had been done with manual instruments, a rigorous statistical treatment of the type of errors involved was undertaken to find the optimum range for an "Autoanalyzer."

There are two independent sources of error with the calibration curve technique, one associated with the instrument and the other with the fitted curve. The types of instrument errors from an automated system are different from those of a manual instrument. In an automated system the baseline and 0%T (T = transmission) are obtained at the start of a run and not reset for each individual measurement, therefore the errors due to these two settings are considered to be zero; only when there is an error in setting 100% and 0% T is there a contribution to the overall error of T.[8,9,10] Any slight random fluctuations in the baseline and zero settings contribute nothing to the error in T. The fitted curve was therefore made to pass through the origin. The present paper deals only with random errors, but systematic errors (such as drift) have to be taken into account when they occur, since they may greatly affect the accuracy. Baseline drift may result from two factors; first, adsorption on the flow-cell may result in a gradual upward drift; secondly, instrumental drift may cause either an upward or downward movement of the baseline.

If adsorption is the prevalent or only factor to cause drift then this can be corrected by subtracting the chart reading of the test solution (I_c) from the baseline chart reading (I_0). The change in baseline can usually be considered as constant over a given time-length of the chart record, which enables the slowly changing baseline to be distinguished from any baseline fluctuations (instrumental noise). If the drift is purely instrumental then transmittance readings (I_c/I_0) will give an adequate correction. A simple case will illustrate why (I_c/I_0) should be measured and not ($I_0 - I_c$) when instrument drift occurs. Let the initial readings for a given solution be $I_0 = 100\%$ and $I_c = 30\%$; if drift occurs so that $I_0' = 95\%$ and $I_c' = 28{\cdot}5\%$, then, $I_0/I_c = I_0'/I_c'$ because the solution will transmit the same fraction of light, but $I_0 - I_c = 70$ and $I_0' - I_c' = 66{\cdot}5$. If adsorption is the main cause of drift then for initial readings of $I_0 = 100$ and $I_c = 30$, the new readings after drift would be $I_0' = 95$ and $I_c' = 25$, *i.e.*, $I_0 - I_c = I_0' - I_c' = 70$, but $I_0/I_c \neq I_0'/I_c'$. In the latter case, the instrument settings will have remained constant.

The cause of drift can be found by setting the baseline with a reagent blank, carrying out a normal run, washing with distilled water or suitable solvents, and finally running the reagent blank again; if there is no instrument drift then the baseline should return to its original setting. Since automated analyses are more prone to adsorption effects than manual methods, paper calibrated in absorbance units should not be used in the chart-recorder when adsorption occurs as there is no easy correction for drift. Other systematic errors which cause deviations from Beer's law can be compensated for by the construction of a calibration curve, but the error from dark-current drift can only be offset by frequent running of the standard solutions. Lastly, since a single continuous-flow cell is used, and left undisturbed during all runs, the errors due to variation in the path-length may be ignored. Even when adsorption on the flow-cell occurs this still applies, for although a high concentration of the test species on the flow-cell walls is enough to cause a significant absorbance (and hence drift), the width of a single layer of the species will cause an insignificant reduction in the flow-cell path-length. Therefore, the volume of solution passing through the cell can be considered to be constant throughout a run.

The variation in repeated measurements[11] of either ($I_0 - I_c$) or (I_c/I_0) is the sum of several independent errors[6] which have so far not been considered since they cannot be analysed separately. However, the overall sum at a given concentration must be analysed to find out whether or not they are independent of the transmission value.

In the present study, three error equations are derived for fitting linear, quadratic or cubic curves.

DERIVATION OF THE RELATIVE ERROR EQUATIONS

Case I. Error for a straight-line fit

A straight line passing through the origin is described by the equation

$$A = mc$$

where A = absorbance, c = concentration, m = the slope.

The equation for propagation of errors is formed by expansion of the function $c = f(A, m)$ in a Taylor series:

$$S_c^2 = \left\{\frac{\partial c}{\partial A}\right\}^2 S_A^2 + \left\{\frac{\partial c}{\partial m}\right\}^2 S_m^2 \qquad (1)$$

where S_c, S_A and S_m are the standard deviations of the concentration, absorbance, and gradient respectively.

Since the instrument responds to a change in transmittance (linear scale), the variance of A is dependent on the transmission variance (S_T^2) as follows.

From Beer's law

$$A = -\log T$$

therefore

$$S_A^2 = (0{\cdot}4343 S_T \,.\, 10^A)^2 \tag{2}$$

On substitution of (2) into (1), the relative error in c ($100S_c/c$) is given by

$$\frac{100S_c}{c} = \left\{\left(\frac{0{\cdot}4343 \,.\, 10^A \,.\, S_T}{A}\right)^2 + \left(\frac{S_m}{m}\right)^2\right\}^{1/2}$$

Case II. The error from a quadratic fit

The equation to be fitted is of the type

$$A = qc + tc^2 \tag{3}$$

The propagation of errors equation is again obtained from the expansion of $c = f(A, q, t)$ in a Taylor series, neglecting the second order powers being neglected since the errors are very small. However, since q and t are not independent (unless an orthogonal polynomial is fitted) the covariances of the polynomial coefficients cannot be neglected:

$$S_c^2 = \left\{\frac{\partial c}{\partial A}\right\}^2 S_A^2 + \left\{\frac{\partial c}{\partial q}\right\}^2 S_q^2 + \left\{\frac{\partial c}{\partial t}\right\}^2 S_c^2 + \frac{2\partial c}{\partial q} \cdot \frac{\partial c}{\partial t}\,\mathrm{cov}(q, t) \tag{4}$$

and by substitution of (2) into (4) the relative error for a quadratic fit is given by

$$\frac{100S_c}{c} = \frac{100}{(q + 2tc)}\left\{S_q^2 + c^2 S_t^2 + 2c\,\mathrm{cov}(q, t) + \frac{0{\cdot}4343 \,.\, S_T\, 10^A)^2}{c^2}\right\}^{1/2}$$

Case III. The error from a cubic fit

The equation to be fitted is of the type

$$A = qc + tc^2 + rc^3$$

By a similar treatment to that for forming the quadratic equation error, the cubic equation error is given by:

$$\frac{100S_c}{c} = \frac{100}{(q + 2tc + 3rc^2)}$$

$$\times \left\{S_q^2 + C^2 S_t^2 + c^4 S_r^4 + 2c\,\mathrm{cov}(q, t) + 2c^2\mathrm{cov}(q, r) + 2c^3\mathrm{cov}(r, t)\right.$$

$$\left. + \frac{(0{\cdot}4343 \,.\, 10^A \,.\, S_T)^2}{c^2}\right\}^{1/2}$$

EXPERIMENTAL

Apparatus

A Technicon "Autoanalyzer" with a chart-recorder fitted with transmission paper was used. Transmission paper was used in order to calculate the transmission variance (S_T^2), although for routine analysis absorbance paper is used. The "Autoanalyzer" is a twin-photocell instrument with a single light-source, the two beams being balanced by a null-point potentiometer.

Method

Standard calibration solutions for silica and alumina were prepared from U S Bureau of Standards Sample No. 99 (Feldspar). Silica was determined by the well-known molybdenum blue method,[12] using a colorimeter fitting with 815-nm filters and silicon photocells. Alumina was determined by a modification of the Eriochrome Cyanine R method developed by Hill,[13] using a colorimeter with 535-nm filters and selenium photocells.

Reagents were introduced into the system and the pen-recorder set first at $I_0 = 99$ and then at 0%T with the sample beam cut off from the sample photocell. A series of standards was then introduced into the system, the lowest concentration standard being introduced first, followed by successively higher concentrations The whole operation was repeated seven times.

RESULTS AND DISCUSSION

The fitted curve was determined from the average of three and two repetitions of the I_0-I_c measurements, for alumina and silica respectively, since each standard is run that number of times during a normal laboratory analysis. The first and last of the seven sets of standards were chosen for this, plus the fourth set in the case of alumina. The baseline was set at $I_0 = 99$ and not at $I_0 = 100$ in case baseline drift occurred. A correction was not made for the reduction in the scale-width (due to the $I_0 = 99$ baseline setting) since absolute values of %T are not required when a calibration method is used. A least-squares fit was computed,[14] and the inverse matrix calculated so that the standard errors of the polynomial coefficients and their covariances could be determined. A test was carried out to find the best-fitting polynomial.[15] Once this had been determined the results were substituted into the appropriate error equation.

The transmission variance is the sum total of several independent errors; these errors may be constant with T, proportional to T, and proportional to $\sqrt{T}$.[6] After correction for the reduction in scale-width, the overall effect of these errors was assessed by calculating the variance of transmission at each concentration level and applying Cochrane's test[16] for homogeneity of variance. If the test shows a non-homogeneity of variance, then the individual variances at each concentration level should be substituted into the appropriate error equation. In the case of silica and alumina the variance was found to be constant over the transmission range investigated. Therefore, these variances are estimates of the same variance and may be combined to yield an improved estimate of S_T^2 by use of the equation

$$S_T^2 = \frac{\sum_{i=1}^{p} \sum_{j=1}^{n} (x_{ij} - \bar{x}_i)^2}{m(n-1)}$$

where p = number of standards, n = number of measurements of each standard, $x = (100 - \%A)/100$, $\%A$ being $100(I_0 - I_c)/I_0$, which corrects %A for the slight reduction in scale-width from the setting of $I_0 = 99$, and $\bar{x}$ = average value of x at each concentration level.

The absorbance values calculated from the fitted curve (Ac) were corrected for the reduction in scale-width and used to calculate the factor 10^A in the error equations.

Table 1 Silica determination

Equation of fitted curve: $A = 0{\cdot}007644C - 0{\cdot}000004C^2$

Concentration of standards, μg/ml	A observed	A calculated	Relative error, %*
9·9	0·073	0·075	0·77
19·9	0·149	0·151	0·51
29·9	0·226	0·225	0·42
39·9	0·300	0·299	0·37
49·9	0·372	0·372	0·34
59·9	0·446	0·444	0·32
69·9	0·516	0·515	0·32
79·8	0·588	0·585	0·33
89·8	0·658	0·654	0·36
99·8	0·726	0·723	0·40
G-1	0·460		0·41†
R-117	0·490		0·39†

* Calculated from the statistics

† Observed for replicate analysis.

Table 2. Alumina determination

Equation of fitted curve $A = 0{\cdot}016883C + 0{\cdot}001942C^2 - 0{\cdot}000054C^3$

Concentration of standards, μg/ml	A observed	A calculated	Relative error, %*
1·91	0·038	0·039	4·12
3·82	0·089	0·089	2·04
7·64	0·217	0·218	0·93
9·56	0·294	0·291	0·80
11·48	0·370	0·368	0·77
15·29	0·516	0·519	0·84
19·11	0·656	0·655	1·14
G-1	0·540		0·91†
R-117	0·450		0·82†

* Calculated from the statistics

† Observed for replicate analyses

Table 1 shows the relative errors for silica, calculated from a quadratic fit and Table 2 that for alumina, calculated from a cubic fit. The relative errors at appropriate absorbance levels may be compared with the errors found for replicate[11] analysis of standards W-1[17] and R-117[18] on a previous occasion (the total error of the standards will therefore include a sample preparation error). Only approximate absorbance readings are given for W-1 and R-117 since they will vary slightly owing to variations in the reagent strengths and instrument settings on the two occasions. The transmission variance will also vary slightly from day to day. However, taking these factors into consideration, the errors compare favourably.

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Zusammenfassung—Die Art und die Verteilung der Fehler wurde untersucht, die beim Ermitteln des optimalen Arbeitsbereichs für die automatisierte Analyse aus einer Eichkurve auftreten. Es werden drei Fehlergleichungen für die Anpassung einer, quadratischen oder kubischen Kurve abgeleitet; dabei wird eine eingehende statistische Analyse der Daten vorgenommen Die Fehler bei einem Satz von Kieselsaure- und Aluminiumoxidstandards, die quadratische bzw kubische Anpassung erfordern, brauchen einen Vergleich mit früher an Standardgesteinen ausgeführten wiederholten Analysen nicht zu scheuen

Résumé—On a effectué une étude des types et de la distribution des erreurs lors de la détermination du domaine de travail optimal à partir d'une courbe d'étalonnage pour analyse automatisée. On a établi trois équations d'erreur pour l'adaptation d'une courbe linéaire, quadratique ou cubique, faisant intervenir une analyse statistique poussée des données. Les erreurs d'un lot d'étalons de silice et d'alumine, nécessitant une adaptation quadratique et cubique respectivement, sont très comparables à des analyses répétées de roches étalons faites à une occasion antérieure.

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SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM WITH *o*-PHENYLENEDIAMINE

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Summary—Platinum(IV or II) reacts with *o*-phenylenediamine, at pH 6 5, to form light blue solutions having maximum absorption at 703 nm The reaction, slow at room temperature, is complete in 3–4 min at temperatures near 100° Use of dimethylformamide in the solution prevents precipitation of the reaction product The colour is stable for at least 24 hr Effects of heating temperature and time, pH, reagent concentration, and other variables have been studied The system conforms to Beer's law over the concentration range investigated Optimum concentration range for measurement in 10-mm cells is 0 4–1·4 ppm of platinum, the molar absorptivity is 9·83 × 10^3 l mole^{-1} mm^{-1} Interference from foreign ions has been evaluated, and methods for removal or masking of interferences have been tested. In the colour-forming reaction, platinum(IV) is reduced by the organic reagent to platinum(II), which is then complexed with the reagent The metal ligand ratio of 1 2 was indicated by solution spectrophotometric measurements, and was confirmed on the solid reaction product by elemental analysis and by mass spectrometric examination

Spectrophotometric methods for the noble metals have been evaluated critically by Beamish,[1] who has also written an important reference work on the analytical chemistry of the noble metals.[2] In reviewing the work up to early 1964, Beamish comments on the deficiency of methods for the more common of the noble metals, namely, gold and platinum. Since that time a few additional spectrophotometric methods for platinum have been published. Chechneva and Podchianova[3] used 1,4-diphenylthiosemicarbazide with platinum(IV) to produce a green solution, followed by extraction of the product into chloroform for measurement of absorbance at 710–750 nm; the molar absorptivity was about 10^3 l. mole^{-1}. mm^{-1}. Senise and Petombo[4] determined platinum by extraction from acidic thiocyanate solution with ethyl acetate, after precipitation with triphenylisopropylphosphonium ion. Absorbance of the extract was measured at 365 nm; the optimum range was 5–20 ppm of platinum, and the absorptivity about 5·6 × 10^2 l. mole^{-1}. mm^{-1}. Hashmi and Rashid[5] used a mixture of isonicotinic acid hydrazide and 2,3,5-triphenyltetrazonium chloride to generate formazan, which produced a pink colour (absorption peak at 480 nm) with platinum(IV) in the 1–5 ppm range; other oxidizing agents also produced the colour. Johnson and Ayres[6] used 3,4-diaminobenzoic acid, at pH 10–12, to give a blue-green solution (absorption maximum at 715 nm); optimum range was 0·35–1·20 ppm of platinum, absorptivity 1·1 × 10^4 l. mole^{-1}. mm^{-1}, and Sandell sensitivity[7] 0·0017 μg/cm. El-Ghamry and Frei[8] formed a red ternary complex with the hexa-ammineplatinum(IV) cation and the counter-ion 2,4,5,7-tetrabromofluorescein ethyl ester at pH 10; absorptivity at 555 nm was about 8 × 10^3 l. mole^{-1}. mm^{-1}.

Work in this laboratory has continued in a search for additional reagents for the platinum elements, in the hope of finding methods that are more sensitive and/or more selective than existing methods. In testing several organic compounds as possible colour reagents for platinum, it was noted that platinum(IV) solutions treated with *o*-phenylenediamine (OPDA) became slightly fluorescent upon standing overnight Addition of dimethylformamide (DMF) to a mixture of platinum(IV) and OPDA produced a light blue solution having a sharp, intense absorption peak at 703 nm; useful absorbance was produced by less than 1 ppm of platinum. This observation initiated the detailed investigation reported herein. In 1960, Sen Gupta[9] reported the use of OPDA as a reagent for platinum(IV) in acetate buffer; the orange solutions were measured at 450 nm. Optimum range was 4–12 ppm of platinum; calculations from his data give an absorptivity of $1{\cdot}1 \times 10^3$ l. mole^{-1}. mm^{-1} and a sensitivity of 0·018 μg/cm (erroneously reported as 0·003 μg/cm). In the present work the solution conditions are radically different from those used by Sen Gupta, and the sensitivity is greater by about one order of magnitude.

EXPERIMENTAL

Apparatus

Spectral scans were made with a Beckman Model DK-1 Recording Spectrophotometer, equipped with a cell-well thermostat. Precision absorbance measurements at a fixed wavelength were made on a Beckman Model DU Quartz Spectrophotometer; matched cells of 10·0 mm optical path were used, and a fixed slitwidth of 0 08 mm

Measurements of pH were made with a Beckman Century SS solid-state pH meter having both standard and expanded scales, and a miniature type calomel–glass electrode system

Analytical weighings were made on either a Mettler Type H5 or a Mettler Micro Type M5 balance, depending upon load and/or accuracy desired. Volumetric ware used for critical transfers and dilutions was of Class A tolerance

Reagents

Standard platinum solutions. Much of the early work in this study used a 10-μg/ml solution of platinum(II), prepared by dissolving the requisite weight of pure K_2PtCl_4 in a small amount of concentrated hydrochloric acid, and diluting to known volume. A stock solution of platinum(IV) was prepared by dissolving 0·49992 g of Grade No 1 platinum thermocouple wire (assay, 99·99% minimum purity) in *aqua regia*, followed by repeated evaporations with hydrochloric acid, and final addition of 5 ml of concentrated hydrochloric acid and dilution to 500 0 ml. The accuracy of this solution was checked by evaporation and hydrogen reduction of aliquots of the solution and weighing of the residual platinum. Concentrations based on weight of platinum taken and platinum residue obtained agreed to better than 1 in 5000 The stock solution, 1 000 mg/ml, or $5\ 125 \times 10^{-3}M$, was diluted volumetrically for working standard solutions

o-Phenylenediamine The OPDA (Eastman Organic Chemicals No. 1700) was initially used as received. Later work showed that an unknown impurity was causing low and variable results Use of a recrystallized reagent eliminated this difficulty The reagent solution finally adopted contained 35 mg of OPDA in 25 ml of DMF

N,N-*Dimethylformamide* Quite late in the investigation it was discovered that the brand of DMF being used was the cause of many confusing results Change to a different source of DMF eliminated this source of error

Buffers Phosphate buffer solutions were prepared so that a 2-ml portion (as used in the recommended procedure) contained 2·75 mg of potassium dihydrogen phosphate, and sodium hydroxide in the amounts requisite to vary the pH over a wide range

All other chemicals were ACS reagent grade

Recommended procedure

A sample containing 4–14 μg of platinum(IV or II) in a volume of 1 ml is taken in a 10-ml volumetric flask One ml of OPDA reagent solution (in DMF) is added, and the pH is adjusted to 6 5 by addition of 2 ml of KH_2PO_4–NaOH buffer. The flask containing the reactants is supported in a boiling water-bath for 4 min, during which time the light blue colour develops DMF is added to bring the solution volume to approximately 10 ml, the flask is removed from the bath and cooled to room temperature, and final adjustment to exactly 10 ml is made with DMF Absorbance of the solution is measured at 703 nm, against a water blank (a reagent blank has no measurable absorption at this wavelength)

RESULTS AND DISCUSSION

Calibration, range, sensitivity, and precision

Data for the calibration curve are shown in Table 1; each absorbance is the average of three closely agreeing measurements. Constant values of A/ppm show that the system follows Beer's law; the calibration curve is a straight line which extrapolates through the origin. The optimum range for measurement in 10-mm cells is 0·4–1·4 ppm. The Sandell sensitivity is 0·002 μg/cm; the specific absorptivity is 0·0504 ppm^{-1}. mm^{-1} and the molar absorptivity is $9{\cdot}83 \times 10^3$ l. mole^{-1}. mm^{-1}. This method, and the method reported by Johnson and Ayres[6] appear to be the most sensitive spectrophotometric methods for platinum thus far, both being about at the theoretical limit of molar absorptivity.[10]

Table 1 Calibration data

Platinum, *ppm*	Absorbance, *A*	*A/ppm*
0·400	0·202	0·505
0·500	0·252	0·504
0·600	0·303	0·505
0·700	0·353	0·504
0·800	0·402	0·502
0·900	0·453	0·503
1·000	0·503	0·503
1·100	0·554	0·504
1·200	0·604	0·503
1·300	0·655	0·504
1·400	0·705	0·504
	Average	0·504

Precision of the method was evaluated by preparing and measuring 20 identical samples containing 1·00 ppm of platinum (a concentration near the middle of the optimum range); the absorbance averaged 0·503, with a standard deviation of 0·002.

Effect of pH

A series of solutions containing 1·00 ppm of platinum(IV) was prepared by the recommended procedure, except for variation in the buffer added. The results are recorded in Table 2. Maximum absorbance (0·504) was reached at pH 6·5; the absorbance was within experimental error over the range pH 6·0–6·7.

Development time, stability

The time required for full colour development depended upon concentration of platinum, concentration of OPDA, pH, and temperature. In samples containing 1·00 ppm of platinum, treated by the recommended procedure, absorbance increased very rapidly during the first minute and reached full development in 3 min; additional heating up to 10 min did not produce further change. A standard development time of 4 min was adopted to ensure full development of all samples. (Exception: cases of certain foreign ions requiring masking with EDTA).

Five samples, each containing 1·00 ppm of platinum, were developed by the recommended procedure and the absorbance was read as soon as the solution was cooled

Table 2. Effect of pH

pH	Absorbance
3·5	0·030
4·0	0·051
4·5	0·131
5·0	0·365
5·6	0·474
6·0	0·501
6·3	0·503
6·5	0·504
6·7	0·503
7·5	0·485
8·0	0·462
9·0	0·398
10·0	0·305

to room temperature (zero time reading). Readings were taken at 1-hr intervals for the next 4 hr, and then at longer time intervals up to a total of 30 hr; all absorbances were within the range 0·501–0·505. Samples that were retained for 4 days showed no change in absorbance. Therefore, no special precautions regarding stability need to be taken, except when rhodium interference is encountered; in that event, the absorbance should be measured promptly after the solution is cooled.

Effect of temperature

The colour developed very slowly at room temperature. As the temperature of the reaction mixture was increased up to about 90°, development was more rapid and the final absorbance (for a given amount of platinum) was greater. From 90° to 100°, development rate still increased, but without increase in final absorbance. Therefore, to attain full development in the shortest time with the simplest equipment, a bath of boiling water was used.

The effect of change in temperature on samples already prepared by the recommended procedure was tested by scanning 1·00-ppm samples with the Beckman DK-1 recording spectrophotometer, using the thermostatic cell holder adjusted to different temperatures in the range 27–81°. Temperature increase caused a decrease in absorbance of about 0·002 per 1°. The change was reversible on decreasing the temperature, and was probably due to the volume change of the solution with change in temperature. Although the temperature coefficient of absorbance is small, it is prudent to make sure that all samples are at the same temperature before absorbance is measured.

Purity and stability of reagent

The solid reagent appeared to be stable under ordinary storage conditions. A melting point test on the reagent as received cast some doubt on its purity. A large amount of the solid OPDA, as received, was dissolved in hot DMF, and the solution was then cooled in an ice-bath. The recrystallized product was separated on a fritted glass funnel, washed with ice-cold water, then dried at 95°. Melting point determination indicated a high-purity OPDA. Use of the recrystallized reagent eliminated the lack of precision of results previously experienced with the original OPDA.

Water solutions of OPDA were not stable for more than 2 hr at room temperature; the stability was increased somewhat by storage in an ice-bath. Aqueous solutions of the reagent were used in some of the early work because they gave more consistent results than solutions in DMF It was later found that the inconsistent results were caused by impure DMF. After a source of pure DMF was found, the OPDA reagent dissolved in DMF was used with excellent results. The reagent solutions in DMF were stable for at least 2 days; solutions kept longer than this began to show some yellow colour of oxidation products of OPDA (probably diaminophenazine). In practice, a fresh solution (35 mg of OPDA in 25 ml of pure DMF) was prepared at least every other day.

Effect of reagent concentration

A series of solutions of 1·00 ppm of platinum was prepared in which the mole ratio of OPDA to platinum was varied from 1 : 1 to 400 : 1. The absorbance reached a constant value at a mole ratio of about 150 : 1. The 1 ml of reagent solution specified in the recommended procedure is equivalent to a mole ratio of 180 : 1 at the maximum platinum concentration used in this study.

Effect of DMF concentration

The product formed by reaction of platinum solution with OPDA at pH >5 is not soluble in water, but is soluble in a few organic solvents, notably in DMF and in dimethylsulphoxide (DMSO). A series of solutions containing 1·00 ppm of platinum was prepared by the recommended procedure, up to the point of addition of DMF. The amount of DMF in the final solution was varied from 20 to 80% v/v. Below 40% v/v DMF the reaction product was only slightly soluble, and more oxidation of the OPDA occurred during colour development. Full colour development was attained at DMF concentrations of 70% and above, which still allowed for an appreciable amount of water from the original solutions. This amount of DMF gave the highest absorbances with good precision, and also improved the stability of the developed samples. Use of a much larger amount of DMF decreased the rate of colour development.

Order of addition

At the pH used in the development procedure, hydrolysis of the platinum solutions took place if the buffer was added before the OPDA. Hence, the order of addition must be platinum solution, OPDA reagent, then buffer. DMF should not be added until the reaction is complete, because it retards the reaction and affects the precision of results.

Effect of foreign ions

These effects were studied by adding the ion in question to the platinum solution (1·00 ppm of platinum in the final solution), then developing by the usual procedure. Cations were added in the form of chlorides, nitrates, or sulphates, to a maximum of 50 ppm; anions were added in the form of sodium or potassium salts, to a maximum of 500 ppm. The tolerance for a given ion is the maximum amount that can be present and produce an absorbance difference no greater than 0·01 absorbance from that for the platinum alone. Table 3 gives the results. If serious interference was observed, an attempt was made to eliminate or minimize it by use of masking agents (see next paragraph); the results are shown in the last column of Table 3.

Table 3 Summary of interference studies

Foreign ion	Tolerance, *ppm* Original	With masking	Masking agent, comments
Pd(II)	0·2	8	200 ppm EDTA
Ir(IV)	2	5	200 ppm EDTA
Rh(III)	1	—	Measure immediately
Os(III)	0·2	—	
Ru(III)	0·3	2	200 ppm EDTA
Au(III)	0·2	3	200 ppm I^-
Fe(III)	5	—	
Ni(II), Co(II)	10	—	>50 ppm with filtering
Pb(II)	15	—	>50 ppm with filtering
Cd(II), Zn(II)	>50	—	
Mn(II)	20	—	>50 ppm with filtering
Cr(III)	12	—	
Cu(II)	0·1	5	200 ppm EDTA
Hg(II)	0·3	6	200 ppm EDTA
Ca(II)	6	20	200 ppm EDTA
NH_4^+	100		
SO_4^{2-}	50		
Br^-, I^-	>500		
NO_3^-, ClO_4^-	>500		
Acetate	>500		
EDTA	200		Double the heating time
Citrate	300		
Tartrate	400		

Removing or minimizing interferences

Elimination of interference from foreign ions can be accomplished by physical removal procedures, such as the following: distillation of ruthenium and/or osmium as their volatile tetroxides; precipitation of palladium as its dimethylglyoximate from acid solution; precipitation of other platinum elements and most base metals as their hydrous oxides, at controlled pH, leaving platinum(IV) in solution. These methods are inconvenient and time-consuming. It is simpler if a reagent or reagents can be found to mask the interference by forming complexes that are more stable than the platinum–OPDA complex of interest. For this purpose, ethylenediaminetetra-acetic acid (EDTA) or, more exactly, its disodium salt, is a useful reagent, in that it forms complexes (of widely different stabilities, to be sure) with practically all metal ions.

All of the other platinum elements, as well as gold, interfered at rather low concentrations. Addition of 200 ppm of EDTA was effective in eliminating or decreasing much of this interference, although it was not effective against interference from osmium or rhodium. Rhodium could be tolerated up to 1 ppm if the absorbance for platinum was measured promptly after colour development. Osmium above 0·2 ppm would require distillation removal. The good results in masking gold(III), palladium(II), iridium(IV), copper(II), mercury(II), *etc.*, were due to the fact that EDTA reacts rapidly with these ions, whereas it reacts quite slowly with platinum solutions.[11] When using this method, EDTA must be added to the sample just before starting the development; the sample and EDTA are heated together for 1 min, then the usual procedure is followed, except that the heating time is doubled.

Interference from copper(II) is of special interest, in that the amount of interference is almost independent of the amount of copper(II) present, even down to very low concentrations. Copper(II) is known to catalyse air oxidation of OPDA,[12] which probably explains this effect. Addition of EDTA prevented the catalytic action of copper(II), but the blue colour of the copper–EDTA complex still caused some interference in the platinum determination. Iron(III) also oxidized OPDA, thus decreasing the concentration available for complexation of platinum. Addition of a larger amount of OPDA reagent decreased iron(III) interference.

Ions of several of the base metals (nickel, cobalt, manganese, lead, *etc.*) interfered by precipitation of their hydrous oxides in the nearly neutral solution used in the procedure. This kind of interference was best removed by simply filtering the mixture after the colour development procedure.

STUDY OF REACTION AND PRODUCT

Absorption spectra

A solution of hexachloroplatinate(IV), $PtCl_6^{2-}$, has a weak absorption band at 460 nm, and strong absorption below 440 nm. Tetrachloroplatinate(II), $PtCl_4^{2-}$, of the same platinum concentration, has a moderately strong absorption band at 405 nm. Neither solution has significant absorption in the 600–800 nm region. Likewise, the OPDA reagent has negligible absorption in the 600–800 nm region. Therefore, any unreacted components will not register in absorbance measurements at 703 nm, the analytical wavelength of the present method. A freshly prepared solution of OPDA had a weak absorption centred at 430 nm; when the solution was aged at room temperature or by heating, the 430 nm absorption increased. Addition of iron(III) to the OPDA solution caused marked increase in the 430-nm absorption, and the solution assumed a pronounced yellow colour due to the oxidation product.

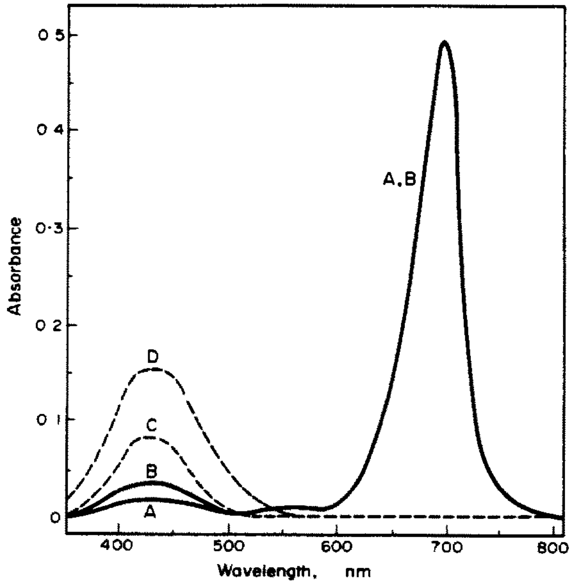


Fig 1 Spectral curves of platinum–OPDA complex and of OPDA reagent. A OPDA + 1·0 ppm of platinum(II), B. OPDA + 1 0 ppm of platinum(IV), C. OPDA after long heating in air, D OPDA oxidized with iron(III)

The absorption spectrum of a solution containing 1·00 ppm of platinum(IV), developed by the recommended procedure and measured against a water blank, showed the intense absorption at 703 nm characteristic of the platinum–OPDA complex, and a weak absorption at 430 nm; see Fig. 1. An identical solution prepared from platinum(II) had an identical absorption curve, except that absorption around 430 nm was negligible. Furthermore, increasing the amount of platinum(IV) caused corresponding increase in the intensity (absorbance) of the 430-nm peak, whereas varying the amount of platinum(II) had no effect on the 430-nm absorbance, provided the heating time was not excessive. It is obvious, therefore, that absorption at 430 nm is due to oxidation product(s) of OPDA, and that the use of this reagent with platinum(IV) involves reduction of the latter to platinum(II) and oxidation of the OPDA, followed by formation of the blue complex. A similar situation has been observed in this laboratory in the reaction of 3,4-diaminobenzoic acid with platinum(IV).[6]

Mole ratio study

Attempts to apply this method[13] gave little useful information, with solutions at the 1 ppm level; a very large excess of OPDA was required to attain constant absorbance, and the great curvature of the 703-nm absorbance *vs.* mole ratio OPDA/platinum plot precluded any meaningful extrapolation of the initial and the final portions of the plot. Application of the method in the converse sense, with OPDA held constant (at $1{\cdot}00 \times 10^{-4}M$) and platinum concentration varied, gave an absorbance *vs.* mole ratio platinum/OPDA plot, the first part of which was linear and identical with the calibration curve of the analytical method. As the platinum/OPDA ratio approached 0·5 the plot assumed considerable curvature and with increasing ratio the absorbance reached a value high enough to establish that the complex could not have a ligand: metal ratio higher than 2 : 1.

In an attempt to gain information concerning the redox reaction between platinum(IV) and OPDA, absorbance measurements at 430 nm (where the oxidation product of OPDA absorbs) were made on a series of solutions in which the concentration of platinum(IV) was held constant at $4{\cdot}1 \times 10^{-5}M$ and the OPDA concentration was varied up to 10 times that of the platinum. Extrapolation of the linear portions of the plot intersected at 0·75 mole of OPDA per mole of platinum(IV), corresponding to a stoichiometry of 3 OPDA to 4 platinum(IV).

Continuous variations method

Application of this method[14,15] was done initially with platinum(II), in order to avoid any complication introduced by oxidation of OPDA by platinum(IV). Figure 2, curves A and B, shows the plots for two different total concentrations of reactants. Extrapolations of the initial and final portions of the curves intersect at 0·67 mole-fraction of OPDA, corresponding to a reaction stoichiometry of 2 OPDA to 1 platinum(II). Curve C of Fig. 2 is the continuous variations plot using platinum(IV) and the same total concentration of reactants as with platinum(II) in curve A; the maximum absorbance attained is the same in the two cases, but with platinum(IV) the curve maximum occurs at 0·73 mole-fraction of OPDA. The marked change of slope at mole-fraction 0·3 is associated with the redox reaction between OPDA and platinum(IV). Based on the OPDA : Pt(IV) = 3 : 4 stoichiometry in the redox reaction (mole-ratio from absorbance measurements at 430 nm) and the OPDA : Pt(II) = 2 : 1 stoichiometry in the complexation reaction [continuous

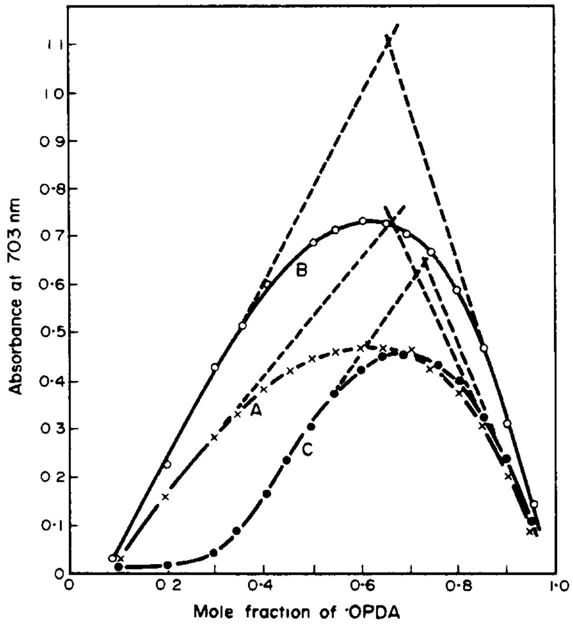


Fig 2 Continuous variations plots. A. OPDA + platinum(II) = 4·1 × $10^{-5}M$, B OPDA + platinum(II) = 6·2 × $10^{-5}M$, C OPDA + platinum(IV) = 4·1 × $10^{-5}M$

variations measurements using platinum(II) and 703 nm absorbances], the overall stoichiometry can be represented as follows:

$$3\ \text{OPDA} + 4\ \text{Pt(IV)} \rightarrow \text{oxidation products} + 4\ \text{Pt(II)}$$
$$8\ \text{OPDA} + 4\ \text{Pt(II)} \rightarrow 4\ \text{Pt(OPDA)}_2\ \text{complex}$$

Total: 11 OPDA + 4 Pt(IV) → oxidation products + 4 Pt(OPDA)_2 Mole-fraction of OPDA = 11/15 = 0·73, as in curve C of Fig. 2.

The heavy curvature of the continuous variations plots indicates that the formation constant of the platinum(II)–OPDA complex is not very large. By calculation analogous to that given by Meites and Thomas[16] the formation constant evaluated from Fig. 2, curve A, is 1·7 × 10^{10}, and from curve B it is 0·86 × 10^{10}, averaging 1·3 × 10^{10}.

Isolation and analysis of the product

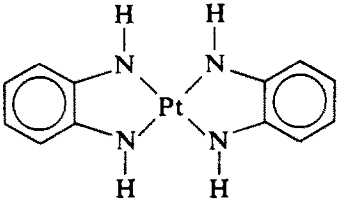
A 0·30-g sample of K_2PtCl_4 was dissolved in a small amount of hydrochloric acid, then diluted to 200 ml with water. A concentrated solution of OPDA containing 10 g of the solid in 20 ml of DMF was added to the platinum solution and the pH was adjusted to nearly neutral with sodium hydroxide. The reaction mixture was heated on a boiling water-bath for 1 hr, during which the colour became dark blue and then purple After cooling in an ice-bath, the mixture was suction-filtered with a sintered glass funnel. The recovered solid was extracted with DMF and again filtered off, the filtrate being received in a clean flask. This solution was filtered through paper, and the filtrate was then centrifuged to ensure complete removal of any solid. To the DMF solution containing the reaction product, water was added until it constituted about

60% by volume. The finely divided precipitate which formed was recovered by centrifugation; it was washed with acetone, redissolved in DMF, and reprecipitated by addition of water. The product was again recovered by centrifugation, washed with acetone, and oven-dried at 95°.

A small amount of the purified complex was dissolved in 70–30 DMF–water solution, and the spectrum of the solution was recorded; it was identical with the spectrum produced by platinum samples developed by the recommended procedure, except that the small absorption at 430 nm observed in the latter case was totally absent. This fact further supports the conclusion that absorption at 430 nm was due to oxidation of the OPDA reagent, and not to the platinum–OPDA complex.

A 0·601-mg sample of the purified complex was dissolved in 10 ml of DMF. Calculations based on the formula weight of the proposed complex (see next section) indicated that diluting 1·0 ml of this solution to a volume of 28·8 ml would give a solution containing 1·00 μg of platinum per ml, or 1·00 ppm. The dilution was made with DMF and water to a final 70% v/v of DMF. The absorbance of this solution was exactly the same as that of a 1·00-ppm platinum solution developed by the recommended procedure.

The question arises as to the mode of formation of the platinum(II)–OPDA complex, whether by simple co-ordinate covalent bonding from the nitrogen atoms of the $-NH_2$ groups, or by loss of one or both hydrogen atoms from one or more $-NH_2$ groups, forming anions associated with the platinum(II) cation, or a combination of these processes. The possible formulae, the formula weights, and the carbon, hydrogen, and nitrogen contents are shown in Table 4. A portion of the purified product was analysed by Galbraith Laboratories, Knoxville, Tennessee; the analysis, included in Table 4, conforms most closely to formula 3, which may be represented thus:



Mass spectrum of the product

A sample of the purified reaction product was analysed on a low-resolution mass spectrometer at 70 eV ionization potential. The largest peak appeared at a mass/charge ratio of 407; slightly smaller peaks appeared at ratios of 406 and 408, and a moderate peak at 410. The ratio of these peak heights is in excellent agreement with the relative natural abundances of the most abundant isotopes of platinum. No particle of mass/charge ratio greater than 410 was found. Another series of peaks was found at *m/e* 203·5, 203, 204, and 205, of intensities in the same ratio as the platinum isotope abundances, corresponding to the doubly-ionized molecules. Table 5 shows that the only composition conforming to the observed mass numbers is $Pt(C_6H_4N_2H_2)_2$, formula weight 407·35, which also agrees with the elemental chemical analysis.

The double ionization of the intact complex is an indication of its considerable stability. A series of small peaks was observed at mass/charge values of 300, 301, and 302,

Table 4 Elemental composition of possible compounds

Possible formula	Formula weight	% C	% H	% N
1 $Pt(C_6H_4N_2H_4)_2$	411 38	35·04	3·921	13·62
2 $Pt(C_6H_4N_2H_3)_2$	409 36	35 21	3·447	13 69
3 $Pt(C_6H_4N_2H_2)_2$	407 35	35·38	2·973	13 76
4 $Pt(C_6H_4N_2H)_2$	405 33	35 56	2·487	13 82
5 $Pt(C_6H_4N_2)_2$	403 31	35 74	2 000	13 89
Analysis found		35 6	3·0	13 7

Table 5 Mass numbers of possible compounds

Platinum isotope	% Natural abundance	Mass/charge of platinum complex with ligand $(\phi N_2H_4)_2$	$(\phi N_2H_3)_2$	$(\phi N_2H_2)_2$	$(\phi N_2H)_2$	$(\phi N_2)_2$
192	0 78	408	406	404	402	400
194	32 8	410	408	406	404	402
195	33 7	411	409	407	405	403
196	25 4	412	410	408	406	404
198	7 23	414	412	410	408	406

these are probably fragments of the original complex that contain only one OPDA group associated with a platinum atom, for example, $Pt(C_6H_4N_2H_2)^+$. This type of fragmentation is not unusual when compounds undergo ionization at 70 eV.

CONCLUSION

The results of this study indicate that in the reaction of platinum(II) with OPDA, each of two ligand molecules loses two hydrogen atoms to form the doubly charged anion of OPDA, which combines with platinum(II) to form a highly coloured neutral complex which is quite stable and insoluble in most solvents except DMF and DMSO. A similar nickel complex, which has been known for some time, has been characterized by mass spectrometry;[17] it is the same as that proposed here for the platinum complex [with nickel(II) substituted for platinum(II)].

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Zusammenfassung—Platin(IV) oder -(II) reagiert bei pH 6·5 mit o-Phenylendiamin zu lichtblauen Losungen mit Absorptionsmaximum bei 703 nm. Die bei Zimmertemperatur langsame Reaktion ist bei Temperaturen in der Nahe von 100° in 3–4 min beendet. Dimethylformamid in der Losung verhindert das Ausfallen des Reaktionsprodukts. Die Farbung ist mindestens 24 h lang stabil. Der Einfluß der Erhitzungstemperatur und -dauer, des pH, der Reagenskonzentration und anderer Variabler wurde untersucht. Das System folgt im untersuchten Konzentrationsbereich dem Beerschen Gesetz. Der optimale Konzentrationsbereich zur Messung in 10 mm-Kuvetten ist 0·4–1·4 ppm Platin, der molare Extinktionskoeffizient betragt 9·83 10^3 l mol^{-1} mm^{-1} Die Storung durch Fremdionen wurde erfaßt und Methoden zur Entfernung oder Maskierung der störenden Ionen geprüft. Bei der farbbildenden Reaktion wird Platin(IV) durch das organische Reagens zu Platin(II) reduziert; dieses bildet dann einen Komplex mit dem Reagens. Das Metall · Ligand-Verhältnis 1 : 2 wurde durch spektrophotometrische Messungen in Losung nahegelegt und wurde am festen Reaktionsprodukt durch Elementaranalyse und massenspektrometrische Untersuchung nachgewiesen.

Résumé—Le platine (IV) ou (II) réagit avec l'*o*-phénylènediamine à pH 6,5, pour donner des solutions bleu clair ayant un maximum d'absorption à 703 nm. La réaction, lente à température ambiante, est complète en 3–4 mn aux températures voisines de 100° L'emploi de diméthylformamide dans la solution évite la précipitation du produit de réaction. La coloration est stable pendant 24 h au moins. On a étudié les influences de la température et du temps de chauffage, du pH, de la concentration en réactif et d'autres variables. Le système suit la loi de Beer dans le domaine de concentrations étudié. Le domaine de concentration optimal pour la mesure dans des cuves de 10 mm est de 0,4–1,4 p.p.m de platine; le coefficient d'absorption moléculaire est 9,83 × 10^3 l. mole^{-1} mm^{-1} On a évalué l'interférence d'ions étrangers, et l'on a essayé des méthodes pour l'élimination ou la dissimultation d'interférences. Dans la réaction de formation de coloration, le platine (IV) est réduit par le réactif organique en platine (II), qui est alors complexé avec le réactif Le rapport métal · complexe de 1 · 2 a été montré par des mesures spectrophotométriques de la solution, et a été confirmé sur le produit solide de réaction par analyse élémentaire et par examen spectrométrique de masse.

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LINEAR CRYSTALLIZATION AND INDUCTION-PERIOD STUDIES OF THE GROWTH OF CALCIUM SULPHATE DIHYDRATE CRYSTALS

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Summary—The linear crystallization of well-formed crystallites of calcium sulphate dihydrate from supersaturated solutions has been studied by a microscopic method at temperatures ranging from 25° to 55° The activation energy is 16 ± 1 5 kcal/mole for the fast-growing faces. Induction periods in the crystallization of calcium sulphate dihydrate have been determined as a function of solution concentration at temperatures of 25° and 90°

The precipitation of calcium sulphate is of considerable importance in processes involving the formation of scale on heat-transfer surfaces. A number of investigations have been made of the influence of additives on the crystallization and nucleation rate,[1–4] but most of the previous work was concerned only with the concentration changes in the supersaturated solutions during the precipitation processes. A study of the seeded crystal growth of calcium sulphate dihydrate from supersaturated solution, by means of a sampling technique, has been published,[5] and a reaction, second-order in relative supersaturation, has been found for the crystallization of this salt both in the presence and in the absence of additives.[6] The dissolution of calcium sulphate dihydrate into subsaturated solution has been followed by a potentiometric method and the diffusion of ions from the surface to the bulk of the solution has been found to be the rate-determining step for the dissolution process.[7]

In studies of the kinetics of crystal growth, in addition to following concentration changes in the supersaturated solution, observation of the growing crystals themselves is clearly of considerable importance. The present study is concerned with the linear crystallization rate of calcium sulphate dihydrate from supersaturated solution. The activation energy of the fast-growing faces has been determined by observing the rate of growth as a function of temperature. In addition, induction periods in the precipitation of calcium sulphate dihydrate have been investigated as a function of the degree of supersaturation, over a range of temperature.

EXPERIMENTAL

Linear growth experiments

Reagent-grade chemicals, grade-A volumetric glassware and triply distilled water were used throughout this work Suspensions of calcium sulphate dihydrate seed crystals were prepared as described previously[5] After the crystals had been washed several times, their morphology was improved by allowing them to grow again in 0·025*M* calcium chloride/0·025*M* sodium sulphate After one hour, the supernatant solutions were decanted and the residual suspensions were washed several times with saturated calcium sulphate solution until the crystals were free from sodium chloride The crystals prepared in this way were well-formed and suitable for further study of the linear crystallization rate of specific faces in supersaturated solutions

Supersaturated solutions were prepared by the slow mixing of solutions containing calcium chloride and sodium sulphate About 7 ml of the solution were then introduced into a microcell of capacity 10 ml, which had a thin microscope slide as its base so that crystals could be observed microscopically (Unitron Series N

Microscope). Water from a thermostat was circulated between the walls of the microcell. After the solutions had reached temperature equilibrium, a small amount of seed suspension was put into the reaction cell. The extent of the reaction was followed by photographing the growing crystal at various times The calcium concentration of the solution was checked before and after each experiment by titrimetric analysis with EDTA, the change of concentration was usually only about 1–3% The linear growth rate R was taken as the average length change of three or four crystals during each experiment.

Induction experiments

Calcium chloride solutions were first brought to temperature equilibrium in a 250-ml reaction vessel, and the required amounts of pre-equilibrated sodium sulphate solutions of the same concentration were quickly added. The induction period was taken as the time interval between the mixing of the solutions and the appearance of the first white cloudy precipitate of calcium sulphate. In order to compare results of experiments at different supersaturations, additions of sodium chloride were made, where necessary, in order to maintain the sodium chloride concentration in the solutions at a constant value

RESULTS AND DISCUSSION

The results of the linear crystallization experiments are summarized in Table 1, and the growth rate is plotted as a function of relative supersaturation in Fig. 1. In Fig. 2 R is plotted against the square of the relative supersaturation, and it is seen that, with the exception of an initial growth surge, equation (1) satisfactorily represents the experimental data:

$$R = k_1(T_{Ca} - T_{Ca}{}^{\circ})^2 \tag{1}$$

Table 1 Linear crystallization rates of the fastest growing face of calcium sulphate dihydrate at 25°C

Expt. No	$T_{Ca} \times 10^2$ M	$(T_{Ca} - T_{Ca}{}^{\circ}) \times 10^2$ M	$R \times 10^2$ *mm/hr*
1	4·24	2·18	3·2
2	3·95	1·91	2·5
3	3·75	1·74	1·6
4	3·49	1·49	1·0
5	3·37	1·39	0·9
6	3·11	1·15	0·6
7	2·86	0·92	0·2
8	2·75	0·83	0·12
9	2·56	0·66	0·09
10	2·28	0·41	0·04

In this equation, k_1 is the rate constant for linear growth, T_{Ca} represents the total calcium concentration of the supersaturated solution, and $T_{Ca}{}^{\circ}$ is the solubility value at the particular ionic strength. An equation similar to (1) has been found to hold for the growth of seed crystals of calcium sulphate dihydrate in supersaturated solutions of the salt in which the rate of growth was expressed in terms of the change in concentration in the supersaturated solutions with time.[5] The results of the direct measurements of the growing crystals are therefore consistent with the previous studies by a different method. The experimental results may be explained in terms of a screw dislocation model[8 9] or the surface adsorption model proposed by Davies,[10] since both models predict the same reaction-order kinetics for the growth of crystals of symmetrical charge-type electrolytes.

The deviation of experimental results from the straight line of the second-order plot at higher supersaturation can be explained in terms of two-dimensional surface nucleation. Troost[11] in a study of crystallization of sodium triphosphate hexahydrate also proposed

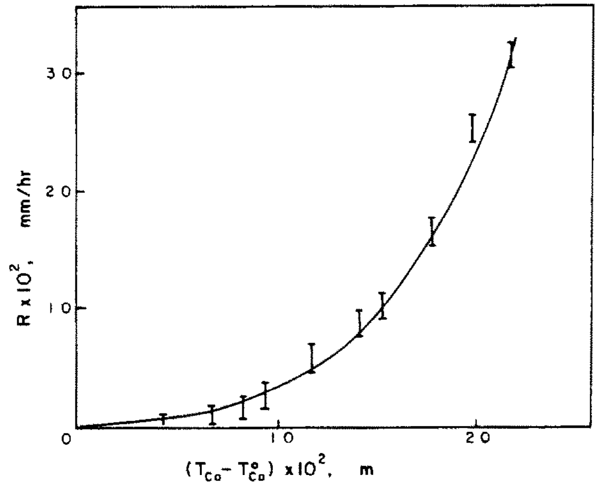

Fig. 1 Plot of the linear growth rate, R, as a function of $(T_{Ca} - T_{Ca}^{\circ})$ for calcium sulphate dihydrate The uncertainties in R are represented as ordinate bars

two mechanisms in determining the rate of growth of 001 faces. He assumed that at low degrees of supersaturation, the growth rate was controlled by the screw dislocation mechanism, while at higher degrees of supersaturation, the formation of two-dimensional nuclei was the rate-determining step. In Fig. 3, the growth of untreated seed crystals in the supersaturated solution is shown. It is interesting to note that if untreated seed crystals are put in the supersaturated solutions, the crystals grow more rapidly at imperfections so that a rapid perfection of the crystal shape takes place in the initial crystallizing step.

A series of experiments was made at a variety of temperatures ranging from 25° to 55° at a constant supersaturation. The results are summarized in Table 2 and the linear growth rate constant is plotted according to the Arrhenius equation in Fig. 4. The

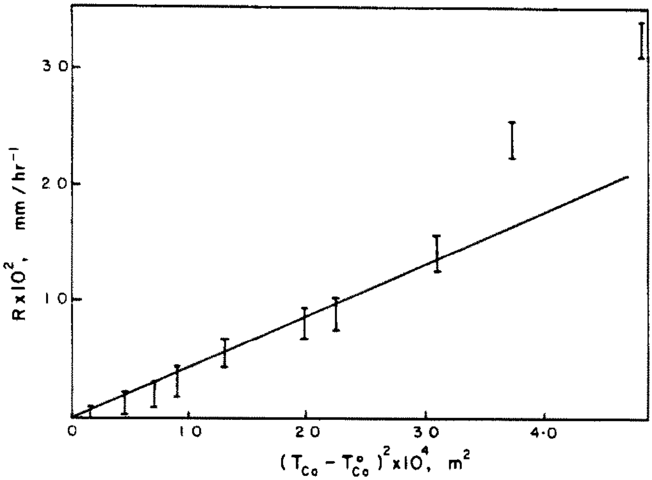

Fig 2 Kinetic plot of growth rate, R, against $(T_{Ca} - T_{Ca}^{\circ})^2$

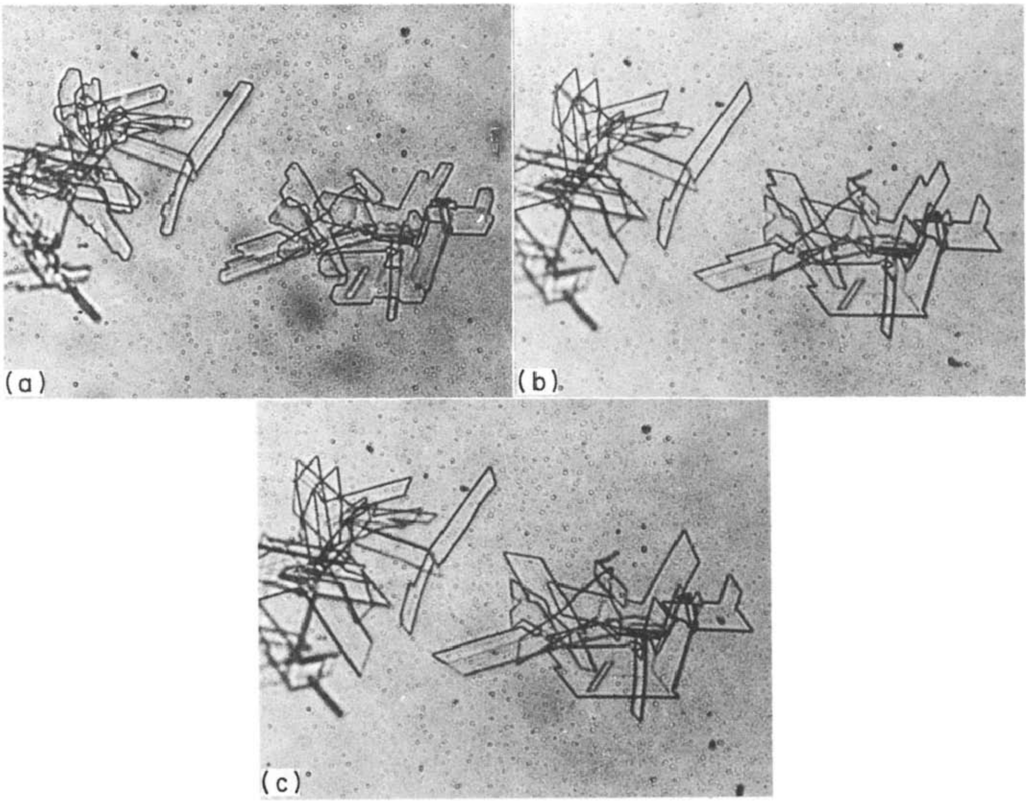

Fig. 3. Crystallization of untreated seed crystals of calcium sulphate dihydrate in 2.85 × $10^{-2}M$ $CaSO_4$ solutions (*a*) at time zero; (*b*) after 20 min; (*c*) after 60 min.

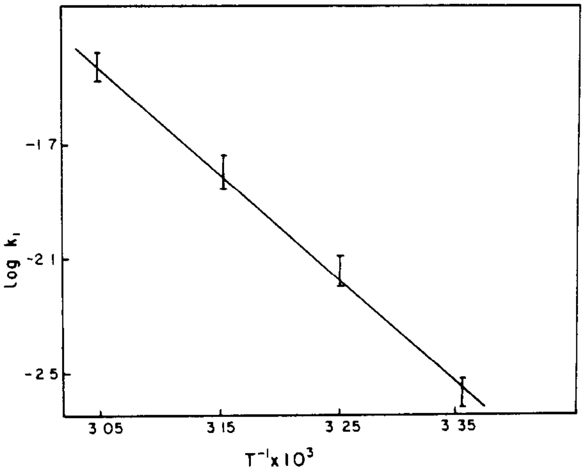

Fig 4 Arrhenius plots of log k_1 against T^{-1} for the linear growth rate of calcium sulphate dihydrate crystals

Table 2 Linear crystallization rates of the fastest growing face of calcium sulphate dihydrate at various temperatures (T_{Ca} 2·86 × $10^{-2}M$)

Temperature °C	$(T_{Ca} - T_{Ca}^{\circ}) \times 10^4$ *M*	$R \times 10^2$ *mm/hr*	$k_1 \times 10^{-2}$ *l mm mole^{-2} hr^{-1}*
55	0·82	2·3	2·8
45	0·76	1·0	1·3
35	0·81	0·45	0·55
25	0·85	0·20	0·23

activation energy obtained is 16 ± 1·5 kcal/mole for the fast growing faces and this value is in satisfactory agreement with that obtained in previous studies.[5]

The induction period in the experiments is the time period between the mixing of solutions containing the lattice ions and the appearance of the first solid phase. The change of induction period with concentration of the supersaturated solutions for calcium sulphate dihydrate precipitation was studied at 25° and 90°. The results are shown in Table 3. The experimental results are satisfactorily treated by equation (2)

$$K = C_o^{(p-1)}t \tag{2}$$

where K is a constant, p the number of ions in the critical nucleus, C_o the concentration of the supersaturated solution and t the induction period. Plots of log t *vs.* log C_o are given in Fig. 5. At a given initial concentration, the length of the induction period decreases appreciably with increase in temperature. If the nucleation rate is inversely proportional to the length of the induction period, the marked decrease of t with increasing temperature may indicate an appreciable activation energy for the nucleation of calcium sulphate dihydrate.

The equation (2) was derived by Christiansen and Nielsen in a non-classical nucleation theory which has been applied in studies of many insoluble salts.[12–14] In the present

Table 3 Induction periods of calcium sulphate dihydrate at various concentrations, in 0·5*M* sodium chloride medium

T_{Ca}, *M*	$-\log C_o$	Induction period, *t, sec*	log *t*
25°C			
0·200	0·700	7	0·85
0·175	0·757	13	1·11
0·150	0·824	25	1·40
0·125	0·903	45	1·65
0·100	1·000	75	1·88
0·090	1·046	120	2·08
0·080	1·097	250	2·40
0·070	1·155	380	2·58
0·060	1·222	1530	3·18
90°C			
0·100	1·000	1	0
0·080	1·097	3	0·48
0·060	1·222	17	1·23
0·050	1·301	55	1·74
0·045	1·347	100	2·00
0·040	1·398	450	2·65

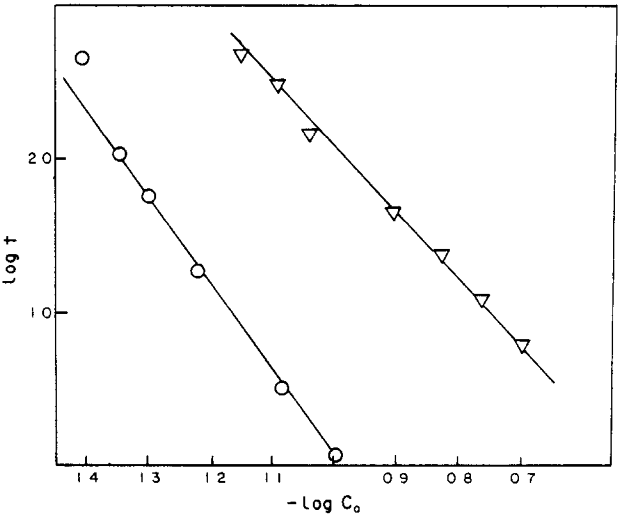

Fig. 5 Plots of log t versus log C_0 for the induction period experiments. ▽, at 25°C. ⊙, at 90°C

study, the lines at 25° and 90° are almost parallel, with slopes of 4·6 and 4·9 respectively. The corresponding p value is therefore approximately 6, and in terms of the model proposed by Christiansen and Nielsen this may correspond to the number of ions in the critical nucleus.

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Zusammenfassung—Die lineare Kristallisation wohlausgebildeter Calciumsulfat-Dihydrat-Kristallite aus ubersattigten Losungen wurde bei Temperaturen von 25° bis 55 mit einer mikroskopischen Methode untersucht. Fur die rasch wachsenden Kristallflachen betragt die Aktivierungsenergie 16 ±1·5 kcal/mol. Induktionsperioden bei der Kristallisation von Calciumsulfat-Dihydrat wurden in Abhangigkeit von der Konzentration der Losung bei 25° und 90° bestimmt

Résumé—On a étudié la cristallisation linéaire de crystallites bien formes de sulfate de calcium dihydraté à partir de solutions sursaturées par une méthode microscopique à des températures allant de 25° à 55° L'énergie d'activation est de 16 ±1,5 kcal/mole pour les faces a développement rapide On a déterminé les périodes d'induction dans la cristallisation du sulfate de calcium dihydraté en fonction de la concentration de la solution aux températures de 25° et 90°

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SHORT COMMUNICATIONS

SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN TELLURIC ACID

(*Received* 7 *March* 1972 *Accepted* 23 *May* 1972)

The radioactive isotope of iodine, ^{131}I, is produced in nuclear reactors by (n, γ) reaction from tellurium. In order to improve the nuclear balance for production of ^{131}I, it is important to have a tellurium target of high purity. Since in our Institute telluric acid has been used as a target, it was necessary to develop a sensitive method for checking its purity. The spectrochemical method has been found to be the most promising for this purpose because of its simplicity and accuracy. Several papers have been published describing either direct spectrographic procedures[1,2] or indirect procedures[3,4] involving preconcentration of the impurities.

Depending on the techniques used for preconcentration, the known indirect methods belong to two groups: in the first are the methods applying a prior physical concentration through vacuum evaporation of the matrix and concentration of the impurities on a graphite matrix, and in the second are the methods using a chemical preconcentration by separation of the impurities with 8-hydroxyquinoline and dithizone.

When the direct methods are applied, a sensitivity of 10^{-4}–10^{-3}% is obtained, while with a chemical preconcentration procedure, the sensitivity is improved to 10^{-7}% with 20-g samples.

In the present work a direct method has been used for spectrographic analysis of the concentration of impurities in telluric acid targets.

EXPERIMENTAL

Preparation of standards and samples

The basic standards were prepared from Johnson and Matthey telluric acid, $H_2TeO_4 \cdot 2H_2O$, dried for 24 hr at 160° to remove the water and obtain metatelluric acid, $(H_2TeO_4)_x$ (x = 1–10), which was then mixed with appropriate amounts of oxides of the elements to be measured. The standards were then mixed with graphite in 3:1 ratio (standard:graphite), with 12% of a spectrochemical buffer (NaCl–KCl) and with 0.1% of GeO_2 as internal standard.

The telluric acid samples are dried and mixed in the same manner as the standards. Ignited telluric acid was used for irradiation.

Spectrographic procedure

Duplicate standards and samples were excited in a 12-A d.c. arc. In order to increase the yield of the sample entering the excitation zone, an NaCl-KCl buffer was added to the telluric acid sample. It has been shown[5,6] that adding alkali metal salts lowers the ionization threshold and increases the sensitivity of determination of impurities.

The spectrograph used was a Jarrel-Ash type with a diffraction grating with 600 lines/mm. The main spectrographic conditions are given in Table 1.

Table 1 Apparatus and operating conditions

Spectrograph	Jarrel-Ash with flat grating
Wavelength region	220–360 nm (first order)
Slit-width	20 μm
Analytical gap	4 mm
Excitation source	Jarrel-Ash Varisource, 12 A, d.c. arc.
Electrodes	Counter-electrode (cathode)—graphite rod, spectral grade, 3·1 mm diam., used as obtained Sample electrode (anode)—graphite, 6·3 mm diam., crater 5 mm deep, 4·5 mm internal diam
Sample charge	70 mg
Preburn time	none
Exposure	40 sec
Emulsion, *etc*	Kodak SA1, developer D-19, 4 min at 20°, using Jarrell-Ash photoprocessor.

The spectrograms were measured on a Jarrell-Ash microphotometer. The analytical lines and concentration ranges are listed in Table 2

Table 2 Analytical lines and concentration ranges of determination

Element	Line, *nm*	Concentration range, *ppm*
Cd	228·8	1–20
Be	234·8	0·1–10
Sb	259·8	4–100
Mg	279·5	0·2–10
Mn	280·1	0·2–10
Pb	283·3	0·2–10
Sn	284·0	0·4–40
Ga	294·3	0·2–40
Cr	301·7	0·4–20
Fe	302·0	0·4–20
Ni	305·0	0·4–20
Pt	306·4	4–100
Bi	306·7	0·4–20
Al	308·2	0·2–20
In	325·6	0·2–20
Ti	334·9	0·4–10
Zr	339·1	1–100
Rh	339·6	0·4–10
Pd	340·4	0·4–10
Co	345·3	0·4–10

The reproducibility of the method, expressed as relative standard deviation, is ±10–25%. The recovery is given in Table 3

Table 3 Recovery

Element	Added, *μg*	Recovered	
		μg	%
Be	2	1·8	90
Fe	2	1·7	85
Mg	2	1·9	95
Mn	2	2·0	100
Sn	2	2·1	105
Cr	2	1·75	88
Ni	2	2·4	120
Ti	2	2·3	115
Pd	2	2·25	113
In	2	1·78	89
Co	2	1·90	95

Results of analyses of telluric acid performed by our method are shown in Table 4. The method proved to be convenient for analysis of telluric acid because of its simplicity and speed

Table 4 Spectrochemical analysis of telluric acid

Element		Be	Cd	Mg	Mn	Pb	Sn	Cr	Ni	Pt	
Concn., *ppm*		<0·1	<1	0·4	0·5	1·5	<0·4	1·5	1·4	10	
Element	Bi	Zr	Pd	In	Rh	Co	Sb	Te	Al	Ti	Ga
Concn. *ppm*	<0·4	1	<0·4	0·6	1·4	<0·4	4	2	5	0·8	0·6

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Summary—An emission spectrographic method is described for determination of 20 elements present as impurities in telluric acid Samples are excited in a 12-A d.c arc with the use of NaCl-KCl as a spectrographic buffer and germanium as internal standard. The limit of determination lies between 10^{-5} and 10^{-2}% The precision of the method calculated as relative standard deviation is 10–25%

Zusammenfassung—Ein emissionsspektrographisches Verfahren zur Bestimmung von 20 Elementen, die als Verunreinigungen in Tellursaure vorliegen, wird beschrieben. Die Proben werden in einem 12 A-Gleichstrombogen mit NaCl-KCl als spektrographischem Puffer und Germanium als innerem Standard angeregt Die Grenze der Bestimmbarkeit liegt zwischen 10^{-5} und 10^{-2}% Die Genauigkeit der Methode, als relative Standardabweichung berechnet, ist 10–25%

Résumé—On décrit une méthode spectrographique d'émission pour le dosage de 20 éléments présents à l'état d'impuretés dans l'acide tellurique Les échantillons sont excités dans un arc à courant continu de 12 A en employant NaCl–KCl comme tampon spectrographique et le germanium comme étalon interne La limite de dosage se situe entre 10^{-5} et 10^{-2}% La précision de la méthode, calculée en écart type relatif, est de 10–25%

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MICROANALYSIS OF SULPHIDE, SULPHITE, SULPHATE AND THIOSULPHATE BY THIN-LAYER CHROMATOGRAPHY AND RING-COLORIMETRY

(*Received* 31 *December* 1971 *Accepted* 29 *May* 1972)

For the micro-separation of inorganic sulphur compounds, paper[1–5] and ion-exchange[6–8] chromatography have been most often used, with little attention being given to thin-layer chromatography (TLC),[9–12] and that only of a qualitative nature

This paper describes an efficient separation of S^{2-}, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ on microcrystalline cellulose, and their subsequent determination by the Weisz ring-oven technique[13] The successful combination of these two techniques by Johri *et al*[14–19] has already been reported

EXPERIMENTAL

Apparatus

Glass plates (200 × 50 × 3 mm) coated with a 0 2-mm thick layer of microcrystalline cellulose without binder (Camag, DSF-O), kept overnight before use

The mini-vacuum-collector devised by Levitt[20] was used for scooping out zones from the chromatograms

Hamilton micro-syringe for spotting the plates

Reagents

Analytical grade sodium sulphide, sulphite, sulphate and thiosulphate were dissolved in doubly distilled water to give 1 mg/ml stock solutions of each

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Hamilton micro-syringe for spotting the plates

Reagents

Analytical grade sodium sulphide, sulphite, sulphate and thiosulphate were dissolved in doubly distilled water to give 1 mg/ml stock solutions of each

Procedure

For the qualitative analysis of the anions, drops of a 1% aqueous zinc acetate solution were applied along the base-line at five different points on the cellulose-coated plate with the help of a pointed paper wick. The plate was dried and then the test solutions of SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and S^{2-} ions were applied in that sequence at the first four points, and a mixture of the four was applied at the fifth point. The volumes applied were in the range 1–5 μl. The plate was developed by the ascending technique in n-propanol–1*M* ammonia–acetone (30 . 20 : 2, v/v) for 30 min at 28–30°, affording a clean separation of the constituent anions. The plate was removed from the jar and dried in a stream of cool air and the respective anionic species were located by spraying with the reagents listed in Table 1 During the spraying with different reagents, glass plates were used to mask those areas of the thin-layer plate which were not to be examined The R_F values were $SO_3^{2-} > S_2O_3^{2-} > SO_4^{2-} > S^{2-}$ No movement of S^{2-} ions were observed since these were precipitated as ZnS.

Table 1. Detection of ions after TLC separation

Ion	Spray reagent	Colour	R_F	Limit of identification, μg
S^{2-}	Aqueous 1% silver nitrate solution	Brown black	zero	0 2
SO_4^{2-}	Aqueous 0·1% barium chloride and aqueous 0·1% sodium rhodizonate solutions	Yellow against a red background	0 28	1 0
$S_2O_3^{2-}$	Aqueous 1% silver nitrate solution	Brown black	0 51	0 5
SO_3^{2-}	Mixture of equal volumes of aqueous 1% cobalt nitrate containing a few drops of dil. acetic acid and saturated sodium azide solution.	Yellow	0 70	0 5

Ring-colorimetric determination of the chromatographed constituents

For the semiquantitative determination of anions, zinc acetate solution was applied at four different points along the base-line on the thin-layer plate, leaving sufficient space between the spots so that there was no sideways overlap of spots during the chromatography. The fifth spot used in the qualitative procedure was not needed since only one visualizing agent, silver nitrate, was employed for both S^{2-} and $S_2O_3^{2-}$ ions (Table 1).

Next, one drop of a known mixture of S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ and SO_4^{2-} ions was applied to each of the first three zinc acetate spots, and a known volume of the test sample to the fourth spot. The plate was developed as described earlier The three developed regions of the known anionic mixture were sprayed respectively with solutions of silver nitrate (for S^{2-} and $S_2O_3^{2-}$ ions), sodium rhodizonate with barium chloride (for SO_4^{2-} ions) and cobalt nitrate with sodium azide (for SO_3^{2-} ions). Next, the regions corresponding to SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ ions on the unsprayed test chromatogram were sucked out by means of a mini-vacuum-collector. The plate was then developed with water for a few cm distance in order to remove all the unreacted zinc ions, taken out of the jar, dried in a hot air stream, cooled, and fumed over bromine to oxidize zinc sulphide to sulphate, which was then also sucked out. The vacuum-collector was dismantled, the inner tube containing one particular anionic species plus cellulose powder was taken out, and the anions from this tube, which would serve as a mini-column, were leached out with water onto a Whatman No 41 filter paper (55 mm diameter) placed on the ring oven heated at 100–110° The anions were then brought into the ring zone by washing with water The same process was repeated for the other anionic species. The individual anion species were then treated with the chromogenic reagents listed in Table 2.

For semiquantitative evaluation, the intensities of the coloured rings obtained with the different anionic species were compared visually with those of standard rings prepared separately,[2] and corresponding to 1–10 μl of standard solution. Results of a few representative determinations are given in Table 2.

The TLC separation gives compact spots for S^{2-}, SO_3^{2-} and SO_4^{2-} ions, and a slightly blurred spot for $S_2O_3^{2-}$ ions. The function of applying zinc acetate in the beginning is to fix S^{2-} ions as ZnS, though the inclusion of zinc acetate in the solvent system causes some tailing due to S^{2-} ions A study of the results (Table 2) suggests that the errors lie within the permissible limits for semi-quantitative analysis Moreover, the combination of the two techniques described offers the advantages of speed and simplicity and at the same time requires only inexpensive apparatus

Table 2 Representative results of determinations

Anion determined	Metal ion employed for the indirect determination of anions	Developing agents for the metal ion	Colour of the ring	Anion taken, *mg/ml*	Anion found, *mg/ml*
S^{2-}	Zinc	Alcoholic 1% diethylaniline and aqueous 1% pottassium ferricyanide solution	Red	4·10	4·3
				2·25	2·3
				1·00	0·95
$SO_4{}^{2-}$	Lead	Aqueous 0·1% sodium rhodizonate and fume over HCl	Blue violet	3·20	3·1
				2·75	2·9
				1·85	1·8
$SO_3{}^{2-}$	Lead	(*a*) Fume over bromine (*b*) Aqueous 0·1% sodium rhodizonate and fume over HCl	Blue violet	2·45	2·5
				3·30	3·2
				1·50	1·5
$S_2O_3{}^{2-}$	—	Aqueous 1% silver nitrate	Brown black	3·50	3·4
				1·10	1·2
				2·60	2·7

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Summary—Clean and rapid analytical separations of microgram quantities of S^{2-}, $SO_3{}^{2-}$, $SO_4{}^{2-}$ and $S_2O_3{}^{2-}$ ions have been accomplished by ascending thin-layer chromatography on microcrystalline cellulose with n-propanol-1*M* ammonia-acetone (30 · 20 . 2) as the solvent system The separated species have been determined by ring-colorimetry

Zusammenfassung—Saubere und rasche analytische Trennungen von Mikrogrammengen S^{2-}, SO_3^{2-}, SO_4^{2-} und $S_2O_3^{2-}$ wurden durch aufsteigende Dunnschichtchromatographie an mikrokristalliner Cellulose mit n-Propanol-1 M Ammoniak-Aceton (30 20 : 2) als Lösungsmittel erzielt. Die getrennten Spezies wurden durch Ring-Kolorimetrie bestimmt

Résumé—On a réalisé des séparations analytiques nettes et rapides de quantités d'ions S^{2-}, SO_3^{2-}, SO_4^{2-} et $S_2O_3^{2-}$ de l'ordre du microgramme par chromatographie en couche mince ascendante sur de la cellulose microcristalline avec le mélange *n*-propanol-ammoniaque 1*M*-acétone (30 : 20 : 2) comme système solvant. Les espèces séparées ont été déterminées par colorimétrie annulaire

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SPECTROPHOTOMETRIC DETERMINATION OF STRYCHNINE AND METHYLATROPINE BY EXTRACTION WITH TETRABROMOPHENOLPHTHALEIN ETHYL ESTER

(*Received* 5 *April* 1972. *Accepted* 15 *May* 1972)

Some acid dyes,[1,2] such as Bromothymol Blue,[3-5] Bromocresol Green[6] or Bromophenol Blue[7,8] have been used for the spectrophotometric determination of amines, alkaloids or quaternary ammonium salts These dyes are dibasic acids, and have serious drawbacks because of their extreme sensitivity to change in acidity; an indeterminate number of 1:1 and 1:2 ion-pairs are formed with resultant poor reproducibility and extreme pH-dependence.

Tetrabromophenolphthalein ethyl ester (TBPE), which has just one acidic group, is able to form only a 1:1 ion-pair complex, which is reproducibly extracted Various amines, alkaloids and quaternary ammonium salts have been extracted with TBPE at pH 7·5 into 1,2-dichloroethane. The colour of the extracts fall into three categories: (*i*) blue (ionic form of TBPE) which is extracted in the presence of many quaternary ammonium salts and alkaloids such as spartein, (*ii*) red which is developed in the presence of alkaloids such as strychnine, physostigmine, quinidine and homatropine, a weak red colour is given by amines such as α-naphthylamine and triethanolamine; (*iii*) yellow (molecular form of TBPE) which is the same colour as the reagent blank even in the presence of aniline, dimethylamine, *N,N'*-dimethylformamide, ethylenediaminetetra-acetic acid, or nitrilotriacetic acid. If the extraction is performed from acidic solution, the colours of the extracts are all yellow even in cases (*i*) and (*ii*).

This paper deals with the determination of methylatropine and strychnine as representatives of the quaternary ammonium salts and the alkaloids, and as widely used medicines (parasympatholytics *etc*) Hexanitrodiphenylamine has been used as a spectrophotometric reagent for alkaloids or quaternary ammonium salts,[9,10] and titrimetric methods have also been investigated[11-14]

EXPERIMENTAL

Reagents

Tetrabromophenolphthalein ethyl ester (*TBPE*) *potassium salt* (*m w* 700·1) Weighed amounts were dissolved in ethyl alcohol.

Standard strychnine and methylatropine solutions. Weighed amounts of strychnine sulphate (dried at 105°) or *N*-methylatropine bromide (dried at 105°) were dissolved in water and diluted to known volume.

Buffer solutions, pH 8 and pH 9·5. Appropriate volumes of 0·4*M* potassium dihydrogen phosphate, 0·06*M* sodium borate and 3*M* sodium hydroxide were mixed

All the chemicals were of reagent grade, and demineralized water was used

Procedures

Strychnine. Transfer 2-10 ml of strychnine solution ($2·0 \times 10^{-5}M$), 2 ml of TBPE solution ($4 \times 10^{-3}M$), and 5 ml of buffer solution (pH 8) into a 100-ml separating funnel, dilute to 25 ml with water and shake the solution for 2 min with 10 ml of 1,2-dichloroethane. After separation of the two layers, run off the extract into a glass tube through a filter paper to remove any droplets of water Measure the absorbance of the extract at 560 nm, using a reagent blank or water as a reference

Methylatropine Transfer 2-10 ml of standard methylatropine solution ($1·0 \times 10^{-5}M$), 2 ml of TBPE solution ($2 \times 10^{-3}M$), and 5 ml of buffer solution (pH 9·5) into a 100-ml separating-funnel Treat the mixture in the same manner as described for strychnine Measure the absorbance at 615 nm.

Résumé—On a réalisé des séparations analytiques nettes et rapides de quantités d'ions S^{2-}, SO_3^{2-}, SO_4^{2-} et $S_2O_3^{2-}$ de l'ordre du microgramme par chromatographie en couche mince ascendante sur de la cellulose microcristalline avec le mélange *n*-propanol-ammoniaque 1*M*-acétone (30 : 20 : 2) comme système solvant. Les espèces séparées ont été déterminées par colorimétrie annulaire

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This paper deals with the determination of methylatropine and strychnine as representatives of the quaternary ammonium salts and the alkaloids, and as widely used medicines (parasympatholytics *etc*). Hexanitrodiphenylamine has been used as a spectrophotometric reagent for alkaloids or quaternary ammonium salts,[9,10] and titrimetric methods have also been investigated.[11–14]

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Methylatropine. Transfer 2–10 ml of standard methylatropine solution ($1\cdot0 \times 10^{-5}M$), 2 ml of TBPE solution ($2 \times 10^{-3}M$), and 5 ml of buffer solution (pH 9·5) into a 100-ml separating-funnel. Treat the mixture in the same manner as described for strychnine. Measure the absorbance at 615 nm.

RESULTS AND DISCUSSION

Absorption spectra

In the absence of methylatropine or strychnine a yellow compound is extracted into dichloroethane, whilst in their presence a blue (λ_{max} 615 nm) or red (λ_{max} 560 nm) one is formed. The change in colour may be attributed to the formation of an ion-pair or addition compound between the TBPE and the quaternary ammonium cation or the alkaloid.

Effect of variables

pH. Methylatropine or strychnine was extracted with TBPE from a series of aqueous solutions buffered at various pH values. The absorbance of the extract was constant when the pH of the aqueous phase lay within the range 9·0–10·5 for methylatropine and 7·0–9·0 for strychnine. Extreme pH-dependence was observed for the determination of quinine or thiamine with Bromophenol Blue[7] or Bromothymol Blue.[3] Similarly, constant absorbance in any pH range could not be obtained when Bromophenol Blue or Bromocresol Green was used as extractant for methylatropine or strychnine.

Reagent concentration. It is found that the concentration of TPBE should be maintained at more than 20-fold molar excess over methylatropine or 40-fold molar excess over strychnine to obtain a maximum and constant extraction. Excess (2–10 ml) of the buffer solution used in the procedure had no influence on the absorbance of the extracts. When the amount of the buffer solution was less than 2 ml, separation of the two layers was poor.

Solvent for extraction. The behaviour of various solvents in the extraction was studied. Solvents were found to fall into the following categories:

(*i*) Those which enhance the extraction, *e.g.*, 1,2-dichloroethane, chloroform.

(*ii*) Those which do not extract the coloured complex even in the presence of quaternary ammonium salts or alkaloids, *e.g.*, carbon tetrachloride, cyclohexane, n-hexane, toluene, monochlorobenzene.

(*iii*) Those with which the blue TBPE is extractable even without quaternary ammonium salts or alkaloids, *e.g.*, butyl acetate, ether, ethyl acetate, isopentyl alcohol, nitrobenzene, methyl isobutyl ketone.

Of these, 1,2-dichloroethane was found to be most suitable for the extraction of the methylatropine or strychnine complexes.

Other variables. Full colour development took about 1 min of shaking. Continued shaking up to 5 min produced no further change in absorbance. The colour intensity of the dichloroethane extracts remains constant for 1 hr.

Fluctuations in room temperature (14–22°) were without measurable effect on the absorbance.

Calibration and precision. A linear relationship was observed between the absorbance of the extract and the concentration of methylatropine ($8·0 \times 10^{-7}$–$4·0 \times 10^{-6}M$, molar absorptivity $1·90 \times 10^5$ $l \cdot mole^{-1} \cdot cm^{-1}$ at 615 nm) or strychnine ($1·6 \times 10^{-6}$–$8·0 \times 10^{-6}M$, molar absorptivity $8·0 \times 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ at 560 nm) in the initial aqueous phase.

The reproducibility was estimated from the results for ten sample solutions, each with a final methylatropine concentration of $4·0 \times 10^{-6}M$. The mean absorbance was 0·761, standard deviation 0·008.

Composition of the coloured species

Continuous variations plots (TBPE + methylatropine = $8 \times 10^{-6}M$, λ = 590, 615 and 630 nm; TBPE + strychnine = $5 \times 10^{-5}M$, λ = 540, 560 and 600 nm) have a maximum at 0·5 mole-fraction of TBPE, indicating a 1:1 TBPE-methylatropine or TBPE-strychnine ratio.

In order to investigate the state of the coloured species in dichloroethane, the electrical conductivity of the extracts was measured. The results obtained shows that the TBPE–methylatropine species is in the ionized state and the TBPE–strychnine species is in the molecular state in dichloroethane. The extracted species, therefore, may be formulated as Strychnine·H(TBPE) and $[\text{Methylatropine}]^+[\text{TBPE}]^-$.

Effect of foreign substances and analysis of practical samples

Potassium nitrate, ammonium sulphate, magnesium chloride, calcium chloride, acetates, citrates, salicylates, glucose, lactose, *o*-cresol, phenol and aniline do not interfere in the determination of methylatropine or strychnine when present at the level of $2 \times 10^{-3}M$. Alkaloids interfere.

The method was applied to a strychnine injection obtained from a drugstore. The result was $2·57 \times 10^{-3}M$ strychnine by the proposed method, and $2·48 \times 10^{-3}M$ by the titrimetric method.[14]

The proposed method has proved applicable to the determination of many quaternary ammonium salts and alkaloids such as spartein, quinine, physostigmine, homatropine, and atropine.

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14. *Ibid.*, p 647

Summary—A new application of monoacidic dyes is reported for the determination of strychnine and methylatropine The method is based on solvent extraction into 1,2-dichloroethane of the ion-pair or addition compound formed between tetrabromophenolphthalein ethyl ester and quaternary ammonium salts or alkaloids. The absorbance of the extracts is linearly dependent on the concentration of strychnine or methylatropine initially present in the aqueous solution

Zusammenfassung—Es wird uber eine neue Anwendung von Farbstoffen mit einer sauren Funktion zur Bestimmung von Strychnin und Methylatropin berichtet. Die Methode beruht auf der Extraktion des Ionenpaars oder der Additionsverbindung aus Tetrabromphenolphthaleinäthylester und quartaren Ammoniumsalzen oder Alkaloiden in 1,2-Dichloräthan. Die Extinktion der Extrakte hangt linear von der Konzentration von ursprunglich in der waßrigen Losung vorliegendem Strychnin oder Methylatropin ab.

Résumé—On rapporte une nouvelle application d'un colorant monoacide au dosage de la strychnine et de la méthylatropine La methode est basée sur l'extraction par solvant en 1,2-dichloréthane de la paire d'ions ou de composé d'addition formé entre l'ester éthylique de la tétrabromophénolphtaléine et les d'ammoniums quaternaires ou les alcaloides Il y a relation linéaire entre l'absorption et la concentration en strychnine ou en méthylatropine initialement présente dans la solution aqueuse

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STUDY OF Cu(II)-HYDRAZINE-6-METHYLPICOLINALDEHYDE SYSTEM: A NEW "*IN SITU*" REACTION

(*Received* 23 *February* 1972. *Accepted* 5 *July* 1972)

The analytical applications of 6-methylpicolinaldehyde azine (6-Me-PAA) and hydrazone (6-Me-PAH) as photometric selective reagents for copper(I) have been reported.[1, 2] This paper reports primary and secondary "*in situ*" reactions between (*i*) copper(II) and 6-Me-PA and hydrazine, and (*ii*) copper(I)-6-Me-PAA with hydrazine or hydroxylamine. These "*in situ*" colour developments sometimes have practical advantages [3-6]

EXPERIMENTAL

Reagents

6-Me-PA, 6-Me-PAA and 6-Me-PAH. Aqueous or ethanolic solutions of 6-Me-PA, hydrazine hydrate, hydroxylamine hydrochloride, 6-Me-PAA, and 6-Me-PAH were used. The synthesis of the latter reagents has been described previously [1, 2]

Buffer solutions Acetic acid–sodium acetate and boric acid–sodium hydroxide mixtures were used as appropriate.

All the reagents used were analytical grade

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Résumé—On rapporte une nouvelle application d'un colorant monoacide au dosage de la strychnine et de la méthylatropine La methode est basée sur l'extraction par solvant en 1,2-dichloréthane de la paire d'ions ou de composé d'addition formé entre l'ester éthylique de la tétrabromophénolphtaléine et les d'ammoniums quaternaires ou les alcaloides Il y a relation linéaire entre l'absorption et la concentration en strychnine ou en méthylatropine initialement présente dans la solution aqueuse

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The analytical applications of 6-methylpicolinaldehyde azine (6-Me-PAA) and hydrazone (6-Me-PAH) as photometric selective reagents for copper(I) have been reported.[1,2] This paper reports primary and secondary "*in situ*" reactions between (*i*) copper(II) and 6-Me-PA and hydrazine, and (*ii*) copper(I)–6-Me-PAA with hydrazine or hydroxylamine. These "*in situ*" colour developments sometimes have practical advantages[3–6]

EXPERIMENTAL

Reagents

6-Me-PA, 6-Me-PAA and 6-Me-PAH. Aqueous or ethanolic solutions of 6-Me-PA, hydrazine hydrate, hydroxylamine hydrochloride, 6-Me-PAA, and 6-Me-PAH were used. The synthesis of the latter reagents has been described previously[1,2]

Buffer solutions Acetic acid–sodium acetate and boric acid–sodium hydroxide mixtures were used as appropriate.

All the reagents used were analytical grade

General procedure

The samples were prepared in 50-ml flasks with varying amounts of copper, buffer solution and reagents. They were diluted to volume with distilled water, and their absorbances measured against blank solutions prepared in the same way but with no copper. If necessary, samples were heated in a water-bath before transfer to the volumetric flasks.

RESULTS AND DISCUSSION

Reaction between Cu(II), hydrazine and 6-Me-PA

Hemerich *et al.*[7] have described the formation of a weak bidentate complex between Cu(II) and 6-Me-PA at pH 4 with release of a proton. At the pH used in the present work, 8·6, this reaction could not be detected. Hydrazine reduces Cu(II) to Cu(I), which precipitates as oxide in the absence of a complexing medium. If 6-Me-PA is added, the precipitate disappears, and the solution becomes brightly coloured.

Several samples were prepared with 5·9 ppm of copper, 2·5 ml of 0·05*M* ethanolic solution of 6-Me-PA, variable volumes of 0·05*M* aqueous solution of hydrazine hydrate and 10 ml of pH 8·6 buffer. The mixtures were heated at 60° for 15 min, the higher temperature favouring the formation of Cu(I)–6-Me-PAA.

The formation of the copper(I) complexes is influenced by pH,[1,2] which for this system should be between 6·5 and 10.

When the molar ratio aldehyde : hydrazine is 2 : 1, the azine is formed (Table 1). This is more soluble in 50% aqueous ethanol than in water.

The Cu(I)–6-Me-PAH complex is formed when the molar ratio between aldehyde and hydrazine is 1 : 1, Table 1, but 2·5 ml of 0·05*M* solutions of the reagents were used to obtain a slight excess. The solutions of both complexes were stable for at least 8 hr and longer heating periods did not improve the stability. If the reaction is carried out at room temperature, the sensitivity is lower and the amount of reagents required is greater.

Reaction between 6-Me-PA and Cu(I)–6-Me-PAH complex

Several samples were prepared with 5 ml of a neutralized 0·1% solution of 6-Me-PAH hydrochloride, 10 ml of pH 8·6 buffer, 10 ppm of Cu(I) and various volumes of 0·5*M* ethanolic solution of 6-Me-PA. On mixing there was an almost instantaneous disappearance of the absorption maximum at 425 nm, due to the Cu(I)–hydrazone complex, and formation of a maximum at 470–80 nm due to the Cu(I)–azine complex. With 0·5 ml of aldehyde solution, the transformation took place in 30 min, and with 1 ml 5 min. Heating the samples was unnecessary.

Table 1. Primary "*in situ*" formation of cuprous complexes

Molar ratio 6-Me-PA/hydrazine	Absorbance 480 nm	Absorbance 425 nm
5·00	0·500	0·338
2·00	0·520	0·325
1·66	0·510	0·360
1·42	0·490	0·380
1·25	0·450	0·430
1·11	0·415	0·507
1·00	0·320	0·620
0·83	0·240	0·630

"In situ" *reactions based on exchange of* $>$C=N— *groups*

Transformation of 6-Me-PAA into 6-Me-PAH in presence of copper. When 1 ml of 0·25*M* hydrazine hydrate solution was added to 5×10^{-5}*M* 6-Me-PAA at pH 8·6, the characteristic azine bands at 309 and 318 nm disappeared and a maximum at 293 nm and a shoulder at 260-5 nm, corresponding to 6-Me-PAH, were formed. There are two isosbestic points, at 299 and 226 nm. To confirm these spectral data, 6-Me-PAH was isolated in a crystalline state from the reaction mixture at greater concentration, and examined.

In the presence of copper, this transformation is detectable in the visible region. A sample containing 10 ppm of copper, 5 ml of 0·1% ethanolic solution of 6-Me-PAA, 10 ml of pH 8·6 buffer and 5 ml of 0·46*M* hydrazine hydrate was prepared. The absorption spectrum of the Cu(I)–azine complex gradually disappeared, as the maximum at 425 nm corresponding to the Cu(I)–hydrazone complex was formed. There are two isosbestic points at 462 and 391 nm but the initial curve without hydrazine does not pass through them.

The optimum conditions are 2 ml of 1*M* hydrazine hydrate and 5 ml of 0·1% 6-Me-PAA solution The solutions were stable for 1–9 hr after their preparation. Prior heating of the samples does not improve their stability. The order of addition of the reagents has no influence.

Transformation of 6-Me-PAA into 6-Me-PAO in presence of copper 6-Methylpicolinaldehyde oxime (6-Me-PAO) has been isolated by heating a suspension of 6-Me-PAA in a hydroxylamine solution at pH 8·6 Its melting point, ultraviolet spectrum and reaction with the cuprous ion are the same as those of 6-Me-PAO prepared by the usual procedure [9] This transformation was checked spectroscopically in the same way as in the previous case, but now 1 ml of neutralized 0·25*M* hydroxylamine hydrochloride was added instead of the hydrazine. The azine spectrum disappeared, and that of the oxime was formed (maxima at 280–6 nm and 244 nm). with isosbestic points at 293 and 224 nm.

This transformation also takes place in the presence of copper under the same conditions as described above The band at 470–80 nm disappears, as a stronger band at 425 nm appears, due to the Cu(I)–oxime complex There are two isosbestic points at 454 and 391 nm.

The variables which influence the reaction were studied and it was concluded that maximum colour development takes place at room temperature, at pH 4·5–5·3 with 3 ml of 1*M* hydroxylamine hydrochloride and 5 ml of 0·1% 6-Me-PAA solution. The solutions were stable for at least 48 hr. The order of addition of the reagents has no influence.

DISCUSSION

The copper(I) complexes of 6-methylpicolinaldehyde azine and hydrazone can easily be obtained by primary "*in situ*" synthesis, from solutions of Cu(II), hydrazine hydrate and 6-methylpicolinaldehyde, according to the proportion of the last

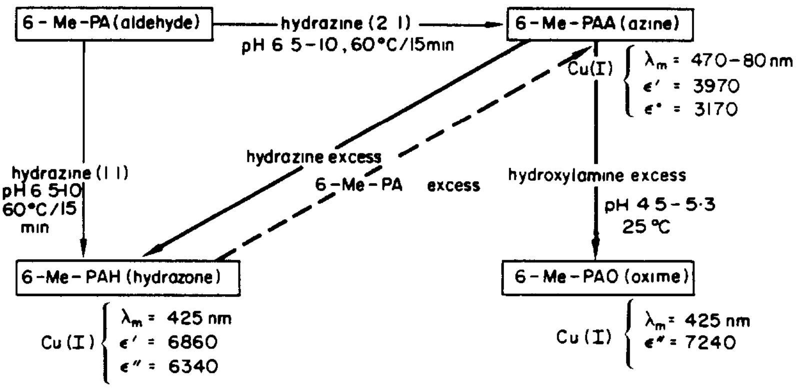
The action of 6-Me-PA on the yellow solutions of the Cu(I)–hydrazone complex was also tested, these solutions are rapidly transformed into red solutions of the Cu(I)–azine complex. The aldehyde interacts with the terminal amino group which does not participate in the formation of the complex, as its nitrogen atom is not included in the "cuproine" grouping of the molecule. The shift of λ_{max} from 425 to 470–80 nm is probably due to the increase of conjugation in the system in the ligand on passing from hydrazone to azine

The exchange between $\gt C{=}N{-}$ bonds has been reported.[10] The formation of a new bond depends on the equilibrium

$$\gt C{=}N{-}R + H_2N{-}R' \rightleftharpoons \gt C{=}N{-}R' + H_2N{-}R$$

which is displaced by the excess of one of the reactants. The conversion of azines into hydrazones by the action of hydrazines has been known for a long time.[11,12] The reaction of an excess of hydroxylamine with 6-Me-PAA leads to the formation of two molecules of oxime in two stages. the formation of hydrazone and oxime, followed by the transformation of hydrazone into another oxime molecule, and a hydrazine molecule. Therefore a lesser amount of hydrazine than hydroxylamine is required to carry out the respective transformations. This may also be the cause of the formation of oxime being much slower than that of hydrazone, which takes place in a single step whereas the Cu(I)–oxime complex is produced more quickly than the corresponding Cu(I)–hydrazone. In all cases a 100 1 molar ratio of amine to 6-Me-PAA was used.

In the diagram the two types of "*in situ*" reaction applied to the Cu(II)–hydrazine–6-methylpicolinaldehyde system, and the optical constants, are summarized: a thin line is used for the reactions based on the reaction of aldehyde with diamine, and a thick line for those based on the exchange of $\gt C{=}N{-}$ bonds



The molar absorptivities found in these photometric reactions (ε' = primary, and ε'' = secondary "*in situ*" reactions) are lower than those found with the previously synthesized reagents:[1,2] $\varepsilon_{\text{azine}} = 4{\cdot}19 \times 10^3$ and $\varepsilon_{\text{hydrazone}} = 6{\cdot}95 \times 10^3$ l.mole^{-1} cm^{-1}. Furthermore, the apsorbtivity value corresponding to the transformations between complexes is lower than that of the normal type

In our numerous experiments with reagents prepared "*in situ*" it has always been observed that the apsorbtivities are lower than those obtained with the previously synthesized reagent A satisfactory explanation of this fact has not yet been found A synthesis of the reagent in insufficient quantity does not seem possible, as the amounts of the components are determined empirically to yield an excess of reagent As the reactive components, in all the cases studied, are able to form less stable complexes with the ions being studied, it can be supposed that the cation is shared between the two complexes in proportion to their stability, and so a small amount of ion would be subtracted for the formation of the "*in situ*" complex This is confirmed considering that in the secondary "*in situ*" reactions, the absorptivity (ε'') decreases relative to the primary "*in situ*" type (ε'), since the starting complex is stable and the competition between ligands in this case is greater

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Summary—The Cu(II)-hydrazine-6-methylpicolinaldehyde system in solution is studied. The "*in situ*" reactions, based on the formation of a ligand by condensation of an amine and an aldehyde in the presence of the metal ion, and the consequent formation of the coloured Cu(I)-azine and Cu(I)-hydrazone complexes are reported. A new mode of homogeneous colour development, based on the exchange of $>$C=N— groups in the ligand with the metal ion present, is also described The results are compared with those obtained with the previously synthesized reagents

Zusammenfassung—Das System Kupfer(II)-Hydrazin-6-Methylpicolinaldehyd wird in Lösung untersucht Es wird über Reaktionen "in situ," die in der Bildung eines Liganden durch Kondensation eines Amins und eines Aldehyds in Gegenwart des Metallions bestehen, und die darauf folgende Bildung der farbigen Kupfer(I)-Azin- und Kupfer(I)-Hydrazonkomplexe berichtet Auch eine neue Art der Farbentwicklung in homogener Lösung wird geschildert, die auf dem Austausch von $>$C=N— Gruppen im Liganden mit dem anwesenden Metallion beruhen. Die Ergebnisse werden mit denen verglichen, die mit früher synthetisierten Reagentien erhalten wurden

Résumé—On étudie le système Cu(II)-hydrazine-6-méthylpicolinaldéhyde en solution On rapporte les reactions "*in situ*", basées sur la formation d'un coordinat par condensation d'une amine et d'un aldéhyde en la présence de l'ion métallique, et la formation consécutive des complexes colorés Cu(I)-azine et Cu(I)-hydrazone On décrit aussi un nouveau mode de développement de coloration homogène, base sur l'échange de groupes $>$C=N— dans le coordinat avec l'ion métallique présent On compare les résultats avec ceux obtenus avec les reactifs synthétisés antérieurement

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STABILITY CONSTANTS OF SOME METAL DITHIZONATES

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The instability and poor solubility of dithizone (diphenylthiocarbazone) in water makes the determination of stability constants of its metal chelates difficult. For that reason, the values of the stability constants are almost unknown[1] despite the excellence of dithizone as a chelating and extraction reagent

We investigated that problem and found a satisfactory solution that is presented in this paper

EXPERIMENTAL

Apparatus

All photometric measurements were made with the DU Beckman spectrophotometer, model 2400 (Fullerton, California). Quartz cells of 1-cm pathlength were used throughout. An Orion model 801 pH-meter (A. H. Thomas Co., Philadelphia. Pa.), with combined glass and calomel electrode, was used for pH measurements

Reagents

Perchlorates of the metals (G. F Smith Co., Columbus, Ohio) were used as 1·00 × $10^{-3}M$ aqueous stock solutions. Dithizone (Fisher Certified Reagent, Fair Lawn, N J) was purified by Welcher's method.[2] Its quality was checked by paper chromatography with methanol–water 10 1 on Chrom AR500 paper (Mallinckrodt Chem. Works, St. Louis, Missouri) and by elemental analysis. The product was chromatographically pure, $R_F = 0·87$ It was analysed with the following results: C 61·0%, H 4 8%, N 21 7%, S 12 4%; required for $C_{13}H_{12}N_4S$: C 60·9%, H 4·7%, N 21·9%, S 12·5%.

The 1·00 × $10^{-3}M$ stock solution of dithizone was prepared by dissolution of 6·4 mg of dithizone in 25·00 ml of 0·1*M* sodium hydroxide and 0·04*M* hydroxylamine hydrochloride. The solution was kept in the dark at 25° It was used during the next three hours, then a new solution was prepared. Solutions of 0·1*M* glycine + 0·05*M* hydroxylamine hydrochloride + 0·095*M* sodium perchlorate and 0·1*M* sodium hydroxide were used to adjust the pH to 5 55–10·02.

Measurement

The sequence of buffer, metal ion and dithizone was adhered to during the preparation of all solutions measured. The ionic strength was kept at 0·1*N* (sodium perchlorate), the temperature at 25 ± 1° The absorbance of solutions was measured against a buffer–reagent blank (or buffer-metal blank when an excess of metal ion was being used).

RESULTS AND DISCUSSION

Stability of dithizone solution

Hydrazine, ascorbic acid, sodium sulphite and hydroxylamine hydrochloride were investigated as stabilizing agents for aqueous solutions of dithizone. The last-mentioned reagent exhibits the most convenient properties It sufficiently stabilizes the solution of dithizone and its masking and reducing effects are negligible for the

Table 1 Stability of dithizone stock solution*

Time *min*	2	8	10	12	17	24	38	48	60	120	180	240	300	
A†	1 019	1 019	1 019	1 019	1 019	1·019	1·019	1 019	1·019	1 019	1 018	1 015	1 009	0 997
A‡	0·985	0·952	0·786	0·419	0 323	0·286	0·273	0·265	—	—	—	—	—	—

* Measured after dilution to 4·00 × $10^{-5}M$, at pH 6 50 and 470 nm

† Stabilized solution.

‡ Unstabilized solution.

concentrations of metal ions used. The time-dependence of absorbance of the stabilized and unstabilized solutions of dithizone is shown in Table 1. It can be seen that the stability of the stabilized solution is quite satisfactory during the first three hours.

Stability of electroneutral complexes

Metal dithizonates are soluble at concentrations of 10^{-5}–$10^{-6}M$ at pH >5·3. Precipitation occurs below that value. Investigating the composition of complexes formed in the range of pH 5·5–6·5 by means of the continuous variation method, we found that electroneutral complexes of ML_n are formed in all cases, where the value of n corresponds to the charge on the metal ion. The occurrence of a single complex of ML_n was checked by the method of Coleman *et al.*,[3] employing the equation

$$\Delta A_1/\Delta A_2 = \Delta\varepsilon_{n(1)}/\Delta\varepsilon_{n(2)} = \text{const} \tag{1}$$

where ΔA_1, ΔA_2 and $\Delta\varepsilon_{n(1)}$, $\Delta\varepsilon_{n(2)}$ are the effective absorbances and molar absorptivities, respectively, measured at two different wavelengths. We have

$$\Delta \mathrm{A}_\lambda = \mathrm{A}_\lambda - \mathrm{A}_{\mathrm{L}(\lambda)} \tag{2}$$

and

$$\Delta\varepsilon_{n(\lambda)} = \varepsilon_{n(\lambda)} - n\varepsilon_{\mathrm{L}(\lambda)} \tag{3}$$

where A_λ and $\mathrm{A}_{\mathrm{L}(\lambda)}$ are the absorbances of the complexing and ligand (dithizone) solution, respectively; $\varepsilon_{n(\lambda)}$ and $\varepsilon_{\mathrm{L}(\lambda)}$ are the molar absorptivities of the complex ML_n and of the ligand.

Plotting the dependence $\Delta A_1 = f(\Delta A_2)$ for equation (1) we obtained straight lines crossing the point $\Delta A_1 = \Delta A_2 = 0$ throughout.

Knowing the value of n for each complex, we determined its overall stability constant β_n, employing the method of stoichiometric dilution.[4] According to that method we have

$$\beta_n = \alpha_{\mathrm{M(Y)}}\alpha^n_{\mathrm{L(H)}}/(y_n n^n c_{\mathrm{M}}{}^n) \tag{4}$$

where $\alpha_{\mathrm{M(Y)}}$ and $\alpha_{\mathrm{L(H)}}$ are the side-reaction coefficients of the metal with the ligand Y of a masking reagent (and buffer) and of the ligand L with hydrogen ions, respectively; c_{M} is the total concentration of the metal and

$$y_n = \frac{(x-1)^{n+1}}{2^n(1-t)(x-t)^n} \tag{5}$$

Table 2. Stability constants of some metal dithizonates*

Complex	pH	λ *nm*	x	log $\alpha_{\mathrm{M(Y)}}$	log β_n	$\Delta\varepsilon_2 \times 10^{-3}$ *cm²/mmole*	u	$-\log v$	log β_1
AgL	8·21	400	1·170	1·76	6·98 ± 0·15	4·05	—	—	—
BiL$_3$	5·60	630	1·300†	15·13‡	32·11 ± 0·22	—	—	—	—
CdL$_2$	6·50	560	1·011†	0·46	15·10 ± 0·15	21·6	9·77	1·22	7·81 ± 0·11
CoL$_2$	6·50	570	1·014	0·59	13·97 ± 0·08	24·1	59·2	2·06	7·52 ± 0·09
CuL$_2$	6·50	570	1·034	6·58	19·18 ± 0·07	22·6	28·0#	1·72	9·35 ± 0·11
FeL$_2$	6·50	570	2·050	0·16	8·99 ± 0·11	16·5	20·0	1·57	4·78 ± 0·15
HgL$_2$	10·02	530	1·005	25·25§	40·3 ± 0·8	19·5	49·0	1·98	20·64 ± 0·16
MnL$_2$	6·50	400	1·500	0·02	9·55 ± 0·07	10·6	12·7	1·33	4·94 ± 0·09
NiL$_2$	6·50	570	1·087	2·36	14·17 ± 0·05	18·0	24·9	1·67	7·42 ± 0·11
PbL$_2$	6·50	560	1·017	0·92	14·16 ± 0·11	21·5	28·0	1·86	7·31 ± 0·09
PdL$_2$	6·50	660	1·012	7·68	21·78 ± 0·08	21·5	52·8	2·01	11·39 ± 0·11
SnL$_2$	5·55	640	1·240	0·39¶	11·99 ± 0·12	8·8	21·2	1·60	6·35 ± 0·15
ZnL$_2$	6·50	590	1·025	1·01	13·96 ± 0·08	32·9	5·52	0·91	6·93 ± 0·09

* For determination of β_n $c_{\mathrm{M}} = 2{\cdot}00 \times 10^{-5}M$, glycine ($c_{\mathrm{Y}} = 0{\cdot}08M$) as masking reagent and a buffer were used for stoichiometric dilution; log $\alpha_{\mathrm{L(H)}} = 0$ throughout. $c_{\mathrm{M}} = 4{\cdot}00 \times 10^{-4}M$, $c_{\mathrm{L}} = 4{\cdot}00 \times 10^{-5}M$ and hexamine buffer of pH 6·20 were used for the determination of β_1. The value of each stability constant is an average of five determinations.

† $c_{\mathrm{M}} = 5{\cdot}00 \times 10^{-6}M$

‡ $c_{\mathrm{Y}} = 0{\cdot}01M$ (EDTA)

\# $c_{\mathrm{M}} = 1{\cdot}25 \times 10^{-2}M$.

§ $c_{\mathrm{Y}} = 0{\cdot}08M$ (DTPA).

¶ $c_{\mathrm{Y}} = 0{\cdot}10M$ (chloride) where

$$x = \Delta A/(2\Delta A') \qquad \text{and} \qquad t = (x/2^n)^{1/(n+1)} \tag{6}$$

ΔA and $\Delta A'$ are the effective absorbances measured for $c_M = c_L/n$ and $c_M' = c_L'/n$ respectively ($c_M = 2c_M'$) According to the same method we have for the effective molar absorptivity

$$\Delta\varepsilon_n = \Delta A(x - t)/[c_M x(1 - t)] \tag{7}$$

and the value of ε_n is calculated by means of equation (3)

All results of this method are collected in Table 2.

Stability of complexes ML of bivalent ions

The overall stability constants of those complexes can be determined by employing an excess of metal ion Since the complexes of ML_n are relatively stable, we may write in that case

$$c_L = [ML] + 2[ML_2] = c_M[L](\beta_1 + 2\beta_2[L]) \tag{8}$$

where c_M and c_L are the total concentrations of the metal and ligand, respectively, and $c_M \gg c_L$ The expressions in the square brackets designate the actual concentrations of the corresponding species, β_1 and β_2 are the overall stability constants of the complexes ML and ML_2 respectively

The effective absorbance of that solution will be

$$\Delta A = \Delta\varepsilon_1[ML] + \Delta\varepsilon_2[ML_2] = c_M[L](\Delta\varepsilon_1\beta_1 + \Delta\varepsilon_2\beta_2[L]) \tag{9}$$

where

$$\Delta A = A - A_M \tag{10}$$

and

$$\Delta\varepsilon_1 = \varepsilon_1 - \varepsilon_M, \ \Delta\varepsilon_2 = \varepsilon_2 - \varepsilon_M \tag{11}$$

A and A_M are the absorbances of the complexing and metal solutions respectively, ε_1, ε_2 and ε_M are the molar absorptivities of the complexes of ML, ML_2 and metal solution respectively. The absorbance and molar absorptivity of the ligand can be ignored, owing to the small concentration of the free ligand

Combining (8) and (9) by elimination of [L] we obtain

$$r = 2\beta_2 c_L r^2/[\beta_1{}^2(2k - 1)c_M] - (2k - 1) \tag{12}$$

where

$$r = 1 - 2\Delta A/(\Delta\varepsilon_2 c_L) \tag{13}$$

and

$$k = \Delta\varepsilon_1/\Delta\varepsilon_2 \tag{14}$$

Using $c_L' = c_L/2$, $c_M' = c_M$ we obtain instead of (12) and (13)

$$r' = \beta_2 c_L r'^2/[\beta_1{}^2(2k - 1)c_M] - (2k - 1) \tag{15}$$

and

$$r' = 1 - 4\Delta A'/(\Delta\varepsilon_2 c_L) \tag{16}$$

Combining (12) and (15) by elimination of k we get

$$2\beta_2 c_L/(\beta_1{}^2 c_M) = 1/[2(u - 1)] + 1/[2(u - 1)]^2 = v \tag{17}$$

where

$$u = (r - r')^{-1} - r'/r \tag{18}$$

In this manner we computed the normalized function of $\log v = f(u)$. It is plotted in Fig 1 To obtain the values of $\log v$ with a precision of $\leq |0{\cdot}2|$ and to keep $r - r' \geq 0{\cdot}01$, u should be $\geq 1{\cdot}05$ and ≤ 100 Assuming $c_M/c_L = 10$ and $u = 100$ as limiting conditions, we obtain $\log \beta_1{}^2/\beta_2 \leq 1{\cdot}59$

The case of $\Delta A = 2\Delta A'$ should be avoided It occurs with improper selection of either the wavelength if $2\Delta\varepsilon_1 = \Delta\varepsilon_2$ [when the equations (8) and (9) become identical] or the ratio c_M/c_L and pH so that only one complex (either ML or ML_2) is formed

Results of the determination of the stability constants of complexes ML are also collected in Table 2

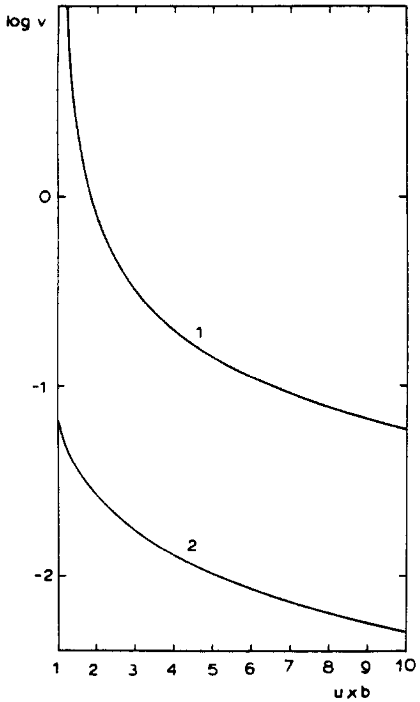

Fig 1 Dependence of log $v = f(u)$ 1 . $b = 1$, 2 · $b = 0$ 1

Conclusions

Employing spectrophotometry as the method of measurement, the use of stoichiometric dilution enables us to keep the concentration of dithizone at a minimum level and to perform the determination of overall stability constants of metal dithizonates in aqueous solution by the method described. In spite of that approach, dithizonates of bismuth and cadmium exhibit a great tendency to precipitate, so their stability constants should be determined at a total metal concentration $c_M = 5{\cdot}00 \times 10^{-6}M$.

Mercury(II) dithizonate is so stable that the use of diethylenetriaminopenta-acetic acid was necessary to adjust its effective stability constant Results in Table 2 indicate that the use of a stronger masking reagent would be desirable, but we could not find a better one Mono- and difunctional ligands containing sulphur donor groups frequently form mixed complexes with dithizone.[5]

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Summary—The overall stability constants of electroneutral dithizonates of bismuth, cadmium, cobalt(II), copper(II), iron(II), lead(II), manganese(II), mercury(II), nickel, palladium(II), silver, tin(II) and zinc were determined by means of stoichiometric dilution in aqueous solution stabilized by hydroxylamine hydrochloride, at pH 5 50–10 02. Stability constants of complexes ML of bivalent metals were determined under similar conditions but with an excess of metal

Zusammenfassung—Die Gesamt-Stabilitatskonstanten der elektrisch neutralen Dithizonate von Wismut, Cadmium, Kobalt(II), Kupfer(II), Eisen(II), Blei(II), Mangan(II), Quecksilber(II), Nickel, Palladium(II), Silber, Zinn(II) und Zink wurden durch stochiometrische Verdunnung in durch Hydroxylamin stabilisierter waßriger Losung bei pH 5 50–10·02 bestimmt. Unter ahnlichen Bedingungen, jedoch mit Metallüberschuß, wurden die Stabilitatskonstanten der Komplexe ML zweiwertiger Metalle ermittelt.

Résumé—On a déterminé les constantes de stabilité globales des dithizonates électroniquement neutres de bismuth, cadmium, cobalt(II), cuivre(II), fer(II), plomb(II), manganèse(II), mercure(II), nickel, palladium(II), argent, étain(II) et zinc au moyen de dilution stoechiométrique en solution aqueuse stabilisée par le chlorhydrate d'hydroxylamine, à pH 5,50–10,02. Les constantes de stabilité de complexes ML de métaux divalents ont été déterminées dans des conditions semblables mais avec un excès de métal.

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ENTHALPIMETRY OF NON-AROMATIC ALKENES

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Enthalpimetry is the analytical technique of determining the amount of a substance present in an unknown sample by allowing it to react quantitatively with some reagent and measuring the amount of heat produced or taken up by the reaction. At constant external pressure, the heat effect is equal to the enthalpy change, hence the name. Although thermodynamics tells us that the ΔH of reaction may be positive, negative or zero, the last is practically never the case and some heat effect is observed for virtually all reactions Because of the ubiquitous heat of reaction, enthalpimetry is an extremely general method, requiring only that the substance sought undergo a quantitative reaction with some reagent.

Although thermochemistry is a very old science, enthalpimetric analysis has attracted wide attention only during the past decade.[1–8] In this work, we have combined the principle of enthalpimetry with the preferred method of olefin determination, that of hydrogenation. Recent work has brought olefin determination by hydrogenation to a high level of sensitivity and accuracy. Brown[9] has been able to analyse samples containing as little 3 μmole of olefin by means of *in situ* generation of hydrogen and catalyst. He reported an error of about 4% for this minute amount. Curran and co-workers have reported determination of between 1 and 2 μmole, using null-point pressurimetry and volumetric addition of sodium borohydride to regenerate the hydrogen consumed[10] More recently, they have determined less than 1 μmole with an error of about 6% by their technique of substituting coulometric regeneration for the sodium borohydride step[11]

The hydrogenation reaction is quantitative and rapid for most simple olefins,[12,13] hence we have used it as the basis of an enthalpimetric method for olefin determination.[14] The purpose of this work was to modify the existing apparatus and procedure so as to take better advantage of the sensitivity due to the large negative ΔH of the hydrogenation reaction We have been able to decrease the working range by more than an order of magnitude from our previous work, to about 2–20 μmole, without significant loss in accuracy Moreover, in another series of experiments, we have decreased the amount of olefin taken to about 0·6 μmole, although at this level the accuracy suffers

EXPERIMENTAL

Reagents

All olefins were obtained from Chemical Samples Co. and certified to be more than 99% pure by the manufacturers Hexane was obtained from Fischer Chemical Co and Matheson, Coleman and Bell supplied the 5% palladium catalyst on powdered charcoal

Summary—The overall stability constants of electroneutral dithizonates of bismuth, cadmium, cobalt(II), copper(II), iron(II), lead(II), manganese(II), mercury(II), nickel, palladium(II), silver, tin(II) and zinc were determined by means of stoichiometric dilution in aqueous solution stabilized by hydroxylamine hydrochloride, at pH 5 50–10 02. Stability constants of complexes ML of bivalent metals were determined under similar conditions but with an excess of metal

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EXPERIMENTAL

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All olefins were obtained from Chemical Samples Co. and certified to be more than 99% pure by the manufacturers Hexane was obtained from Fischer Chemical Co and Matheson, Coleman and Bell supplied the 5% palladium catalyst on powdered charcoal

Apparatus

The electrical circuitry,[15] essentially a simplified version of what is used in elementary physical-chemical laboratories,[16] does not necessitate electrical calibration because all measurements are made relative to a standard Thus the enthalpy change of an unknown is always compared with that of a known material taken under the same conditions and in the same calorimeter, causing many errors to cancel out between the two measurements.

The cell (calorimeter) is similar to that previously described[14] except that it is fitted with two rubber septa, one a soft septum, fashioned from a serum-bottle cap, and one much harder, fashioned from a #1 rubber stopper The modified cell is shown in Fig 1

The micrometer burette was of 0·25 ml capacity and had a hypodermic needle cemented to the male portion of the Luer joint as shown in Fig 1

The original thermistor–thermistor well arrangement[14] was replaced by a stainless-steel liquid immersion probe of 1/8-in diameter designed for fast response time (time constant 2.5 sec, Cole-Parmer Inst Co, Model 8436) The probe was inserted through a small hole drilled in the hard septum The apparatus for hydrogen injection, stirring and insulation of the calorimeter was as previously described.[14]

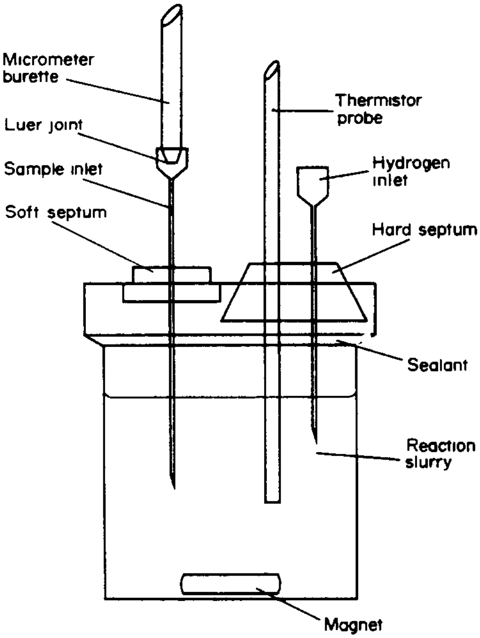

Fig 1. Modified hydrogen calorimeter

Procedure

Twenty-five ml of hexane and 0·6 g of 5% palladium catalyst on charcoal were placed in the calorimeter along with a stirring magnet, the chamber was closed and the screw cap was sealed down with "Silastic 732" sealing compound (Dow Chemical Co) After 1/2–1 hr setting time for the sealant, hydrogen was allowed to flow for ~5 sec through the tube which conveyed it from the tank to the inlet needle so as to clear the tube of air The inlet needle was then thrust through the harder of the two septa as shown in Fig. 1 and the hydrogen pressure within the calorimeter was adjusted to 20 psig by means of the tank valve The valve remained open throughout all subsequent steps, maintaining a constant pressure over the reaction mixture With vigorous magnetic stirring, the catalyst was activated in about 5 min with considerable evolution of heat Residual air within the calorimeter caused no interference with catalyst activation or subsequent steps About 1/2 hr was allowed for the calorimeter to return to thermal equilibrium (about 25°) with the surroundings, while hydrogen pressure remained constant and stirring was continued at a constant rate of 400–500 rpm. The method is not affected by small variations in ambient temperature or stirring speed Thermal equilibrium was indicated by a steady baseline recorded by the potentiometric recorder, showing that the Wheatstone bridge was in balance and that there was minimal heat leak to or from the calorimeter.

The microburette was then filled with an approximately 20% solution, in hexane, of the olefin to be investigated. Its needle was thrust through the soft septum into the reaction slurry and it was clamped into place, as shown in Fig. 1 Between 1 and 20 μl of olefin solution were delivered into the reaction slurry, causing a wave in the time-temperature curve as shown in Fig. 2. The potentiometer deflection was measured by extrapolating the "fore" and "after" temperature-drift curves to obtain the vertical line shown in Fig 2, in accordance with accepted practice.[17] After discard of the first few readings, further readings of potentiometer deflection were tabulated as a function of the injected sample size in μl.

Because of the very small temperature changes involved, 10^{-2}–10^{-3}K, thermistor reponse was assumed to be linear with temperature. For the same reason, the calorimeter was not always allowed to come to thermal equilibrium between injections, but, particularly with the smaller samples, successive injections were made at a rate of about one per minute, the baseline being re-established by fine adjustments of the bridge or the zero control of the recording potentiometer. If, after a series of such measurements, it was desired to re-establish thermal equilibrium, cold carbon dioxide gas was allowed to flow over the calorimeter in accordance with a procedure previously described[14] until the initial bridge and potentiometer settings were reproduced

Note. If the microburette is equipped with rubber seals, these are attacked by hexane, necessitating frequent replacement.

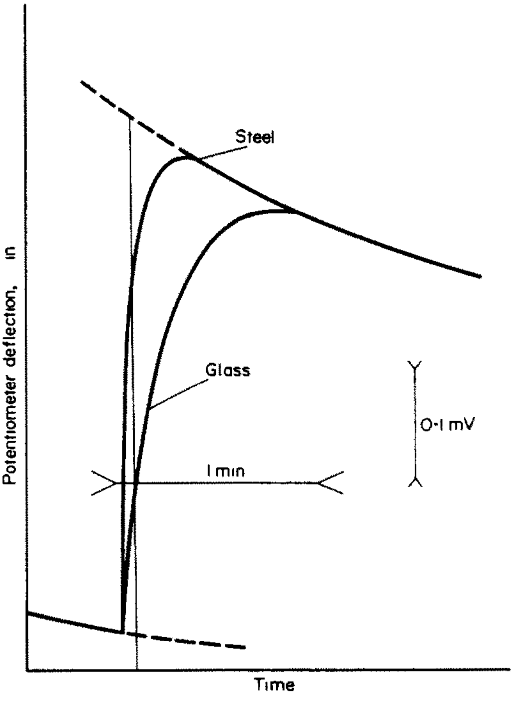

Fig. 2. Time-temperature curves for thermistors encased in glass and steel

RESULTS AND DISCUSSION

Figure 2 shows that the new thermistor resulted in much steeper time-temperature curves, indicating, in the cases studied here, that thermistor response-time was the controlling factor for their shape. Typical time-temperature curves are shown in Fig 2 for a thermistor contained in a glass well and the present thermistor encased in thin stainless steel The new thermistor is also more sensitive than the previous one and shows a much more stable baseline than a thermistor suspended directly in the reaction slurry Increased baseline stability is observed because the rigid probe transmits to the bridge less background noise due to stirring than does a freely-suspended thermistor Decreased response time makes the extrapolation process in Fig 2 more accurate, hence we were able to work at olefin concentrations which averaged an order of magnitude lower than our previous work.[14 18] Table 1 shows the results for several olefins in quantities of 1 39–37 5 μmole. Tabulated results of amount and corresponding potentiometer deflection were fitted by a standard least-squares technique to obtain the "best" linear function satisfying the points and to obtain the

Table 1 Standard deviation from linearity for potentiometer deflection as a function of alkene taken in amounts from 1·4 to 37·5 μmole

Compound	Amount, *μmole*	Replicates	Rel std dev, %
Cyclopentene	7·44–37·5	17	2·0
2-Pentene	2·35–21·2	27	2·0
Cyclohexene	1·98–15·8	26	1·4
Heptene	1·39–13·9	17	2·0
Methylallylbenzene	1·61–28·9	22	2·4
Hexene	1·53–15·3	25	3·2
Hexene	1·67–16·7	24	2·7

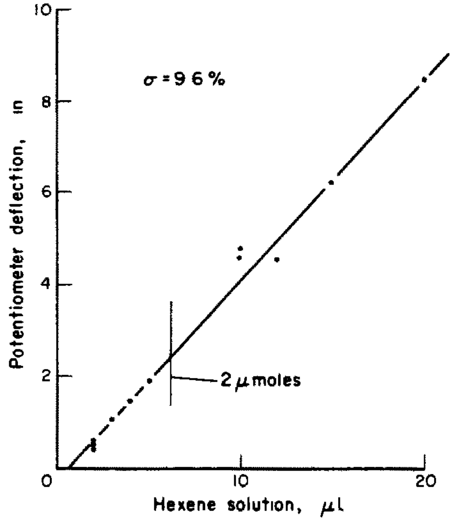

Fig 3. Ultramicro determination of micromolar quantities of hexene in hexane: potentiometer deflection as a function of amount taken

standard deviation, σ, from the function A simple published programme[19] was used to achieve this with G00D = 0 so that no points were discarded, no matter what their deviation

Sensitivity and accuracy are comparable with those of Brown's results[9] and those obtained by Curran and co-workers[10,11] Simplicity and speed seem to be superior to the best contemporary methods, so we decided to attempt further increase in sensitivity

The result was only partly successful, as is shown in Fig 3. Our method of increasing sensitivity was one of almost trivial simplicity but one which rests on unassailable thermodynamic grounds: we made the calorimeter smaller so as to reduce its heat capacity The results in Fig. 3 were obtained with a calorimeter of about 8–10 ml capacity, all other details of apparatus and procedure being unchanged

We were able to collect significant results for amounts below 2 μmole and to extend the lower limit of the method to about 0·6 μmole but at a significant increase in the relative standard deviation, which rose to 9·6%

CONCLUSION

We have developed a method of quantitative analysis of olefins which is comparable in accuracy and sensitivity to the best of contemporary methods and seems to have the advantage in speed and simplicity Its principal disadvantage is one it shares with all hydrogenation methods, that of non-specificity; with the exception of aromatic double bonds, the method does not, in general, differentiate between different olefinic linkages

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Summary—A method of increased sensitivity for hydrogen enthalpimetry of olefins in μmole quantities is reported. The method depends on a linear relationship between the amount of alkene present and the heat given off on hydrogenation at slightly more than 2 atm pressure over palladium catalyst on charcoal. Least-squares analysis of the results shows that the measured heat effect is a linear function of amount of alkene taken, with a relative standard deviation of 1–3% for samples ranging in size from 1·4 to 37·5 μmole. Extension of the method to samples in submicromolar quantities was only partially successful; in a series of measurements extending to a minimum amount of 0·64 μmole, the relative standard deviation rose to 9·6%.

Zusammenfassung—Ein Verfahren zur Wasserstoff-Enthalpimetrie von Olefinen in μMolmengen mit erhohter Empfindlichkeit wird angegeben. Es beruht auf der linearen Beziehung zwischen der anwesenden Alkenmenge und der bei der Hydrierung abgegebenen Wärmemenge, wenn die Hydrierung bei etwas uber 2 atm Druck uber einem Palladiumkatalysator auf Aktivkohle ausgeführt wird. Die Analyse der Ergebnisse nach der Methode der kleinsten Quadrate zeigt, daß die gemessene Warme linear von der eingesetzten Alkenmenge abhangt; die relative Standardabweichung betragt 1–3% bei Proben, die von 1·4 bis 37·5 μMol groß sind Die Ausdehnung des Verfahrens auf Proben unter einem μMol war nur teilweise erfolgreich, in einer Meßreihe, die sich bis zu einer kleinsten Menge von 0·64 μMol erstreckte, stieg die relative Standardabweichung auf 9·6% an.

Résumé—On rapporte une méthode de sensibilité accrue pour l'enthalpimétrie d'hydrogène d'oléfines en quantités de l'ordre de la μmole. La méthode repose sur une relation linéaire entre la quantité d'alkène présent et la chaleur dégagée par hydrogénation à une pression légèrement supérieure à 2 atm sur catalyseur au noir palladié. L'analyse des résultats par la méthode des moindres carrés montre que l'effet calorifique mesuré est une fonction linéaire de la quantité d'alkène, avec un écart type relatif de 1–3% pour des échantillons de dimensions comprises entre 1,4 et 37,5 μmole. L'extension de la méthode à des échantillons en quantités submicromolaires n'a été que partiellement couronnée de succès; dans une série de mesures allant jusqu'à une quantité minimale de 0,64 μmole, l'écart type relatif s'est élevé à 9,6%

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SEPARATION OF LITHIUM FROM DEAD SEA BRINES BY GEL PERMEATION CHROMATOGRAPHY

(*Received* 19 *June* 1972 *Accepted* 3 *August* 1972)

Dead Sea brines are concentrated solutions of a mixture of salts (30–40% salts, specific gravity *ca* 1·3), mainly halides of the alkaline and alkaline earth metals To date, their principal value is as a source of potash and bromine, but there is also considerable interest in the extraction of the rarer elements dissolved in them, such as caesium, rubidium, and lithium

Of these three elements lithium is present in relatively high concentrations—20 ppm in the water of the Sea and about 40 ppm in the so-called "end brine", which is a concentrated salt solution obtained after evaporation of the water in solar ponds and the subsequent crystallization of the potash.

Of all separation techniques available for such a concentrated salt solution, gel permeation chromatography seemed to the authors the most promising In that method use is made of the differential migration of cations, the difference being most pronounced between the migrations of univalent and bivalent metal ions, especially on polyacrylamide gels.

Studies of the gel permeation chromatography of simple cations and anions were first carried out by Egan,[1] who used polydextran and polyacrylamide gels Ohashi[2–4] has investigated solute-gel interactions and the influence of eluting agents on the chromatograms obtained. In these works a certain degree of selectivity was achieved This study examines the possibility of utilizing such separations to obtain lithuim-enriched fractions.

The main problems to which an answer was sought by the authors were

(1) whether it is possible to separate lithium chloride from the other chlorides in the very concentrated solutions available;
(2) the determination of the purity of the lithium so obtained in the concentrated fractions,
(3) whether some degree of preconcentration can be achieved in addition to the separation.

EXPERIMENTAL

Materials

Polyacrylamide gel, Bio-Gel P-2, molecular weight exclusion limit about 2600. Bio-Rad Laboratories, Richmond, California.

Blue Dextran 2000, average molecular weight 2 × 10^6 Pharmacia Fine Chemicals, Sweden

Separation procedure

Dry Bio-Gel P-2 was immersed in distilled water and allowed to swell for 24 hr. The gel thus wetted was introduced into a 200-cm long column of 3·5 cm internal diameter. The bed length was 147 cm. Before use the column was rinsed for several hours with distilled water

The void volume, V_0, determined by measuring the elution volume of Blue Dextran 2000, was found to be 400 ml The total volume V_t was 1385 ml

After introduction into the column, at a flow-rate of 1 ml/min, the sample of Dead Sea water was allowed to soak completely into the gel phase. For elution, distilled water was used. Ten-ml fractions were collected from the column, and each fraction was analysed for lithium, sodium, potassium, calcium, and magnesium.

Analytical methods

Lithium Since the lithium content of Dead Sea brines is very low compared with that of the other salts, its atomic-absorption signal is ordinarily suppressed, but with the method of standard additions quantitative results can be achieved

The measurements were made on a Perkin–Elmer Model 403 Atomic Absorption Spectrophotometer with a lithium hollow-cathode lamp at wavelength 335 nm.

Potassium and sodium These were measured by flame photometry, using the same instrument as for lithium but at wavelength 589 nm for sodium and 766 5 nm for potassium.

Calcium and magnesium These were titrated in an ammonia buffer with a standard solution of EDTA, with Eriochrome Black T as indicator

Qualitative tests In order to follow the elution process, qualitative tests for chloride were made throughout Thus the fraction in which the brine begins to emerge and the point at which it is completely eluted from the column can be established

Further qualitative tests, for magnesium and calcium, were carried out with carbonate in order to determine the fraction in which these elements first emerge from the column. Fortunately, they do so after the lithium.

RESULTS AND DISCUSSION

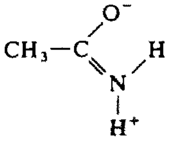
The great difficulty encountered in this separation stems from the very high overall salt concentration and from the high viscosity and density of both Dead Sea Water and the end brine. Table 1 lists the average salt compositions of these solutions.

Table 1. Salt composition of Dead Sea water (D.S.W.) and end brine (E.B.)

Sample	Sp. gr at 17°C	Li^+ conc. *ppm*	Br^- conc *g/l*	Salt concentration, *g/l* $MgCl_2$	$CaCl_2$	NaCl	KCl
D.S.W.	1.22	18	4.8	155	46.3	100.3	13.6
E.B.	1.337	36	11.2	348	108	6.9	3.8

Both Dead Sea water and end brine were chromatographed on a column of Bio-Gel P-2, and the cations were eluted with water. The chromatograms are shown in Figs. 1 and 2. In both cases the order of appearance in the effluent fractions was K^+, Na^+, Li^+, Mg^{2+}, Ca^{2+}, thus confirming the findings of Egan[1]. The chromatograms clearly indicate that separation is feasible and that there are a number of fractions which contain high concentrations of lithium chloride. These fractions also contain small amounts of NaCl and KCl, but no salts of either calcium or magnesium.

This is significant, as these latter two ions are the ones that are present in the highest concentrations. The fact that these two bivalent cations emerge last from the column can be explained by their stronger interaction with the negatively charged oxygen atom of the resonance form of the polyacrylamide gel



Indeed, the distribution coefficients—as shown in Table 2—are all smaller than unity, indicating that this interaction, though relatively weak, is yet stronger than with the univalent cations.

Table 2. Distribution coefficients of Dead Sea brines on Bio-Gel P-2

Sample	K^+	Na^+	Li^+	Mg^{2+}	Ca^{2+}
D.S.W	0·46	0·53	0·59	0·71	0·87
E.B.	0·37	0·46	0·49	0·60	0·75

Distribution coefficients ($K_{available}$) were calculated from the chromatogram by the formula developed by Laurent and Killander[5]

$$K_{av} = \frac{V_e - V_0}{V_t - V_0}$$

where V_e is the eluted volume of the solute, V_0 the void volume, and V_t the total liquid volume.

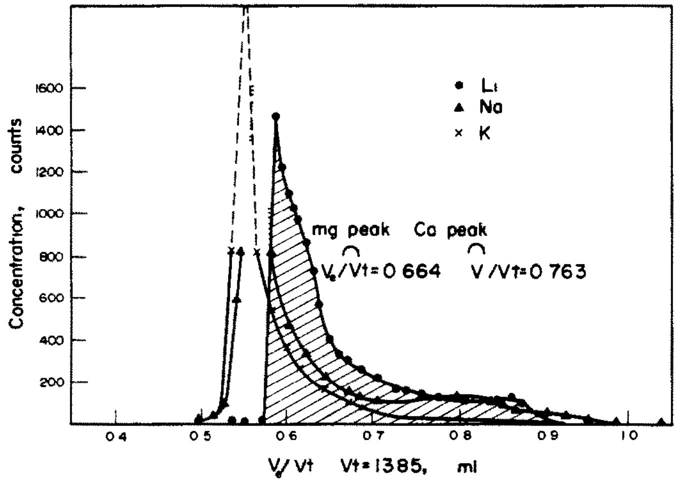


Fig 1 Fractionation of Dead Sea water on Bio-Gel P-2 Magnesium and calcium peaks have not been drawn in because of their great height, but their locations have been indicated

From a practical point of view it seems better to separate lithium from the end brine, because there the concentration of lithium is higher, and that of potassium and sodium lower, than in the natural Dead Sea water Table 3 presents a comparative study of both solutions as regards the degree of separation and preconcentration achieved with them

The results shown in Table 3 indicate that the aims set in the introduction were achieved to a certain extent Of the 130 10-ml fractions collected there are four or five that are rich in lithium and contain only small quantities of potassium and sodium but no magnesium or calcium. A degree of preconcentration was also achieved

It seems preferable, as was stated before, to separate lithium from the end brine, because of its higher initial concentration and the presence of lower quantities of sodium potassium. On the other hand the viscosity of the end brine is higher than that of natural Dead Sea water and its migration through the column consequently slower

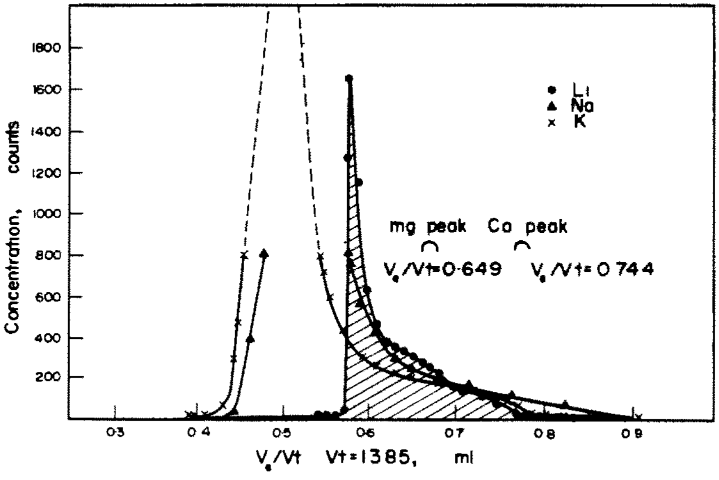


Fig 2 Fractionation of end brine on Bio-Gel P-2 Magnesium and calcium peaks have not been drawn in because of their great height, but their locations have been indicated

Table 3 Composition of the lithium-enriched fractions of Dead Sea water and end brine

	D.S W	E B
Initial Li$^+$ conc.	18 ppm	38 ppm
Li$^+$ conc. in enriched fractions	49 ppm	62 ppm
Li$^+$/Na$^+$ in original solution	1 5550	1 181
Li$^+$/Na$^+$ in concentrated fraction	1 11	1 8
Li$^+$/K$^+$ in original solution	1 756	1 100
Li$^+$/K$^+$ in concentrated fractions	1 10	1 3
Li$^+$/Mg^{2+} in original solution	1 . 8611	1 9150
Li$^+$/Mg^{2+} in concentrated fractions	1 1	no magnesium present
Li$^+$/Ca^{2+} in original solution	1 2572	1 2840
Li$^+$/Ca^{2+} in concentrated fractions	1 : 1	no calcium present

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Summary—Fractionation of Dead Sea brines by differential migration through a polyacrylamide gel is shown to be feasible. Lithium-enriched fractions obtained in the process contain no calcium or magnesium and only small quantities of sodium and potassium

Zusammenfassung—Es wird gezeigt, daß Solen aus dem Toten Meer durch differentielle Wanderung durch ein Polyacrylamidgel fraktioniert werden konnen Durch dieses verfahren erhaltene, an Lithium angereicherte Fraktionen enthalten kein Calcium oder Magnesium und nur wenig Natrium und Kalium

Résume—Il a ete montré que le fractionnement de saumures de la Mer Morte par migration différentielle à travers un gel de polyacrylamide est possible Les fractions enrichies en lithium obtenues dans le processus ne contiennent pas de calcium ou de magnésium et seulement de petites quantités de sodium et potassium.

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SYNERGISTIC INFLUENCE OF Zn(II) IN THE EXTRACTION-ATOMIC-ABSORPTION DETERMINATION OF TRACE CADMIUM IN WATERS

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Solvent extraction is well recognized as a powerful method for effecting analytical separations, owing to its capability of removing the analyte from interferences, as well as for the potential concentration of the analyte in the organic phase Both these effects are important in determining trace elements in waters Schaller *et al* [1] and Kuwata *et al* [2] used methyl isobutyl ketone to extract cadmium from waters by using ammonium pyrrolidinedithiocarbamate and sodium diethyldithiocarbamate respectively, Robinson *et al.*[3] used the method of standard additions in the determination of cadmium with 2-mercaptobenzothiazole and n-butyl acetate

A more sensitive development of this last extraction system is described, which provides high precision and almost total extraction of cadmium from natural waters, at the ng/ml level and below.

EXPERIMENTAL

Apparatus

A model AA5 Varian Techtron atomic-absorption spectrophotometer (AAS) fitted with a DI-30 digital indicator was used with a 100 × 0·5 mm AB51 burner and an ASL cadmium hollow-cathode lamp.

The optimum working conditions were

Wavelength	228 8 nm
Lamp current	2 mA
Slit	0 20 mm
Air	15 psig, flow-rate 9·0 L/min
Acetylene	10 psig, flow-rate such that flame was just non-luminous when butyl acetate was aspirated
Scale expansion	× 10

Reagents

Cadmium standard solution Pure cadmium (100 0 mg) was dissolved in a minimum excess of hydrochloric acid and the solution diluted to 1 litre Dilute standards were prepared from this

2-Mercaptobenzothiazole (MBT) solution A 1% solution in butyl acetate, purification was not required for either reagent.

Zinc acetate dihydrate Reagent grade

Buffer solution, pH 10 Ammonium chloride (7 g) and concentrated ammonia solution (57 ml) diluted to 100 ml

Extraction conditions

Several solvents were investigated for the extraction besides butyl acetate (e.g. methyl isobutyl ketone, ethyl acetate) but butyl acetate was considered to have optimum balance between enhancement of the absorption signal relative to aqueous solutions, solution equilibrium with water, and flame stability after extraction

Maximum extraction efficiency was obtained at above pH 9, so all aqueous solutions for analysis were buffered at pH 10

Procedure

Volumes of standard 0 01 μg/ml Cd solution from 0 to 30 ml were diluted to 250 ml in 500-ml separating-funnels with water drawn from the water supply mains which had previously been verified to contain an undetectable concentration of cadmium This served to provide a matrix for the extractions Four series of extractions were undertaken

(*A*) To the 250-ml solutions were added 10 ml of buffer solution, 0·1 g of zinc acetate and 10 ml of MBT solution The mixtures were extracted vigorously for 2 min, allowed to settle for 15 min, and the organic layers were then separated and aspirated through the flame with the instrument set for maximum sensitivity against a zero reference of pure butyl acetate.

(*B*) Procedure (*A*) was repeated but without the addition of the Zn(II).

(*C*) Procedure (*A*) was repeated but with 5 ml of MBT solution added

(*D*) Procedure (*C*) was repeated but without the addition of the Zn(II)

RESULTS AND DISCUSSION

The effect of addition of Zn(II) on the extraction of Cd(II) from waters is illustrated in Table 1 for 10-ml additions of MBT solution, and in Table 2 for 5-ml additions The effective zinc concentration, where Zn is added, is 120 μg/ml

Table 1. Effect of presence of 120 μg/ml Zn(II) on Cd absorbance after extraction by 10 ml of 1% MBT-BuOAc

Cd, *ng/ml*	Absorbance without Zn(II)	Absorbance with Zn(II)
0·0	0·0016	0·0070
0·4	0·0036	0·0118
0·6	0·0042	0·0142
0·8	0·0051	0·0156
1·0	0·0062	0·0188
1·2	0·0076	0·0218

Table 2. Effect of presence of 120 μg/ml Zn(II) on Cd absorbance after extraction by 5 ml of 1% MBT-BuOAc

Cd, *ng/ml*	Absorbance without Zn(II)	Absorbance with Zn(II)
0·0	0·0131	0·0149
0·2	0·0174	0·0207
0·4	0·0194	0·0260
0·6	0·0231	0·0323
0·8	0·0238	0·0389

Phase equilibria

Equilibrium between the Cd-MBT complex in the organic phase and the unextracted Cd is achieved relatively slowly, the extent of equilibration being dependent on the vigour and time period of the extraction—this is viewed as being fairly consistent with the low distribution coefficient, *D*, (as discussed by Brooks *et al.*[4]) of about 30. The effect of the presence of the large excess of Zn(II) is to shift the equilibrium almost completely in favour of the organic phase, resulting in an effective distribution coefficient in excess of 3000, so allowing rapid, quantitative extractions at very low trace cadmium levels

Precision

Comparison of the results in Tables 1 and 2 shows that it is feasible to obtain an increase in sensitivity by using 5 ml of added MBT solution instead of 10 ml, as would be expected, but for all practical purposes the higher volume would be more suitable as it yields a greater volume of solution to deal with As an indication of the precision that can be expected, a series of identical solutions containing 1·2 ng/ml Cd were treated according to procedure (*A*) and were found to have a standard deviation of 0·01 ng/ml, so that the limit of determination would be 0·02 ng/ml

Stability

The synergistic influence of Zn(II) also becomes apparent in the increased stability of the extracted Cd when compared with the extractions without the Zn(II) present. Although the latter solutions exhibited good stability for 3-4 weeks, the "synergistic" solutions had not degenerated after 5 weeks standing at room temperature.

Interferences

No interferences due to the water matrix were present However, attention was given to the effect of cyanide ions as this is often associated with Cd in various waste waters, and has been found to be a positive interference by Kuwata *et al*[2] In the presence of a 600-fold excess of cyanide, the extraction of 20 ng/ml Cd was found to be enhanced, which is an effect attributed by Robinson *et al*[3] to the suppression of Cd adsorption on the walls of the glass vessels, but in the presence of a 100,000-fold excess of cyanide this quantity of Cd remains completely unextracted The synergistic procedure however, permits the complete extraction of the Cd in the presence of a 100,000-fold excess of CN^- The extraction efficiency is improved and this is possibly also due to the lack of adsorption effects

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Summary—A very simple and rapid procedure is described in which the addition of a large amount of Zn(II) to a water sample before extraction by 2-mercaptobenzothiazole into n-butyl acetate brings about almost total extraction of Cd and allows determination of concentrations down to at least 0·02 ng/ml High precision is achieved, and the interference of cyanide is also overcome

Zusammenfassung—Ein sehr einfaches und rasches Verfahren wird angegeben, bei dem die Zugabe einer großen Menge von Zn(II) zu einer Wasserprobe vor der Extraktion mit 2-Mercaptobenzthiazol in *n*-Butylacetat die nahezu vollständige Extraktion von Cd bewirkt Dies erlaubt die Bestimmung von Konzentrationen bis herunter zu mindestens 0·02 ng/ml Man erreicht eine hohe Genauigkeit, und die Störung durch Cyanid wird ebenfalls ausgeschaltet.

Résumé—On décrit une technique très simple et rapide dans laquelle l'addition d'une forte quantité de Zn(II) à un échantillon d'eau avant extraction par le 2-mercaptobenzothiazle en acetate de *n*-butyle entraîne une extraction presque totale du Cd et permet le dosage de concentrations descendant jusqu'à 0,02 ng/ml au moins Une haute précision est atteinte, et l'interference du cyanure est aussi surmontée

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APPLICATIONS INVOLVING THE IODIDE ION—X DETERMINATION OF COPPER AND ANALYSIS OF CATION MIXTURES AND ALLOYS

(*Received* 5 *January* 1972 *Revised* 9 *June* 1972 *Accepted* 17 *August* 1972)

The present work is an extension to the application of potentiometric back-titration of excess of iodide with mercury(II), which was recently applied to the determination of oxidizing agents,[1] silver,[2] or ions reduced with iodide[3] In the classical iodometric determination of copper error may arise from loss of iodine, since CuI adsorbs some of it,[4] leading to earlier end-points even in presence of thiocyanate Copper determinations based on EDTA titration often lack selectivity The most important separation methods for copper in more than microgram amounts involve electrolysis or precipitation with sulphide or organic reagents The present method involving selective separation of copper(I) as the iodide is suitable for amounts in the range 1-35 mg of copper, either alone or mixed with other cations

Interferences

No interferences due to the water matrix were present However, attention was given to the effect of cyanide ions as this is often associated with Cd in various waste waters, and has been found to be a positive interference by Kuwata *et al*[2] In the presence of a 600-fold excess of cyanide, the extraction of 20 ng/ml Cd was found to be enhanced, which is an effect attributed by Robinson *et al*[3] to the suppression of Cd adsorption on the walls of the glass vessels, but in the presence of a 100,000-fold excess of cyanide this quantity of Cd remains completely unextracted The synergistic procedure however, permits the complete extraction of the Cd in the presence of a 100,000-fold excess of CN^- The extraction efficiency is improved and this is possibly also due to the lack of adsorption effects

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Summary—A very simple and rapid procedure is described in which the addition of a large amount of Zn(II) to a water sample before extraction by 2-mercaptobenzothiazole into n-butyl acetate brings about almost total extraction of Cd and allows determination of concentrations down to at least 0·02 ng/ml High precision is achieved, and the interference of cyanide is also overcome

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EXPERIMENTAL

Reagents

Solutions of copper(II) (0·1–0·01*M*), iodide (0·1–0·02*M*), mercury(II) (0·05–0·01*M*), and all metal ions involved, were prepared from high purity chemicals and twice distilled water, and standardized by recommended procedures None of the solutions contained chloride ions

Procedure for copper in pure solution or in cation mixtures

To appropriate volumes of copper(II) solution (1–5 ml), in a 100-ml beaker, add 15–20 mg of sodium sulphite, 5*M* sulphuric acid (1 ml) and distilled water (5 ml), then add, with constant stirring, iodide solution (3–8 ml), coagulate the white precipitate of CuI by heating on a water-bath for 10–15 min, which gives sufficient time for expulsion of any excess of sulphurous acid Filter off on a Whatman No 42 filter paper, wash thoroughly with water till the washings are free from iodide (usually five washes suffice) and titrate unreacted iodide in the filtrate and washings with Hg(II) (delivered from a microburette with its tip immersed in the solution), using silver amalgam as the indicator electrode and saturated calomel as the reference electrode.

Procedure for copper in alloys

From knowledge of the expected amount of copper in the alloy prepare a 0·03–0·07*M* copper solution by dissolution in nitric acid, digestion on a water-bath, separation of hydrous stannic oxide and lead sulphate and dilution to volume; determine copper in a fraction (2–4 ml) by the procedure above.

RESULTS AND DISCUSSION

Tables 1 and 2 list results for copper alone, in presence of a variety of cations, and in alloys, indicating the selectivity and reliability of the method.

With alloy No. 3 (copper taken, 7·47 mg) the results of copper determination in 9 parallel experiments were 7·49, 7·48, 7·48; 7·45, 7·45, 7·44, 7·44, 7·46, and 7·43 mg; with alloy No. 4 (copper taken, 7·36 mg) the results were 7·35, 7·35, 7·35, 7·32, 7·33, 7·34, 7·34, 7·37 and 7·37, showing respective standard deviations 0·021 and 0·017 mg, the relative standard deviations being 0·28 and 0·23%.

In determining copper by the present method, CuI was separated to avoid the metathesis $2\,CuI + Hg^{2+} = HgI_2 + 2\,Cu^+$ which is due to the lower solubility of HgI_2 ($8{\cdot}8 \times 10^{-7}$ mole/l. at 18°)[2] than that of CuI ($1{\cdot}05 \times 10^{-6}$ mole/l. from $K_{sp} = 1{\cdot}1 \times 10^{-12}$)[5], as verified experimentally

The method has the advantages that, (*a*) any oxidizing agent or higher oxidation state cation such as Fe(III) will not interfere, in the presence of added sulphite, (*b*) it is possible to titrate iodide selectively in presence of large amounts of a variety of cations, with accurate and precise potentiometric end-point determination, with equilibrium potentials obtained instantaneously, (*c*) the titrated species is iodide which, unlike iodine, is non-volatile, and (*d*) it can be successfully applied to the analysis of copper-containing alloys and related materials.

Table 1 Determination of copper

No.	Cu, *mg* Taken	Found	Error (± %)	Potential break, *mV*/0·1 *ml*
1	26·42	26·33	0·34	363
2	21·14	21·07	0·33	382
3	14·09	14·04	0·35	367
4	12·72	12·78	0·50	410
5	6·36	6·36	0·00	390
6	2·54	2·53	0·39	285
7	38·13	38·04	0·19	434
8	28·18	28·05	0·46	335
9	9·54	9·52	0·20	328
10	6·36	6·34	0·31	395
11	3·18	3·17	0·31	388

Nos. 1–11 0·099*M* I^- + 0·05*M* Hg(II) Also present No 7; 60 mg of Co; No. 8· 35 mg each of Ni, Co and Mg; No 9 40 mg of Al + 35 mg of Fe(III) + 40 mg of Ni; No 10: 50 mg of Zn + 30 mg of Ni + 40 mg of Cd, No. 11 40 mg of Cd + 30 mg of Cr(III) + 40 mg of Ni

Table 2 Determination of copper in alloys

Alloy No	Cu, *mg*		Cu%	
	Taken	Found	(*a*)	(*b*)
1	9·18	9·12	100·0	99·4
	13·77	13·86	100·0	100·7
	18·36	18·28	100·0	99·6
2	4·64	4·63	47·2	47·1
	6·96	6·94	47·2	47·1
	9·28	9·33	47·2	47·5
3	7·47	7·43	58·8	58·5
	11·21	11·18	58·8	58·7
	14·95	14·96	58·8	58·8
4	7·36	7·35	85·5	85·4
	11·04	10·99	85·5	85·1
	14·72	14·66	85·5	85·2
5	7·18	7·21	74·3	74·6
	10·77	10·75	74·3	74·2
	14·36	14·30	74·3	74·0
6	7·98	7·95	95·0	94·7
	11·96	11·92	95·0	94·7
	15·95	15·89	95·0	94·6
7	8·92	8·88	82·8	82·5
	13·38	13·38	82·8	82·8
	17·84	17·77	82·8	82·5
8	7·63	7·62	88·0	87·8
	11·45	11·42	88·0	87·7
	15·26	15·23	88·0	87·8

(*a*) Copper known by certified analysis (Chemical Department, Ministry of Industry) (*b*) Copper found by the present method Nos. 1–8 respectively, copper 100%, cupronickel 51·1% Ni, 0·72% Fe and 0·05% Zn, 33·9% Zn, 1·62 Al, 1·03% Mn, 1·01% Ni, 0·71% Fe and 0·78% Pb, bronze 9·96% Sn, 1·86% Zn, 1·83% Pb, 0·24% Sb, 0·07% Fe, 0·04% Ni, 0·06% As, 0·43% P, 6·8% Sn, 4·2% Pb, 4·6% Zn, 0·05% Fe, 0·02% Al, 0·07% P, 4·26% Ni, 0·006% Fe, 0·007% Pb; 7·08% Pb, 7·48% Sn, 0·021% Fe, 0·045% P, 0·35% Ni, rest Zn; 10·24% Sn, 1·37% Pb, 0·39% Ni, 0·02% P, 0·002% Fe.

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Summary—A rapid, accurate and highly selective method has been developed for estimation of copper, based on separating it as the slightly soluble copper(I) iodide, and potentiometric back-titration of unreacted iodide, in the filtrate, with mercury(II) By its aid binary, ternary and quaternary mixtures as well as a variety of copper alloys have been successfully analysed

Zusammenfassung—Eine rasche, genaue und hochselektive Methode zur Bestimmung von Kupfer wurde entwickelt. Sie beruht auf seiner Abtrennung als nur schwach losliches Kupfer (I)-jodid und potentiometrischer Rucktitration des nicht verbrauchten Jodids im Filtrat mit Quecksilber (II) Mit ihrer Hilfe wurden binare und quaternare Gemische sowie verschiedene Kupferlegierungen mit Erfolg analysiert

Résumé—On a élaboré une méthode rapide, précise et hautement sélective pour le dosage du cuivre, basée sur sa séparation sous forme d'iodure de cuivre (I) faiblement soluble, et le titrage potentiométrique en retour de l'iodure non réagi, dans le filtrat, par le mercure (II). A l'aide de cette technique, on a analysé avec succès des mélanges binaires, ternaires et quaternaires ainsi qu'une variété d'alliages de cuivre

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NOUVELLE MICROMETHODE COLORIMÉTRIQUE DE DOSAGE DE L'ION I^- DANS LES EAUX ET LES SUBSTANCES ORGANIQUES

(*Reçu le* 9 *mai* 1972 *Accepté le* 16 *août* 1972)

Parmi les méthodes proposées pour le dosage de faibles quantités d'iodures les colorimétries offrent un intérêt certain.[1-10] En particulier, Lange et Ward[1,2] ont décrit une détermination de I_2, I^- et IO_3^- en présence l'un de l'autre utilisant comme réactif une solution alcoolique d'*o*-tolidine et la formation d'une coloration vert-bleu. La méthode est toutefois laborieuse et la coloration obtenue instable. C'est pourquoi Johannesson[3] a retenu comme réactif une solution chlorhydrique d'*O*-tolidine, la coloration étant alors jaune

Selon nos essais, effectués dans le but de doser de faibles quantités d'ion I^- dans les produits naturels, une microcolorimétrie peut être réalisée sur le principe d'une oxydation de I^- en I_2 par l'eau oxygénée, à pH 3,5–4,5 et développement d'une coloration bleue stable avec l'*o*-tolidine.

PARTIE EXPERIMENTALE

Réactifs

Solution d'*o*-tolidine obtenue en dissolvant 0,1 g d'*o*-tolidine dans 4 ml d'alcool éthylique à 96%, ajoutant 0,1 g d'acide salicylique, complétant à 100 ml avec de l'eau puis filtrant Le réactif dont le pH est compris entre 3,5 et 4,5 est stable pendant plusieurs mois. L'*o*-tolidine peut être purifiée si nécessaire par dissolution en acide chlorhydrique ou sulfurique dilué, décoloration par un charbon actif et précipitation par l'hydroxyde de sodium

Solution aqueuse à 20% de carbonate de potassium

Eau oxygénée concentrée (30%).

Solution étalon d'iodure de potassium à 0,6541 pour 1000 (500 μg I^-/ml) dont la dilution fournit les solutions à 0,1–1 μg I^-/ml.

Solution de sulfamate d'ammonium obtenue en dissolvant 20 g de sulfamate d'ammonium dans 50 ml d'eau, ajoutant 10 ml de solution aqueuse à 5% d'acide sulfamique et complétant à 100 ml avec de l'eau

Solution tampon pH = 4,5–4,6 contenant 10 g de phosphate disodique, 2 ml d'acide phosphorique à 83% (d = 1,70 g/ml) dans 100 ml.

Mode opératoire

Dans le cas des eaux potables, des effluents (non chlorés) ou des eaux minérales (éventuellement privees d'hydrogène sulfuré par barbotage d'un courant de CO_2 après acidification) 50–100 ml sont alcalinisés dans une capsule de nickel par la solution à 20% de carbonate de potassium puis évaporés au bain-marie jusqu'à siccité Si le residu n'est pas parfaitement blanc, il convient de le calciner au four électrique a 500–550°

Pour les produits organiques, alimentaires ou biologiques, la prise d'essai, 1–5 g, (1 ml dans le cas du sang ou de l'urine) est desséchée, finement divisée puis additionnée de 2 ml de solution a 20% de carbonate de potassium. Après homogénéisation, puis dessiccation au bain-marie on procède à la calcination à 500–550° jusqu'à cendres pratiquement blanches

Dans tous les cas, le résidu de calcination est repris par trois fois avec 3 ml d'alcool à 96% puis après filtration les solutions sont évaporees en étuve à 80° jusqu'à siccité Si la teneur en NaCl est importante, il convient de répeter l'extraction alcoolique

Zusammenfassung—Eine rasche, genaue und hochselektive Methode zur Bestimmung von Kupfer wurde entwickelt. Sie beruht auf seiner Abtrennung als nur schwach losliches Kupfer (I)-jodid und potentiometrischer Rucktitration des nicht verbrauchten Jodids im Filtrat mit Quecksilber (II) Mit ihrer Hilfe wurden binare und quaternare Gemische sowie verschiedene Kupferlegierungen mit Erfolg analysiert

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Pour les produits organiques, alimentaires ou biologiques, la prise d'essai, 1–5 g, (1 ml dans le cas du sang ou de l'urine) est desséchée, finement divisée puis additionnée de 2 ml de solution a 20% de carbonate de potassium. Après homogénéisation, puis dessiccation au bain-marie on procède à la calcination à 500–550° jusqu'à cendres pratiquement blanches

Dans tous les cas, le résidu de calcination est repris par trois fois avec 3 ml d'alcool à 96% puis après filtration les solutions sont évaporees en étuve à 80° jusqu'à siccité Si la teneur en NaCl est importante, il convient de répeter l'extraction alcoolique

Tableau 1

I^- ajouté, μg	Précision recherchée	t	Intervalle de confiance, $E \pm S_{\bar{x}} t$
0,2	95%	2,57	0,028 ± 4,3 10^{-3}
0,4	95%	2,57	0,061 ± 3,0 10^{-3}
0,6	95%	2,57	0,090 ± 4,0 10^{-3}
0,8	95%	2,57	0,121 ± 5,0 10^{-3}
1,0	95%	2,57	0,150 ± 3,3 10^{-3}

Le résidu d'évaporation est alors additionné de 0,4 ml de solution de sulfamate d'ammonium puis soumis à une nouvelle dessiccation On ajoute 1 ml de solution tampon, 1 ml de solution d'*o*-tolidine, 0,2 ml d'eau oxygénée à 30% puis abandonne au repos pendant 25 minutes On complète à 5 ml avec de l'eau, homogénéise et soumet au spectrophotomètre à 626 nm La coloration est stable pendant 30 minutes

En effectuant la même réaction avec des solutions étalons d'iodure de potassium puis traçant la courbe d'étalonnage (Tableau 1) on en déduit la teneur en I^- dans la prise d'essai

DISCUSSION

L'instabilité de la coloration que nous avons observée avec la méthode de Lange et Ward semble due à la présence d'alcool dans le réactif. Par contre les colorations obtenues sont stables si le réactif à l'*o*-tolidine contient de l'acide salicylique. Celuici permet d'obtenir un pH de 3.5–4 5, optimal pour la réaction.[7]

Les conditions opératoires doivent être respectées à d'autres pH les colorations obtenues varient du jaune au bleu avec diminution de la sensibilité. De même la quantité d'eau oxygénée ajoutée ne doit pas excéder 0,2 ml pour éviter les colorations parasites Il convient d'ailleurs d'effectuer un témoin réactif qui doit être incolore La sensibilité de la méthode est de 0,02 μg I^-/ml

La réaction à l'*o*-tolidine est perturbée par les ions Br^- et Cl^- qui développent tous deux une coloration bleue (l'ion Cl^- en catalysant une réaction entre l'*o*-tolidine et l'eau oxygénée) Les bromures et chlorures sont en fait éliminés en mettant à profit leur insolubilité dans l'alcool à 96%

Les ions Fe^{3+} et NO_2^- développent également avec l'*o*-tolidine la même coloration bleue L'ion Fe^{3+} est, toutefois, éliminé par le carbonate de potassium ou complexé par la solution de tampon phosphate et l'ion nitrite est éliminé par le mélange sulfamate-sulfamique Ils n'apportent de ce fait pas de gêne dans le dosage des iodures

La méthode a été appliquée à divers produits agro-alimentaires et les résultats sont réunis dans le tableau 2

Tableau 2 Vérification de la méthode pour les produits agro-alimentaires récoltés de différentes régions

Nature de l'échantillon	Subst pesée, g	I^- contenu dans l'épreuve, μg	I^- ajouté, (a) μg	I^- trouvé, (b) μg	Différence ($b - a$)
carottes (S)	1,6095	1,74	0,60	2,27	1,67
carottes (V)	1,0000	0,40	0,60	1,00	0,40
carottes (A)	1,0000	0,20	0,60	0,80	0,20
carottes (R)	1,0000	0,60	0,80	1,33	0,53
haricots	5,1220	0,50	0,80	1,33	0,53
haricots	5,0000	0,46	0,50	0,93	0,43
mais (H)	5,0000	0,60	0,20	0,86	0,66
mais (H)	5,0000	0,60	0,40	1,00	0,60
mais (R)	5,0000	0,87	0,80	1,65	0,85
chou (R)	1,0000	0,37	0,60	0,97	0,37
blé (R)	5,0000	0,60	1,00	1,50	0,50
oignon (R)	2,0000	1,07	1,00	2,00	1,00

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Résumé—Un microdosage de l'ion I⁻ dans les eaux et les produits organiques est fondé sur son oxydation par l'eau oxygénée en iode, qui développe avec l'*o*-tolidine à pH 3,5–4,5 une coloration bleue. Sa sensibilité est de 0,02 μg I⁻/ml

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Zusammenfassung—Eine Mikroermittlung von Jodid in Wasser und in organischen Stoffen gründet sich auf Oxydierung mit Wasserstoffperoxid zu Jod, was eine blaue Farbung mit *o*-Tolidin bei pH 3,5–4,5 ergibt. Die Genauigkeit ist 0,02 μg/ml.

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ACENAPHTHENEQUINONE MONOXIME(AQM) AS A SELECTIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM(IV) BY SOLVENT EXTRACTION

(*Received* 31 *December* 1971. *Accepted* 31 *May* 1972)

Reviews of methods[1–4] for the colorimetric determination of platinum show that there is a real need for a reagent which can be used to determine platinum, particularly in the presence of other platinum metals, cobalt, nickel and copper

Acenaphthenequinone monoxime, which has already been used for the spectrophotometric determination of ruthenium,[5] osmium,[6] rhodium[7] and cobalt[8] was examined to see if it satisfies this need.

EXPERIMENTAL

Reagents

Standard platinum solution was prepared by dissolving 1 g of grade 1 platinum thermocouple wire (99·99% pure) in hot *aqua regia* The resultant solution was evaporated almost to dryness. A small amount of hydrochloric acid was added and the solution was again evaporated to dryness. The treatment was repeated three or four times in order to destroy any nitroso complexes After the final evaporation, 5 ml of hydrochloric acid were added and the solution was made up to 500 ml with doubly distilled water More dilute solutions were prepared, as needed, by dilution of the stock solution Two standard platinum solutions prepared by exactly the same procedure were found to give the same spectrophotometric readings

Acenaphthenequinone monoxime (AQM) 0·1*M* solution in ethanol

Chloroform, reagent grade, was used after distillation

Buffer solutions with pH values ranging up to 5·0 were prepared by mixing 0·5*M* acetic acid and 0 5*M* sodium acetate in different proportions

Procedure

The pH of a solution containing 19·5–156·0 μg of platinum and 2 ml of $1 \times 10^{2-}$*M* reagent solution is adjusted to between pH 1 9 and 3 2 with acetic acid–sodium acetate buffer (5 ml) and diluted to 10 ml with doubly distilled water (The acid present in the platinum solution accounts for the low pH values) The contents

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Chloroform, reagent grade, was used after distillation

Buffer solutions with pH values ranging up to 5·0 were prepared by mixing 0·5*M* acetic acid and 0·5*M* sodium acetate in different proportions

Procedure

The pH of a solution containing 19·5–156·0 μg of platinum and 2 ml of $1 \times 10^{2-}M$ reagent solution is adjusted to between pH 1·9 and 3·2 with acetic acid–sodium acetate buffer (5 ml) and diluted to 10 ml with doubly distilled water (The acid present in the platinum solution accounts for the low pH values) The contents are heated for 2 hr on a boiling water-bath, then cooled to room temperature, and 10 ml of chloroform are added The contents are equilibrated by shaking for 5 min and then left for 1 min to allow the two phases to separate. The organic phase is separated and centrifuged to remove water droplets, and the absorbance is measured against the corresponding reagent blank prepared under identical conditions From the absorbance, the amount of platinum is deduced from the calibration curve.

RESULTS AND DISCUSSION

Optimum conditions

The rate of reaction of platinum(IV) with AQM is slow at room temperature, but it increases at 100°, the absorbance of the chloroform extracts becoming constant after about 2 hr

The absorbance remains constant over the pH range 1·0–3·2, so a buffer solution of pH 2 5 ± 0·1 was adopted for the working procedure.

At pH 2·5 an eightfold molar excess of the reagent is sufficient for full colour development However, a tenfold molar excess of the reagent was generally employed

Optical constants and composition of the complex

The absorption spectra are shown in Fig 1. All measurements were made at 390 nm The extraction procedure was followed and the absorbance of the organic phase was measured Beer's law was obeyed up to 23·4 ppm of platinum. The accurate range for determination of platinum, as evaluated from a Ringbom plot, is 1·95–15·6 ppm of platinum, and the sensitivity of the reaction at 390 nm is 0·021 μg/cm^2 for log $I_0/I = 0{\cdot}01$. The colour is stable for at least 24 hr.

Eight determinations on a solution of 11 7 ppm of platinum resulted in a mean absorbance of 0·566 with an average relative deviation of ±0·2%. The method of continuous variations[9,10] and the mole-ratio method[11] were employed to establish the stoichiometry of the complex Both complexes showed the existence of 1 · 2 (Pt . AQM) complex

Effect of diverse ions

The effect of foreign ions on the determination of platinum was studied by adding known amounts of foreign ions to samples containing 15·6 ppm of platinum and extracting the complex into chloroform by the working procedure Interference from large amounts of ruthenium(III), osmium(VIII), rhodium(III) and iridium(III) ions was sufficient to warrant their removal, but they could be tolerated at the 10-ppm level Tartrate and citrate have been successfully used as masking agents for some metals, since they themselves are tolerated even in large amounts Oxalate has also been used as a masking agent but since oxalate interferes, a relatively small excess was used Results of the study of diverse ions are shown in Table 1.

Determination of platinum in presence of palladium

The reaction between platinum and acenaphthenequinone monoxime takes place at elevated temperatures while palladium is completely precipitated at room temperature. Based on this behaviour of the two metals,

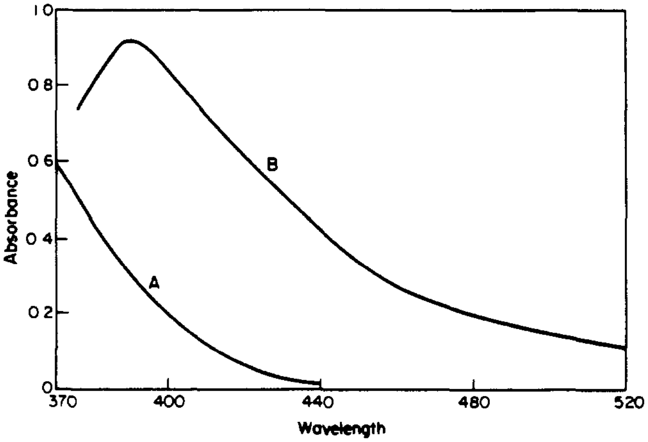

Fig 1 Absorption spectra of platinum-AQM complex
Platinum, 1 × $10^{-4}M$, reagent, 15 × $10^{-4}M$
A Reagent *vs* chloroform B Platinum–AQM complex *vs.* reagent

Table 1. Determination of platinum in presence of foreign ions
Amount of Pt = 15·60 ppm; pH = 2·0
Absorbance in absence of foreign ions = 0·752

Foreign ion	Amount of foreign ion added, *ppm*	Absorbance	Deviation in absorbance	Foreign ion	Amount of foreign ion added, *ppm*	Absorbance	Deviation in absorbance
Sulphate	5000	0·752	0·000	Strontium(II)	600	0·754	+0·002
Citrate	1000	0·752	0·000	Barium(II)	600	0·754	+0·002
Tartrate	1000	0·752	0·000	Calcium(II)	600	0·754	+0·002
Nitrate	6200	0·752	0·000	Copper(II)	60	0·758	+0·006
Phosphate	80	0·752	0·000	Uranium(VI)*	230	0·752	0·000
Pyrophosphate	160	0·751	−0·001	Iron(III)	100	0·752	0·000
Perchlorate	2500	0·752	0·000	Silver(I)	34	0·760	+0·008
Nitrate	40	0·752	0·000	Ruthenium(III)†	10	0·753	+0·001
Borate	160	0·754	+0·002	Rhodium(III)†	10	0·754	+0·002
Fluoride	1500	0·760	+0·008	Iridium(III)	10	0·754	+0·002
Thiocyanate	80	0·765	+0·013	Osmium(VIII)	10	0·754	+0·002
Oxalate	200	0·765	+0·013	Gold(III)	30	0·752	0·000
Bromate	160	0·740	−0·012	Vanadium(V)	54	0·752	0·000
Zinc(II)	140	0·760	+0·008	Molybdenum(VI)	20	0·752	0·000
Cadmium(II)	140	0·765	+0·0013	Mercury(II)§	34	0·761	+0·009
Nickel(II)	2000	0·752	0·000	Chromium(III)	30	0·752	0·000
Cobalt(II)	1600	0·752	0·000	Thorium(IV)†	40	0·760	+0·008
Magnesium(II)	180	0·752	0·000	Lead(II)	40	0·770	+0·018

* Oxalate used as masking agent
† Citrate used as masking agent
§ Fluoride used as masking agent

palladium was extracted into chloroform before heating. The remaining aqueous solution was heated for 2 hr and the platinum complex was extracted into chloroform. The absorbance of the extracted complex was identical with that found in absence of palladium. The results are recorded in Table 2.

Comparison with other methods$^{1-4}$

The *p*-nitrosodimethylaniline–iodide method is more sensitive but less selective than acenaphthenequinone monoxime and it requires more reagent and is more sensitive to the time of heating, change of pH and the amount of buffer. The AQM method is less sensitive than those based on tin(II) chloride and *o*-phenylenediamine, but it is more selective.

Acknowledgement—One of the authors (SKS) is thankful to the Council of Scientific and Industrial Research (India) for the award of a fellowship

Table 2. Determination of platinum in presence of palladium
Absorbance in absence of palladium = 0·752

Palladium, *ppm*	Platinum, *ppm*	Absorbance after separation
10·0	15·6	0·752
20·0	15·6	0·749
30·0	15·6	0·751
40·0	15·6	0·752
50·0	15·6	0·751
60·0	15·6	0·752

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Summary—Acenaphthenequinone monoxime has been found to be a selective reagent for spectrophotometric determination of 1–16 ppm of platinum in the pH range 1·90–3·20. With excess of the reagent, a 1 2 (metal : ligand) complex is formed with an absorption maximum at 390 nm and molar absorptivity of $9·0 \times 10^3$ l mole^{-1}·cm^{-1}. The effect of foreign ions has been investigated and other platinum metals do not interfere if present in similar amounts to the platinum

Zusammenfassung—Es wurde gefunden, daß Acenaphthenchinonmonoxim ein selektives Reagens zur spektrophotometrischen Bestimmung von 1–16 ppm Platin bei pH 1·90–3 20 ist Mit einem Reagensuberschuß wird ein 1 · 2(Metall:Ligand)-Komplex mit Absorptionsmaximum bei 390 nm und einem molaren Extinktionskoeffizienten von $9·0 \times 10^3$ 1 mol^{-1} cm^{-1} gebildet. Der Einfluß von Fremdionen wurde untersucht. andere Platinmetalle storen nicht, wenn sie in ahnlichen Mengen wie Platin vorliegen

Résumé—On a trouvé que la monoxime de l'acénaphtènequinone est un réactif sélectif pour le dosage spectrophotométrique de 1–16 p.p.m de platine dans le domaine de pH 1,90–3,20 Avec un excès de réactif, il se forme un complexe 1 : 2 (métal : coordinat) avec un maximum d'absorption à 390 nm et un coefficient d'absorption molaire de $9,0 \times 10^3$ 1 mole^{-1} cm^{-1}. On a étudié l'influence d'ions étrangers et les autres métaux de la mine du platine ne gênent pas s'ils sont présents en quantités similaires au platine

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TELLURATE AND PERIODATE SOLUTIONS AS MEDIA FOR PAPER ELECTROPHORESIS OF CARBOHYDRATES

(*Received* 3 *July* 1972. *Accepted* 29 *August* 1972)

Some years ago one of us[1] described an exploratory study of the electrophoretic behaviour of sugars and other polyhydroxy compounds in 0·05*M* telluric acid adjusted to pH 8–11 with sodium hydroxide. Although the compounds were found to migrate as anions, considerable elongation of spots was observed and the method was not recommended at that time as an analytical technique since far better separations were obtained by using other complex-forming electrolytes[2] The continuing interest in electrophoretic separation of polyols, as shown by periodic reviews of the subject,[3,4] has prompted us to re-examine the use of tellurate solutions in an attempt to find conditions under which they could be employed as satisfactory complexing media Extensive studies of the thermodynamics and kinetics of the polyol–tellurate reaction have been reported by Edwards and co-workers, who showed that a 1 . 1 anionic complex forms[5] but at a rate which is rather low compared to the very rapid reaction occurring in borate solutions, the most popular media for electrophoresis of polyols Although the formation constant for the polyol–tellurate complex decreases with increase in temperature[6] the reaction is base-catalysed and its rate increases markedly with the temperature[7]

In the absence of strong adsorption upon the support medium, an elongation of polyol spots during electrophoresis may be reasonably ascribed to incompleteness of complexing. Thus, the above-mentioned studies would suggest that a suitable modification in pH, concentration of tellurate, and temperature, might provide better conditions for complex formation and lead to more discrete spots. One of the objects of the present work was to test this possibility experimentally

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The extension of our investigations to periodate solutions was prompted by the report[6] that the ability of periodate ions to bind simple 1,2-diols such as propylene glycol is greater than that of tellurate, which in turn is greater than that of borate. The use of periodate for the oxidation of carbohydrates and other polyols is now well established,[8] and extensive studies of the mechanism of such reactions have indicated that a necessary intermediate is a periodate–polyol anionic complex,[9] although the exact nature of the latter has not yet been ascertained. The optimum reaction conditions depend on the compound to be oxidized but are known to require a pH in the range 2·5–5·0. In contrast, the formation constant of the anionic complex increases with pH, while at the same time the rate of decomposition into oxidation products decreases.[10] Maximum complexing and minimum oxidation appear to take place above pH 9

EXPERIMENTAL

Apparatus

Shandon high-voltage electrophoresis instrument, model L.24.

Procedure

Before loading, the filter paper (Whatman No. 3 MM, 57 × 23 cm) was wetted with electrolyte and the excess was evenly blotted. The test compounds (1% aqueous solutions) were then applied to the baseline by means of capillaries, the sample volumes being approximately 0·01 ml (100 μg of carbohydrate) in periodate solutions, and about twice this quantity in tellurate solutions. During electrophoresis the paper was cooled by water circulating either from a tap or from a thermostatic bath. Although the apparatus can produce up to 10000 V, in practice the relatively high conductances of the solutions restricted the work to 1000–2000 V in order not to exceed the maximum permissible current (100 mA). Migrations towards the positive electrode were expressed relative to the movement of D-ribose, with 2,3,4,6-tetra-*O*-methyl-D-glucose as a non-migrating marker. The extent of migration was taken as the distance between the leading edges of the spots for the test compound and the marker.

Reagents

The electrophoretic media were prepared by dissolving laboratory reagent grade telluric acid or sodium metaperiodate, $NaIO_4$, in distilled water and adjusting the pH with solid sodium hydroxide.

Ammoniacal silver nitrate[11] was found to be a very satisfactory detecting reagent in periodate solutions for all the compounds investigated, but it is dangerous to store this reagent. An ethanol/sodium hydroxide mixture followed by silver nitrate/acetone will do equally well. Immediately after spraying, each compound gave a clear white spot on a brown background, and its position could be marked before the entire paper became brown. Incubation at 110° for about 5 min produced black deposits of silver in the previously white positions, and the paper was then "fixed" by washing in 10% sodium thiosulphate solution and then water. Silver nitrate cannot be used in presence of tellurate, but good results were obtained with an aniline phosphate spray[12] although it was necessary to locate the alcohols under an ultraviolet lamp

RESULTS

In a series of preliminary electrophoretic runs using tellurate solutions, various combinations of the following conditions were used: concentration of telluric acid 0·05–0·20*M*, pH 9–11, temperature 25–60° Spots of satisfactory compactness were obtained at 25° by using 0·20*M* tellurate at pH 10, and these conditions were chosen for all subsequent investigations. The highest potential difference attainable was only 1000 V (about 17 V per cm of paper) since the current rose from approximately 50 to 95 mA during each 1-hr electrophoresis period. The corresponding migration of the reference compound, D-ribose, was about 9 cm A temperature increase improves the compactness of the spots to some extent, even if the tellurate concentration is reduced to 0·10*M*, but the improvement was not considered to be commensurate with the increased experimental difficulty Sodium tellurate is not very soluble, and tends to precipitate out of the more concentrated solutions after 24 hr. However, it is easily redissolved by heating, to give a usable but turbid solution. There is some decomposition of tellurate in the cathode compartment of the apparatus, a black deposit being obtained.

Periodate solutions were prepared in the concentration range 0·03–0·07*M*, and in the pH range 6–13 The finally adopted conditions were 0·07*M* periodate at pH 11, the electrophoresis being performed at the temperature of tap water (13–18°). A voltage of 2000 V (approx. 35 V/cm) could be applied for 30 min, during which time D-ribose migrated about 10–12 cm and the current rose from 60 to nearly 100 mA After standing for 24 hr the periodate solutions deposit crystals which cannot be redissolved by heating. The relative mobilities (M_R) selected from closely concordant repetitions in tellurate and periodate solutions under the finally chosen conditions are given in Table 1

Table 1 Relative mobilities (M_R) in tellurate (0·2*M*, pH 10, 25°C) and in periodate (0·07*M*, pH 11, 13–18°C) solutions. (Reference compound: D-ribose)

Test compound	M_R (tellurate)	M_R (periodate)	Test compound	M_R (tellurate)	M_R (periodate)
D(−)Arabinose	0·86	1·01	Cellobiose	0·33	0·65
L(+)Arabinose	0·86	1·01	Lactose	0·55	0·82
D(−)Ribose	1·00	1·00	Maltose	0·41	0·73
D(+)Xylose	0·66	1·00	Sucrose	0·15	0·30
D(+)Galactose	0·90	1·00	Raffinose	0·46	0·62
D(+)Glucose	0·50	1·00	α-Methyl glucoside	0·15	0·35
D(+)Mannose	1·00	1·01	β-Methyl glucoside	0·13	0·37
L(+)Rhamnose	0·86	0·99	Pentaerythritol	0·15	—
D(−)Fructose	0·92	1·01	Mannitol	1·00	1·02
L(−)Sorbose	0·80	1·00	Dulcitol	1·00	1·05
			Sorbitol	0·93	1·05
			Inositol	0·80	0·96

It is known that periodate solutions slowly decompose in the presence of light, giving iodate and ozone[8] Also, it has been reported[2] that carbohydrates migrate in 0·1*M* sodium hydroxide media In order to ensure that electrophoresis in periodate solutions was not due simply to the basic nature of the solution, or to the possible presence of iodate, runs were carried out with sodium hydroxide and 0·07*M* sodium iodate solutions, both adjusted to pH 11 However, migration under these conditions was found to be negligible

DISCUSSION

The considerable stability of periodate complexes of most of the compounds studied is suggested by the fact that after moderate spraying with ammoniacal silver nitrate the periodate–polyol white spots persist for about 30 sec and the complex does not immediately break down to give brown silver periodate. If the paper is oversprayed and left in the oven for longer periods before fixing, a diffuse region of slight blackening appears beyond the leading edge of each spot. This silver deposit was ascribed to oxidation products, which, being of lower molecular weight, would be expected to migrate faster Nevertheless, judging from the low intensity of such blackening, the extent of oxidation under the conditions chosen for electrophoresis appears to be rather slight In spite of this complication the components of a separated mixture can be quite easily located with the spray reagent on the basis of the transitory white spots

Electrophoretic behaviour in tellurate solutions qualitatively confirms previous reports[6] that complexing between polyols and the tellurate ion is weaker than that with the periodate ion, as indicated by the much lower concentrations of periodate necessary to obtain compact spots under conditions which are otherwise similar for the two electrolytes

These results appear to provide two additional electrophoretic methods for the analysis of polyols, which should be considered in cases where a satisfactory separation is not obtained by use of the more conventional complexing media

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Summary—Electrophoretic separations of sugars and other polyhydroxy compounds may be performed in 0·2*M* telluric acid media adjusted to pH 10 with sodium hydroxide, and in 0·07*M* sodium metaperiodate at pH 11. Oxidation by periodate appears to be only slight under these conditions. Migration rates of 21 compounds are reported relative to the movement of D-ribose In both electrolytes the compounds form anionic complexes.

Zusammenfassung—Zucker und andere Polyhydroxyverbindungen konnen in 0·2 M Tellursauremedien, die mit Natriumhydroxid auf pH 10 eingestellt sind, und in 0·07 M Natriummetaperjodat bei pH 11 elektrophoretisch getrennt werden Unter diesen Bedingungen fallt die Oxidation durch Perjodat offenbar nur geringfügig ins Gewicht. Die Wanderungsgeschwindigkeiten von 21 Verbindungen werden relativ zur Bewegung von D-Ribose angegeben In beiden Elektrolyten bilden die Verbindungen anionische Komplexe.

Résumé—On peut effectuer des séparations électrophorétiques de sucres et d'autres composés polyhydroxylés en milieux acide tellurique 0,2*M* ajustés à pH 10 par la soude, et en métaperiodate de sodium 0,07*M* à pH 11. L'oxydation par le periodate paraît n'être que légère dans ces conditions. On rapporte les vitesses de migration de 21 composés par rapport au mouvement du D-ribose Dans les deux électrolytes, les composés forment des complexes anioniques

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SULPHOLANE AS A SOLVENT FOR TITRATION OF BARBITURATES AND SULPHA DRUGS

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Sulpholane (tetramethylenesulphone, TMS) is a dipolar aprotic solvent with a moderately high dielectric constant (44).[1] It has been widely used as a titration medium[2–6] and has been recommended for use as a differentiating solvent for acid-base titrations.[5] Because of its high stability, perchloric acid-sulpholane solution has been suggested for use as a titrant.[3]

Recent studies in these laboratories investigated the titration of barbiturates and sulpha drugs in tetramethylurea.[7] The titration of barbituric acid in sulpholane was shown to be feasible with various electrode systems.[9] To continue our investigation of sulpholane as a medium for the analysis of weak acids, as well as to further expand our studies with barbiturates and sulpha drugs, this investigation was undertaken

EXPERIMENTAL

Apparatus

An Orion Model 601 digital pH/mV meter equipped with an Orion Model 605 electrode switch and Orion Model 615 Digital Volt-Ohmmeter Converter for scale expansion was the potential-measuring device Sargent 30050-15c glass indicator electrodes were used in conjunction with Sargent 30080-15c fibre-type calomel reference electrodes. The saturated aqueous potassium chloride solutions were replaced with saturated potassium chloride solutions in ethanol. All electrodes were soaked for several days in sulpholane and used for only one titration before resoaking, to improve the stability of the potential readings The titrations were performed with a 10-ml burette graduated in 0·02-ml increments, and a 200-ml Berzelius beaker fitted with a stopper containing the electrodes, burette tip, and a nitrogen purge-line.

Reagents

TMS was obtained from Phillips Petroleum Company and vacuum distilled from over sodium hydroxide pellets as described earlier[9] Tetrabutylammonium hydroxide (Eastman, 25% solution in methanol) was diluted tenfold with TMS and standardized against benzoic acid Barbituric acid was Eastman reagent grade Barbital was Merck U.S P All other barbiturates and sulpha drugs were Eli Lilly U.S.P All drugs were dried *in vacuo* before use Because of the limited quantities, further purification was not attempted

Procedure

Between 20 and 50 mg of the acid were weighed into the beaker and dissolved in approximately 50 ml of TMS. The electrodes were allowed to stabilize for about 15 min and titrant added Readings were taken after the potential had stabilized to ±0·1 mV (2–5 min). It is not really necessary to reach such a high level of stability, as ±1 mV was found to be adequate for recoveries as good as those listed below The titrations may then be performed in 10–15 min The drift observed was approximately 1 mV/hr

Summary—Electrophoretic separations of sugars and other polyhydroxy compounds may be performed in 0·2M telluric acid media adjusted to pH 10 with sodium hydroxide, and in 0·07M sodium metaperiodate at pH 11. Oxidation by periodate appears to be only slight under these conditions. Migration rates of 21 compounds are reported relative to the movement of D-ribose. In both electrolytes the compounds form anionic complexes.

Zusammenfassung—Zucker und andere Polyhydroxyverbindungen können in 0·2 M Tellursäuremedien, die mit Natriumhydroxid auf pH 10 eingestellt sind, und in 0·07 M Natriummetaperjodat bei pH 11 elektrophoretisch getrennt werden. Unter diesen Bedingungen fällt die Oxidation durch Perjodat offenbar nur geringfügig ins Gewicht. Die Wanderungsgeschwindigkeiten von 21 Verbindungen werden relativ zur Bewegung von D-Ribose angegeben. In beiden Elektrolyten bilden die Verbindungen anionische Komplexe.

Résumé—On peut effectuer des séparations électrophorétiques de sucres et d'autres composés polyhydroxylés en milieux acide tellurique 0,2M ajustés à pH 10 par la soude, et en métaperiodate de sodium 0,07M à pH 11. L'oxydation par le periodate paraît n'être que légère dans ces conditions. On rapporte les vitesses de migration de 21 composés par rapport au mouvement du D-ribose. Dans les deux électrolytes, les composés forment des complexes anioniques.

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RESULTS AND DISCUSSION

Table 1 lists the recoveries for the barbiturates and sulpha drugs studied

Recoveries and precision

The only one of these drugs previously titrated in sulpholane is barbituric acid[9] No significant difference was found between these results with the glass–calomel electrode system and those of the Pt–hydrogen or Ag/AgCl electrode systems. Overall, the recoveries are as good or better than those previously reported for tetramethylurea and dimethylformamide, while the precision is in the same range[7,8] The precision and recovery are also similar for other acids in TMS[9] Two other sulpha drugs, sulphamethazine and sulphathiazole, were tried but the recoveries were high It is suspected that appreciable acid impurities were present in these materials

Indicators

No visual end-point determinations were attempted. It has been shown that several of the most common indicators used in non-aqueous titrations do not change colour in the vicinity of the end-point in TMS medium[6]

Acid strength

Although no exact pK_a values can be determined without further study, it is possible to make approximations of acid strengths from the size of the break in the titration curve near the end-point (see Fig. 1) The order of relative acid strengths is barbituric acid > phenobarbital ~ sulpha drugs > amobarbital > barbital > secobarbital The respective changes in potential are 550, 470, 470, 360, 240 and 210 mV The sulpha drugs are all levelled to the same acid strength, as was reported for tetramethylurea.[7] The breaks are much larger however, and hence make the end-point more easily determined The break for barbituric acid is not as large as was reported previously; the difference is probably because of the differing electrode responses

As noted above, perchloric acid in sulpholane has been recommended as a stable titrant for non-aqueous titrations Tetrabutylammonium hydroxide in TMS as prepared above was found to retain its titre

Table 1 Recovery of barbiturates and sulpha drugs

Acid	Taken, *mmole*	Found, *mmole*	Recovery, %
Barbituric acid	0·2828	0·2813	99·6 ± 0·3
	0·1583	0·1585	
	0·2464	0·2448	
Phenobarbital	0·1581	0·1593	100·4 ± 1·4
	0·1312	0·1290	
	0·0920	0·0940	
Amobarbital	0·1395	0·1383	99·5 ± 0·3
	0·0860	0·0855	
	0·1695	0·1693	
Barbital	0·1766	0·1748	99·8 ± 0·6
	0·1776	0·1787	
	0·0990	0·0987	
Secobarbital	0·1005	0·1002	99·5 ± 0·3
	0·1467	0·1453	
	0·1456	0·1453	
Sulphapyridine	0·1438	0·1430	99·7 ± 0·4
	0·0805	0·0808	
	0·1008	0·1002	
Sulphadiazine	0·0987	0·1002	100·9 ± 0·5
	0·1108	0·1118	
	0·1864	0·1864	
Sulphamerazine	0·1040	0·1033	99·6 ± 0·6
	0·1501	0·1484	
	0·0744	0·0746	

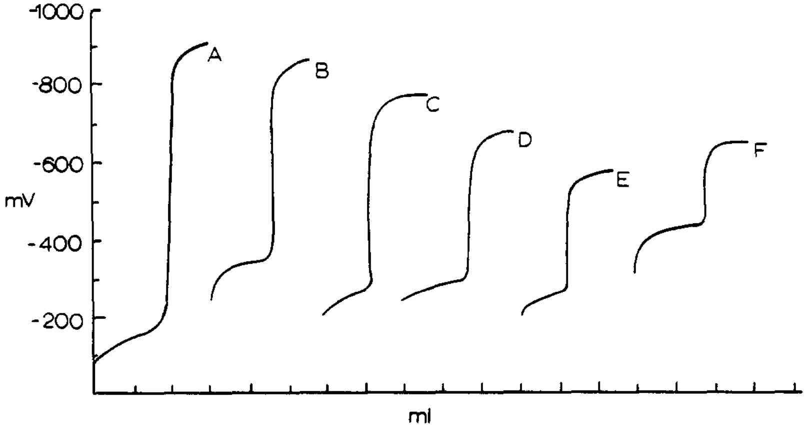

Fig. 1 Titration curves for *A*, barbituric acid; *B*, phenobarbital; *C*, sulphapyridine, *D*, amobarbital, *E*, barbital, *F*, secobarbital.

for at least two weeks. The combination of titrant stability, large potential changes at the end-point, ease of solvent purification, and good solubility characteristics indicate TMS is a solvent with high potential for important practical applications.

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Summary—Sulpholane (tetramethylenesulphone) has been used as the medium for non-aqueous potentiometric titration of barbiturates and sulpha drugs with tetrabutylammonium hydroxide Recoveries for 0 1–0 3 mmole of barbituric acid, phenobarbital, amobarbital, barbital, secobarbital, sulphapyridine, sulphadiazine and sulphamerazine were generally in the range 99–101%. A glass-calomel electrode system was used: common acid-base indicators give no colour change in the medium used.

Zusammenfassung—Sulfolan (Tetramethylensulfon) wurde als Medium fur die nichtwaßrige potentiometrische Titration von Barbituraten und Sulfa-Arzneimitteln mit Tetrabutylammoniumhydroxid verwendet. Die Ergebnisse lagen fur 0·1–0·3 mmol Barbitursaure, Phenobarbital, Amobarbital, Barbital, Secobarbital, Sulfapyridin, Sulfadiazin und Sulfamerazin im allgemeinen bei 99–101%. Ein System mit Glas- und Kalomelelektrode wurde verwendet· gebrauchlicke Saure-Basen-Indikatoren geben in dem verwendeten Medium keinen Farbumschlag

Résumé—On a utilisé le sulfolane (tétraméthylènesulfone) comme milieu pour le titrage potentiométrique en milieu non aqueux de barbiturates et de médicaments sulfamidés avec l'hydroxyde de tétrabutylammonium Les récupérations de 0,1–0,3 mmole d'acide barbiturique, phénobarbital, amobarbital, barbital, secobarbital, sulfapyridine, sulfadiazine et sulfamérazine ont été géneralement dans le domaine 99–101%. On a utilisé un système électrodes de verre et calomel · les indicateurs acide-base communs ne donnent pas de changement de coloration dans le milieu utilisé.

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DEVELOPMENT AND PUBLICATION OF NEW METHODS IN KINETIC ANALYSIS

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Summary—A review is made of the various factors, such as the mathematical basis, measurement instrumentation, reaction mechanism, synergistic effects, *etc*, affecting the accuracy and precision of kinetic-based analytical methods. Recommendations are made concerning the research involved in developing new methods and/or applications and concerning the manner of presentation of the results for publication.

Although the concept of using analytical methods based on kinetics or reaction rates goes back over fifty or sixty years to the early literature in biochemistry, radiochemistry and gas-phase diffusion,[1] and there has been extensive use of enzymatic and other catalytic reactions[2] in analysis, especially in clinical applications,[3] it was not until 1951 in the work of Lee and Kolthoff[4] that the broad inherent possibilities and advantages of kinetic-based analytical methods with respect to conventional equilibrium methods in many chemical situations were pointed out clearly to chemists. This work stimulated considerable fundamental development and special application research by Siggia,[5–7] Reilley,[8–10] Guilbault[3,11] and others,[1,9,12–17] particularly in the area of *in situ* analysis of complex systems. There have been several books,[1–3,18,19] monograph chapters[9,13–15,20] and reviews[11,16,21–23] published during the last ten years which summarize the research efforts in this field.

It is somewhat surprising in view of the potentialities of kinetic-based techniques and the considerable amount of fundamental method development published, that there has not, except for continued massive use in clinical assays, been any significant application of kinetic-based techniques to routine and/or practical analytical problems. However, there are two main reasons for this lack of application of kinetic techniques. First of all, almost all commercial instrumentation for chemical measurement is designed for steady-state or equilibrium measurement and does not perform satisfactorily when used for quantitative time-dependent measurement. Thus, analysts often found it necessary to modify or completely build the instrumentation for analytical rate-based determinations. Secondly, it is felt that many of the fundamental method-development papers reported during the past ten years did not fully explain applicability and limitations of the individual methods and, thus, it was not clear to other analytical chemists how they could modify or adapt these methods to their particular system or analysis problem.

A very striking example of this occurred at a recent symposium on "reaction-rate methods of analysis." After one talk on the principles of a particular method for the simultaneous *in situ* analysis of closely related mixtures, someone in the audience made the following comment: "I tried this method on mixtures of amines. The rate constants, ratio of rate constants and ratio of reactant concentrations were ideal according to the discussion in this talk. However, the analytical results were terrible. Why?"

The first problem, instrumentation, has essentially been overcome. Now that inexpensive analogue and digital integrated circuitry and minicomputer systems are readily available, considerable research on the basic concepts of stable accurate instruments for kinetic measurement has been reported[15,20,24–32] and automated quantitative instruments are beginning to become available (or easily built). However, the general guidelines for carrying out research to develop kinetic-based analytical procedures and for reporting the data and results have never been given in one place. Thus, this paper will attempt to present recommendations concerning important points that should be covered and investigated during a research project in this area.

MATHEMATICAL BASIS OF KINETIC METHODS OF ANALYSIS

The past few years have seen the development of a very large number of methods for the calculation of the initial concentration(s) of the species of interest from reaction rate data. These methods involved, in general, the simple mathematical manipulation and rearrangement of the usual differential or integral forms of the classical reaction-rate equations to put them in a convenient form for the calculation of initial concentration(s) of the unknown reactant(s). With few exceptions most of these mathematical treatments or methods have been reported within the past 5–10 years. Such methods can be classified into two main categories: methods for a single species and methods for the simultaneous *in situ* analysis of mixtures. Within each of these two categories, the methods can be subdivided according to the kinetic order of the reactions employed: pseudo zero-order or initial-rate methods, first-order and pseudo first-order methods, and second-order techniques. The principles, mathematical treatments, applicability and limitations of these methods have been discussed in the book by Mark, Rechnitz and Greinke[1] and the monograph chapters by Mark, Papa and Reilley,[9] Blaedel and Hicks,[13] Pardue,[15] and Crouch.[20]

Although these various methods are generally classified by most investigators as zero-order (initial reaction-rate), first-order, or second-order reaction-rate methods,[1,9,20,23] the actual mechanisms for the chemical reactions employed in virtually all of these methods (except those involving radiochemical decay reactions[1] and catalytic reactions[20]) are bimolecular reactions of the type:

$$A + R \underset{k_b}{\overset{k_f}{\rightleftarrows}} P \tag{1}$$

[where A is the species of analytical interest, R is the added reagent, and P is the product (or products)] and the general differential rate expressions have the form:

$$-\frac{d[A]_t}{dt} = -\frac{d[R]_t}{dt} = \frac{d[P]_t}{dt} = k_f[A]_t[R]_t - k_b[P]_t \tag{2}$$

(where $[A]_t$, $[R]_t$, and $[P]_t$ represent the concentrations of these species at any time t). Thus, the nomenclature zero-, first- and second-order actually refers to the experimental conditions under which the rate measurements are made and/or the relative concentrations of the reactants A and R.

If the rate data are taken only during the initial 1–2% completion of the total reaction, then the concentrations of A and R during this initial reaction period are virtually unchanged and equal to the initial concentrations $[A]_0$ and $[R]_0$ respectively and the reverse reaction can be ignored, as only a negligible amount of product is formed. Thus the differential rate expression (2) simplifies, under these initial rate conditions, to a pseudo zero-order form:

$$\left(\frac{\mathrm{d}[\mathrm{P}]_t}{\mathrm{d}t}\right) \sim k_{\mathrm{f}}[\mathrm{A}]_0[\mathrm{R}]_0 \sim \text{Constant} \tag{3}$$

[Note that only the rate of initial change of concentration of product(s) is followed experimentally, as the change in concentration of A or R is small and, therefore d[A]/dt or d[R]/dt cannot be measured accurately.] If the reaction (1) is run under such conditions that the initial concentration of one of the reactants (either A or R) is very large compared to the other, then either $[\mathrm{A}]_t$ or $[\mathrm{R}]_t$ will remain virtually unchanged as the reaction proceeds to equilibrium and can be considered equal to its initial concentration. Also, the reverse reaction can usually be neglected as the large excess of one of the reactants drives the reaction to virtual completion. Under these conditions the reaction is a pseudo first-order reaction and the differential rate expression takes the form

$$-\frac{\mathrm{d}[\mathrm{A}]_t}{\mathrm{d}t}\left(\text{or } -\frac{\mathrm{d}[\mathrm{R}]_t}{\mathrm{d}t}\right) \sim k_{\mathrm{f}}[\mathrm{R}]_0[\mathrm{A}]_t \text{ (or } k_{\mathrm{f}}[\mathrm{A}]_0[\mathrm{R}]_t) \tag{4}$$

$$\sim k'_{\mathrm{f}}[\mathrm{A}]_t \text{ (or } k'_{\mathrm{f}}\ [\mathrm{R}]_t) \tag{5}$$

where $k'_{\mathrm{f}} = k_{\mathrm{f}}[\mathrm{R}]_0$ (or $k_{\mathrm{f}}[\mathrm{A}]_0$). If the rate of reaction (1) is measured during a significant degree of completion under conditions where $[\mathrm{A}]_0$ is of the same order of magnitude as $[\mathrm{R}]_0$, then the method is called a second-order method and the exact differential rate expression (2) must be employed in the data analysis. Note also that only when the reaction mechanism is virtually irreversible can the reverse reaction be ignored in equation (2). Also, for the special case $[\mathrm{R}]_0 = [\mathrm{A}]_0$, a modified form of the calculation of initial concentrations must be employed.[33]

It is obvious from the discussion above that any complete research and/or report on a kinetic-based analytical procedure must carefully take into account the degree of approximation made in the use of equation (2) with respect to the time period of data measurement and relative initial concentrations of reactants and, in some cases, the reversibility of the reaction(s). For example, care must be taken when using a pseudo first-order method when the initial concentrations of the unknown varies over several orders of magnitude. The error introduced in assuming the validity of the pseudo first-order approximation of equation (2) is a function of $[\mathrm{A}]_0$. Although the reaction mechanism for enzyme and other catalysed reactions and, hence, the rate equations, seem somewhat more complex,[1,2,20] similar assumptions, simplifications and therefore, restrictions in validity are made on the rate-measurement techniques employed in the analytical use of these systems.[20,34]

Within each of the zero-order, first-order and second-order classifications of reaction-rate methods there are a large variety of different methods of display and/or mathematical manipulation of the reaction-rate data or equations in order to calculate the initial concentration(s) of the species being determined. The selection of the technique of calculation can have very significant effects on the accuracy of the analysis.[1,9,20,34,35] For example, Crouch[20,34] has pointed out that the kinetic role of the determinand species in methods employing first-order and enzyme or other catalysed reactions has a strong effect on the choice of measurement of the reaction-rate data. It was shown that a fixed-time approach[1,13,15] is superior for pseudo first-order reaction conditions and for the determination of the substrate in any type of pseudo zero-order catalysed reactions. However, in the cases where the enzyme or other catalyst is to be determined (under pseudo zero-order conditions), the variable-time procedure[1,13,15] yields better results. The choice of rate data reduction method in the simultaneous *in situ* analysis of mixtures is even more critical with respect to accuracy of the analyses. There have been numerous results in the literature[1,4,8,9,12,35,36] which have shown that both the relative and absolute values of the rate constants and the initial concentrations of the species to be determined dictate the choice of data treatment for the calculation of the initial concentrations. Furthermore, within the mathematical framework of each of these calculation procedures, there are generally optimum and/or limited times at which rate data should be taken in order to minimize the effects of random and absolute error in measurement.[1,9,12,35] The choice of procedure and optimization of the measurement is very complex and no simple rules can be given here. However, very detailed discussions of this problem are available.[1,9,12,35] Thus, any research on the development of new analytical methods should include a very comprehensive analysis of the choice of data measurement and reduction procedures.

THE REACTION MECHANISM

In most equilibrium-based analytical methods, the success or failure of a determination is not affected by the reaction mechanism provided that the reaction is either quantitative or the measured parameter at equilibrium is linearly proportional to initial concentration of the species of interest. This is not the case in reaction-rate methods. Any report of a new kinetic method should include, if possible, a *complete* study of the mechanism of the reaction(s) involved in the procedure (some reactions, such as catalytic reactions, are so complicated that complete elucidation of the mechanism would be impossible). It should also include a detailed study of the effects of typical sample matrix components, which can act as catalysts, induce side-reactions, alter the activity of the reactants, *etc.* The rates and rate constants for chemical reactions are very sensitive to low concentrations of " spectator " species, *etc*, and hence, samples containing the same true initial composition of the species of interest but coming from different sources can very often give quite different apparent concentrations. Unless the experimenter is completely aware of the total reaction mechanism and all possible factors that can affect either the activation energy and the reaction path, erroneous analytical results could be obtained under certain circumstances which may not be detected. A detailed investigation of the simultaneous *in situ* analysis of binary amine mixtures illustrates this point.[37]. (It should be mentioned here that most systems will be less error-prone than the example given.) It was found that rate constants for the reaction of many individual organic amines with methyl iodide in acetone solvent had ideal differentiation and range of absolute values when the reactions were conducted under pseudo first-order conditions with respect to the methyl iodide. The data reduction method of Roberts and Regan[38] and the simple and accurate data acquisition system employing a continuously recording conductivity instrument[39,40] seemed to indicate that almost ideal analytical results would be attained. However, it was found, just as had been reported by the analyst who commented at the symposium mentioned in the introduction to this paper, that most binary mixtures gave very poor results when analysed by this procedure.

A careful examination of the reaction mechanism of the system revealed that there were numerous unexpected sources of error. First, it was found that the acetone used as a solvent underwent a Schiff-base type reaction with some primary amines at a rate comparable to the methylation reaction of the method. This resulted in the variation of the composite rate constant, K^*,[37,38] during the course of the reaction of mixtures containing such primary amines, as shown in curve 1 of Fig. 1. As the calculation of initial concentration from K^* by the method of Roberts and Regan[38] requires K^* to remain constant over the total reaction time, serious errors are introduced by this side-reaction. As added water would suppress the Schiff-base reaction, acetone–water mixtures were then used as the solvent systems. While this improved the results obtained for several amine mixtures, those containing high molecular weight amines still gave poor results. For example, K^* is not constant over the whole reaction for n-butylamine–tributylamine mixtures, as shown in curve 2 of Fig. 1. In this case the addition of water results in the formation of small suspended micelles of amine in the solution, which alters the reaction rates. Thus, it was necessary to go to a less basic solvent system, DMSO–n-propyl alcohol, which had no significant tendency to react with primary amines[41] and in which most amines are soluble.[37] Curve 3 of Fig. 1 shows that K^* for the n-butylamine–tributylamine mixture is then constant and, thus, accurate initial concentrations are obtained.[37]

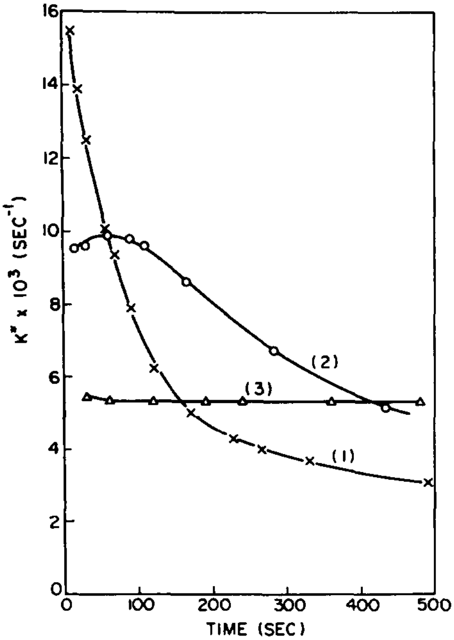

Fig. 1. Variation of K^* for n-butylamine–tributylamine mixture (71.2% n-butylamine) as a function of time, for three different solvent systems.[37]
Curve 1—100% acetone
Curve 2—89% acetone–11%water
Curve 3—70% DMSO–30% n-propyl alcohol
(Reprinted by permission of the American Chemical Society)

However, certain amine mixtures, generally those containing methylamime, still gave poor analyses. It was found that such mixtures were slightly hygroscopic and samples often contained traces of water. This trace water acted as a catalyst in the methylation reaction. Thus, the rate constants obtained from the reactions of standard dry amine solutions and used in the calculation of initial concentrations of unknown mixtures containing traces of water were not valid for the unknown mixture reactions. The addition of water to the solvent system (10% or more) was found to swamp out these variations of rate constants in unknown amine mixtures. Recall, however, that the addition of water can result in solubility complications for some amines. This investigation also revealed that a synergistic effect, probably caused by changes in the activity of the amines by the build-up of product, resulted in variation of K^* during the reaction when the amine mixture concentration was high. Other sources of error arose from the reaction of the reagent methyl iodide with the DMSO solvent system on storage, and loss of measurement sensitivity when conducting impurities were present in the unknown.[37]

The point here is that no simple general reaction procedure for this method can be given that is universally applicable to all types of amine mixtures. This is probably true in general for any procedure for a kinetic-based method. Thus, in reporting a new method, it is necessary to have investigated the chemistry of the reactions employed so that other analysts trying to use the method for their samples can anticipate possible sources of errors resulting from the chemical nature and/or composition of their samples.

INSTRUMENTATION FACTORS

Of course, the accuracy and precision of the instrumental and/or experimental measurement is equally important to both kinetic-based and equilibrium analytical methods and should be discussed in any publication concerning these methods. However, there are a few special instrumental and/or experimental factors that are of critical importance in the kinetic-based methods and quantitative information concerning them should be included in any report about a new method. Those factors particularly important to reaction rate methods are listed below.

Instrumental stability

Although high-frequency noise in an instrument used in measuring reaction rates can be a problem, it can generally be eliminated by simple electronic filtering, as the frequency of the noise is generally very high compared to the rate of change of the signal, which is proportional to the rate of reactions employed in analytical procedures.[23,32,42] Weichselbaum *et al.*,[32,42] Pardue *et al.*,[15,24,25] and Crouch[20] have discussed in detail the circuitry, design criteria and magnitude of the effects of low-frequency drift on analytical results, in spectrophotometric rate-measurement. The principles discussed are applicable to any type of instrumental measurement.

Linearity of transducer response

Most transducers which convert chemical concentration into an electrical signal have a non-linear response. For example, potential and optical transmission are not proportional to concentration. In general, this non-linearity is easily and simply corrected in equilibrium analytical measurements. However, Weichselbaum *et al.*,[32,40] and Crouch[20] have shown that it is considerably more difficult to linearize instrumentally the response–concentration function in reaction rate methods and often this transformation can introduce significant errors into the analytical results.[32,42] For example, Weichselbaum *et al.* have shown that simple non-linear feedback elements employed in log-response operational amplifier circuits are not sufficiently accurate in the transformation of transmittance into absorbance, to be used for many analytical purposes. They found it necessary to go to a very elaborate servomechanical system to circumvent this problem. Crouch[20,34] in an extensive analysis of the various data measurement and reduction procedures in kinetic methods has shown that the variable-time approach can be used advantageously in the case of non-linear response, as the measured reaction rate in this procedure is linearly proportional to *initial* concentration of the species of interest in spite of the fact that the actual transducer response is not proportional to concentration. This is because the time required to reach a fixed concentration level is the parameter measured and, thus, linearity of the overall response–concentration curve is not necessary. Thus, it is not necessary to resort to instrumental linearization of signal response when the variable-time method is used. The point here is that in some cases the instrument and not the chemical reaction can dictate the method used.

Rise-time of the instrument

As mentioned above, high-frequency noise can often be eliminated by simple electronic filtering. However, caution is necessary and the investigator should be very familiar with the actual effective rise-time of the instrument used, over all operating ranges. Obviously, a fixed filter time constant cannot be applicable over a large range of initial concentrations as the rate of the reaction at any time is a function of initial concentration.[32] Thus, a report of a new rate method should include a quantitative evaluation of the rise-time of the instrument under all conditions of damping employed and a comparison with the maximum reaction rates measured under each setting of the filter time constant.

Data acquisition mode

Most reaction rate methods reported[1,2,15,20] utilize only a small number of actual data points (from one to about four) in the calculation of the initial concentration(s) of the species of interest. Clearly this approach throws away a considerably amount of data that could be used advantageously. For example, Margerum and co-workers have discussed the parameters affecting the accuracy of the simultaneous analysis of mixtures by pseudo first-order reaction methods.[30,31,43,44] Their results point out that a continuous data-utilization approach to the problem is the superior data-analysis method in several examples of the use of reaction rate methods for analyses. In the early development of reaction rate methods for analysis of closely related mixtures, the procedures used chemical reactions which were not suitable for continuous automatic measurement of the entire rate-response curves.[1,9] Also, all calculations at that time in the development of the reaction rate methods attempted to limit the number of data points taken and to predetermine the optimum times, *etc*, for taking this minimal amount of data.[1,9] However, in recent years the advances in the field of electronic circuitry and computer technology has had a tremendous influence on the design of instrumentation for kinetic analysis. These instrumental advances have also had a strong influence on the principles of and approaches to differential rate methods. Margerum and co-workers (and also Weichselbaum and co-workers[32,42]) have shown conclusively that the use of built-in computation systems allows continuous analysis of the entire reaction-rate data curve throughout the course of the reaction. The data are thus processed with both ensemble-averaging and smoothing routines in real time. Experimental results and detailed error analysis study have shown that this approach to data acquisition, reduction, and display leads to a much greater accuracy and precision of the analytical results.[30,31,43,44] In fact, good results can be obtained for fast reaction differential rate analyses where the usual finite or minimal data-point methods fail completely.[43,44] Thus, any new report of a reaction rate method should include a comparison of results calculated from both a finite and a continuous number of data points. This will warn others that certain methods will fail under limited data point computation.

Temperature control

The rate of a chemical reaction is considerably more sensitive to temperature variation than the position of the equilibrium (provided the formation constant is very large and the reaction can be considered to be "quantitative"). Thus, temperature control is critical in reaction rate analytical methods and quantitative data concerning this control must be given in any publication describing a new method. Also, the effect of temperature fluctuation on the accuracy and precision of the analytical results should be discussed.

Two factors in temperature control must be considered. The accuracy of the temperature control in the thermostated jacket of the reaction cell is the initial consideration, of course.[45,46] However, as chemical reactions are either exothermic or endothermic, Pardue and Rodriguez,[24] Weichselbaum *et al.*,[47] and Feil *et al.*[48] have shown that rapid temperature exchange and equilibration of the reaction solution with the thermostated cell jacket is also an extremely important consideration in obtaining analytical-quality rate data.

Automation of operations

It is very obvious that automated control of solution mixing, measurement sequences, *etc*, will minimize time-measurement errors compared to those arising from manual control and solution handling and, hence, will increase the accuracy of a given reaction rate procedure.[23,25,29,32] Thus, a report of a new rate method should cover the variation of the analytical results under varying increase in automatic control, going from hand operation to complete computer control of operation and optimization.[29] Thus, again there will be warning about the experimental limits and operational controls under which the method is applicable. It would also be valuable to include a quantitative discussion of the relative merits and limitations of *continuous flow*[13,15] and *discontinuous-sampling* automated systems.[20,50-54]

CONCLUSIONS

Useful general guidance on the information that should be included in a published paper on an analytical method can be found in articles by Wilson,[55,56] Chalmers,[57,58] and others.[59,60,61] The specific requirements unique for the development and description of kinetic based analytical methods are discussed in detail above and are summarized here for convenience and emphasis. The points listed are those that *must* be examined and reported in publication of a new method.

1. *Mathematical basis of the method.* The complete reaction order, relative concentrations of reactants, identification of species followed during reaction, mathematical basis of data reduction and assumptions or simplifications should all be discussed. The selection of optimum conditions, such as the times of data collection, must be justified. Evidence must be given for the choice of data-reduction procedure.
2. *The reaction mechanism.* A complete description of the mechanism and reaction-order of all reactions involved in the kinetic method must be given wherever possible, as it is important to demonstrate the effect of any potential impurities on the reaction mechanism or path. The stability of reagent–solvent systems as well as synergistic effects related to concentration are also important.
3. *Trace impurities as catalysts or inhibitors.* It is necessary to examine the effects of trace

amounts of all conceivable impurities that might be expected to be present in the types of samples that the method is designed for.

4. *Instrumental factors.* Any publication must include data concerning the long-term stability of the instrumentation employed, the linearity of the transducer response over the concentration ranges to be expected and its effect on the data-reduction procedure, the rise-time of the instrument with respect to desired data-taking rates, the number of data points taken and utilized in the data-reduction procedure, the temperature control of the reaction solution under dynamic conditions, and the effect of automation on accuracy of analyses.

The following points must also be covered in the publication of any new kinetic method. These points were not specifically discussed above in this paper as they are essential to the report on any type of new analytical method.

5. *Accuracy and precision.* As the accuracy and precision of kinetic-based methods is, in general, less than that of equilibrium techniques, it is essential that a statistical analysis of repetitive analyses be given. It would also be necessary to give statistical evidence in support of the choices of optimum measurement parameters. Simple theoretical considerations alone are generally not sufficient as they often neglect unsuspected effects.[1,9,10]
6. *Applications.* Procedures suitable for various sample matrices should at least be discussed. Also, matrices that are at least potentially unsuited for the method should be pointed out.
7. *General.* The value of the method must be realistically compared, in terms of speed, accuracy, selectivity, simplicity, cost, *etc*, with other methods for the same species.

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Zusammenfassung—Es wird eine Übersicht über die verschiedenen Faktoren gegeben, die Genauigkeit und Richtigkeit von analytischen Methoden auf kinetischer Basis beeinflussen, wie mathematische Grundlage, Meßinstrumente, Reaktionsmechanismus, synergistische Effekte usw. Für Arbeiten, die neue Methoden und/oder Anwendungen entwickeln wollen, sowie für die Art der Publikation ihrer Ergebnisse werden Empfehlungen ausgesprochen.

Résumé—On effectue une revue des divers facteurs, tels que la base mathématique, l'instrumentation de mesure, le mécanisme de réaction, les effets synergiques, etc. . . , qui affectent la précision et la fidélité de méthodes analytiques basées sur la cinétique. On fait des recommandations concernant la recherche impliquée dans le développement de nouvelles méthodes et / ou applications et concernant la manière de présenter les résultats pour publication.

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CHROMATOGRAPHIC BEHAVIOUR OF 47 METAL IONS ON TITANIUM(IV) ARSENATE PAPERS

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Summary—Titanium arsenate papers with As/Ti ratios 0·2–2·2 have been prepared and 47 metal ions chromatographed on these papers in 10^{-5}–$4M$ nitric acid. The effect of pH and of the Ti/As ratio on the R_f values has been studied. A new quantity R_t ($R_t = R_f$ on untreated papers minus R_f on treated papers) has been defined. The effect of the concentration of the loading reagents on the Ti/As ratio of the ion-exchanger precipitated on the papers has been determined. Contrary to Alberti, it is shown that Lederer's equation is obeyed by titanium arsenate papers in the sodium form if the activity of Na^+ ions is considered instead of their concentration. It has also been demonstrated that the selectivity sequence for cations on titanium arsenate papers is not the same as that on titanium arsenate columns.

Chromatography on papers impregnated with inorganic ion-exchangers of zirconium phosphate type has recently been reviewed.[1] Some interesting possibilities for the separation of alkaloids and amino-acids on zirconium phosphate papers have also been reported.[2] In the earlier reports[3,4,5,6] from this laboratory it was observed that these papers are highly selective and they give rapid separations with simple aqueous systems. The selectivity of the papers is greatly enhanced if mixed solvent systems are used in place of the aqueous systems.[7] Quantitative separations were also achieved by Qureshi and co-workers.[8] Alberti found that the R_M/pH ratio increases with valency of the ion on zirconium phosphate papers, but that Lederer's equation, *i.e.*, $n\text{pH} = R_M + \text{constant}$, does not hold, as zirconium phosphate is a weak ion-exchanger. Alberti,[9] however, showed that if zirconium phosphate papers in the Na^+ form are eluted with solvents containing increasing concentrations of Na^+ (or K^+) ions then the equation $-n\log[Na^+] = R_M + \text{constant}$ is obeyed. These results were confirmed by Prášilová and Šebesta for ammonium tungstophosphate paper[10] but they have not been extended to other ion-exchange papers.

These studies on ion-exchange papers have the following limitations.

(1) The ion-exchangers deposited on the papers have not been analysed and therefore the inference of Nunes da Costa[11] that $ZrPO_4$ papers and $ZrPO_4$ columns show analogous behaviour is not very convincing and needs further examination.

(2) No study has been made on ion-exchange papers in which the precipitated material has varying cation to anion ratio.

(3) No systematic studies in nitric acid systems have been reported. Sastri used $3{\cdot}0M$ nitric acid to separate U(IV) from U(VI), $1{\cdot}0M$ nitric acid to separate As(III) from As(V), and $0{\cdot}1M$ nitric acid to separate Hg(I) from Hg(II). Zhang Zhu separated Y(III) from Sr(II), using $0{\cdot}1$–$2{\cdot}0M$ nitric acid media.

The present work was therefore undertaken to overcome these limitations. Papers with different As/Ti ratios have been prepared and 47 cations have been chromatographed on them, with 0·1*M* nitric acid as the developer; 10^{-5}–4*M* nitric acid media have also been used for systematic studies of these ions on papers impregnated with titanium arsenate exchanger having Ti:As ratio 1 : 1·7. The results are summarized in the following report.

EXPERIMENTAL

Apparatus

Chromatography was performed on 15 × 3·5 cm Whatman No. 1 paper strips in 20 × 5 cm glass jars.

Reagents

Chemicals and solvents were analytical reagent grade.

Preparation of ion-exchange papers

Aqueous solutions (0·5*M*) of titanium(IV) chloride and sodium arsenate were prepared. Paper strips of the required size were first impregnated in the titanium(IV) chloride solution for 3–5 sec and excess of reagent was removed by placing the strips on sheet filter paper. The strips were allowed to dry for 15 min at room temperature. They were then dipped in the sodium arsenate solution for 15 sec. The excess of solution was drained off and the strips were placed over a filter sheet. The strips were converted into the Na^+ form by dipping in 0·5*M* sodium nitrate and then washed thrice with demineralized water in order to remove the excess of reagents. Finally the strips were dried at room temperature and used for chromatography.

Test solutions

Solutions (0·1*M*) of chlorides, nitrates or sulphates of most of the cations were prepared in 0·1*M* solutions of the corresponding acids. The 0·1*M* antimony and bismuth chloride solutions were prepared in 30% v/v and 3·7*M* hydrochloric acid respectively. The 2% solution of gold chloride was prepared in 4*M* hydrochloric acid. Niobium pentachloride solution (1%) was prepared in 10% tartaric acid solution. Selenium dioxide was dissolved in water and made alkaline with 1*M* potassium hydroxide. Sodium molybdate, sodium tungstate, potassium chloride, caesium chloride and rubidium chloride solutions, all 0·1*M*, were prepared in water. Ceric sulphate (0·1*M*) was prepared in 3·6*N* sulphuric acid, stannous chloride was dissolved in 4*M* hydrochloric acid and a piece of tin was added to the 0·1*M* tin solution to prevent oxidation.

Detection

Pb^{2+}, Ag^+, Hg^{2+}, Tl^+, Bi^{3+}, Cd^{2+}, Sb^{3+}, Cu^{2+} and Sn^{2+} zones were detected with yellow ammonium sulphide solution. Fe^{3+}, V^{4+}, UO_2^{2+} were detected with aqueous potassium ferrocyanide solution. To detect Mg^{2+} the paper was dipped first in alcoholic quinalizarin solution and then washed with 2*M* sodium hydroxide. Aqueous potassium ferricyanide solution was used to detect Fe^{2+}. A 1% alcoholic diphenylcarbazide solution was used to detect Ir^{3+}, Cr^{3+}, Mn^{2+} and Zn^{2+} spots and 0·1% alcoholic Alizarin Red S solution for Y^{3+}, Zr^{4+}, Th^{4+}, Ce^{3+}, La^{3+}, In^{3+}, Nb^{5+}, Ca^{2+} and Hf^{4+} spots. A fresh solution of sodium cobaltinitrite was used to detect K^+, Rb^+ and Cs^+. For detecting Al^{3+}, Be^{2+} and Ga^{3+} the strips were dipped in aqueous Aluminon solution and then they were washed with aqueous ammonium acetate solution. A fresh aqueous sodium rhodizonate solution in neutral medium was used to detect Ba^{2+} and Sr^{2+}, 0·1*M* stannous chloride in 4*M* hydrochloric acid to detect Se^{4+}, Mo^{6+}, W^{6+}, Pt^{4+} and Au^{3+}, 2% thiourea in 2*M* hydrochloric acid to detect Ru^{3+} and 1% alcoholic dimethylglyoxime solution to detect Ni^{2+} and Co^{2+}.

Procedure

One or two spots of the test solutions were spotted on the paper with thin glass capillaries. The paper was then conditioned for 15 min. The solvent ascent was always 11 cm. The front (R_L) and rear (R_T) R_f values were measured.

The paper strips were dissolved in a mixture of perchloric, nitric and sulphuric acid (3 : 1 : 4) and the solution was evaporated to dryness. The residue was dissolved in hydrochloric acid. The solution was then diluted to 50 ml and arsenic determined as arsenic sulphide.[12] Titanium was determined in the filtrate by reducing it to Ti(III) with aluminium foil and titrating with ferric ammonium sulphate, with ammonium thiocyanate as indicator.[13]

RESULTS

The results are summarized in Table 1.

Table 1. Composition of titanium(IV) arsenate papers prepared by varying the concentration of reagents.

No.	Concentration of reagents $TiCl_4$, *M*	 Na_2HAsO_4, *M*	Temperature	Ti:As
1	0·01	0·01	Room	1 : 0·21
2	0·05	0·05	Room	1 : 0·32
3	0·1	0·1	Room	1 : 0·42
4	0·1	0·25	Room	1 : 1·7
5	0·5	0·5	Room	1 : 2·2
6	0·5	0·5	70 ± 1°C	1 : 1·8

The Ti:As ratios of titanium arsenate deposited on papers are compared with those of titanium arsenate[14] precipitated by mixing the equimolar reagents in the ratio of 1 : 1 (Fig. 1).

In all, 47 cations were chromatographed on paper impregnated with titanium(IV) arsenate (on papers Nos. 4 and 5) with various concentrations of nitric acid and sodium nitrate as solvent.

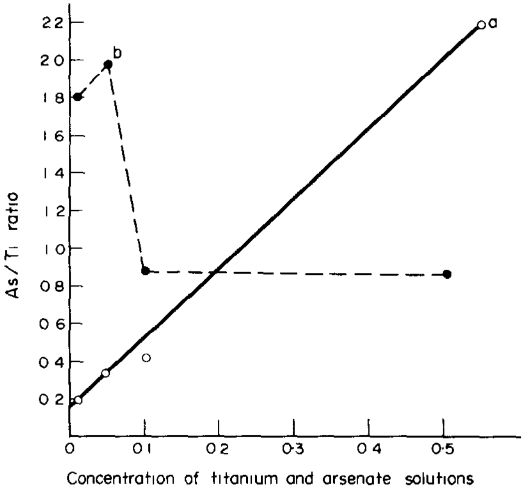


Fig. 1. Composition of titanium arsenate prepared with various reagent concentrations. (*a*) Composition on papers; (*b*) composition of precipitates.

Chromatography on paper No. 4

The following solvent systems were used to study the effect of pH on the R_M values and to find important separations.

(1) 1·0*M* HNO_3
(2) 2·0*M* HNO_3
(3) 3·0*M* HNO_3
(4) 4·0*M* HNO_3
(5) 0·1*M* HNO_3
(6) 0·01*M* HNO_3
(7) 10^{-3}*M* HNO_3
(8) 10^{-5}*M* HNO_3
(9) 1·0*M* NH_4NO_3 + 0·1*M* HNO_3 (1 : 1)
(10) Demineralized water

The greatest number of important separations was obtained with 0·1*M* nitric acid as eluent. R_f values of metal ions in this system are plotted in Fig. 2. The more important separations achieved on paper No. 4 are given in Table 2; all separations took 30 min.

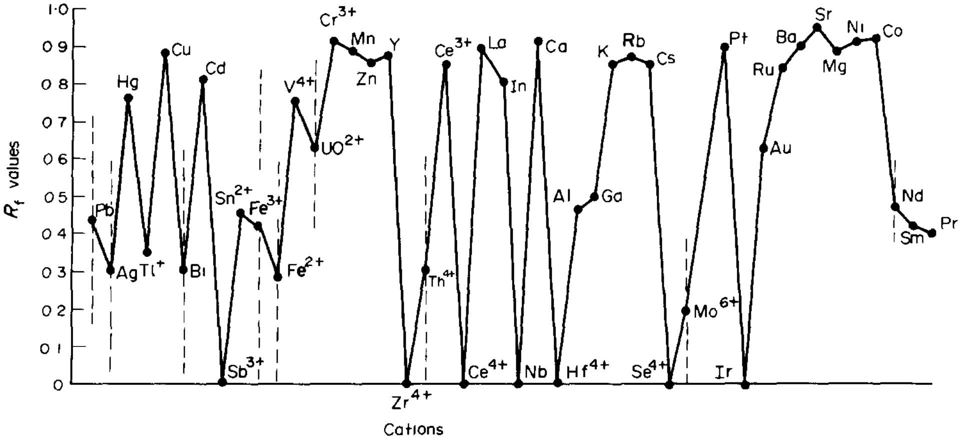


Fig. 2. Plot of R_f values for 47 cations, with 0·1*M* nitric acid as solvent.

Table 2. Separations achieved on titanium(IV) arsenate paper No. 4.

No.	Separation of (R_f)	Separation from (R_f)	Solvent
1	Fe^{3+}(0·0–0·28)	Cr^{3+}(0·65)	0·001*M* HNO$_3$
2	Bi^{3+}(0·0)	Cu^{2+}(0·86) Hg^{2+}(0·46–0·75)	0·01*M* HNO$_3$
	Th^{4+}(0·1)	Y^{3+}(0·55)	0·01*M* HNO$_3$
3	Pt^{4+}(0·85)	Ir^{3+}(0·00), Au^{3+}(0·55)	0·1*M* HNO$_3$
	Sb^{3+}(0·0)	Cu^{2+}(0·85), Cd^{2+}(0·64)	0·1*M* HNO$_3$
	Cd^{2+}(0·62)	Tl^{+}(0·0–0·3)	0·1*M* HNO$_3$
	Bi^{3+}(0·08)	Cd^{2+}(0·65)	0·01*M* HNO$_3$
	Ag^{+}(0·0)	Cu^{2+}(0·69) Au^{3+}(0·85)	0·01*M* HNO$_3$
	Th^{4+}(0·0–0·2)	La^{3+}(0·51)	0·01*M* HNO$_3$
	Ca^{2+}(0·89)	Al^{3+}(0·4)	0·1*M* HNO$_3$
4	Nb^{5+}(0·0–0·28)	Zr^{4+}(0·85), UO$_2^{2+}$(0·70)	1·0*M* HNO$_3$
5	Sb^{3+}(0·06)	Cu^{2+}(0·90), Cd^{2+}(0·92)	2·0*M* HNO$_3$
6	Au^{3+}(0·55)	Sb^{3+}(0·08)	3.0*M* HNO$_3$
	Sb^{3+}(0·06)	Sn^{2+}(0·75)	3·0*M* HNO$_3$
7	Sb^{3+}(0·15)	Numerous	4·0*M* HNO$_3$
8	Ag^{+}(0·0)	Pt^{4+}(0·84)	1·0*M* NH$_4$NO$_3$$^+$ 0·1*M* HNO$_3$
9	Pt^{4+}(0·76)	Ir^{3+}(0·10)	Water
	Pt^{4+}(0·81)	Pb^{2+}(0·07), Bi^{3+}(0·05) Ni^{2+}(0·07), Co^{2+}(0·0) Ag^{+}(0·0)	Water

Chromatography on paper No. 5 in the Na^+ form

Eight different concentrations (1, 2, 3, 4, 1·5, 0·5, 0·1 and 0·01*M*) of sodium nitrate were used to study the R_M values as a function of concentration of sodium ion, For most cations the R_f values were zero. In some cases movement was observed (Table 3). A plot of $-\log a_{Na^+}$ *vs.* R_M is given in Fig. 3.

Table 3. R_f and R_M values of some cations as function of a_{Na}

		R_f				R_M			
No.	$-\log a_{Na^+}$	K^+	Rb^+	Cs^+	Ni^{2+}	K^+	Rb^+	Cs^+	Ni^{2+}
1.	+0·4868	0·06	0·06	0·06	0·10	1·19	1·19	1·19	0·95
2.	+0·2168	0·16	0·12	0·12	0·17	0·72	0·86	0·86	0·69
3.	+0·0516	0·20	0·18	0·16	0·44	0·60	0·66	0·72	0·10
4.	−0·0630	0·22	0·15	0·21	0·48	0·55	0·75	0·57	0·03
5.	−0·2340	0·41	0·33	0·34	0·63	0·08	0·16	0·28	−0·2
6.	−0·5003	0·48	0·52	0·53	—	0·03	−0·04	−0·02	—

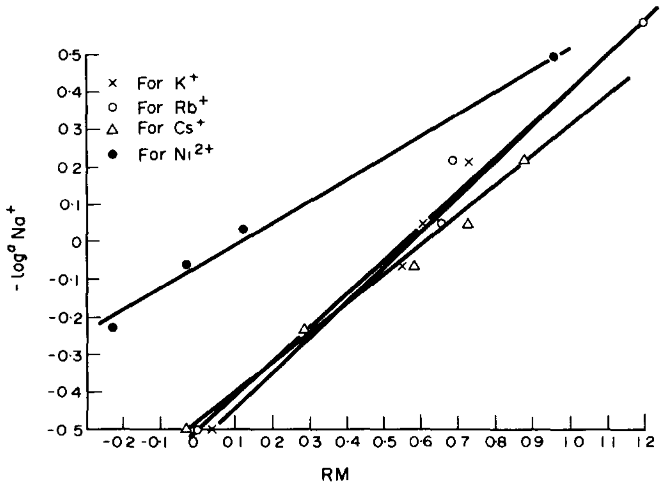


Fig. 3. Plot of R_M *vs.* $\log a_{Na^+}$.

Table 4. Separations achieved on titanium(IV) arsenate paper No. 5 in the Na^+ form (50 min chromatography).

	Separation		
No.	of (R_f)	from (R_f)	Solvent
1.	Pt^{4+}(0·65–0·80)	Pd^{2+}(0·0–0·22)	0·1*M* $NaNO_3$
2.	Pt^{4+}(0·65–0·80)	Numerous	0·1*M* $NaNO_3$
3.	Hg^{2+}(0·6–0·75)	Numerous	0·1*M* $NaNO_3$

DISCUSSION

The results given in Tables 2 and 4 show the high specificity of titanium arsenate papers even in simple aqueous systems. Thus Sb^{3+} can be separated from 43 metal ions with 4·0*M* nitric acid. Binary mixtures of Sb^{3+} with Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+},

Co^{2+}, Au^{3+}, Mn^{2+} and Zn^{2+} were successfully separated, the ΔR_f in each case being more than 0·4. The only interferences were from Tl^+, Se^{4+} and Mo^{6+}. The titanium arsenate papers in the sodium form are almost specific for Pt^{4+} and Hg^{2+}. All other cations have R_f values below 0·2. Therefore Pt^{4+} or Hg^{2+} can be separated from 45 metal ions, because Pt^{4+} is present as an anion and Hg^{2+} as an uncharged species. When the papers are developed with 0·1*M* sodium nitrate almost all the cations have zero or very low R_f values, because the exchanger is in the ionized form and therefore cations with a charge greater than unity are adsorbed in preference to Na^+ ions. It will be interesting to see whether other papers in the Li^+, Rb^+ and Cs^+ forms show the same results when developed with the corresponding metal nitrate solution.

Elemental analysis (Table 1) shows that the As/Ti ratio increases as the concentration of the loading reagents increases. This may be explained as follows. The papers are first dipped in the titanium chloride solution, which is uniformly adsorbed by the paper. When the titanium-impregnated strips are dipped in the arsenate solution, titanium arsenate is precipitated on the paper. The rate of precipitation, however, is proportional to the concentration of the arsenate solution and the As/Ti ratio increases as the arsenate concentration increases. If this explanation is correct the As/Ti ratio should be higher for papers first dipped in the arsenate and then in the titanium solution. To test this hypothesis, papers were prepared by dipping first in 0·05 and 0·1*M* arsenate. These papers were then dipped in 0·05 and 0·1*M* titanium solutions respectively. It was found that the As/Ti ratio for the "0·05*M*" paper was 1·7 and for the "0·1*M*" 2·21, which is about 5 times that observed when the order of immersion is reversed. The comparison of these results with the As/Ti ratio of titanium arsenate precipitated from solution is interesting. In all cases the As/Ti ratio is greater than for papers which have first been immersed in the titanium solution, because in solution the titanium arsenate reaction is allowed to proceed almost to equilibrium. When we consider titanium and arsenate solutions of the same concentration, a plot of the mean ion concentration *vs.* As/Ti ratio gives a linear plot (Fig. 1) and it is possible to adjust the As/Ti ratio as desired, by changing the concentration of the loading reagents. When the cation and anion solutions have different concentrations the composition of the precipitated material is not so easy to predict.

As the concentration of the loading reagents increases, the R_f values are also lowered. Therefore papers impregnated with 0·5*M* titanium and 0·5*M* arsenate solutions are probably the best for studying the effect of the counter-ion concentration on R_M values and to test the validity of the relation

$$-n \log [Na^+] = R_M + \text{constant}.$$

The results (omitted to save space) show that the slope increases with charge on the cation, but the relation above does not hold. This is because in concentrated solutions the availability of Na^+ ions is not given by their concentration. A better approach is to use activities instead of concentrations. A plot of $-n\log a_{Na^+}$ *vs.* R_M (Fig. 3) is linear. It will be interesting to see whether this is true for other papers also.

The plots in Fig. 4 show some very interesting trends. Of the 32 cations studied, only 8 give compact spots at pH 5. In most cases there is only a slight change in R_f value as the pH is altered from 3 to 2. At this pH the concentration of H^+ ions is still small and the cations compete successfully for the exchange sites. When the pH is changed from 2 to 1 there is an increase in the concentration of H^+ ions and a decrease in ionized exchange

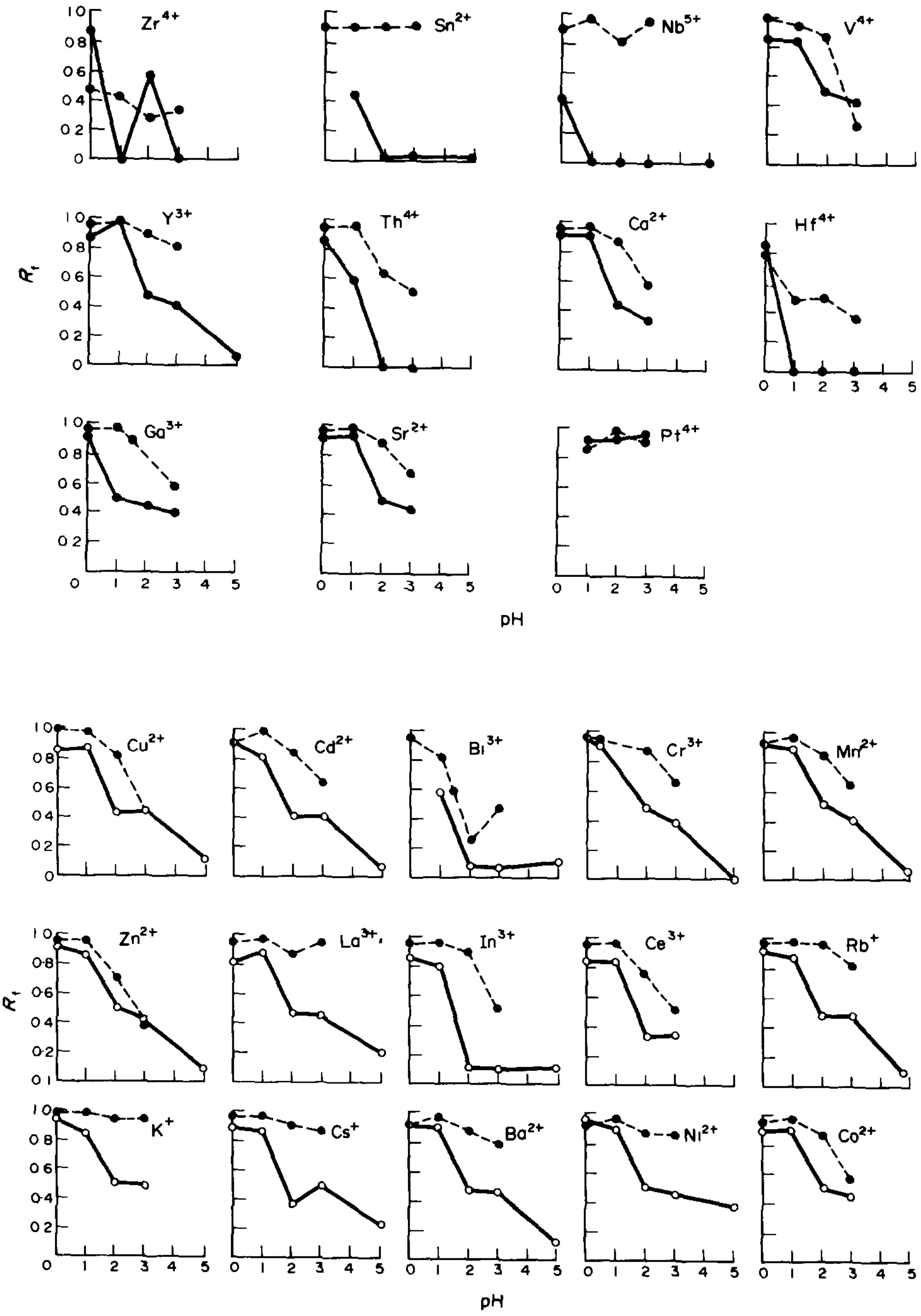


Fig. 4. Comparison of R_f values at various pH values on Whatman No. 1 paper (---) and on paper impregnated with titanium arsenate (—).

sites, hence the H^+ ions compete successfully and there is a sudden increase in R_f value. If the pH is further lowered from one to zero the ion-exchanger is now only slightly ionized and there is a negligible increase in R_f value. The ions which are not hydrolysed, *e.g.*, Ba^{2+}, Mg^{2+}, Rb^+ and Cs^+, show a considerable change in R_f values when the pH is altered from 5 to 4. For ions which are more extensively hydrolysed, *e.g.*, Bi^{3+}, Sn^{2+}, In^{3+} and Nb^{5+}, there is very little change in R_f values over the same pH range. These ions have zero R_f value at pH 3 because, as is clear from Fig. 5, the acid front has an almost zero R_f at this pH.

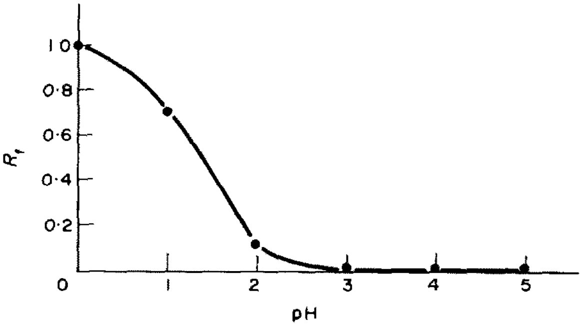


Fig. 5. R_f values of the acid front as a function of pH, for titanium arsenate papers.

A comparison of R_f values on treated papers (R_{FT}) and on untreated papers (R_{FU}) shows very clearly that at pH 0 the ion-exchange papers behave as untreated papers. This is because titanium arsenate is a weak ion-exchanger and at pH 0 it is not ionized and therefore it behaves only as a sorbent and not as an ion-exchanger. It is also apparent from Fig. 6 that ($R_{FU} - R_{FT}$) increases with increase in pH. This is because with increase in pH the concentration of hydrogen ions is decreased and more ion-exchange sites are available for exchange.

It is therefore useful to define a new property $R_i = (R_{FU} - R_{FT})$. R_i is a measure of the ion-exchange effect. A plot of R_i *vs.* pH shows that the maximum ion-exchange effect is obtained at pH 2. The results we have obtained for titanium arsenate should be valid for other ion-exchangers of the weak acid type. The value of R_i can also help in estimating the charge on the ion. Thus in the case of Pt^{4+} R_i is zero at all pH values, showing that no ion-exchange occurs in this case, and therefore the ion is either uncharged or has a negative charge. The results given in Table 5 show that only for Ba^{2+}, Sr^{2+} and Ca^{2+} is the sequence of K_d values the same as predicted from the R_f values. If we consider that the sequence of elution can be predicted from K_d values it follows that the R_f values are not reliable for such prediction. The reasons for this discrepancy are as follows.

1. In paper chromatography the solvent ascent is too fast for equilibrium to be achieved.
2. There are some ions which definitely interact differently with the paper than with the ion-exchange material.
3. The material deposited on the paper has different composition from that obtained by precipitation from solution. Since the K_d values depend upon the composition of the material they are found to be different.

Owing to the facts mentioned above it is difficult to agree with Alberti[15] that the elution sequence can be predicted from that R_f values. At best the R_f values are a rough guide and then only when they differ from one another considerably.

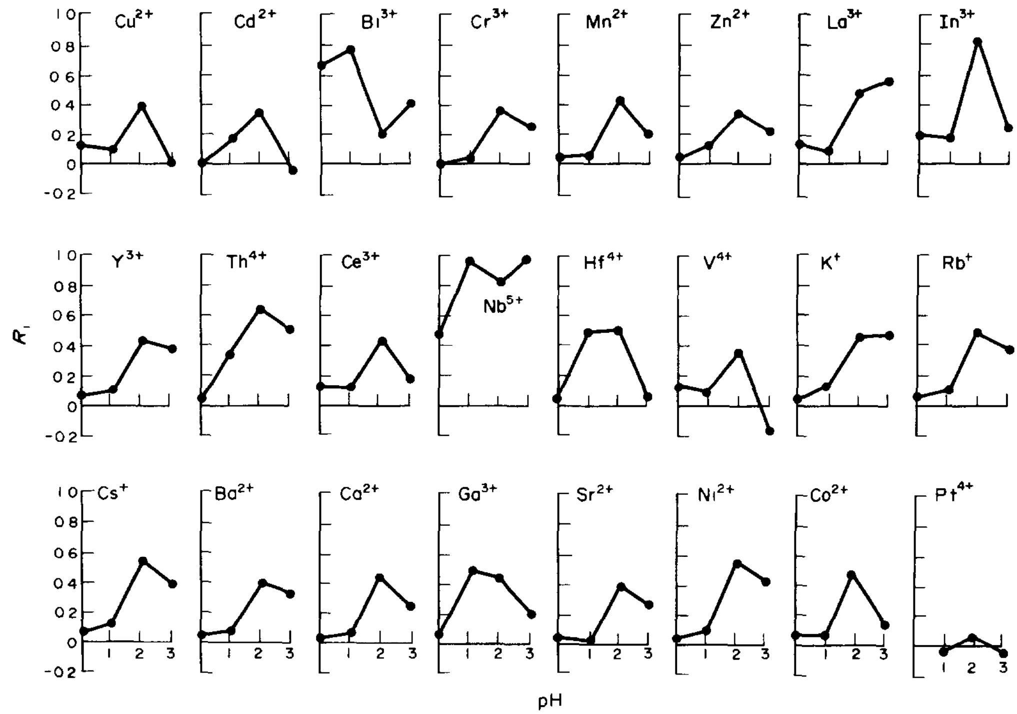
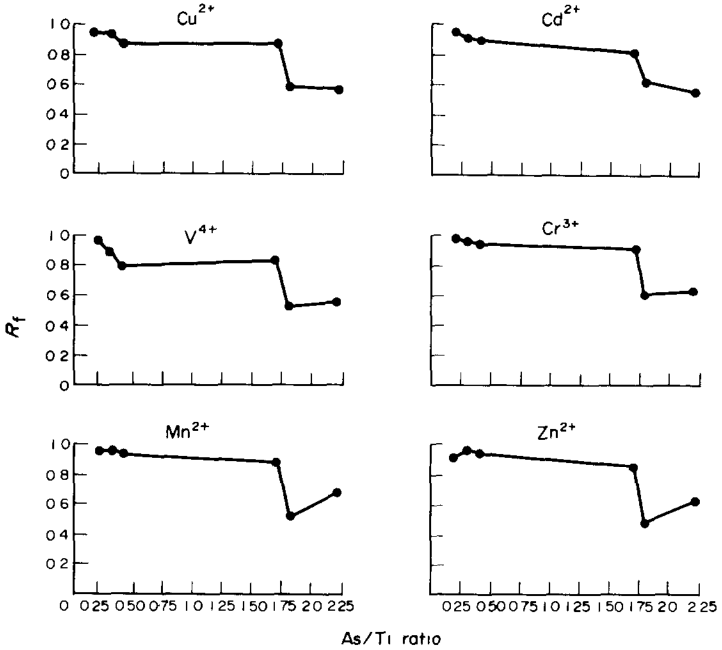


Fig. 6. Plot of R_f *vs.* pH.

Since 0·1*M* nitric acid gave the best separations, numerous cations were chromatographed in this solvent on papers with different As/Ti ratios. Almost all the plots (Fig. 7) show the same trends. Thus for papers with As/Ti between 0·20 and 1·7 there is very little change in R_f values because the amount of arsenate is insufficient for the ion-exchange reaction. However, as the As/Ti ratio increases from 1·7 to 1·8 there is a sudden decrease in the R_f value as considerable ion-exchange probably takes place at this stage. Further increases in the arsenic content does not have much effect on the R_f value, since there is no further increase in ion-exchange.

Table 5. Comparison of K_d values and R_f values of some metal ions on titanium(IV) arsenate.

Medium	K_d	R_f values
Water	$Ba^{2+} > Sr^{2+} > Ca^{2+}$ $Fe^{3+} > Ni^{2+} > V^{4+} >$ $Zn^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+}$ $Hg^{2+} > Cd^{2+} > Zn^{2+}$	$Ca^{2+} > Sr^{2+} > Ba^{2+}$ $Fe^{3+} > V^{4+} > Zn^{2+} =$ $Mn^{2+} = Ni^{2+} > Cu^{2+} > Co^{2+}$ $Hg^{2+} > Zn^{2+} > Cd^{2+}$
0·01*M* HNO_3	$Ca^{2+} = Sr^{2+} = Ba^{2+}$ $Fe^{3+} = Ni^{2+} = V^{4+} = Zn^{2+}$ $= Co^{2+} = Mn^{2+} = Cu^{2+}$ $Hg^{2+} > Zn^{2+} > Cd^{2+}$	$Sr^{2+} > Ba^{2+} > Ca^{2+}$ $Mn^{2+} > Zn^{2+} = Co^{2+} = V^{4+} >$ $Ni^{2+} > Cu^{2+} > Fe^{3+}$ $Zn^{2+} > Cd^{2+} > Hg^{2+}$
0·1*M* HNO_3	Zero	$Ba^{2+} > Ca^{2+} > Sr^{2+}$ $Cu^{2+} > Ni^{2+} > Co^{2+} >$ $Mn^{2+} > Zn^{2+} > V^{4+}$ $Zn^{2+} > Cd^{2+} > Hg^{2+}$



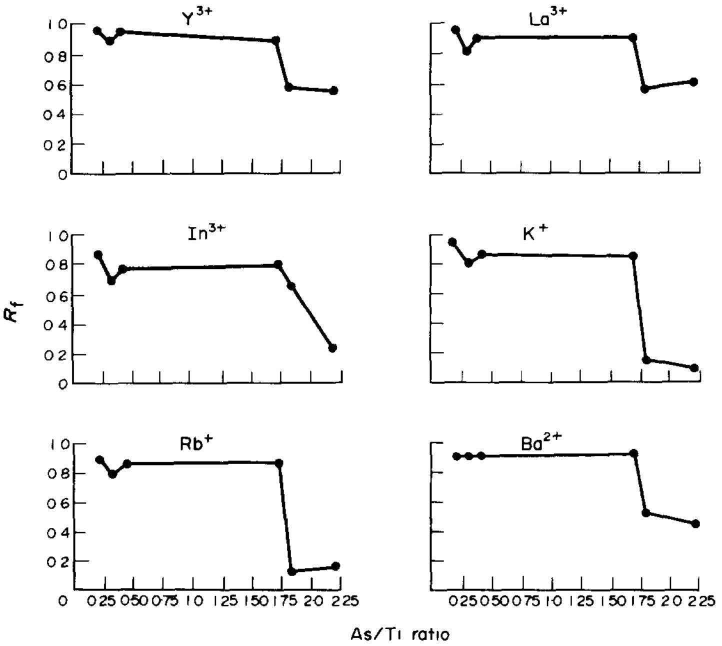


Fig. 7. Variation of R_f with concentration of arsenic on titanium arsenate papers with 0·1*M* nitric acid as solvent.

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Zusammenfassung—Titanarsenatpapiere mit As/Ti-Verhaltnissen von 0·2–2·2 wurden hergestellt und auf diesen Papieren 47 Metallionen in 10^{-5}-4M Salpetersäure chromatographiert. Der Einfluß von pH und Ti/As-Verhältnis auf die R_f-Werte wurde untersucht. Eine neue Größe R_t ($R_t = R_f$ auf unbehandelten minus R_f auf behandelten Papieren) wurde eingeführt. Der Einfluß der Konzentration der Ladereagentien auf das Ti/As-Verhältnis des auf den Papieren niedergeschlagenen Ionenaustauschers wurde ermittelt. Im Gegensatz zu Alberti wird gezeigt, daß Titanarsenatpapiere in der Natriumform die Gleichung von Lederer erfüllen, wenn man die Aktivität der Na^+-Ionen betrachtet und nicht die Konzentration. Es wurde ferner gezeigt, daß die Selektivitätsreihenfolge von Kationen auf Titanarsenatpapieren nicht dieselbe wie an Titanarsenatsaulen ist.

Résumé—On a préparé des papiers à l'arséniate de titane avec des rapports As/Ti 0,2–2,2, et chromatographié 47 ions métalliques dur ces papiers en acide nitrique $10^{-5} - 4$ *M*. On a étudié l'influence du pH et du rapport Ti/As sur les valeurs de R_f. Une nouvelle quantité R_t ($R_t = R_f$ sur papiers non traités moins R_f sur papiers traités) a été définie. On a déterminé l'influence de la concentration des réactifs de charge sur le rapport Ti/As de l'échangeur d'ions précipité sur les papiers. On montre que, contrairement à Alberti, l'équation de Lederer est suivie par les papiers à l'arséniate de titane sous la forme sodium si l'on considère l'activité des ions Na^+ au lieu de leur concentration. On a aussi démontré que la séquence de sélectivité pour les cations sur les papiers à l'arséniate de titane n'est pas la même que celle sur colonnes d'arséniate de titane.

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A PHOSPHORIMETRIC INVESTIGATION OF THE EXTERNAL HEAVY-ATOM EFFECT IN AQUEOUS SOLUTION AND ITS CORRELATION WITH PHOSPHORESCENCE INTENSITY AND QUANTUM YIELD*

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Summary—Excitation and emission phosphorescence spectra, lifetimes, and relative quantum yields of benzene and ten monosubstituted benzenes were determined at 77 K in methanol/water 10/90 v/v and in sodium iodide/methanol/water solutions. Substituents —CHO, —$COCH_3$, —COC_2H_5, —OH, —OCH_3, —CH_3, —C_2H_5, —CH_2OH and —$N(CH_3)_2$ were investigated. Aqueous sodium iodide solutions were found to be a suitable heavy-atom solvent for phosophorimetry. Heavy-atom enhancement factors ranged from 1·2 to 8·3 according to the molecular structure and a marked decrease of the lifetime was observed for nine compounds in aqueous sodium iodide solution. A linear log–log correlation was obtained between the relative corrected phosphorescence signal and the heavy-atom enhancement factor of the monosubstituted benzenes. A similar correlation was found between the quantum yields and the heavy-atom enhancement factors. The analytical usefulness of these correlations is evident for the prediction of the magnitude of the heavy-atom effect.

The introduction of a heavy atom into a solvent system has been shown to improve in several cases the sensitivity of the analytical method of phosphorimetry.[1–5] This external heavy-atom effect is mainly due to the increase of the spin-orbit coupling of excited singlet and triplet states, resulting in the increase of the rate constant of intersystem crossing between the singlet and triplet states.[6] Weak complexes between a phosphorescent molecule and a perturbing heavy atom have been postulated to interpret these effects physically.[6] In the absence of increased quenching by collision between the phosphorescent species and the heavy-atom solvent and of a change in the rate of radiationless internal conversion from the lowest triplet state, theoretically a decrease of the fluorescence quantum yield and an increase of the phosphorescence quantum yield of the luminescing molecules are expected in an heavy-atom solvent. However, until now, the analytical use of these interesting effects has been very limited in phosphorimetry, mainly because of the requirements of the heavy-atom solvent systems, which had to form clear, rigid glasses at low temperature to give reproducible phosphorescence signals. Another major inconvenient characteristic of the mixtures of EPA (*i.e.*, diethyl ether, isopentane and ethanol and iodomethane[1,2] or ethanol and iodoethane[3,4] (which have previously been used most as heavy-atom solvents)

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was their strong absorption of excitation radiation below about 330 nm, leading therefore to a reduction of the phosphorescence intensity of the ultraviolet-absorbing compounds. The importance of this ultraviolet wavelength cut-off in the heavy-atom enhancement of phosphorescence was pointed out by McCarthy and Dunlap.[5] These authors showed that mixtures of ethanol and chlorinated or brominated hydrocarbons were more suitable than the iodine-containing solvent systems for the study of the phosphorescence of polycyclic aromatic hydrocarbons, because of the better ultraviolet transmission characteristics of the former.[5] Nevertheless, large and unexplained variations of the value of the heavy-atom enhancement of the intensity of phosphorescence were observed from one compound to another. For example, in the case of the more favourable solvent used (bromoethane/ethanol 50/50), enhancement factors ranged from 0·55 to 52;[5] and variations could not be attributed to the solvent filter effect, as all the compounds studied were excited at longer wavelengths than the wavelength cut-off of this solvent.

New technological improvements in phosphorimetry[7,8] have permitted the use of predominantly aqueous solvents forming snowed matrices at low temperatures and excellent analytical results have been obtained under these conditions.[8–10] In a recent study,[11] we have demonstrated that a few per cent by weight of sodium iodide in a methanol–water mixture or in water resulted in phosphorescence signals several orders of magnitude greater than the phosphorescence signal of the same compound in pure water solution. Although most of this increase was due to a matrix effect, the phosphorescence signal was enhanced by a factor of 3–6 for two of the three compounds studied, when 1*M* sodium iodide medium was used instead of methanol–water (10/90) and this could be reasonably attributed to the heavy-atom effect.[11]

In the present paper, we want to report on the study of the heavy-atom effect of the iodide upon the phosphorescence of a series of substituted aromatic hydrocarbons in predominantly aqueous solvent, and to discuss the analytical utility of the sodium iodide–methanol–water solvent system in phosphorimetry. A thorough study of the variation of the heavy-atom enhancement factors with the phosphorescence signals of substituted benzenes has indicated to us the existence of a correlation between the intensity of the heavy-atom effect and the phosphorescence quantum yield of the compounds studied.

EXPERIMENTAL

Apparatus

Phosphorescence intensity and relative quantum yield measurements were performed with an Aminco-Bowman spectrophotofluorometer with an Aminco-Keirs phosphoroscope attachment (American Instrument Co., Silver Spring, Md., U.S.A). The instrument was equipped with a 150-W xenon arc lamp, a potted RCA-1P28 multiplier phototube (American Instrument Co.) and an Aminco Model 1620-827 X-Y recorder. Phototube signals were measured with a low-noise nanoammeter previously described.[12] The xenon lamp was powered by a Harrison Lab Model 6268A power supply (Hewlett-Packard, Palo Alto, Calif.), and the phototube was powered by a Keithley Model 244 high-voltage supply (Keithley Instruments, Cleveland, Ohio). Rotating quartz capillary sample tubes were used as previously described.[8] The capillary tubes were made from T21 Suprasil capillary tubing (Amersil Inc., Hillside, N.J.), 5 mm o.d. and 0·9 mm i.d. Excitation light was polarized by means of a thin-film quartz plate polarizer (Polacoat Inc., Cincinnati, Ohio) in order to decrease the background phosphorescence of the quartz tubes.

Phosphorescence spectra were obtained with an Aminco-Bowman spectrophotofluorometer equipped with an Aminco-Ratio Photometer and with an Aminco-Keirs phosphoroscope attachment. A Moseley Model 135A X-Y recorder (F. L. Moseley, Pasedena, Calif.) was used to record the phosphorescence spectra.

A calibrated standard tungsten lamp (Model EPUV-1068, Eppley Laboratory, Newport, R.I.) was used to calibrate the emission of the monochromator photomultiplier tube system. Ultraviolet absorption spectra were obtained on a Beckman DB-G spectrophotometer (Beckman Instruments, Fullerton, Calif., U.S.A.).

Phosphorescence lifetimes greater than 1 sec were measured by using the Aminco Model 1620-827 X-Y recorder in the time-base mode. Lifetimes of less than 1 sec were measured with the pulsed-source time-resolved system recently described.[13,14]

Reagents

Reagents used without further purification were: ethylbenzene, propiophenone (reagent grade; Matheson, Coleman, and Bell, East Rutherford, N.J., U.S.A.); phenol, acetophenone (reagent grade, J. T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.); benzyl alcohol, anisole (reagent grade, Fisher Scientific Co., Fairlawn, N.J., U.S.A.); *N,N*-dimethylaniline (reagent grade, Eastman Organic Chemicals, Rochester, N.Y., U.S.A.); benzaldehyde (Baker reagent, Allied Chemical, New York, N.Y., U.S.A.); benzoic acid (reagent grade, Mallinckrodt Chemical, St. Louis, Mo., U.S.A.); benzene, toluene, methanol (spectroquality, Matheson, Coleman, and Bell, East Rutherford, N.J., U.S.A.). Ultrapure sodium iodide was used in the heavy-atom effect studies (Alfa Inorganics, Beverly, Mass., U.S.A.). Demineralized water was obtained directly from a commercial ion-exchange column.

Procedures

Stock solutions of all compounds were approximately $10^{-2}M$. All stock solutions were prepared in absolute methanol solvent except for benzoic acid which was prepared in pure aqueous solution. Successive dilutions of the stock solutions were prepared in 10% v/v methanol–water as solvent. Final dilutions of the compounds studied were prepared in 10% methanol–water and 10% methanol–water that was $0{\cdot}75M$ in sodium iodide. The concentrations of all solutions were in the range 10^{-5}–$10^{-4}M$ as determined by the intensity of the phosphorescence signal of the particular compound.

Phosphorescence spectra and relative intensity measurements for the molecules studied were obtained with the quartz capillary sample tube suspended in liquid nitrogen in a quartz-window Dewar flask. The slit arrangement for intensity and relative quantum yield measurements was 3, 4, 3, 3, 4, 3 (all in mm, corresponding to 17 and 22 nm spectral half-band pass).

Calibration of the instrumental system was accomplished as follows. The emission monochromator-photomultiplier tube system was corrected for the transmission characteristics of the optical system, the spectral response of the photomultiplier tube, and the relative bandwidth used, by means of a standard tungsten lamp according to the method of Parker (without a magnesium oxide screen).[15] The entrance and exit slitwidths of the emission monochromator were set at 3 mm, and the total entrance slit area was illuminated with light from the tungsten lamp. The intensity was reduced by means of neutral density filters, and the signal from the phototube, R_{SL}, in amperes, was recorded at 10-nm intervals obtained by manually rotating the wavelength disc. The wavelength accuracy of the emission monochromator system had previously been calibrated with a mercury vapour pen-lamp. Because the flux output $[dE/d\lambda]_{SL}$ in watts per unit wavelength interval, for the standard tungsten lamp, was known at wavelength λ, the spectral response characteristic of the emission system, S_λ, in amperes per quanta, was obtained by means of equation (1).

$$S_\lambda = \frac{R_{SL}}{\lambda\left(\frac{dE}{d\lambda}\right)_{SL}} \tag{1}$$

The transmission characteristics of the excitation monochromator and the xenon lamp output were corrected for by placing a shiny aluminium strip diagonally in the fluorescence cell holder of the instrument and measuring the response of the phototube to the excitation light scattered from the aluminium strip into the emission monochromator. It is assumed that the aluminium strip reflects all wavelengths equally. The intensity (flux) of exciting radiation, I°, in quanta, at wavelength λ could then be obtained by using equation (2).

$$I_\lambda^\circ = \frac{R_{SL}}{S_\lambda} \tag{2}$$

Corrected emission spectra for the determination of relative quantum yields were determined by correcting the observed spectra for the response of the emission system point by point at 10-nm intervals, and replotting the points. The integrated intensity for each emission spectrum was obtained by cutting out and weighing the area under the resulting curve.

RESULTS AND DISCUSSION

Characteristics of the heavy-atom effect in aqueous solvent

Previous study[11] showed that the addition of very small amounts of sodium iodide (about 1% in weight) to pure water solutions increased the phosphorescence signal by about two orders of magnitude, and a smaller increase in phosphorescence signal was observed when sodium iodide was added to methanol–water (10/90 v/v) solution. To distinguish the iodide heavy-atom effect from the matrix effect produced by the addition of small amounts of methanol or sodium iodide to pure water solutions, in the present work methanol–water 10/90 v/v solutions were used rather than pure water solutions. In order to define more accurately the nature of the variation of phosphorescence intensity with sodium iodide concentration in aqueous solutions, the phosphorescence signal was measured at various sodium iodide concentrations, over the range 0–0·8*M*. The result obtained for phenol is presented in Fig. 1. A region of gradual increase of the signal occurs from 0 to about 0·75*M* sodium iodide, and a plateau at higher concentrations. As similar curves are expected for the other monosubstituted benzenic compounds studied, a heavy-atom solvent in the composition range of the plateau (methanol/water 10/90 v/v–0·75*M* in sodium iodide) was used for all other studies.

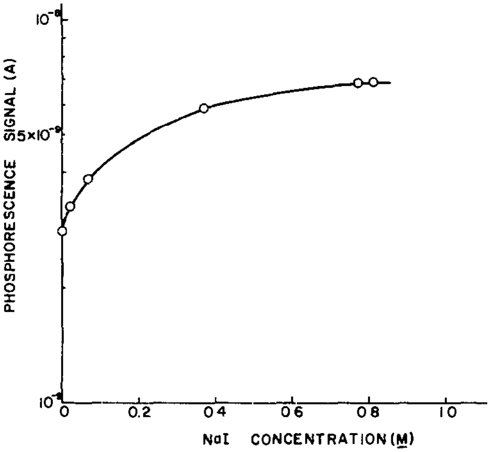

Fig. 1. Phosphorescence signal of phenol ($2{\cdot}2 \times 10^{-5}M$) as function of sodium iodide concentration in methanol–water 10/90 v/v at 77 K.

Phosphorescence excitation and emission spectra and lifetimes were obtained for all the monosubstituted benzenes at 77 K in snowed matrices, with and without sodium iodide. Phosphorescence characteristics are given in Table 1. No significant effect on the position of the long excitation wavelength or emission peaks in sodium iodide solution is apparent. The only noticeable changes in the shape of the excitation spectra are the 10–15 nm red-shift of the ${}^{1}L_{a}$ band in the case of the carbonyl substituted benzenes and benzoic acid (see Fig. 2) and its disappearance or its decrease for benzene and the other substituted benzenes upon addition of sodium iodide (Fig. 3). These slight changes are very probably due to the solvent filter effect of the sodium iodide solutions, which strongly absorb the incident light of wavelength below about 250 nm. Previously, even more severe red-shifts of the phosphorescence excitation wavelength were observed in iodine or bromine-containing heavy-atom solvents[1–5] and were also attributed to filter effects of these solvents.[5] However, such undesirable effects, which can also reduce the heavy-atom enhancement of phosphorescence efficiency, are minimized in our case by the much shorter absorption wavelength of the sodium iodide solutions; for example, in the present studies, it was found that the 90% transmission wavelength of the sodium iodide

Table 1. Sodium iodide effect on phosphorescence characteristics of monosubstituted benzenic compounds

	10% MeOH/H_2O			10% MeOH/H_2O–0·75*M* NaI		
Compound	λ_{ex},* *nm*	λ_{em},* *nm*	τ, *sec*†	λ_{ex},* *nm*	λ_{em},* *nm*	τ,† *msec*
Anisole	~200, *265*	385	3·4 (3·0)	*265*	385	10·7
Benzene	~200, *260*	365	7·0 (7·0)	*255*	365	58
Benzoic acid	240, *280*	395	2·7 (2·5)	250, *280*	395	3·6
Benzyl alcohol	~200, *250*	380	6·2	*250*	380	13·7
N,*N*-Dimethylaniline	240, *290*	405	2·3	235, *285*	400	36·0
Ethylbenzene	~200, *255*	375	8·8	*255*	380	5·8
Phenol	~200, *270*	380	2·8 (2·9)	*265*	375	122
Toluene	~200, *261*	383	8·2 (8·8)	*260*	383	30·2
Acetophenone	255, *285*	420	0·0041 (0·004)	265, *290*	415	4·9
Benzaldehyde	255, *290*	425	0·0035 (0·0023)	~270, 290	425	4·9
Propiophenone	250, *285*	415	0·37	260, *285*	415	15·5

* All peak wavelengths: error ±3 nm. Wavelengths in italics were used for phosphorescence intensity measurements.

† Lifetime: error ±10%. Times are in msec for the solvent containing NaI. Values in parentheses are for EPA media, and taken from R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley, New York, 1969.

methanol/water solutions was about 255 nm, compared to corresponding values of 365 and 295 nm for the better iodinated and brominated hydrocarbons previously used as heavy-atom solvents.[5] Because of their extended transmission range, the sodium iodide methanol/water solutions constitute suitable heavy-atom solvents for phosphorescent compounds with excitation wavelength above about 255 nm, while until now heavy-atom solvents were only analytically useful for compounds with excitation wavelength greater than about 300 nm.

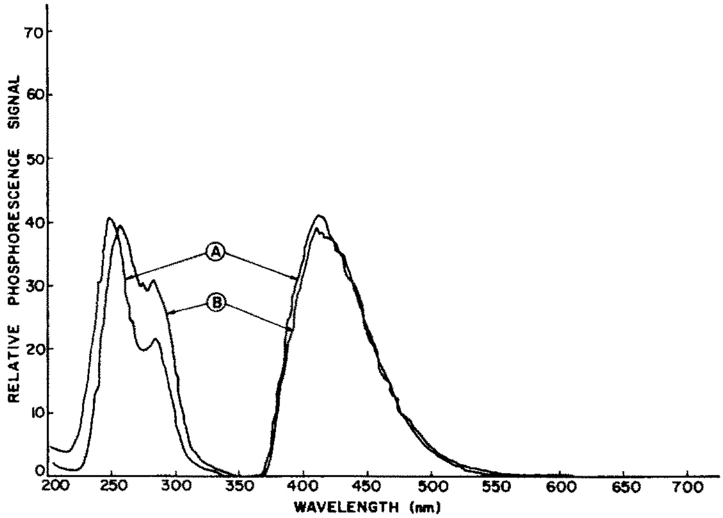

Fig. 2. Phosphorescence excitation and emission spectra of propiophenone at 77 K, in methanol/water v/v 10/90 (Curve A, emission wavelength 415 nm, excitation wavelength 250 nm) and in methanol/water v/v 10/90, sodium iodide 0·75*M* solutions (Curve B, emission wavelength 415 nm, excitation wavelength 260 nm).

Sensitivity of the ratio photometer = 3 and sensitivity vernier = 15. Concentration of propiophenone = $6{\cdot}14 \times 10^{-4}M$.

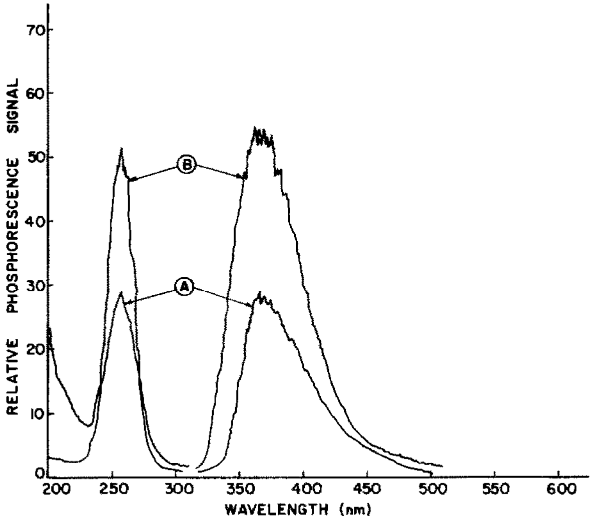

Fig. 3. Phosphorescence excitation and emission spectra of benzene at 77 K, in methanol/water v/v 10/90 (Curve A, emission wavelength 365 nm, excitation wavelength 260 nm) and in methanol/water v/v 10/90, sodium iodide 0·75*M* solutions (Curve B, emission wavelength 365 nm, excitation wavelength 255 nm).

Sensitivity of the ratio photometer = 0·3 (Curve A) and 1·0 (Curve B), and sensitivity vernier = 50 (Curve A) and 20 (Curve B). Concentration of benzene = $2{\cdot}14 \times 10^{-3}M$.

Phosphorescence lifetimes of all benzenic compounds, except acetophenone and benzaldehyde, were found to decrease greatly in sodium iodide solutions, an effect which is typical of the enhancement of the spin-orbit coupling by an external heavy atom.[6a] The absence of significant change in the short phosphorescence lifetimes of acetophenone and benzaldehyde upon addition of sodium iodide is in agreement with the prediction of a very small external heavy-atom effect on the singlet–triplet transition probability and on the lifetime of the n,π^* triplet state of these carbonyl compounds.[6b,16] The longer phosphorescence decay-time of propiophenone and its marked decrease in sodium iodide solution would indicate that, in contrast to the other carbonyl-substituted benzenes, the triplet state of propiophenone is probably of π, π^* type; this phenomenon may be due to the inversion of the n,π^* and π,π^* triplet-state energy levels by the polar solvent (methanol/water) used. It is also of interest to observe that the phosphorescence decays of all the compounds in sodium iodide media were found to be exponential over 3–4 half-lives; this behaviour is different from the non-exponential decay observed by several authors for mixtures of EPA or ethanol and iodinated or brominated hydrocarbons[1,2,5] combinations of halonaphthalenes and propyl halides,[17] and in perdeuterated benzenes in alkali halides.[18] Two effects may explain the exponential character of phosphorescence decays in sodium iodide solutions.

(*i*) The effect of specific crystal geometry and density characteristics of aqueous sodium iodide snowed matrices upon the decay of phosphorescence is expected to be different[16] from that of the heavy-atom glasses[1–5] or cracked glasses[19] previously used.

(*ii*) Triplet-state equilibrium complexes occurring in the sodium iodide solutions may be very different from the charge-transfer equilibrium complexes postulated to explain the non-exponential nature of phosphorescence decay in the cracked glasses of halonaphthalenes and propyl halides,[17] because of the different conditions of solvent polarity, solute ionic dissociation, and solvation in water–methanol sodium iodide medium.

The phosphorescence signal was markedly enhanced for all compounds in sodium iodide solutions (see Table 2), and the room-temperature fluorescence of the fluorescent monosubstituted benzenes was markedly quenched. These results are also typical of an external heavy-atom effect, characterized by the increase of the triplet population by radiationless intersystem crossing and of the triplet-to-singlet transition probability.

Variation of the sodium iodide heavy-atom effect with phosphorescence signal

Phosphorescence signals and heavy-atom enhancement factors of all monosubstituted benzenes studied are presented in Table 2.

Phosphorescence relative signals ($I_{\mathrm{p,r}}$) are defined as the ratio of the phosphorescence molar signals (expressed in A.l.mole^{-1}) of the sample and of the reference compound (phenol) and are corrected for the exciting radiation intensity, according to the equation

$$I_{\mathrm{p,r}} = \beta_\lambda\left(\frac{i_{\mathrm{S}}c_{\mathrm{R}}}{i_{\mathrm{R}}c_{\mathrm{S}}}\right) \tag{3}$$

where i is the absolute phosphorescence signal (in A) of the sample S and of the reference R, c is the concentration (mole/l.) of the species of interest S, and reference

Table 2. Heavy-atom enhancement factors and phosphorescence quantum efficiencies of monosubstituted benzenes

Compound	Molar absorptivity, ε_λ[a]	Relative phosphorescence signals[f]		Enhancement factor, $I_{\mathrm{p}}^{\mathrm{NaI}}/I_{\mathrm{p}}$	Relative quantum yield, ϕ_{p}[g]
		$I_{\mathrm{p,r}}$	$I^{\varepsilon}_{\mathrm{p,r}}$		
Anisole	1,480 (269)[b]	1·56	1·53	2·8	0·11
Benzene	204 (254)[b]	0·0136	0·0962	8·3	0·01 (0·20)[h]
Benzoic acid	970 (269)[b]	2·9	4·34	1·7	0·76 (0·27)[i]
Benzyl alcohol	176 (258)[c]	0·126	1·04	2·8	0·29
N,*N*-Dimethylaniline	1,300 (291)[d]	0·36	0·404	6·2	0·04
Ethylbenzene	215 (262)[c]	0·180	1·21	3·0	0·23
Phenol	1,450 (270)[b]	1·00	1·00	3·8	0·17 (0·37)[i]
Toluene	225 (261)[b]	0·210	1·42	3·4	0·27
Acetophenone	1,172 (278)[e]	3·52	4·35	1·3	0·74 (0·74)[h]
Benzaldehyde	1,585 (280)[e]	1·3	1·64	1·3	0·14 (0·56)[h]
Propiophenone	1,120 (280)[e]	2·98	3·87	1·2	0·66

[a] Absorption wavelength values, in nm, are given in parentheses; ε in l.mole^{-1}.cm^{-1}.

[b] From H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962 (for aqueous medium).

[c] Values measured in 10% methanol–water at room temperature.

[d] From *Sadtler Standard Spectra*, Sadtler Research Laboratories, Philadelphia, Pa. (for aqueous media).

[e] From *Organic Electronic Spectral Data*, Vols. I–IV, eds, O. H. Wheeler and L. A. Kaplan, Interscience, New York, 1946–1959. (Acetophenone; water as solvent: propiophenone and benzaldehyde; ethanol as solvent).

[f] Relative to phenol = 1·00.

[g] Relative to $\phi_{\mathrm{p}} = 0{\cdot}74$ for acetophenone in EPA at 77 K.

[h] Values in parentheses taken from R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley, New York, 1969 (for EPA media at 77 K).

[i] Values in parentheses taken from C. A. Parker, *Photoluminescence of Solutions*, Elsevier, London, 1968 (for EPA media at 77 K).

R, and β_λ is the ratio of the exciting radiation intensity ($I^{\circ}_{\lambda,\mathrm{R}}$) at the excitation wavelength of the reference to the same quantity ($I^{\circ}_{\lambda,\mathrm{S}}$) at the excitation wavelength of the sample [see equation (2) for the determination of I°_{λ} values].

Corrected relative phosphorescence signals ($I^{\varepsilon}_{\mathrm{p,r}}$), taking into account the molar absorptivity of the compounds, were obtained from the equation

$$I^{\varepsilon}_{\mathrm{p,r}} = \beta_\lambda\left(\frac{i_{\mathrm{S}}c_{\mathrm{R}}\varepsilon_{\mathrm{R}}}{i_{\mathrm{R}}c_{\mathrm{S}}\varepsilon_{\mathrm{S}}}\right) \tag{4}$$

where ε_{S} and ε_{R} are the molar absorptivities of the sample S and of the reference R and other notations are as in equation (3). It is assumed[15] that the molar absorptivities for the sample at 77 K are identical to those at room temperature.

Sodium iodide heavy-atom enhancement factors ($I_{\mathrm{p}}^{\mathrm{NaI}}/I_{\mathrm{p}}$) are defined as the ratio of the molar phosphorescence signals in methanol–water–sodium iodide solutions and in methanol–water and were determined from the equation

$$I_{\mathrm{p}}^{\mathrm{NaI}}/I_{\mathrm{p}} = \beta_\lambda'\left(\frac{i_{\mathrm{S}}^{\mathrm{NaI}}c_{\mathrm{S}}}{i_{\mathrm{S}}c_{\mathrm{S}}^{\mathrm{NaI}}}\right) \tag{5}$$

where $i_{\mathrm{S}}^{\mathrm{NaI}}$ and $c_{\mathrm{S}}^{\mathrm{NaI}}$ are respectively the absolute phosphorescence signal (in A) and

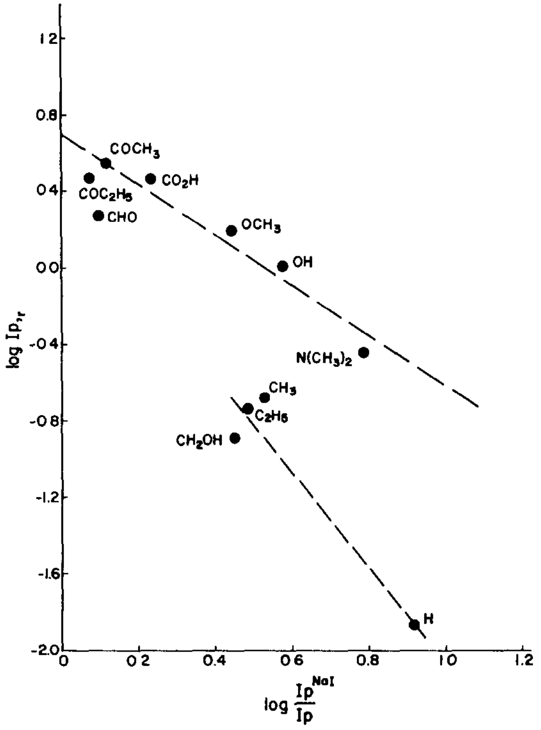

Fig. 4. Relative phosphorescence signal of the monosubstituted benzenes as function of their heavy-atom enhancement factor.

---●---Least-squares line for the compounds with molar absorptivity ≥ 1000 (correlation coefficient = 0·97 and standard deviation = 0·10).

---o---Least-squares line for the compounds with molar absorptivity < 230 (correlation coefficient = 0·95 and standard deviation = 0·21).

(Benzaldehyde was not included in the calculation).

the concentration (mole/l.) of the species of interest S in methanol–water–sodium iodide solution; β_λ' is the ratio of the exciting radiation intensity ($I^\circ_{\lambda,\mathrm{S}}$) at the exciting wavelength of the sample in methanol–water solution to the same quantity ($I^{\circ\,\mathrm{NaI}}_{\lambda,\mathrm{S}}$) at the exciting wavelength of the sample in methanol–water–sodium iodide solution. It is assumed in equation (5) that the molar absorptivities are identical in the iodide and non-iodide solvents.

Heavy-atom enhancement factors of all monosubstituted benzenes were found to be larger than unity; $I_\mathrm{p}^\mathrm{NaI}/I_\mathrm{p}$ values ranged between 1·2 for propiophenone and 8·3 for benzene. Even though excitation wavelengths are taken in the wavelength region above 255 nm, in which no solvent filter effect[1–5] should occur, enhancement factors vary appreciably with the molecular structure of the compound. It is worthwhile to note that the variation of heavy-atom enhancement factors is parallel to the change in phosphorescence relative signals; there is definitely a trend in the increasing phosphorescence signals with a decrease in the heavy-atom enhancement factors, and partial correlations are obtained between the logarithms of these quantities for the compounds with similar molar absorptivity (see Fig. 4). In order to take this last factor into account, the phosphorescence signals were corrected for the absorptivity according to equation (4) and a satisfactory correlation was found between the logarithms of the corrected phosphorescence signal values and of the heavy-atom enhancement factors (see Fig. 5), *i.e.*,

$$\log I^\varepsilon_{\mathrm{p,r}} = -1{\cdot}80 \log I_\mathrm{p}^\mathrm{NaI}/I_\mathrm{p} + 0{\cdot}93 \qquad (6)$$

For ten compounds, a correlation coefficient of 0·95 and a standard deviation of 0·16 were obtained. This correlation indicates that for molecules with a heavily populated triplet state, the sodium iodide does not have a large effect upon the intersystem crossing from the singlet to the triplet state. This is the case for the very phosphorescent carbonyl-substituted benzenes and benzoic acid. On the contrary, for a molecule with a poorly

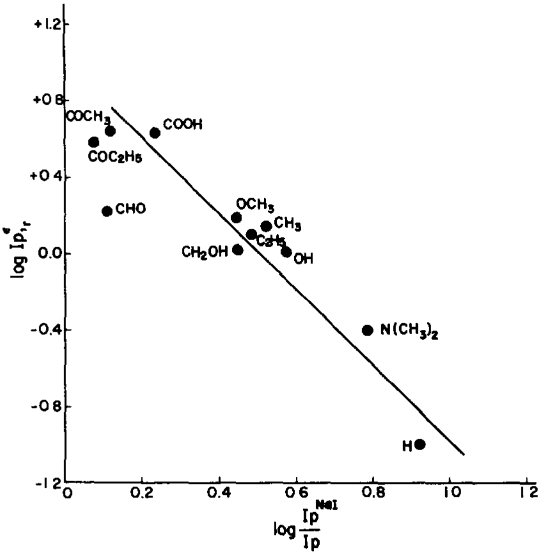

Fig. 5. Correlation between the corrected relative phosphorescence signal ($I^\varepsilon_{\mathrm{p,r}}$) and the heavy-atom enhancement factor ($I_\mathrm{p}^\mathrm{NaI}/I_\mathrm{p}$) of monosubstituted benzenes. (Benzaldehyde was not included in the calculation of the least-squares line).

populated triplet state, sodium iodide would facilitate a very large increase of the intersystem crossing transition from the singlet excited state, as in the case of the weakly phosphorescent benzene.

The correlation [see equation (6)] is also of great interest from an analytical point of view. Indeed, it is possible to predict the heavy-atom enhancement factor for any substituted benzene within an error of 20%, by means of equation (6). The only data which need to be known for a particular compound are the relative phosphorescence signals and molar absorptivity values of the compound with phenol as reference. The application of equations of this type would allow prediction of the analytical usefulness of the heavy-atom effect for the improvement of sensitivity of phosphorimetry.

Correlation of the quantum yield with the heavy atom effect

Relative quantum yields (ϕ_S) were determined[18] from equation (7)

$$\phi_S = \phi_R \times \beta_\lambda \left(\frac{F_S c_R \varepsilon_R}{F_R c_S \varepsilon_S} \right) \tag{7}$$

where ϕ_R is the phosphorescence quantum yield of the reference species R (acetophenone), F_S and F_R are the corrected areas under the phosphorescence emission spectra for sample, S, and reference R, c is the concentration (M) of the species indicated and β_λ, ε_R and ε_S are as previously defined.

All relative quantum yield values are presented in Table 2. The phosphorescence quantum yield of acetophenone in EPA was taken as the reference, because no quantum yield data were known for methanol–water 10/90 v/v. Compared with the

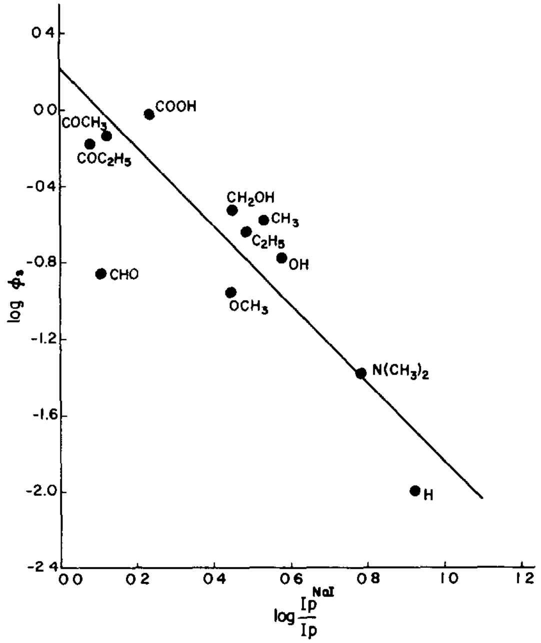

Fig. 6. Correlation between the relative quantum yield (ϕ_s) and the heavy-atom enhancement factor (I_p^{NaI}/I_p) of monosubstituted benzenes. (Benzaldehyde was not included in the calculation of the least-squares line).

literature data, which were all obtained in EPA medium, our values are consistently smaller except in the case of benzoic acid; this difference may be due to the different radiationless deactivations of the triplet state according to the matrices used and to the change in solvation as well as due to solvent absorption which was not corrected for in Table 2. For example, it may be expected that benzene will be less solvated in predominantly aqueous solution ($\phi_S = 0{\cdot}01$) than in EPA ($\phi_S = 0{\cdot}20$). Quantum yield values spread over a large range from 0·01 for benzene to 0·76 for benzoic acid and were found to be correlated relatively well with the heavy-atom enhancement factors:

$$\log \phi_S = -2{\cdot}06 \log I_p^{\mathrm{NaI}}/I_p + 0{\cdot}22 \qquad (8)$$

for ten compounds, with correlation coefficient 0·93 and standard deviation 0·24. The negative slope of the correlation (Fig. 6) shows that heavy-atom enhancement is larger for compounds with low phosphorescence quantum yield. A correlation of the heavy-atom enhancement factors with the quantum yields is obtained which is nearly as good as with the phosphorescence signals, which indicates that the vibrational components of the phosphorescence (included in the total emission area) are affected in the same way by the heavy-atom effect as is the maximum phosphorescence signal. Therefore, it seems reasonable that the substituent sequences of phosphorescence signals and quantum yields fall in approximately the same order.

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Zusammenfassung—Phosphoreszenzanregungs- und -emissionsspektren, Lebensdauern und relative Quantenausbeuten von Benzol und zehn monosubstituierten Benzolen wurden bei 77°K in Methanol/Wasser 10/90 (V/V) und in Natriumjodid/Methanol/Wasser-Lösungen bestimmt. Die Substituenten $—CHO$, $—COCH_3$, $—COC_2H_5$, $—CN$, $—OCH_3$, $—CH_3$, $—C_2H_5$, $—CH_2OH$ und $—N(CH_3)_2$ wurden untersucht. Es wurde gefunden, daß wäßrige Natriumjodidlösungen ein geeignetes Schweratom-Lösungsmittel für die Phosphorimetrie sind. Die Schweratom-Verstärkungsfaktoren reichten je nach der Molekülstruktur von 1·2 bis 8·3; für neun Verbindungen wurde in wäßriger Natriumjodidlösung eine beträchtliche Verkürzung der Lebensdauer beobachtet. Im doppeltlogarithmischen Maßstab wurde eine lineare Beziehung zwischen der relativen korrigierten Phosphores-zenzintensität und dem Schweratom-Verstärkungsfaktor der monosubstituierten Benzole gefunden. Eine ähnliche Beziehung wurde zwischen den Quantenausbeuten und den Schweratom-Verstärkungsfaktoren gefunden. Der analytische Nutzen dieser Beziehungen ist für die Voraussage der Größe des Schweratomeffekts offenkundig.

Résumé—On a déterminé les spectres d'excitation et d'émission de phosphorescence, les temps de vie et les rendements quantiques relatifs du benzène et de dix benzènes monosubstitués à 77°K en solutions méthanol/eau 10/90 v/v et iodure de sodium/méthanol/eau. On a étudié les substituants $-CHO$, $-COCH_3$, $-COC_2H_5$, $-OH$, $-OCH_3$, $-CH_3$, $-C_2H_5$, $-CH_2OH$ et $-N(CH_3)_2$. On a trouvé que les solutions aqueuses d'iodure de sodium sont un solvant à atome lourd convenable pour la phosphorimétrie. Les facteurs d'exaltation par atome lourd se sont situés de 1,2 à 8,3 selon la structure moléculaire et un abaissement notable du temps de vie a été observé pour neuf composés en solution aqueuse d'iodure de sodium. On a obtenu une relation log-log linéaire entre l'intensité de phosphorescence corrigée relative et le facteur d'exaltation par atome lourd des benzènes monosubstitués. On a trouvé une relation semblable entre les rendements quantiques et les facteurs d'exaltation par atome lourd. L'utilité analytique de ces relations est évidente pour la prévision de la grandeur de l'effet d'atome lourd.

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2,2′-DIMERCAPTODIETHYLSULPHIDE: A POTENTIAL ANALYTICAL REAGENT

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Summary—The compound 2,2′-dimercaptodiethylsulphide has been investigated with regard to the stability of its solutions to air oxidation, its acid strength, its reactivity towards metal ions, the nature of its Ni(II) and Pd(II) complexes in solution, and its applicability to the determination of small amounts of Ni(II) and Pd(II). Studies on the Ni(II) complex extend the work reported previously by others and are not in complete accord with it. The results presented show that 2,2′-dimercaptodiethylsulphide is a promising analytical reagent.

The compound 2,2′-dimercaptodiethylsulphide (or 2,2′-thiodiethanethiol, hereafter referred to as TDT) has received only sparse attention as a possible analytical reagent. Two analytical applications have been reported to date. One of these involves the formation of the red Ni(II) complex as a sensitive and specific test for mustard gas[1] and the other involves the determination of nickel.[2] Because the compound is a liquid at room-temperature, its potential as a chelating extraction solvent has been recognized[3] but no such studies have yet been reported.

In the present study, we have further examined TDT as an analytical reagent and report, on the stability of its solutions to air oxidation over a wide pH range, its acidity in solution, its reactivity towards metal ions, the nature of its Ni(II) and Pd(II) complexes in solution, and on its potential as a reagent for nickel and palladium. With respect to the Ni(II) complex, our findings add substantially to those reported earlier.[2]

EXPERIMENTAL

Apparatus

pH Meter. Radiometer Type PHM 4C meter equipped with Radiometer glass (G 202B) and saturated calomel (K401) electrodes.

Spectrophotometry. Spectrophotometric measurements for the determination of nickel and palladium were made with a Hitachi Perkin–Elmer UV-VIS Spectrophotometer, Model 139. The cell compartment was kept at 25·0 ± 0·5°. Spectrophotometric measurements of TDT in the ultraviolet range and of its Ni(II) and Pd(II) complexes in solution were made with a Cary Model 14 recording spectrophotometer. High-quality 1-cm quartz cells were used for all measurements. *Molecular-weight Determinations.* Mechrolab Vapour Pressure Osmometer, Model 301A.

Reagents

All common laboratory chemicals were either analysed grade or of sufficient purity for the purpose intended. Distilled water passed through a mixed-bed ion-exchanger was used in all experiments.

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TDT. The commercially available compound (Aldrich) was purified by distillation under reduced pressure (nitrogen atmosphere). The boiling point was 135–136° at 10 mmHg (lit.,[2] 138°, 13 mmHg). The purified material was kept under nitrogen in glass-stoppered bottles stored in a refrigerator. The nitrogen atmosphere was replaced after every opening.

Dioxan. Reagent-grade 1,4-dioxan was purified as described elsewhere.[4]

1,2-*Dichloroethane.* Samples were redistilled and the fraction collected over the range 82·4–83·0° was used.

Benzil, recrystallized from ethanol (*m.p.* 93·8–94·5°).

Stock solution of Ni(II), 9·78 ± 0·02 × $10^{-3}M$. Prepared from the hydrated perchlorate and standardized by EDTA titration.[5] The EDTA solution was initially standardized against a standard Zn(II) solution prepared from pure zinc metal.[6]

Pd(II) stock solution (9·480 ± 0·007 × $10^{-3}M$). The solution contained 0·425 g of anhydrous palladium chloride, 0·29 g of sodium chloride and 0·20 ml of $12M$ hydrochloric acid in 250 ml. Heating was necessary for dissolution. The solution was standardized by PFHS as the dimethylglyoximate.[7]

Procedures

Stability of TDT in 50% v/v aqueous dioxan. Sufficient TDT was weighed out to allow preparation of solutions of known concentration (10^{-3}–$10^{-4}M$) in 50% v/v aqueous dioxan. Solutions were prepared at pH 6·0 (no buffer present), pH 9·8 (ammonia/ammonium chloride) buffer, and pH 13·4 (0·01M sodium hydroxide) and their spectra recorded over the range 220–320 nm (Fig. 1). The effect of time was studied at each pH value. At pH 6·0, a maximum soon developed at 250 nm and reached constant intensity after 165 hr. At pH 9.8, the absorbance at 235 nm decreased rapidly to a minimum while the absorbance at ~250 nm increased to a maximum. The changes were complete after 21 hr. At pH 13·4, the absorbance at 235 nm decreased to a constant value (~0·1) after 45 hr. Plots of absorbance *vs.* time (at specific wavelengths) allowed extrapolation to $t = 0$ (*i.e.*, time immediately after solution preparation) and provided corrected absorbance values for calculation of the following molar absorptivities (ε in l. $mole^{-1}.cm^{-1}$): at pH 6·0, $\varepsilon = 365$ (235 nm), 108 (250 nm); at pH 9·8, $\varepsilon = 1{\cdot}40 \times 10^3$ (235 nm); at pH 13·37, $\varepsilon_{max} = 1{\cdot}24 \times 10^4$ (235 nm).

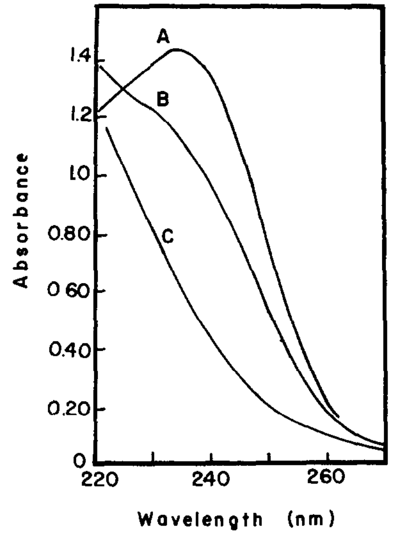

Fig. 1. Ultraviolet specta of TDT in 50% v/v aqueous dioxan 15 min after preparation of solution. A, pH 13·4 (1·2 × $10^{-4}M$); B, pH 9·8 (1·3 × $10^{-3}M$); C, pH 6·0 (1·7 × $10^{-3}M$).

The changes in the spectra with time reflect the relative rates of oxidation of the ligand in the various solutions. A qualitative estimate of the relative reaction rates was obtained by graphically evaluating the time ($t_{1/2}$) required for the initial absorbance, A_t (A at $t = 0$), to decrease to $A_{1/2} = 1/2(A_t - A_f)$ at pH 9.8 and 13.4 at 235 nm, and to increase to $A_{1/2} = 1/2(A_f - A_t)$ at pH 6·0 (250 nm). A_f is the (constant) final absorbance observed and it was assumed that oxidation was complete at this point. The results are discussed below.

Acid dissociation constants. The acid dissociation constants of TDT were determined both potentiometrically and spectrophotometrically in 50% v/v aqueous dioxan at 25° and ionic strength 0·1 (adjusted with sodium perchlorate). The potentiometric technique and procedure were essentially as described previously.[8] The correction factor for converting the pH-meter reading into [H^+] was −0·07. Because the two

pK_a values are not well separated, refined values were obtained by the least-squares fit of equation (4) in reference 8; the pK_a values obtained were 10·32 ± 0·01 and 11·43 ± 0·02.

The spectrophotometric procedure was a straightforward one in which the ε values (235 nm) at pH 6·0 and 13·4 were taken to be ε_{H_2A} and $\varepsilon_{A^{2-}}$, and ε_{HA^-} was assumed to be equal to $\frac{1}{2}\varepsilon_{A^{2-}}$.[9] Simple simultaneous equations involving first C_{H_2A} and C_{HA^-} as unknown pairs of concentrations at pH 9·76 and then C_{HA^-} and $C_{A^{2-}}$ at pH 12·02 were solved. Substitution into the K_a expression yielded the pK_a values 10·35 ±0·05 and 11·47 ± 0·04. All absorbance values were corrected to $t = 0$.

Reaction with metal ions. Tests for reactivity were made in test-tubes at three pH values by adding 0·4 ml of metal-ion solution (0·02*M*, prepared from the chloride, nitrate or perchlorate) and 0·4 ml of TDT solution (0·07*M*, in dioxan) to 10 ml of buffer solution. Each test was compared with a blank containing only the metal ion and buffer solution. The formation of a colour or precipitate was taken as a positive test for reaction. The results are summarized in Table 1. The following class (a) ions gave negative tests at all pH values: Mg(II), Sr(II), Y(III), La(III), Ce(III), Th(IV), U(VI), Ti(IV), Al(III).

Table 1. Reaction with metal ions

Ion	pH*				Colour§
	2·1	5·6	8·5	10·3	
Mn(II), Cr(III)	−	−	−	+	w,g
Co(II), Ni(II), Fe(II), Fe(III)	−	+	+	+	g–b,r,g,g
Ag(I), Cu(II)†, Pd(II), Cd(II), Hg(II)	+	+	+	+	w,w,o,w,w
Zn(II)	−	+	+	−	w
Rh(III)†, Pt(IV)†	+	+	+		o,b
Tl(I)		−	+		y
Pb(II), Bi(III)	−	+	+		y,y

* The pH values were fixed by appropriate concentrations of the following buffers: pH 2·1, H_2SO_4; pH 5·6, acetic acid/sodium acetate; pH 8·5, ammonium acetate/ammonia; pH 10·3, ammonium chloride/ammonia. A positive test is indicated by +, negative by −, and a blank signifies a test was not tried.

§ The colours designated are in the same order as the ions listed: r(red), o(orange), y(yellow), g(green), b(brown), w(white).

† With Cu(II) in excess, a mauve precipitate formed. With Rh(III) and Pt(IV), the reaction at room temperature was slow. For Rh(III), heating was required to obtain appreciable reaction.

Preparation of solid Ni(II) and Pd(II) complexes. Bis(2,2′-dimercaptodiethylsulphide)dinickel(II) was prepared from alkaline solution essentially as described by Harley-Mason.[1] The Pd(II) complex was prepared as follows: palladium(II) chloride ($1{\cdot}62 \times 10^{-3}$ mole) was dissolved with heat in 100 ml of water containing sodium chloride ($5{\cdot}20 \times 10^{-3}$ mole) and a few drops of concentrated hydrochloric acid. The brown solution was filtered to remove traces of undissolved material. To a solution containing TDT ($1{\cdot}61 \times 10^{-2}$ mole), 10 ml of 0·25*M* perchloric acid, 40 ml of water and 150 ml of dioxan, the Pd(II) solution was added over a period of 20 min. with stirring. An orange precipitate formed immediately and was washed by decantation with 50% v/v aqueous dioxan, filtered off, and washed with aqueous dioxan, ethanol and ether in succession. The compound was dried overnight *in vacuo* at 55° (yield, 52%).

The following results were obtained for elemental analysis. Calculated for $NiC_4H_8S_3$: C, 22·77%; H, 3·82%; 2, 45·58%; Ni, 27·83%. Found: C, 23·0%; H, 4·0%; S, 45·4%; Ni, 27·8%. Calculated for $PdC_4H_8S_3$: C, 18.57%; H, 3·12%; S, 37·18%; Pd, 41·13%. Found: C, 18·4%; H, 3·2%; S, 37·0%; Pd, 40·3%.[*]

Molecular-weight determinations were made with a vapour-phase osmometer calibrated with solutions of benzil in freshly-distilled 1,2-dichloroethane. It was necessary to protect the benzil solutions from sunlight to prevent photolysis, otherwise the calibration curves were not reproducible. For the nickel complex, the molecular weight obtained was 425 ± 7 (2 determinations). The calculated molecular weight for the dimer $Ni_2(C_4H_8S_3)_2$ is 422. Reliable estimates could not be obtained for the molecular weight of the Pd(II) complex, because of the very low solubility (0·2–0·3 mg/ml) in dichloroethane, but the results (650 ± 150) at least suggest the formation of a polymeric species. Magnetic susceptibility measurements (Gouy method) confirmed that both complexes are diamagnetic.

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[*] The low result for Pd was due to volatilization during ignition to Pd metal.

Ni(II) and Pd(II) complexes in solution. The formation of the Ni(II) and Pd(II) complexes was studied as a function of pH in 50% v/v aqueous dioxan at ionic strength 0·1 (adjusted with sodium perchlorate) and 25°. For the Ni(II) complex, the analytical concentrations of Ni(II) and TDT in the final solution were $5{\cdot}87 \times 10^{-4}$ and $3{\cdot}28 \times 10^{-3}M$ respectively; for the Pd(II) complex, the values were $9{\cdot}48 \times 10^{-5}$ and $8{\cdot}20 \times 10^{-4}M$. For solutions of the Ni(II) complex, the pH ranged from 2·3 to 12·4. The pH was adjusted by use of dilute sulphuric acid, acetic acid/acetate, ammonia/ammonium chloride or dilute sodium hydroxide solutions. For the Pd(II) complex, the pH range was 0-12·4; the low pH values were obtained by addition of 2·5*M* hydrochloric acid.

The spectra of all solutions were recorded over the range 300–600 nm. Typical spectra are shown in Figs. 2 and 3. Spectrum A, Fig. 2, is representative of the Ni(II) complex at pH values up to pH 7·3 (the solutions were red.) At high pH values (*e.g.*, 12·4, spectrum B), the spectrum was significantly different and the solution was yellow-orange. At pH 9·4, the spectrum (not shown) was intermediate in appearance. On standing overnight, the yellow-orange solutions turned red and the spectra changed accordingly. For the red Ni(II) complex, characteristic ε values (l.mole^{-1}.cm^{-1}) are: 1310 (378 nm); 1060 (505 nm); 1160 (414 nm). For the yellow-orange species, $\varepsilon_{max} = 740$ l.mole^{-1}.cm.$^{-1}$ at 463 nm.

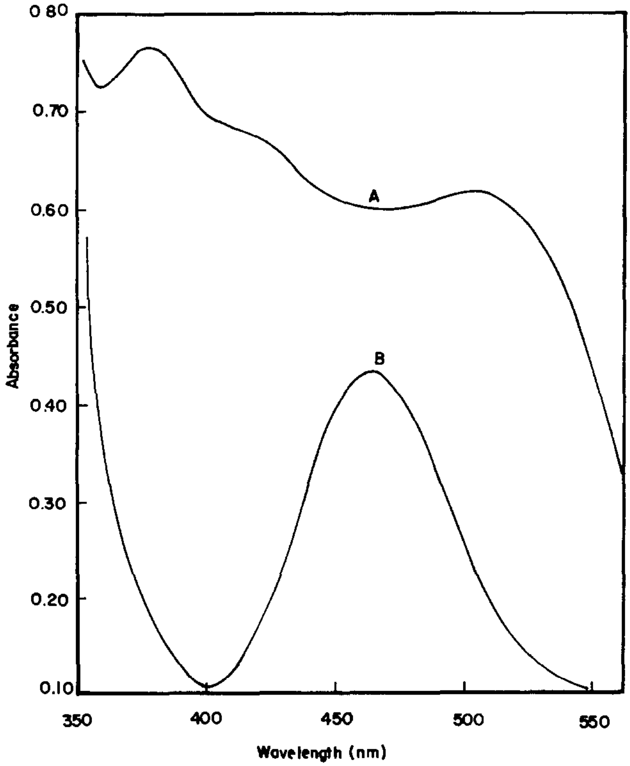

Fig. 2. Spectra of Ni (II)–TDT complex in 50% v/v aqueous dioxan, TDT : Ni ratio ~6 : 1. A, pH 6·6 (red solution); B, pH 12·4 (yellow-orange solution).

Spectrum B, Fig. 3, is typical of the Pd(II) complex for the pH range 1·0–7·8 (yellow-green solution). The spectra in strongly acid solution (spectrum A, deep yellow solution) and in alkaline solution (>pH 9, spectrum C, pale greenish-yellow) are also shown, together with the spectrum of palladium (II) chloride. Characteristic ε values (l. mole.$^{-1}$ cm^{-1}) are: at pH 0, $7{\cdot}81 \times 10^3$ (310 nm); pH 1·0–7·8, $7{\cdot}38 \times 10^3$ (340 nm); pH> 9, $5{\cdot}83 \times 10^3$ (335 nm).

The formation of the red Ni(II) complex and the greenish-yellow Pd(II) complex as a function of pH is shown in Fig. 4.

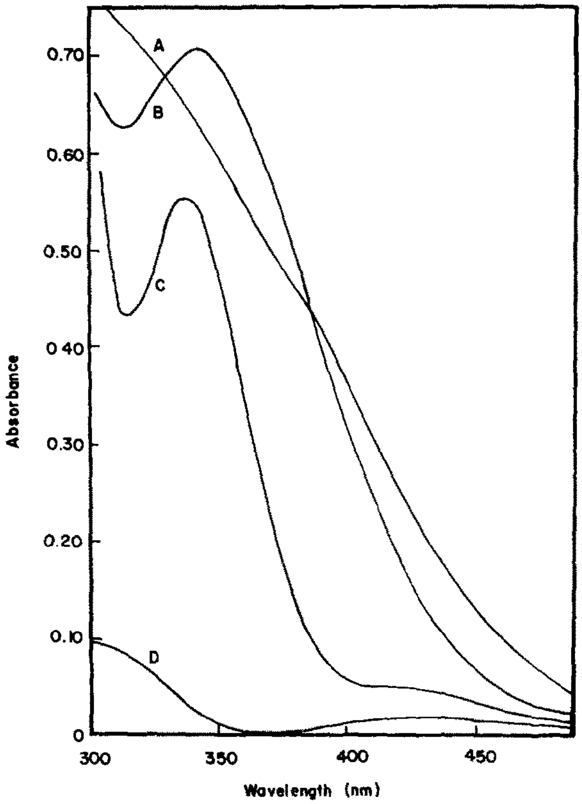

Fig. 3. Spectra of Pd(II)–TDT complex in 50% v/v aqueous dioxan, TDT : Pd ratio ~9 : 1. A, pH 0; B, pH 2·2; C, pH 12·4; D, $PdCl_2$ solution ($9{\cdot}48 \times 10^{-5}M$) at pH 2·1 (TDT absent).

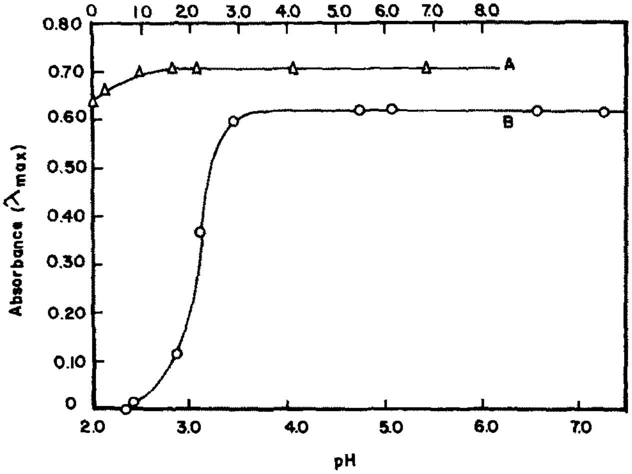

Fig. 4. Complex formation in 50% aqueous dioxan as a function of pH. A, Pd(II) complex, $\lambda_{max} = 340$ nm, TDT : Pd ratio ~9 : 1 (upper pH scale); B, Ni(II) complex, $\lambda_{max} = 505$ nm, TDT : Ni ratio ~6 : 1 (lower pH scale).

Extraction of the Ni(II) complex into 1,2-dichlorethane was studied as follows. Water and the appropriate buffer solution and 3·00 ml of the Ni(II) stock solution were placed in a 100-ml separatory-funnel (total volume of aqueous phase, 40 ml) and extracted with three 10-ml portions of $2{\cdot}0 \times 10^{-2}M$ TDT in 1,2-dichloroethane. Shaking for 1–2 min with each portion was sufficient. The aqueous phase was washed with a 10-ml portion of pure solvent and then the pH was measured. The organic extracts (red) were combined and diluted to 50 ml and the spectrum was recorded. The spectrum of the extracted complex was essentially as shown in spectrum A, Fig. 2, with small shifts (~5–10 nm) in the maxima. The dependence of the extraction on pH is given in Fig. 5. At pH 10·3, the aqueous phase was yellow after extraction; only repeated washing with pure solvent removed the yellow colour, imparting a pink colour to the organic phase. At all lower pH values, the aqueous phase was colourless after extraction and a single washing. Benzyl alcohol was also shown to be an effective extractant (Fig. 5).

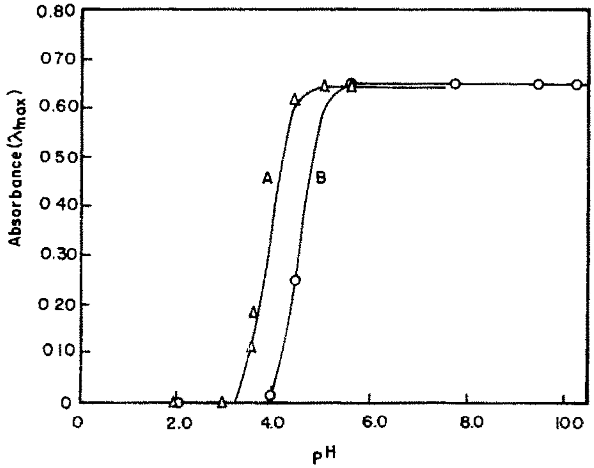

Fig. 5. Extraction of Ni (II) complex as a function of pH. A, benzyl alcohol, $\lambda_{max} = 508$ nm; B, 1,2-dichloroethane, $\lambda_{max} = 512$ nm.

The Pd(II) complex was only partially extracted into 1,2-dichlorothane, but extraction into benzyl alcohol was complete at pH 1·5 and higher. The aqueous phase consisted of appropriate volumes of 0·25M perchloric acid, 30 ml of water and 5·0 ml of $4{\cdot}74 \times 10^{-4}M$ Pd(II) solution. The organic phases (greenish yellow) were diluted to 50 ml. The spectra were identical to spectrum B, Fig. 3.

The composition of the Ni(II) complex was determined at pH 6·8 and 12·1, adjusted by an acetic acid/acetate buffer and 0·05M sodium hydroxide respectively. Five-ml portions of Ni(II) solutions ($5{\cdot}87 \times 10^{-3}M$) and varying volumes of dioxan solution of TDT ($2{\cdot}53 \times 10^{-2}M$) were diluted to 50 ml, and the absorbance was measured at 505 nm (negligible absorbance of TDT and free Ni(II)). The mole-ratio diagrams are given in Fig. 6. At pH 6·8 (curve A), a sharp break occurs at mole ratio = 1·08. At pH 12·1, the solutions were red up to a TDT : Ni ratio of 2·25 and the spectra were identical to A, Fig. 2; however, at high ratios (*e.g.*, 4·00, 6·00) the solutions were yellow-orange and the spectra were identical to B, Fig. 2. Overnight, the solutions became red and the spectra reverted to A.

The stoichiometry of the Pd(II) complex was studied at pH 2·3, adjusted with 0·25M perchloric acid. Five-ml portions of Pd(II) solution ($4{\cdot}74 \times 10^{-4}M$) and appropriate volumes of reagent solution ($7.97 \times 10^{-3}M$), water and dioxan were mixed to give a final volume of 50 ml. The spectra varied with mole ratio; with increasing mole ratio, the absorbance at 410 nm decreased by ~60% and that at 340 nm increased by ~20%. The absorbance at 340 and 410 nm was measured and plotted against pH (curves A and B, Fig. 7). The study was repeated in the absence of chloride ion [Pd(II) perchlorate was used in place of $PdCl_2$ and the stock solution contained no chloride]. At 340 nm, a curve identical to A was obtained; at 410 nm, the curve (C, Fig. 7) was similar to B.

Potentiometric titrations of the Ni(II) and Pd(II)–TDT systems in 50% v/v aqueous dioxan were made in the usual way.[10] The quantities of reactants used were $4{\cdot}89 \times 10^{-5}$ mole of Ni(II)/7.63×10^{-5} mole of TDT and $4{\cdot}78 \times 10^{-5}$ mole of Pd(II)/$3{\cdot}79 \times 10^{-4}$ mole of TDT. The formation of the Ni(II) complex began at ~pH 2·5; no precipitation occurred during the titration. Two protons per Ni(II) ion were released in complex formation. The Pd(II) complex formed and precipitated* on mixing of the reagents. Two protons

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*As discussed later, the solid complex is a 1:1 trimer.

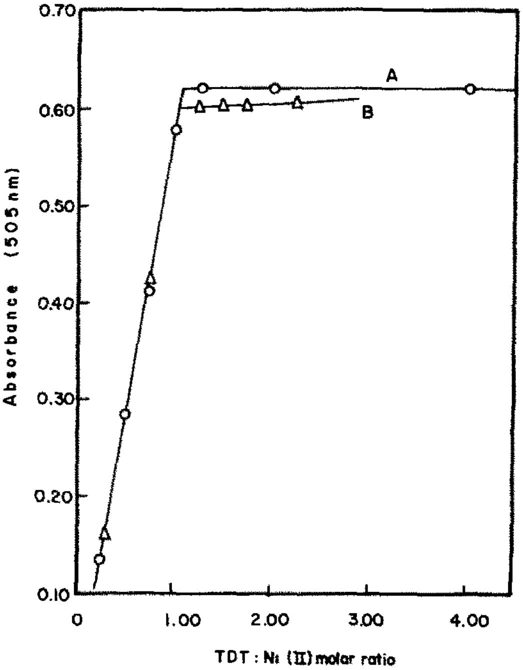

Fig. 6. Mole-ratio diagrams of TDT : Ni(II) system in 50% v/v aqueous dioxane. A, pH 6·8; B, pH 12·1.

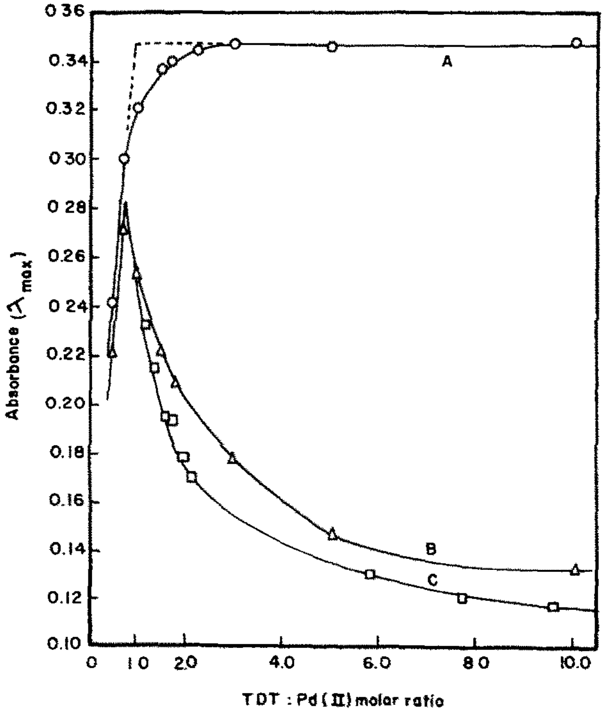

Fig. 7. Mole-ration diagrams of TDT : Pd(II) system in 50% v/v aqueous dioxan at pH 2·3: A, λ_{max} = 340 nm (chloride present or absent); B, λ_{max} = 410 nm (chloride present); C, λ_{max} = 410 nm (chloride absent).

per Pd(II) ion were released in acid solution. At pH ~ 8–9, an inflection was observed that corresponds to one additional proton per Pd(II). Nearly complete dissolution of the precipitate occurred in this pH range.

Investigation of analytical applications

Determination of nickel. A calibration curve for the determination of nickel was obtained as follows. Appropriate aliquotes of the Ni(II) stock solution to give amounts of Ni(II) ranging from 0·3 to 2·3 mg were placed in 100-ml separatory-funnels containing 10 ml of buffer solution (0·02*M* ammonia, 0·15*M* ammonium chloride) and diluted to 50 ml. The Ni(II) was then extracted with three 10-ml portions of a 1,2-dichlorethane solution of TDT (~2·5 × $10^{-2}M$). Each portion was shaken with the aqueous phase for 1–2 min and then drained through a glass-wool plug in the stem of the funnel. The residual aqueous phase was washed with one 10-ml portion of pure solvent. The organic phases were collected in a 50-ml flask and diluted to volume at 25·0°. The absorbance was measured at 512 nm against a solvent blank. The pH of the residual aqueous phase was 7·6 ± 0·2. The results yielded an excellent calibration plot; Beer's law was obeyed over at least the concentration range studied. The absorbance of the solutions remained constant for at least 40 hr.

Solutions containing 0·29, 1·15 and 1·72 mg of Ni(II) together with 0·5 mg of Pd(II) and 1·4 mg of Fe(III) were tested as follows. The pH of the aqueous solution was adjusted to 1·5–2·0 with 0·25*M* perchloric acid (~4–5 ml) and diluted to 50 ml. The Pd(II) was extracted with two 10-ml portions (shaking for 1–2 min) of a benzyl alcohol solution of the reagent ($10^{-2}M$). The aqueous phase was then washed with two 5-ml portions of benzyl alcohol followed by one 10-ml portion of 1,2-dichloroethane to remove residual alcohol. Aqueous ammonia (1 + 1) was added to the aqueous phase to precipitate Fe(III) and with the pH about 8, 10 ml of the buffer solution were added. The Ni(II) was extracted as before and the absorbance measured. The pH of the residual aqueous phase was 8·4 ± 0·3. The amounts of Ni(II) found were 0·29, 1·14 and 1·71 (±0·01) mg.

Determination of palladium. The absorbance of the Pd(II) complex was found to obey Beer's law by the following experiment. Aliquots (20·0–5·0 ml) of 0·06*M* hydrochloric acid and 25·0 ml of a dioxan solution of TDT (1·93 × $10^{-2}M$) were transferred by pipette into 50-ml volumetric flasks. Corresponding volumes (5·00–20·00 ml) of a Pd(II) solution (1·90 × $10^{-4}M$, 0·06*M* in hydrochloric acid were added. The amounts of Pd(II) taken ranged from 0·1 to 0·5 mg. The solutions were diluted to volume at 25·0° with 50% v/v aqueous dioxan and the absorbance measured at 340 nm against a solvent blank. The pH of the final solution was 1·67 ± 0·01. A plot of the results was linear and passed through the origin. The absorbance of the solutions remained constant for at least 15 hr.

The method above was applied to a solution known only to contain Pd(II) at a high concentration. This solution was diluted 50-fold and exactly 20 ml were taken for analysis. By reference to the calibration curve, the Pd concentration of the unknown was found to be 1·00 ± 0·01 mg/ml. Standardization of the same solution by the established procedure of homogeneous preciptation as the dimethylglyoximate gave 1·01 ± 0·00 mg/ml.*

The effect of the foreign ions Ni(II), Co(II) and Fe(III) was investigated. The quantities of all metal ions taken and results obtained are given in Table 2.

Table 2. Effect of Ni(II), Co(II) and Fe(III) on Pd(II) determination

Pd(II), *μg/ml* Taken	Found	Deviation %	Foreign ions present, *μg/ml*	Foreign ion : Pd molar ratio
6·05	6·04*	−0·2	Ni(23·0)	6·9
8·05	8·22	+2·1	Ni(34·5)	7·8
3·94	3·96*	+0·5	Ni(57·5)	26·4
6·05	6·05	0	Co(23·2)	6·9
5·91	6·05	+2·4	Co(23·2)	7·1
3·94	4·11	+4·3	Co(58·0)	26·6
6·05	6·05	0	Fe(16·9)	5·3
3·94	3·89	−1·3	Fe(67·6)	32·8
3·93	3·96	+0·8	Ni(11·5), Co(11·6)	5·3, 5·3
3·93	3·93	0	Ni(11·5), Fe(11·3)	5·3, 5·5
3·93	4·15*	+5·5	Cl(11·6), Fe(11·3)	5·3, 5·5
3·93	4·13	+5·1	Ni(11·5), Co(11·6), Fe(11·3)	5·3, 5·3, 5·5
5·91	6·31	+6·8	Ni(23·0), Co(23·2), Fe(16·9)	7·0, 7·1, 5·5
6·05	6·49	+7·3	Ni(23·0), Co(23·2), Fe(16·9)	6·9, 6·9, 5·3

* Average of two determinations.

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*This value was furnished by O. E. Hileman, McMaster University.

DISCUSSION

Stability of TDT

Segall *et al.* have reported that TDT and its chloroform solutions show no deterioration after twelve months when stored at room temperature in glass-stoppered bottles.[2] We have found that the purified reagent does not keep for such periods unless stored in a refrigerator under a dry nitrogen atmosphere. Under routine laboratory conditions, a white deposit forms after a few weeks. Solutions of the reagent (10^{-3}–$10^{-4}M$) in chloroform, petroleum ether and 1,4-dioxan are only moderately stable in routine use. For example, after two weeks the absorbance at 250 nm increased by about 8%. Because of the subsequent work in 50% v/v aqueous dioxan, the stability of the reagent in this solvent was studied more thoroughly. The mild oxidation of a mercaptan usually gives rise to the corresponding disulphide, characterized by a low-intensity, broad absorption band at about 250 nm.[11,12] This band was observed to develop when the reagent was kept at pH 6·0 and 9·8 and is strong evidence for air-oxidation of the dithiol to disulphide species. When reagent was kept at pH 13·4, the band was not observable, perhaps because a lower initial reagent concentration was used on account of the high absorbance at this pH, but the strong maximum of TDT at 235 nm was greatly reduced. The rate of oxidation is pH-dependent. The half-life at pH 6·0 is about 85 hr, 1 hr at pH 9·8 and 15 hr at pH 13·4 at the concentrations specified in Fig. 1. The pH-dependence of the rate of oxidation of mercaptans is complex and not well understood.[13]

In summary, TDT may be used in analytical applications in neutral 50% v/v aqueous dioxan solutions without special precautions against air-oxidation. In basic solutions, its use is more limited.

Acid dissociation constants

Because of rapid air-oxidation at about pH 10 in aqueous dioxan, the potentiometric titrations for the determination of the pK_a values of TDT were performed rapidly under an atmosphere of dry nitrogen. The pK_a values were confirmed spectrophotometrically. The acid dissociation constants of TDT have not previously been reported; the values reported here should prove to be useful in analytical studies.

Reaction with metal ions

TDT forms metal complexes with numerous metal ions (Table 1) and possesses no apparent selectivity beyond that expected for a ligand containing "soft" donor atoms.[14,16] Hence there is no reaction with the class (a) acceptors listed above. Reactions occur only at higher pH values with borderline acceptors [e.g., Mn(II), Cr(III)] while strong class (b) acceptors [*e.g.*, Pd(II), Ag(I), Cd(II), Hg(II)] react at low pH values. Ions with a d^{10} configuration [Ag(I), Cd(II), Hg(II), Zn(II)] form white insoluble complexes. The complex derived from Cu(II) (TDT in excess) is likely a Cu(I) complex since it is colourless, and oxidation of mercaptans by Cu(II) is well known.[17] The mauve complex that forms when Cu(II) is in excess may be a Cu(II) derivative of the disulphide or a complex containing copper in both oxidation states. Fe(II) and Fe(III) each react to give a green complex. Presumably, this is an Fe(II) complex since Fe(III) is known to oxidize mercaptans to disulphides.[13,18]

Ni(II) complex in solution

The formation of the red Ni(II) complex was complete in 50% v/v aqueous dioxan at about pH 4 (B, Fig. 4). Correspondingly, the extraction of Ni(II) with TDT into benzyl alcohol or 1,2-dichloroethane was quantitative at about pH 5.5 and 5, respectively (Fig. 5). Thus, both formation and extraction of the Ni(II) complex were complete at a much lower pH value than previously reported (above pH 10).[2] The stoichiometry at pH 6·8 was 1 : 1 and only one species existed in solution at all TDT: Ni molar ratios (0·25–4) investigated (A, Fig. 6). Elemental analysis showed the stoichiometry of the solid complex to be 1 : 1, as reported by others.[1,19,20] Also, since the complex in 1,2-dichloroethane was dimeric, as indicated by the molecular weight determination, it probably is dimeric in other solvents, such as 50% v/v aqueous dioxan. This is consistent with the dimeric structure of the solid, found by X-ray analysis.[19–22]

In alkaline solution (pH 12), the red 1 : 1 complex formed at TDT: Ni ratios of up to 2·25 (B, Fig. 6). At higher ratios, the solution became yellow-orange (*e.g.*, B, Fig. 2). This dependence on pH and TDT: Ni ratio is consistent with the addition of another ligand molecule to yield a complex with a ligand: metal ratio >1. This addition was not detected by potentiometric titration but it could have been obscured by titration of the excess of reagent in the same pH region. The yellow-orange complex was still extracted, however, as the 1 : 1 red complex into the organic phase.

The observation that solutions initially yellow-orange became red on standing overnight is probably the result of lowering of the reagent: Ni ratio through oxidation of the reagent. Appreciable oxidation of the reagent (see above) would occur in the pH region (9·4–12·4) over which the yellow-orange complex was observed. Thus, as the reagent is oxidized, the complex would be converted into the red 1 : 1 complex. The formation of the yellow-orange complex may account for the 2 : 1 stoichiometry reported by Segall *et al.*[2]

Pd(II) complex in solution. Formation of the Pd(II) complex was complete at about pH 1·5 (A, Fig. 4) in the presence of a large excess of TDT. Extraction into benzyl alcohol was also quantitative at this pH value. The molecular-weight data, although imprecise, suggest the formation of a dimer or trimer in solution. In an X-ray structural study,[19,23] the solid was found to be trimeric (and extremely insoluble in common solvents); thus the species in solution is probably a trimer. Elemental analysis confirmed the 1 : 1 stoichiometry of the trimeric solid, but as discussed below, the stoichiometry of the species in solution could not be obtained with certainty.

In solution, appreciable amounts of more than one complex can exist, depending on the pH and TDT: Pd(II) molar ratio. Figure 3 shows the dependence of the spectra on pH, at a mole ratio of ~9 : 1. At pH < 1·0, the solution was (deep) yellow (A). In the pH range 1–7, a yellow-green complex was formed (B). In alkaline solution (pH > 9), a further change occurred (C) which probably corresponds to the addition of one hydroxyl ion per Pd(II) ion. This change is consistent with the potentiometric titration, which showed that in the pH range 8–9 one proton was released per Pd(II) ion. Since at this point the 1 : 1 trimer which had precipitated earlier in the titration redissolved, the species in solution can be reasonably formulated as $[Pd_3L_3OH_3]^{3-}$.

The deep yellow and yellow-green species can also be produced by varying the TDT: Pd(II) molar ratio at constant pH. Thus, at pH 2·3 and mole ratio <1, the solution was deep yellow and absorption maxima* at 340 and 410 nm were obtained. At values >3, the solution was yellow-green and the absorbance at 340 nm was increased while that at 410 nm decreased. At mole ratio above 3 (and up to at least 60), the absorbance at 340 nm was constant (A, Fig. 7). The absorbance at 410 nm attained a maximum value at a mole ratio of

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* TDT does not absorb at 340 and 410 nm and the absorbance of uncomplexed Pd(II) is negligible.

~0·8† and then decreased to a constant value (B, Fig. 7). This behaviour suggests the presence of at least two distinct species in equilibrium in solution. The interconversion of the species is not essentially dependent on chloride ion, since similar behaviour was observed in the absence of chloride (Fig. 7).

Potentiometric titration of the TDT: Pd(II) system at mole ratio ~12 showed that 2 protons were released per Pd(II) ion in acid solution. This is consistent with the formation of a 1:1 complex. Since no evidence has been produced for the formation of a higher complex either in solution or solid, the yellow-green species is probably a 1:1 species. (The orange 1:1 trimer also yielded a yellow-green solution when dissolved in aqueous dioxan.) These observations can then be explained on the basis that with increasing mole ratio, the yellow (polymeric) species with a TDT: Pd(II) ratio <1 (*e.g.*, $Pd_3L_2{}^{+2}$, $Pd_4L_3{}^{2+}$, *etc.*) were converted into the 1:1 trimeric species. Interestingly, extrapolation of the linear segments of curve A (Fig. 7) yields a TDT: Pd(II) ratio of 1.0. The break in curve B at ~0.8 suggests a ratio <1 for the yellow species. However, these observations must be treated with caution since the mole-ratio method has limited application when more than one species is present in solution.

For the determination of Pd(II) with TDT as outlined above and discussed below, Fig. 7 is essential. It illustrates that absorbance measurements at 340 nm must be made on solutions containing a large excess of TDT (> 10-fold). At such high excesses, the yellow species are essentially fully converted into the 1:1 complex; the constant residual absorbance at 410 nm (Fig. 7) is due primarily to the 1:1 yellow-green complex.

Analytical applications

Determination of nickel. The investigation of the solution properties of the Ni(II) complex resulted in an analytical procedure somewhat improved over that reported by Segall *et al.*[2] For example, the extraction of Ni(II) into 1,2-dichloroethane is best carried out in the pH range 6–9. The upper pH limit circumvents the formation of the yellow-orange species in the aqueous phase, which is rather difficult to extract. Also, the interference from Pd(II) is easily overcome by prior extraction of the ion (even in large amount) from strongly acid solution into benzyl alcohol with TDT. The use of one reagent for both the removal of Pd(II) and for the Ni(II) determination is convenient. Interference from Fe(III) can be avoided by adjusting the pH of the aqueous phase to about 8, after extraction of Pd(II) from acid solution. The Fe(III) is not extracted into 1,2-dichlorethane and remains in the aqueous phase as the hydroxide.

Segall *et al.*[2] did not investigate the effect of many class (b) metal ions on the nickel determination. Since these ions react strongly with the reagent (Table 1), they would be expected to interfere. However, the Pt(IV) complex (although it forms slowly at room temperature) can be extracted from acid solution into benzyl alcohol together with the Pd(II). Also, the white complexes of Cu(I) [from the reduction of Cu(II)], Zn(II), Ag(I), Cd(II) and Hg(II), are insoluble in 1,2-dichloroethane (and also in benzyl alcohol), and should not be extracted along with the Ni(II) complex. Even if the white complexes were extracted, they would not absorb at 512 nm. It would be necessary, of course, to use large excesses of reagent in the organic phase if several ions that react with the ligand were present.

Segall *et al.* found that in addition to the ions discussed above the following cations and anions do not interfere: alkali and alkaline earth metals, Pb(II), Sn(II), Mn(II), Sb(III),

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† Spectra of solutions with mole ratio <0·5 could not be recorded because of the formation of a black suspension, indicative of reduction to Pd metal.

Cr(III), Al(III), Cl^-, NO_3^-, CH_3COO^-, SO_4^{2-}, and PO_4^{3-}. The improved procedure presented in this work should not alter the effect of these ions. Co(II) interferes in the nickel determination. It must therefore be removed, perhaps by the method suggested by Segall *et al.*[2]

TDT shows considerable promise as an analytical reagent for nickel. In addition to its simplicity, the method is accurate and precise over the concentration range studied (6–45 ppm, with respect to the aqueous phase before extraction). Future investigations on a variety of samples are necessary to assess the high degree of selectivity suggested above.

Determination of palladium. The spectrophotometric determination of Pd(II) with TDT, as far as developed in the present work, is accurate and precise over the concentration range studied (2–10 ppm in the final solution), and appears to have advantages over several existing spectrophotometric methods[24] for palladium. Unlike most other reagents for palladium, TDT does not absorb in the visible region. Also, Fe(III) and Ni(II), which are common interferences, do not interfere even when present in relatively large amounts (Table 2). Furthermore, Co(II), which also commonly interferes, may be present at least up to a Co/Pd ratio of 7. If the molar ratio is large (*e.g.*, Co/Pd = 27), the error becomes appreciable (4.3%). Except when Co(II) and Fe(III) occur together, only small errors are produced when combinations of Ni(II), Co(II) and Fe(III) are present with Pd(II). The simultaneous presence of Co(II) and Fe(III) leads to positive errors of about 5–7%. Larger errors are incurred if the absorbance measurements are not made promptly after preparation of the solution. When Co(II) is present in the absence of Fe(III), the solutions are stable for at least 3 hr. The interference may be due to the formation of stable Co(III) complexes[25] in acid solution through oxidation of Co(II) by Fe(III).

Examination of the data in Table 1 permits speculation on the effect of other foreign ions. Since Cr(III), Mn(II), Fe(II), Zn(II), Pb(II) and Tl(I) do not react with TDT at pH 2, they should not interfere in the Pd(II) determination—provided that the respective aquated ions do not absorb significantly at 340 nm. Ions of definite class (a) behaviour such as the alkali and alkaline earth metals, Al(III), the lanthanides and actinides do not react with the reagent and as a result, should not interfere.

The metals that normally interfere most seriously in palladium determinations are typically class (b) such as Pt, Ir, Au, Rh, Ag and Hg.[24] The reaction of Pt(IV) and Rh(III) with TDT is slow at pH 2 and room temperature and may permit the Pd(II) determination in their presence. The d^{10} ions, Cu(I), Ag(I), Cd(II) and Hg(II), form insoluble white compounds in strongly acid solution and can be removed by filtration before the dilution to volume. Thus, interference from several class (b) ions can perhaps be avoided by a combination of favourable rate and solubility effects. The potential of TDT as a reagent for the spectrophotometric determination of palladium cannot be fully realized until these possibilities have been investigated.

Many methods exist for the spectrophotometric determination of palladium. In a comprehensive review,[24] 65 such methods have been listed, making justification for a new method for palladium difficult. A survey of the methods reported in this review reveals that nearly all are subject to interferences from common metals such as chromium, iron, cobalt, nickel and copper, and from noble metals, particularly platinum. In a few methods, common anions such as chloride interfere. Only one method (involving *p*-nitrosodiphenylamine) seems relatively free from these interferences. About six methods are promising but more restrictive. Another method with promise, not mentioned in the review, involves 4,4′-bis(dimethylamino)thiobenzophenone.[26] Thus, a new method for palladium would be warranted if interferences from first-row transition and noble metals were minimal. The present work shows that TDT could fulfil this criterion and further studies to apply this promising reagent should be made.

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Zusammenfassung—Die Verbindung 2,2′-Dimercaptodiäthylsulfid wurde bezüglich der Stabilität ihrer Lösungen gegen Oxidation an der Luft, ihrer Säurestärke, ihrer Reaktivität gegenüber Metallionen, der Natur ihrer Komplexe mit Ni(II) und Pd(II) in Lösung sowie ihrer Verwendbarkeit bei der Bestimmung kleiner Mengen Ni(II) und Pd(II) untersucht Die Arbeiten am Nickel(II)-Komplex erweitern früher von anderen Autoren mitgeteilte Ergebnisse und stehen nicht vollkommen mit diesen in Einklang. Die vorgelegten Ergebnisse zeigen, daß 2,2′-Dimercaptodiäthylsulfid ein vielversprechendes analytisches Reagens ist.

Résumé—On a étudié le composé 2,2′-dimercaptodiéthylsulfure quant à la stabilité de ses solutions à l'oxydation par l'air, sa force acide, sa réactivité vis-à-vis des ions métalliques, la nature de ses complexes Ni(II) et Pd (II) en solution, et sa possibilité d'application au dosage de petites quantités de Ni (II) et Pd (II). Les études sur le complexe Ni (II) développent le travail rapporté antérieurement par d'autres et ne sont pas en accord complet avec lui. Les résultats présentés montrent que le 2,2′-dimercaptodiéthylsulfure est un réactif analytique prometteur.

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STRIPPING VOLTAMMETRY WITH COLLECTION AT A ROTATING RING–DISK ELECTRODE

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Summary—A new electroanalytical technique is described, called "stripping voltammetry with collection." The technique involves the use of a rotating ring–disk electrode and is an improvement over traditional voltammetric stripping at a single electrode in that it is characterized by a lower limit of detection and that the period of deposition before stripping can be shorter. The use of the technique is illustrated by the determination of $10^{-10}M$ Ag^+ in $0{\cdot}1M$ H_2SO_4 by use of a ring–disk electrode having a disk electrode constructed of glassy carbon and a ring electrode constructed of platinum.

The electroanalytical technique known as stripping voltammetry at a single electrode has been shown to be useful for the determination of many species present in aqueous solutions at very low concentrations. The theory and application of stripping voltammetry have been adequately reviewed.[1–3] In principle, the technique involves the accumulation of the substance sought in the form of a metal or a sparingly soluble compound on the surface of the electrode in the test solution. The accumulation may proceed for a long period of time so that a significant quantity of material is deposited even though the concentration of the species in the bulk of the solution is very low. Following the accumulation, the potential of the electrode is varied (scanned) in such a manner that the deposit undergoes electrochemical dissolution (stripping), and the current–potential (I–E) or current–time (I–t) curve for the process at the electrode is recorded. The curves are characterized by a sharp current peak in the potential region where the dissolution occurs. The area of the stripping peak can be related to the quantity of the original deposit and to the analytical concentration of the species sought in the test solution. The technique has a high sensitivity, especially when the accumulation is continued for a long period of time at a high rate of stirring. Stripping voltammetry has been applied to the analysis of very dilute solutions (below $10^{-8}M$) in biological, semiconductor, metallurgical, and environmental research, and for the determination of impurities in highly purified chemicals.[2] As an example of the applicability of the technique for trace analysis, Fedosuva and Stromberg[4] used liquid–liquid extraction followed by stripping voltammetry for the determination of bismuth at $5 \times 10^{-11}M$ concentrations.

In practice, the limit of detectability by voltammetric-stripping analysis is set by the uncertainty in the determination of the current in the electrode due to processes other than the stripping of the desired species. These "background" processes include (*i*), charging of the electrical double-layer at the electrode–solution interface during the variation of the

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applied potential, (*ii*), oxidation and/or reduction of impurities in the solution or adsorbed at the surface of the electrode, and (*iii*), electrochemical reactions of the electrode itself, *e.g.*, formation or dissolution of oxide on a platinum electrode. The background current is usually estimated by drawing a smooth curve under the stripping peak, superimposed on the portions of the I–t curve on each side of the peak. This, of course, requires an estimation by the analyst and is a great source of uncertainty since the background current is usually a function of the potential of the electrode and is, therefore, not constant during the recording of the I–t curve. The problem is not solved by recording the I–t curve for the voltammetric scan when no deposition has been allowed, because the background currents are not usually reproducible from one scan to the next unless the treatment of the electrode before the recording of the I–E curves is identical. Furthermore, a large variation in the background current caused by change in applied potential dictates the use of a low sensitivity on the recorder. As a result, long deposition times are necessary if perceptible stripping peaks are to be obtained.

In this paper we describe the use of a rotating ring–disk electrode (RRDE) for the determination of concentrations lower than the limit of detection for stripping voltammetry at a single electrode. The technique is called stripping voltammetry with collection (SVWC). In principle, SVWC requires the accumulation and stripping of the species sought, at the disk electrode, according to the accepted procedures for stripping voltammetry at a single electrode. The potential of the ring electrode is fixed at a value such that deposition of the species sought is limited by convection and diffusion and the current–time curve for the ring electrode (I_r–t) is recorded during the voltammetric stripping of the deposit from the disk electrode. A fraction of the species stripped from the disk electrode is carried by convection and diffusion to the ring electrode where it is redeposited. Because the potential of the ring electrode is constant during the voltammetric stripping, the background current for the redeposition is nearly constant. Consequently, the background can be compensated electronically and the I_r–t curve obtained with a very high sensitivity used on the recorder. The collection of very small quantities of species stripped voltammetrically from the disk electrode still produces significant peaks on the I_r–t curve even when the stripping peak on the I–t curve at the disk electrode is nearly imperceptible against the background current.

The instantaneous current for the deposition of a chemical species from a solution onto the disk electrode of an RRDE by a convection/diffusion-limited process, I_d, is related to the concentration of the species in the bulk of the solution, C_b, by equation (1),[5] where n and F have their usual electrochemical significance, ω is the angular velocity of the electrode rotation,

$$I_d = 0{\cdot}62nF\pi R_1{}^2\omega^{1/2}\nu^{-1/6}D^{2/3}C_b \tag{1}$$

ν is the kinematic viscosity of the solution, and D is the diffusion coefficient for the species in solution. The total charge passed at the disk electrode due to deposition, Q_d, during the deposition period, t_{dep}, is given by equation (2).

$$Q_d = \int_0^{t_{dep}} I_d \, dt \tag{2}$$

If ω and C_b remain constant during t_{dep}, equation (2) can be written as equation (3). The charge passed at the ring electrode due to collection and deposition of the species produced by voltammetric stripping at the disk electrode, Q_r is given by equation (4). The negative sign is due

$$Q_d = I_d \cdot t_{dep} \tag{3}$$

$$Q_r = -NQ_d$$

$$= -NT_{dep}0{\cdot}62nF\pi R_1{}^2\omega^{1/2}\nu^{-1/6}D^{2/3}C_b$$

to the fact that the current for the deposition is of opposite polarity to that for the dissolution. In equation (4), N is the fraction of the species produced at the disk, which can be collected at the ring. N is called the collection efficiency and can be calculated from the respective radii of the disk and ring electrodes.[6]

No reference has been found in the chemical literature to the quantitative analysis of solutions for species at trace levels by using the technique of SVWC at an RRDE. Several studies were reported in which the ring electrode of an RRDE was used for detection and electrochemical characterization of small quantities of chemical species produced at the disk electrode. Bruckenstein and Tindall[7,8] studied the electrochemical behaviour of monolayer and submonolayer deposits of copper and silver on a platinum electrode in acidic media. Johnson, Napp and Bruckenstein[9] detected small amounts of Pt(II) produced at the anodized platinum disk electrode of an RRDE during the reduction of the surface oxide. Johnson and Bruckenstein[10] used the ring electrode of an RRDE to determine small quantities of HOBr produced by oxidation of submonolayer quantities of bromide previously adsorbed at the platinum disk electrode from 1·0*M* sulphuric acid. Johnson[11] extended the study of the electrochemistry of halides adsorbed on platinum electrodes in 1·0*M* sulphuric acid and determined the adsorption and desorption of submonolayer quantities of iodide and iodine on the disk of an RRDE.

Kopanica and Vydra[12] used voltammetric-stripping analysis at a rotating, glassy-carbon disk electrode for the determination of Ag^+ in acidic, neutral, and alkaline media. They reported that Ag^+ could be determined "with sufficient accuracy" at a concentration of $1 \times 10^{-9}M$ provided the deposition time was sufficiently long. They did not show the I–t curve for that concentration. Here we report the use of stripping voltammetry with collection for the determination of down to $1{\cdot}0 \times 10^{-10}M$ Ag^+ in 0·1*M* sulphuric acid. The distinct advantages of using SVWC at an RRDE are discussed.

EXPERIMENTAL

Notation

Subscripts d and r to symbols for current, I, and potential, E, represent the corresponding quantities at the disk and ring electrodes, respectively. Superscripts a and c used with E_d designate the anodic and cathodic limits of potential scan. The potentials of the disk and ring electrodes used for the deposition of silver are $E_{d,dep}$ and $E_{r,dep}$, respectively. Cathodic current is considered a positive and anodic current a negative quantity. All electrical currents are given in microamperes (μA) and quantity of charge in microcoulombs (μC). All electrode potentials were measured and are given in volts *vs.* the saturated calomel electrode (SCE).

Instrumentation

The ring–disk electrode used was from Pine Instrument Co. of Grove City, Pa. The electrode had a glassy-carbon disk and a platinum ring. The pertinent geometric parameters,[6,13] were: $R_1 = 0{\cdot}379$ cm, $R_2 = 0{\cdot}399$ cm, $R_3 = 0{\cdot}421$ cm, $\alpha = 0{\cdot}168$, $\beta = 0{\cdot}211$, and $N = 0{\cdot}170$. The synchronous rotator used was Model PIR from Pine Instrument Co. The rotator has nine speeds between 400 and 10,000 rpm. The cell was constructed of quartz with a fritted-quartz membrane separating the main compartment from the chamber for the platinum counter-electrode. Glassware was cleaned with hot nitric acid and rinsed thoroughly with triply distilled water. The reference electrode was a Beckman SCE in electrical contact with the solution through a quartz capillary.

The electronic control circuitry was constructed with use of operational amplifiers according to Bruckenstein's[13] and modification[14] to the disk circuit, but instead of use of a potentiometric input for the recording of current in the ring electrode, as indicated by Fig. 1 of Ref. 13, the recorder was driven by the output of a difference amplifier which measured the difference in the signals at the outputs of amplifiers F-2 and A-2. All resistors used for measurement of current were standardized by the Physics Instrument Services of Iowa State University and all voltages were measured with instruments calibrated against sources standardized by the Physics Instrument Services. The X-Y recorder was a Plotomatic 815 from Bolt, Beranek and Newman, Inc., of Santa Ana, Cal. The areas of collection peaks were determined by integration of the original curves with a Keuffel and Esser Compensating Polar Planimeter.

Reagents

All solutions were made up in triply distilled water prepared with a demineralization after the first distillation, and the second distillation being made from alkaline permanganate. The supporting electrolyte was $0{\cdot}1M$ sulphuric acid prepared from Mallinckrodt Reagent Grade sulphuric acid. Test solutions of Ag^+ were prepared by addition to the supporting electrolyte of aliquots of a $0{\cdot}00100M$ stock solution of silver nitrate prepared from Baker Analyzed Reagent. The stock solution was stored in a polyethylene bottle with the exterior painted black.

Pretreatment of the electrode

The ring–disk electrode was polished at the start of the research with Buehler Handimet 600 strips followed by 30-μm and 6-μm Buehler AB Metadi Diamond on nylon lubricated with Buehler Metadi Fluid. The electrode was washed carefully with detergent on a cotton swab and rinsed thoroughly with distilled water after each step in the polishing procedure. Before each day of research, the electrode was polished with 1-μm diamond dust. To remove particles of platinum embedded in the glassy-carbon disk during previous stages of polishing and to prevent transfer of platinum from the ring to the disk during this last stage in polishing, the electrode was rotated at 400 rpm and the polishing cloth moved radially from the centre of the rotating electrode. No portion of the polishing cloth was used twice. The surface of the electrode was then cleaned as described above. An I_d–E_d curve was obtained after the polishing to confirm the absence of platinum on the disk electrode. The absence of platinum was verified when a peak for reduction of platinum oxide was not observed on the cathodic potential sweep following anodization.

The rotating electrode was then lowered into the test solution and deaeration with dispersed nitrogen begun. E_d was cycled for 10 min between $E_d^c = -0{\cdot}40$ V and $E_d^a = +1{\cdot}20$ V at a rate of 5·0 V/min with E_r maintained at $+0{\cdot}80$ V.

Impurity in test solutions

The supporting electrolyte was found to contain traces of Ag^+ varying from $5 \times 10^{-10}M$ to $5 \times 10^{-9}M$. The source of the impurity was first thought to be the silver-loaded graphite used for making electrical contact to the upper portion of the metallic cylinder on which the ring electrode was mounted in the usual construction of the RRDE. This contact is directly above the cell for the rotator used. A large disk of Teflon, having an outer diameter greater than the opening of the cell through which the RRDE was inserted, was drilled to an inner diameter just sufficient to permit the Teflon disk to be slipped onto the Teflon shroud of the RRDE. Rubber O-rings were placed on the shroud of the RRDE above and below the Teflon disk to hold it in place. In use, the RRDE was lowered into the cell so that the Teflon disk was just slightly above the opening of the cell and did not rub on the cell during rotation. With this protection, it was impossible for particles of the ring contact to fall into the solution. No decrease in the level of the impurity of Ag^+ occurred when the Teflon disk was used and it was concluded that the contact for the ring electrode was not the source of the impurity. The use of the protecting Teflon disk was continued, however. The sulphuric acid was thought not to be the source of the trace impurity since addition of more acid directly to the test solution did not result in an increase of the level of the impurity. Other procedures were used for cleaning the glassware with no effect on the level of impurity and the glassware was concluded not to be the source. The water for preparing solutions was analysed before the demineralization stage in the procedure for purification and the content of Ag^+ was $5 \times 10^{-8}M$. It was concluded that the water was the source of the impurity. Triply distilled water from one other source in the department was analysed and found to contain Ag^+ as an impurity at approximately $2 \times 10^{-9}M$.

Experimental procedure

The procedure for the determination of Ag^+ by SVWC at the RRDE was as follows. The cyclic scan of E_d for the pretreatment of the disk electrode was halted at the desired value of $E_{d,\,dep}$, and E_r was stepped to the desired value of $E_{r,\,dep}$ for collection of Ag^+. With the expiration of t_{dep}, E_d was scanned anodically at a rate of 5·0 V/min and the I_r–E_d curve recorded. Since the rate of scan for E_d was constant, the I_r–E_d curve was also an I_r–t curve. The background current during the collection was estimated by drawing a smooth curve superimposed on the I_r–E_d curve on either side of the collection peak, and the area of the peak was determined and Q_r calculated. The procedure was repeated for $t_{dep} = 0{\cdot}00$ min and the area of the corresponding peak determined. A small amount of silver was deposited at the disk electrode at $t_{dep} = 0$ min with the deposition occurring (*i*), during the cathodic portion of the cyclic scan of E_d before reaching the value of $E_{d,\,dep}$, and (*ii*), during the time that E_d was being scanned anodically from $E_{d,\,dep}$ to the value where stripping commenced. The value of Q_r was corrected by subtracting the area of the collection peak for $t_{dep} = 0{\cdot}00$ min from the area for the non-zero value of t_{dep}. For $t_{dep} = 3{\cdot}00$ min, the correction was approximately 3% for a rate of scan of E_d equal to 5·0 V/min. Further correction of the value of Q_r was made when preparing a calibration plot. The value of Q_r obtained for the impurity of Ag^+ in the supporting electrolyte was subtracted from the values of Q_r obtained after the intentional additions of standard Ag^+.

Standard additions of the stock solution of Ag^+ to the supporting electrolyte were made with 2·000-ml and 0·2000-ml micrometer syringes.

RESULTS AND DISCUSSION

Current–potential curves

I–E curves for glassy-carbon electrodes in mineral acids are shown and discussed in Ref. 15 and curves for platinum electrodes are discussed in Ref. 9. They will not be further described here. I_d–E_d and I_r–E_d curves obtained by using SVWC at an RRDE for $1{\cdot}00 \times 10^{-6}M$ Ag^+ are shown in Fig. 1. Silver deposited at the disk electrode was electrochemically stripped at $E_d > 0{\cdot}1$ V with the peak of the anodic current at approximately 0·25 V. In comparison to the stripping peak on the I_d–E_d curve, the collection peak on the I_r–E_d curve is shifted slightly to a more positive value of E_d. This is the result of the use of a

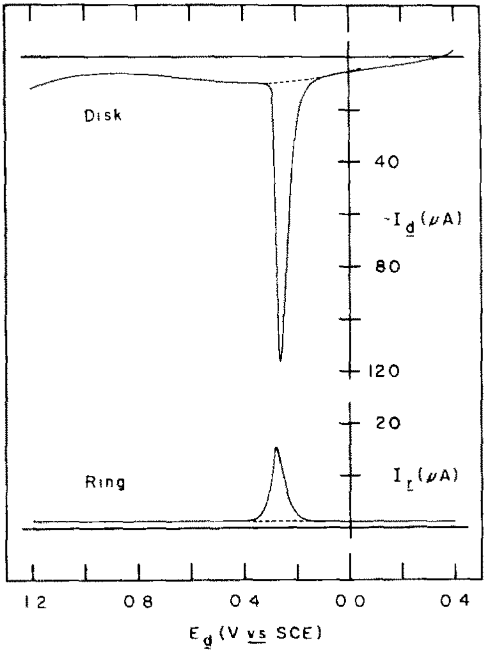

Fig. 1. I_d–E_d and I_r–E_d curves for stripping voltammetry with collection in $1{\cdot}00 \times 10^{-6}M$ Ag^+. $t_{dep} = 5{\cdot}00$ min, $E_{d,\,dep} = -0{\cdot}400$ V; $E_{r,\,dep} = 0{\cdot}000$ V, $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$, rate of anodic scan of $E_d = 5{\cdot}0$ V/min; ———— *I–E* curves, ------------ constructed baselines.

high rate of anodic scan of E_d (5·0 V/min) and a low rate of rotation of the RRDE (400 rpm). A finite amount of time is necessary for species produced at the surface of the disk electrode to be transported by convection and diffusion to the surface of the ring electrode. Consequently, the peaks in the currents for stripping and collection do not coincide. For a concentration of $1{\cdot}00 \times 10^{-6}M$, the contribution to Q_d and Q_r from the impurity of Ag^+ in the supporting electrolyte was negligible. From the values of the areas of the stripping and collection peaks, Q_d and Q_r were calculated to be 71·5 and 11·3 μC, respectively. On the basis of these values, the experimental value of N was calculated to be 0·158. Both the stripping and collection peaks for high concentrations of Ag^+, such as illustrated by Fig. 1, are sufficiently distinct in comparison to the background currents for both Q_d and Q_r to be used for an accurate calculation of $C_{b,\,Ag^+}$.

To determine the *I–E* curve for the electrodeposition of silver at the glassy-carbon disk electrode, SVWC was performed in $1{\cdot}00 \times 10^{-6}M$ Ag^+ for varying values of $E_{d,\,dep}$ with $E_{r,\,dep} = 0{\cdot}000$ V. The values of Q_r are plotted in Fig. 2 as a function of $E_{d,\,dep}$ for $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$. The value of $E_{1/2}$ for the deposition is approximately 0·03 V. The standard reduction potential for the Ag^+/Ag couple is 0·55 V *vs.* SCE. The moderate irreversibility of the deposition of Ag does not prevent successful application of SVWC since values of $E_{d,\,dep} < -0{\cdot}3$ V appear to be sufficiently cathodic for the deposition to occur at a rate limited by convection and diffusion. A value of $E_{d,\,dep} = -0{\cdot}400$ V was used for all subsequent determinations.

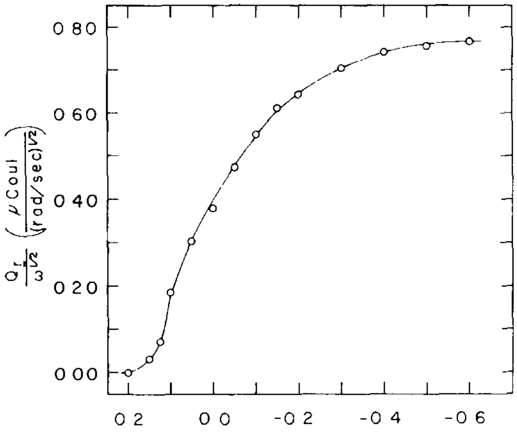

Fig. 2. *I–E* curve for electrodeposition of Ag on a glassy-carbon disk electrode. $C_{b,\,Ag^+} = 1{\cdot}00 \times 10^{-6}M$, $E_{r,\,dep} = 0{\cdot}000$ V *vs.* SCE, $t_{dep} = 2{\cdot}00$ min, $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$, rate of anodic scan of $E_d = 5{\cdot}0$ V/min.

To determine a value of $E_{r,\,dep}$ at which deposition of silver at the ring electrode occurs at a rate limited by convection and diffusion, SVWC in $1{\cdot}00 \times 10^{-6}M$ Ag^+ was repeated for various values of $E_{r,\,dep}$. The plot of Q_r *vs.* $E_{r,\,dep}$ is shown in Fig. 3 for $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$. The value of $E_{1/2}$ for the deposition at the platinum ring electrode is approximately 0·27 V. The value of Q_r is not zero for 0·8 V > $E_{r,\,dep}$ > 0·4 V. The deposition of silver at a platinum electrode at underpotentials has been investigated and discussed by Bruckenstein

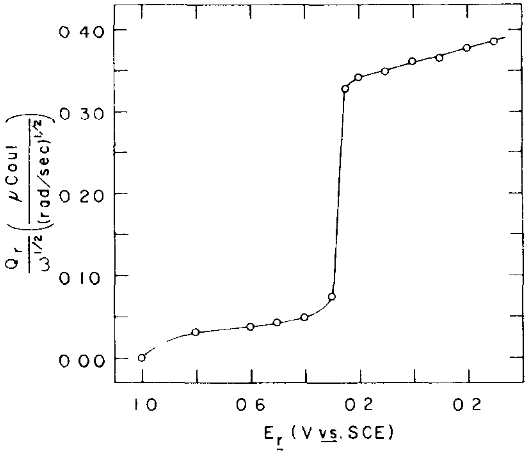

Fig. 3. *I–E* curve for electrodeposition of Ag on platinum ring electrode. $C_{b,\,\mathrm{Ag}^+} = 1{\cdot}00 \times 10^{-6}M$, $E_{\mathrm{d,\,dep}} = -0{\cdot}400$ V *vs.* SCE, $t_{\mathrm{dep}} = 2{\cdot}00$ min, $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$, rate of anodic scan of $E_{\mathrm{d}} = 5{\cdot}0$ V/min.

and Tindall.[7,8] The deposition of silver is more reversible at the ring electrode than at the glassy-carbon disk electrode and a value of $E_{\mathrm{r,\,dep}} = 0{\cdot}000$ V was used for all determinations.

Verification of equation (4)

According to equation (4), it is predicted that Q_{r} should be a linear function of t_{dep}. Corrected values of Q_{r} were obtained for SVWC in $1{\cdot}00 \times 10^{-6}M$ Ag for $0{\cdot}50 \text{ min} \leq t_{\mathrm{dep}} \leq 5{\cdot}50$ min and did in fact give a good linear plot with a slope of 4.4 μC/min for $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$.

To determine the effect on Q_{r} of changes in the value of $\omega^{1/2}$, SVWC was performed in $1{\cdot}00 \times 10^{-6}M$ Ag$^+$ for $6{\cdot}47 \text{ (rad/sec)}^{1/2} \leq \omega^{1/2} \leq 32{\cdot}4 \text{ (rad/sec)}^{1/2}$. The corrected values of Q_{r} plotted *vs.* $\omega^{1/2}$ gave a straight line which intersected the origin in agreement with equation (4).

Q_{r} is not predicted to be dependent on the rate of scan of E_{d} used during the process of electrochemically stripping the deposit of silver from the disk electrode. A corrected value of $Q_{\mathrm{r}} = 0{\cdot}84$ for SVWC in $1{\cdot}00 \times 10^{-6}M$ Ag$^+$ was observed for scan rates between 2 and 9 V/min. The results are consistent with equation (4).

Variation of $C_{\mathrm{b,\,Ag^+}}$

SVWC was performed for $1{\cdot}00 \times 10^{-10}M \leq C_{\mathrm{b,\,Ag^+}} \leq 1{\cdot}00 \times 10^{-6}M$. The concentration values were calculated on the basis of standard addition and values of Q_{r} were corrected as already described. The plot of Q_{r} *vs.* $C_{\mathrm{b,\,Ag^+}}$ on a log-log scale is a straight line in agreement with equation (4). The determinations of Q_{r} for $C_{\mathrm{b,\,Ag^+}} < 10^{-9}M$ were performed at a time when the blank was advantageously low (approximately $5 \times 10^{-10}M$). Several days later a fresh supporting electrolyte was prepared for which the blank was approximately $2 \times 10^{-10}M$. Values of the area of the collection peak for five determinations of the blank had an average relative deviation of 25%. Values of the area of the collection peak for five determinations following the addition of $1{\cdot}0 \times 10^{-10}M$ Ag$^+$ had an average relative deviation of 7·4%.

The diffusion coefficient for Ag^+ in 0·1*M* sulphuric acid was calculated by using equation (4) and the results previously obtained and found to be $1{\cdot}29 \times 10^{-5}$ cm²/sec, in good agreement with the value of $1{\cdot}30 \times 10^{-5}$ cm²/sec found by Johnson[16] for 0·1*M* potassium nitrate medium.

Comparison of SVWC with stripping voltammetry at a single electrode

The effect of the background current in limiting the application of stripping voltammetry at a single electrode was discussed in the introductory paragraphs. The possibility of applying SVWC at an RRDE for the determination of concentrations lower than those amenable to voltammetric stripping at a single electrode is illustrated by the I_d–E_d and I_r–E_d curves shown in Fig. 4. These curves were obtained for $6{\cdot}0 \times 10^{-9}M$ Ag^+. The large anodic peak on the I_d–E_d curve is due to background processes and not the voltammetric dissolution of a deposit. The small shoulder at about 0·2V is due to the stripping of the silver deposit. Even though the sensitivity is relatively high on the scale used for recording the I_d–E_d curve, no possibility exists of accurately determining the area of the stripping peak. The background current at the ring electrode is much more independent of E_d than is the background current at the disk electrode. Consequently, the I_r–E_d curve was recorded with a very high sensitivity. The collection peak is very distinct and integration of the peak can be performed accurately.

The rapid change of the background current on the I_r–E_d curve for $-0{\cdot}4\ V < E_d < 0{\cdot}0\ V$ is due to electronic instrumentation and not a consequence of the production of any electroactive species at the disk electrode. Proper alignment of the electronic circuit is described in

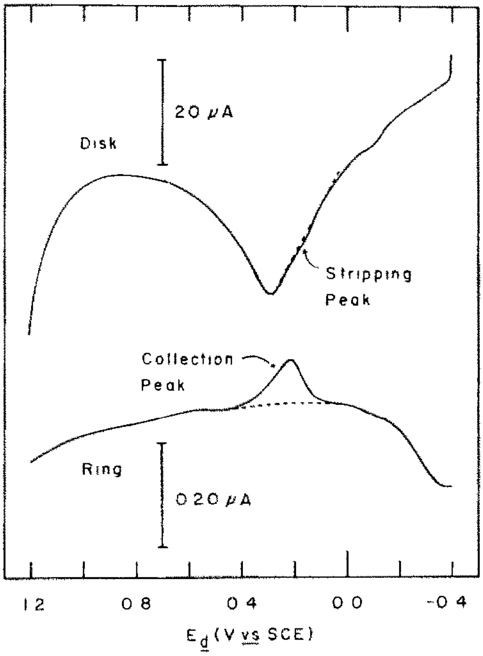

Fig. 4. I_d–E_d and I_r–E_d curves for $6{\cdot}0 \times 10^{-9}M$ Ag^+.
$E_{d,dep} = -0{\cdot}400$ V *vs.* SCE, $E_{r,dep} = 0{\cdot}000$ V *vs.* SCE, $\omega^{1/2} = 6{\cdot}47$ (rad/sec)$^{1/2}$, $t_{dep} = 10{\cdot}0$ min, rate of anodic scan of $E_d = 5{\cdot}0$ V/min; ——— *I–E* curves, ············ constructed baselines.

Ref. 13 and involves adjustment of resistor R_4 so that E_r does not change while E_d is scanned. Proper alignment is essential, particularly if it is desired to measure very small electrical currents in the ring electrode. Even with maximum care in alignment we found it impossible to prevent a small change in E_r (1–3 mV) while scanning E_d in the vicinity of 0·0 V. The small fluctuation in E results in background current as shown in Fig. 4.

Conclusions

The applicability of an RRDE for decreasing the already dramatically low detection limits for analyses based on stripping voltammetry has been demonstrated. There are at least two additional advantages of SVWC at an RRDE over the conventional method at a single electrode.

First, the time of analysis is greatly decreased because Q_r can be determined accurately even though the quantity of deposit accumulated is very small. This allows use of SVWC for routine analysis without the need for irritatingly lengthy depositions.

Secondly, the difficulties in simultaneous determination of two or more metallic species resulting from formation of intermetallic compounds at the electrode surface may be largely circumvented. This follows since the maximum coverage of the electrode by the deposit need never approach a complete monolayer and, therefore, the chance of inter-element reactions is greatly reduced or eliminated.

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Zusammenfassung—Ein neues elektroanalytisches Verfahren wird beschrieben und "inverse Voltametrie mit Sammlung" genannt. Es verwendet eine rotierende Ring–Scheiben-Elektrode und stellt gegenüber der traditionellen inversen Voltametrie an einer einzelnen Elektrode insofern eine Verbesserung dar, als es eine niedrigere Nachweisgrenze besitzt und daß die Abscheidungszeit vor dem Wiederauflösen kürzer sein kann. Die Anwendung des Verfahrens wird am Beispiel der Bestimmung von 10^{-10} M Ag^+ in 0·1 M H_2SO_4 gezeigt. Dabei wird eine Ring-Scheiben-Elektrode mit Scheibenelektrode aus glasigem Kohlenstoff und Ringelektrode aus Platin verwendet.

Résumé—On décrit une nouvelle technique électroanalytique, appelée "voltammétrie de dissolution avec collection". La technique comprend l'emploi d'une électrode rotative à disque-anneau et est une amélioration par rapport à la dissolution voltammétrique traditionnelle sur une seule électrode en ce sens qu'elle est caractérisée par une limite de détection inférieure et que la période de dépôt avant dissolution peut être plus courte. L'emploi de la technique est illustrée par le dosage d'Ag 10^{-10} *M* en H_2SO_4 0,1 *M* par l'emploi d'une électrode rotative à disque-anneau ayant une électrode à disque construite en carbone vitreux et une électrode annulaire en platine.

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MASS SPECTROMETRIC STUDY OF THE DETERIORATION OF POLYSTYRENE-BASED ION-EXCHANGERS

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Summary—A mass spectrometric study of the aging effects in polystyrene-based ion-exchangers has been made. Fragments in the *m/e* range 10–70 were examined and attributed to OH^+, H_2O^+, CO^+, CO_2^+, supplemented by SO^+ and SO_2^+ from sulphonic-acid cation-exchangers. Ion-current intensities were found to be dependent on the state of the resin.

Cation- and anion-exchangers based on copolymers of styrene and divinylbenzene are frequently found to contain fragments which are detrimental to certain applications.[1–3] The fragments are unlikely to be introduced during the manufacture of the exchangers, but side-reactions occurring at that time may lead to their subsequent production. Time-dependent deterioration is readily observable from periodic washing of the resin and examination of the wash-liquids.[3,4] The fragments thus released show structural similarity to the resin and have properties associated with electrolytes although non-electrolytes could also be present. The processes which eventually results in fragmentation, modify the constitution of the ion-exchange beads. It has been reported[5] that a cation-exchanger of the sulphonic-acid type may have up to 5% of its exchange capacity represented by carboxylic acid groups. Direct evidence for the presence of carboxyl groups has not been reported to date. Nevertheless trace metal-ion distribution studies[6,7] with cation- and anion-exchangers support the view that a secondary cation-exchange capacity exists even in the highest quality commercial resins.

In order to obtain information throwing light on the origin of the additional exchange capacity and the nature of the reactions leading to eventual fragmentation, a mass spectrometric study has been made of a range of polystyrene-based ion-exchangers and related substances.

EXPERIMENTAL

Materials

Commercially available resins were used in this study. They were obtained from the Permutit Co. Ltd., London, the Rohm and Haas Co., Philadelphia and the Dow Chemical Co., Midland, Michigan. Samples of each were dried in air at 80° for 24 hr. Portions (about 10 g) of the resins were placed in separate glass columns, converted into the hydrogen or chloride form by the passage of 300 ml of 2*M* hydrochloric acid, washed copiously with distilled water and dried over phosphorus pentoxide at 25°. Divinylbenzene (DVB) 8% cross-linked polystyrene was kindly made available by The Permutit Co. Ammonium toluene-*p*-sulphonate, laboratory reagent grade, was obtained from British Drug Houses Ltd., Poole, England.

Apparatus

Mass spectra were obtained with a G.E.C.-A.E.I. MS 902 mass spectrometer employing an electron energy of 70 eV and source temperatures in the range 140–180°. An *m/e* range from 10 to 70 was examined at a resolution of 2500. The probe temperature to which the samples were subjected was generally in the range 140–250°.

A precise mass analysis of certain prominent peaks was done with the aid of a "trial and error" type of computer programme. The maximum deviation permitted in the assignment of a test formula to an experimental *m/e* value was 5 ppm. Calculations were performed on a PDP8/E computer.

RESULTS AND DISCUSSION

Results are presented in Figs. 1–5 in which relative intensities of ion current on a common scale are plotted against *m/e*. The spectra of the sulphonic-acid cation-exchangers have peaks at *m/e* values of 17, 18, 28, 44, 45, 48, 50, 64 and 66 (Figs. 1–3). The peaks at *m/e*-17 and 18 are due to the species OH^+ and H_2O^+ respectively. Examination revealed the presence of a doublet at *m/e*-28, the major and minor components of which are attributable to CO^+ and N_2^+ respectively. Consideration of precise masses led to the conclusion that the peak at *m/e*-44 is due to CO_2^+ and that at *m/e*-45 to the fragment $C_2H_5O^+$. The peaks at *m/e*-48 and 50 are due to SO^+; they occur in the

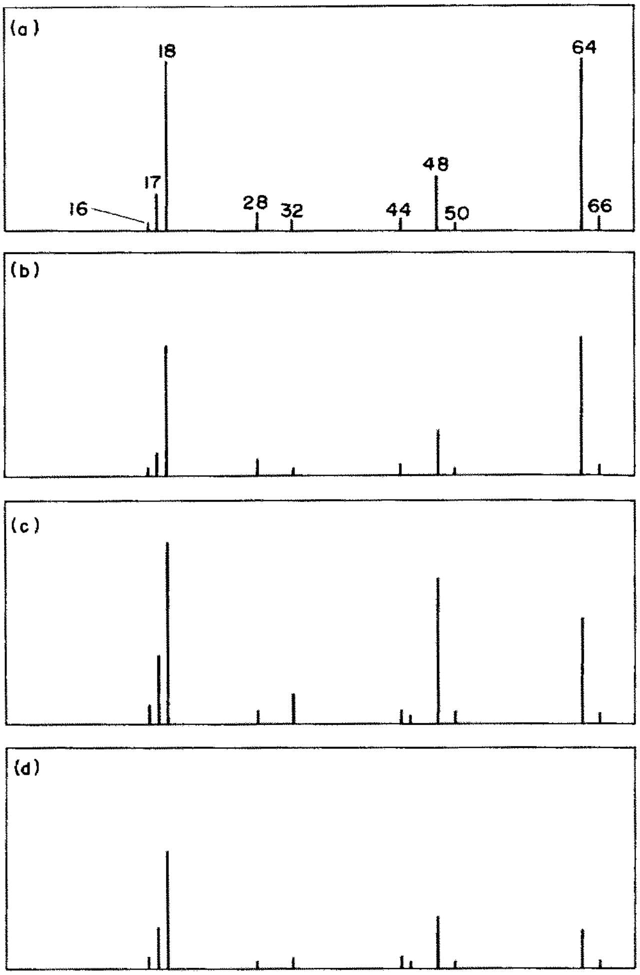

Fig. 1. Mass spectra for Zeo-Karb 225 (SRC series) exchangers. (*a*) 1%, (*b*) 2%, (*c*) 4–5%, (*d*) 12% DVB cross-linking.

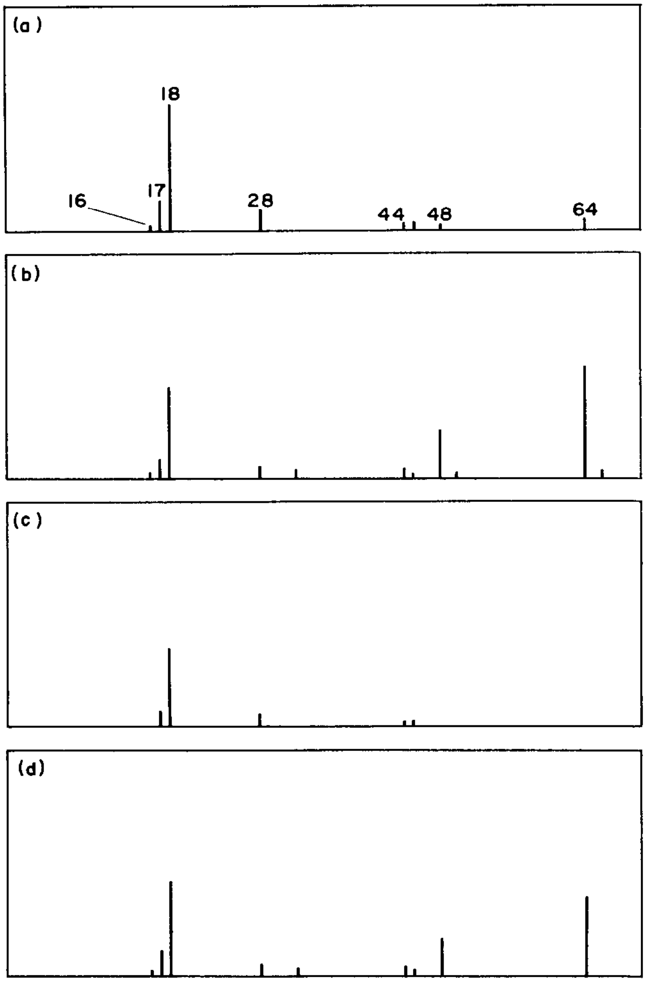

Fig. 2. Mass spectra for Zeo-Karb 225 (SRC series) exchangers. (*a*) 1%, (*c*) 2% cross-linking after conditioning (*b*) 1%, (*d*) 2% cross-linking, after three months storage.

intensity ratio expected from typical natural isotopic abundances for ^{32}S and ^{34}S. The peaks at *m*/*e*-64 and 66 are due to SO_2^+.

In Fig. 1 spectra are reproduced for cation-exchangers of the sulphonic-acid type taken from the shelf and dried at 80°. An increase in the degree of cross-linking causes a steady decrease in the intensity of peaks at *m*/*e*-28 and 64 but similar trends are not observed for ion currents at other masses. A comparison of the spectra in Fig. 1*a* with those in Fig. 2*a* and in Fig. 1*b* with those in Fig. 2*c* shows the effect of careful conditioning of the resin; all the peaks from the conditioned samples are considerably reduced except those due to water. Changes in the spectra due to aging of a resin sample are illustrated in Fig. 2. It is seen from Fig. 3 that resin samples carefully freed from water-soluble fragments, (*e.g.*, Amberlite IR 122), and converted into the sodium form, gave very "clean" spectra after two years' storage in amber bottles.

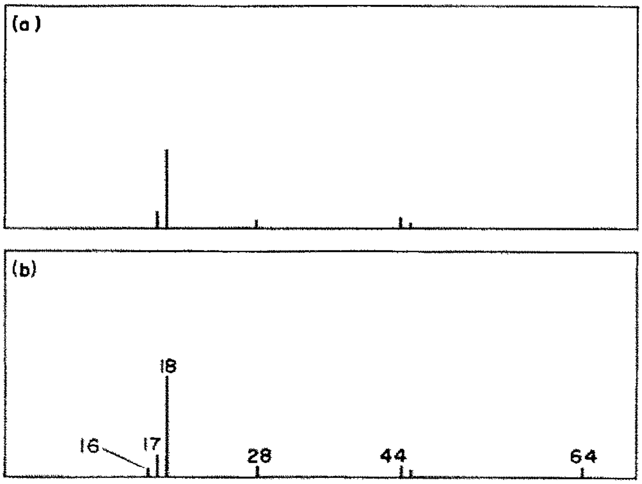

Fig. 3. Mass spectra of (*a*) Amberlite IR 122 (10% cross-linking) and (*b*) IR 124 (12% cross-linking) after two years storage.

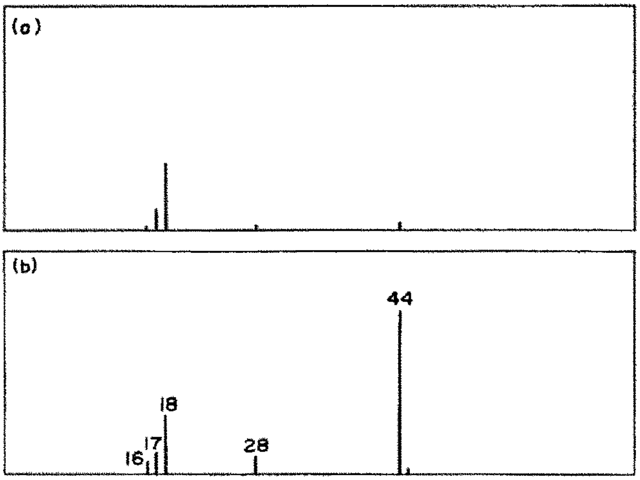

Fig. 4. Mass spectra of Zeo-Karb 226 (SRC 47) at probe temperatures of (*a*) 150° and (*b*) 195°.

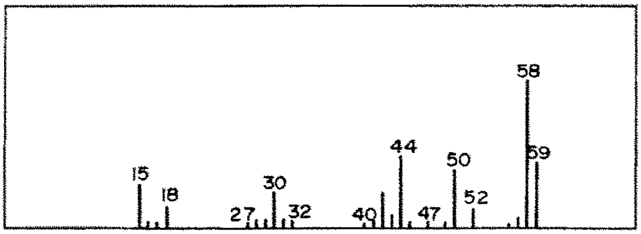

Fig. 5. Mass spectrum of aged De-Acidite FF (SRA 71).

The presence of the peak at m/e-44 in most of the spectra is noteworthy and experiments were performed in an attempt to establish its origin. The spectrometer background in this region was very low. A spectrum was obtained for ammonium toluene-*p*-sulphonate; a peak was not observed at m/e-44. This rules out the possibility that CO_2 could originate from "cracking" and "reforming" processes in the resin samples. Analyses of the doublets at m/e-28 eliminate the possibility that the CO_2 is derived from the atmosphere, at least for the cation-exchangers in the hydrogen form. The CO_2 must therefore arise from the resin framework or fragments from it. Spectra were obtained at two different probe temperatures (Fig. 4) for a cation-exchanger having carboxylic-acid exchange groups. Each spectrum has peaks at m/e-28 and 44, which may be due to decarboxylation. At the higher probe temperature they are very intense relative to those from other resin samples.

The spectrum for a sample of rather old (several years) anion-exchanger nominally in the chloride form, dried at 80° but otherwise untreated, had a characteristic peak-pattern which was nevertheless quite different from that of the cation-exchangers (Fig. 5). A very prominent peak at m/e-44 was attributed to carbon dioxide derived from the atmosphere. This was confirmed by the effervescence produced by the addition of hydrochloric acid and by chemical testing of the gas evolved. [Precise mass measurements indicated clearly that the peak (Fig. 5) at m/e-44 was due to CO_2^+ and not, for example, to $(CH_3)_2N^+$ although the latter was observed at higher probe temperatures.] Treatment of the resin with dilute hydrochloric acid, followed by washing with water and drying, reduced the peak height considerably but did not altogether eliminate it. In view of the apparent tendency of the resin in the chloride form to take up atmospheric carbon dioxide a categoric interpretation of the origin of this residual peak would not be justified. Other evidence, however, would support the view that carboxyl groups are present.

The structure of polyacrylic acids with DVB cross-linking is different from that of polystyrene-based sulphonic-acid exchangers. Fragmentation induced naturally, and thermal decomposition patterns, will not necessarily be exactly the same. In the latter, carboxyl groups may reside on the aromatic nucleus, or be formed by oxidative cleavage of the aliphatic "backbone" of the polymer, especially at points where cross-linking occurs. Carboxyl groups could arise[8] from oxidation of ethyl groups introduced during the formation of the resin in ethylstyrene, a common contaminant[9] of commerical DVB. It is also possible that divinylbenzene becomes incorporated into the polymer chain at one end, leaving a readily oxidized ethylenic group. Some carboxyl groups are undoubtedly introduced at the time of sulphonation[5,8] but careful choice of sulphonating conditions is claimed[5] to reduce such oxidation considerably.

It has been found that for a cation-exchanger having sulphonate functional groups, the distribution ratio at constant ionic strength of a carrier-free radioactive cation depends on the pH of the solution.[6,7] This behaviour is also observed for DVB cross-linked polystyrene beads and for strong base (quaternary ammonium) anion-exchangers.[6] (A unifunctional strong acid or base exchanger would be expected to give a distribution ratio independent of pH in the absence of cation hydrolysis.) It is explicable if carboxylic acid groups are present and the size of the additional exchange capacity created above the threshold pH can be assessed by suitably designed loading experiments. Evidence available from mass spectrometric and exchange distribution studies is therefore consistent with the presence of carboxyl groups on polystyrene-type exchangers. This interpretation would explain the retention of traces of rare-earth metal ions by an anion-exchanger and the proposed[10] separation of ^{140}La from ^{140}Ba.

The appearance of SO^+ and SO_2^+ in the spectra of aged resins but not in those of recently washed resins would indicate that the sulphur-containing groups on the polymer matrix are quite stable relative to those on the fragments. Examination of the peaks resulting from these ions in the spectra taken at suitably chosen probe temperatures would permit a rapid means of assessing qualitatively the general condition of a batch of sulphonic-acid type resin. Information can be obtained on thermal stability of a resin by variation of the probe temperature of the spectrometer.

Acknowledgement—The authors wish to record their gratitude to Mr. R. B. Turner who has been responsible for the operation of the mass spectrometer.

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Zusammenfassung—Die Alterungseffekte in Ionenaustauschern auf Polystyrolbasis wurden massenspektrometrisch untersucht. Fragmente mit m/e = 10–70 wurden überprüft und OH^+, H_2O^+, CO^+ und CO_2^+ zugeordnet. Dazu kamen SO^+ und SO_2^+ bei Kationenaustauschern mit Sulfonsäuregruppen. Die Ionenstromintensitäten hingen vom Zustand des Harzes ab.

Résumé—On a effectué une étude spectrométrique de masse des effets de vieillissement dans les échangeurs d'ions à base de polystyrène. On a examiné les fragments dans le domaine m/e 10–70 et les a attribués à OH^+, H_2O^+, CO^+, CO_2^+ complétés par SO^+ et SO_2^+ des échangeurs de cations acide sulfonique. On a trouvé que les intensités de courant d'ions dépendent de l'état de la résine.

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EMISSION SPECTROMETRIC DETECTION OF METAL CHELATES SEPARATED BY GAS CHROMATOGRAPHY

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Summary—An emission spectrometric detector is used in the determination of metal acetylacetonates. Spectra are excited in the plasma of a 2450 MHz electrodeless discharge. Measuring the intensities of the atomic emission lines of aluminium, beryllium and chromium after gas chromatography provides a highly sensitive and selective method for the determination of the acetylacetonates of these metals. Detection limits are 100 ng for aluminium, 0.01 ng for beryllium and 1 ng for chromium. An analytical procedure is proposed for beryllium down to 10 ppm in aluminium.

During the past decade, studies have been made of the gas chromatography of volatile metal chelates[1,2] and it has been successfully used for inorganic analysis.[3,4] Many workers have employed the electron-capture detector for metal fluorinated β-diketonates because of its exceptional sensitivity to halogenated organic compounds. This detector, however, lacks selectivity for metal chelates, and it responds to a variety of organic compounds with polar functional groups. Juvet and Durbin[5] suggested the flame photometric detector as a more selective detector for metal chelates, but its sensitivity is not satisfactory for trace analysis. Recently, Wolf *et al.*[6] employed gas chromatography-mass spectrometry in the determination of chromium and beryllium at the picogram level. The emission spectrometric detector was devised by McCormack *et al.*[7] and applied to the analysis of organic compounds containing sulphur, phosphorus and halogens.[8] It was also used to detect mercury compounds,[9] but a report of its application to the determination of metal chelates has not been found in the literature. The present study was initiated to explore the applicability of emission spectrometry in a microwave-powered inert-gas plasma to the determination of volatile metal chelates separated by gas chromatography. Detection of acetylacetonates of aluminium, beryllium, chromium, copper, iron and vanadium, and the application to the determination of traces of beryllium in aluminium were investigated.

EXPERIMENTAL

Instrumentation

The apparatus and operating conditions in this study are summarized in Table 1. The thermal conductivity detector was removed from the gas chromatograph and a discharge tube (quartz capillary) was connected directly to the outlet of the column. To prevent the effluent from condensing in the inlet portion of the discharge tube, this was heated to about 200° with a small nichrome-wire heater. The light emitted from the discharge was focused by means of a quartz lens ($f = 80$ mm, magnification = 1) on the entrance slit of a monochromator. The discharge tube was positioned horizontally (perpendicular to the slit), because the spectral emission was not uniform along the discharge.[10] The discharge was initiated by means of a Tesla coil.

Table 1—Apparatus and operating conditions

Gas chromatography	Hitachi KGL-2.
Column	Stainless-steel tubing: 4 mm i.d., 72 cm long, packed with glass microbeads (60–80 mesh) coated with 0·5% SE-30.
Column temperature	160°.
Injection port temperature	200–210°.
Carrier gas	Argon (99·99%), flow-rate of 150 ml/min unless otherwise stated.
Spectrometer	Nippon Jarrell-Ash JE-50E, 0·5-m Ebert-mounting scanning monochromator with 1180 rulings/mm grating and Hamamatsu TV R-106 photomultiplier. Reciprocal linear dispersion of 16 Å/mm.
Slit-width	20 μm.
High-voltage power supply	Hamamatsu TV, HTV-C447.
Amplifier and recorder	Toa Dempa PM-18C and EPR-2T.
Microwave generator	Ito Chotampa KTM-150, 2450 MHz, operated at an anode current of 55 mA (~50 W output, stabilized electronically).
Discharge tube	Quartz capillary: 1·6 mm i.d., 4·2 mm o.d., 25 cm long.
Microwave cavity	Tapered rectangular type with a slot to accept the discharge tube (NBS No. 1 type).

Reagents

Metal acetylacetonates were purchased from Wako Pure Chemical Ind. [Al(III), Be(II)], Tokyo Kasei Kogyo [Cr(III), V(IV)] and Nakarai Chemicals [Cu(II), Fe(III)], and were used without further purification. The column packing (SE-30 on glass microbeads) was obtained from Nippon Kuromato Ind.. Standard aluminium and beryllium solutions were prepared by dissolving 99.999% pure aluminium metal and 99% pure beryllium metal in *aqua regia* and hydrochloric acid, respectively, and diluting to appropriate concentrations with water.

Operating procedure

The metal acetylacetonates were dissolved in chloroform and the solutions were introduced into the gas chromatograph with a 10-μl microsyringe. Sample sizes ranged from 0·5 to 5 μl. The wavelength of the monochromator was set by maximizing the emission signal from the appropriate electrodeless discharge tube. The discharge was initiated before sample introduction. When the solvent began to elute, the discharge was extinguished. The discharge was ignited again after almost all of the solvent had been eluted. The peak heights of the recorder response were measured because the precision was not improved by peak area measurement.

Procedure for determining beryllium in aluminium

To the slightly acidic sample solution containing 1 mg of aluminium and 10–100 ng of beryllium, add 1 ml of acetylacetone. Dilute the solution to about 25 ml with water, and adjust the pH to 7·0 with 1*M* sodium hydroxide. Transfer the solution to a separating funnel, shake twice with 5-ml portions of chloroform for 3 min, and collect the extracts in a 10-ml volumetric flask. Take a 5-ml aliquot in a 10-ml bottle, vaporize the solvent under reduced pressure (30–100 mmHg) for 30 min, and then expel free acetylacetone under vacuum for 30 min at room temperature. Dissolve the residue in 1 ml of chloroform and inject a 2-μl aliquot into the gas chromatograph.

RESULTS AND DISCUSSION

Chromatograms of aluminium, beryllium and chromium acetylacetonates

Figure 1 shows chromatograms of a mixture of beryllium, aluminium and chromium acetylacetonates measured at 234·9 nm (Be I), 396·2 nm (Al I), 425·4 nm (Cr I) and 388·3 nm (CN band). Although no nitrogen was added, cyanogen yielded the most intense band system. The source of nitrogen was probably impurities in the argon. The measurements at 388·3 nm provide a non-selective detection for organic material.[7] Attempts to chromatograph acetylacetonates of copper(II), iron(III) and vanadium(IV) (as vanadyl acetylacetonate) were unsuccessful. In an attempt to chromatograph the iron complex, a broad peak, not separated from the solvent peak, appeared in the chromatogram when the detector was operated at 388·3 nm, but no atomic line due to iron could be observed. The cyanogen band peak was caused by decomposition of the complex.

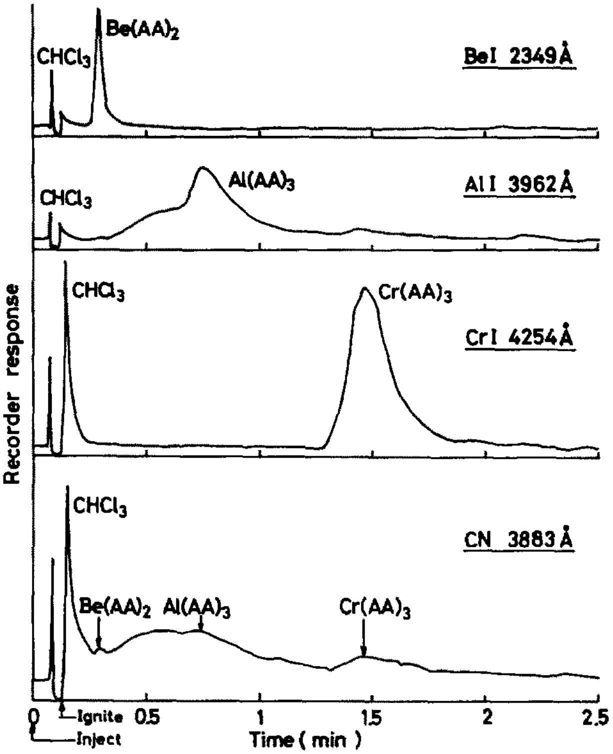

Fig. 1. Chromatograms of a mixture of $Be(AA)_2$, $Al(AA)_3$ and $Cr(AA)_3$. Ar flow-rate: 100 ml/min. Sample: 1 μl of chloroform (containing 0·002 μg of Be, 0·5 μg of Al and 0·1 μg of Cr).

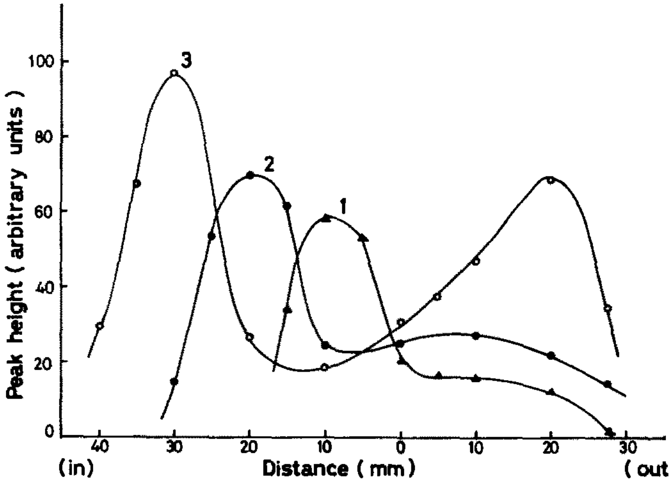

Fig. 2. Effect of microwave power on the recorder response of the Cr 425·4 nm line as a function of the position in the discharge. The abscissa designates a distance from the centre of the cavity. Sample: 1 μl of chloroform (containing 100 ng of Cr) Microwave power (W): *1*-30, *2*-50, *3*-70.

Effect of microwave power

In Fig. 2 the variation of the intensity of a chromium emission line is plotted against distance along the discharge tube. The position where the intensity was maximum moved toward the inlet as the power increased. Similar effects were observed with the other elements though the maximum positions were somewhat different. Beryllium and aluminium emissions were observed only at the inlet side of the discharge tube.

Effect of the argon flow-rate

The flow-rate of carrier gas affected the intensity distribution along the discharge tube as well as the retention time. In Fig. 3 the effect of the argon flow-rate on the intensity distribution of a beryllium line is shown. This behaviour of the intensity distribution may cause the detector response to depend greatly on carrier gas flow if the light emitted is measured at a fixed position.[7]

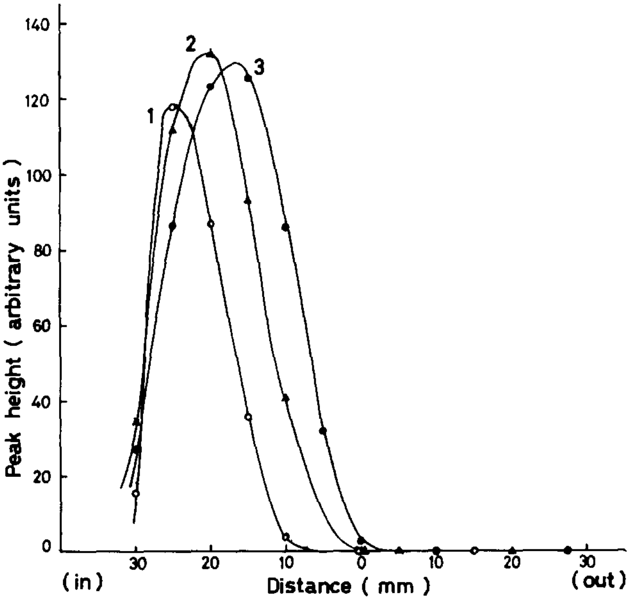

Fig. 3. Effect of argon flow-rate on the recorder response. Sample: 1 μl of chloroform (containing 10 ng of Be). Ar flow-rate (ml/min): *1*–50, *2*–100, *3*–150.

Calibration curves and detection limits

The calibration curves for aluminium, beryllium and chromium are shown in Fig. 4. Log-log calibration curves were linear over two orders of magnitude for beryllium and chromium. However, the linear range of the calibration curve for aluminium was very narrow and its slope was extremely steep. The mechanism of this response is as yet unknown. The maximum amounts of metals used in preparing the calibration curves were limited by the fact that the discharge became unstable as the sample emerged. The detection limits (signal/noise ratio of 2) for aluminium, beryllium and chromium are 100 ng, 0·01 ng and 1 ng, respectively. The relative standard deviations of the recorder response were 10–15%.

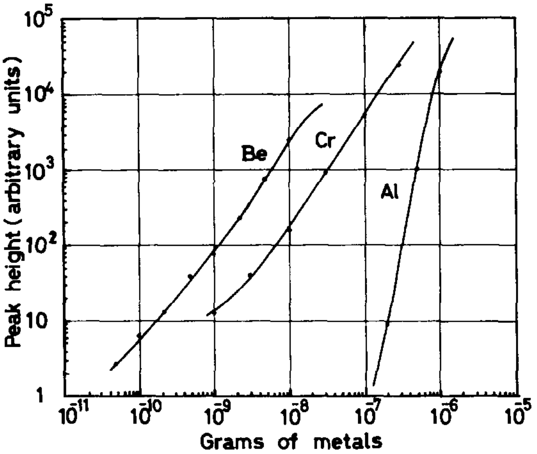

Fig 4. Calibration curves for Be, Cr and Al measured at Be I 234·9 nm, Cr I 425·4 nm and Al I 396·2 nm, respectively.

Interferences

There are many complex bands in the emission spectra of organic compounds,[7] which may interfere with the atomic emission lines. For instance, the peak due to acetylacetone appeared near that of beryllium acetylacetonate measured at 234·9 nm when more than 0·01% of acetylacetone was present. This type of interference can be greatly decreased by decreasing the slit-width of the monochromator. Another example of interference was the enhancement effect of aluminium acetylacetonate on beryllium and chromium emissions as shown in Fig. 5. This is due to the incomplete separation of the peaks.

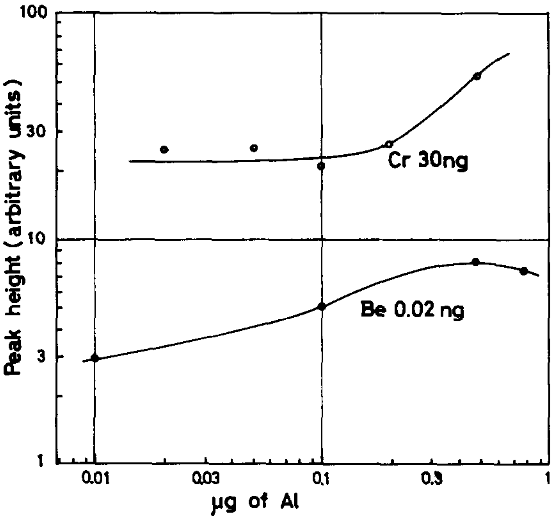

Fig. 5. Effect of aluminium content in the sample on the recorder responses of Cr 425·4 nm and Be 234·9 nm lines.

Determination of beryllium in aluminium

Sievers[11] could detect 0·0059 μg of beryllium in the presence of 2000 times as much aluminium with a thermal conductivity detector (in the gas chromatography of metal trifluoroacetylacetonates). However, it is difficult with conventional detectors to detect one metal in the presence of much larger amounts of others. Owing to its inherent selectivity and high sensitivity, the emission spectrometric detector can be used to determine trace metals without prior separation of the major constituents. The calibration curve constructed by carrying standard solutions containing known amounts of beryllium and aluminium through the entire procedure described above is linear but does not pass through the origin. The calibration curve prepared with chloroform solutions of mixtures of the acetylacetonates is a straight line passing through the origin. Moreover, the slope of the latter curve is about 1·6 times that of the former. The discrepancy between the two is probably due to the formation of unknown compounds during the extraction step. Nevertheless, down to 10 ppm of beryllium in aluminium (0·01 ng of beryllium in the presence of 1 μg of aluminium) could be determined with a relative standard deviation of about 15%.

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Zusammenfassung—Bei der Bestimmung von Metall-Acetylacetonaten wird ein emissionsspektrometrischer Detektor verwendet. Die Spektren werden im Plasma einer elektrodenlosen 2450 MHz-Entladung angeregt. Die Messung der Intensität der Atomemissionslinien von Aluminium, Beryllium und Chrom nach der Gaschromatographie ergibt eine hochempfindliche und selektive Methode zur Bestimmung der Acetylacetonate dieser Metalle. Die Nachweisgrenzen sind 100 ng für Aluminium, 0,01 ng für Beryllium und 1 ng für Chrom. Eine Analysenvorschrift zur Bestimmung von Beryllium in Aluminium bis herunter zu 10 ppm wird vorgeschlagen.

Résumé—On utilise un détecteur spectrométrique d'émission dans la détermination d'acétylacétonates métalliques. Les spectres sont excités dans le plasma d'une décharge sans électrode de 2450 MHz. La mesure des intensités des raies d'émission atomique de l'aluminium, du béryllium et du chrome après chromatographie en phase gazeuse apporte une méthode hautement sensible et sélective pour la détermination des acétylacétonates de ces métaux. Les limites de détection sont 100 ng pour l'aluminium, 0,01 ng pour le béryllium et 1 ng pour le chrome. On propose une technique analytique pour le béryllium, pouvant descendre jusqu'à 10 p.p.m. dans l'aluminium.

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SHORT COMMUNICATIONS

SOME ASPECTS OF THE WINKLER DETERMINATION OF OXYGEN IN WATER

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The Winkler method for the determination of dissolved oxygen in water has been used for this purpose since 1888[1] either in its original form or as modified by various workers.[2] The basic method, which is fast and accurate when properly carried out, makes use of the three reactions:

$$\mathrm{Mn(II)} + \mathrm{O_2} \xrightarrow{\mathrm{OH^-}} \mathrm{MnO_2} \tag{1}$$

$$\mathrm{MnO_2} + 4\mathrm{H^+} + 2\mathrm{I^-} \longrightarrow \mathrm{I_2} + \mathrm{Mn(II)} + 2\mathrm{H_2O} \tag{2}$$

$$\mathrm{I_2} + 2\mathrm{S_2O_3^{2-}} \longrightarrow \mathrm{S_4O_6^{2-}} + 2\mathrm{I^-} \tag{3}$$

Despite its accuracy, the Winkler method does have some disadvantages. It cannot be used to monitor dissolved oxygen continuously. Continuous monitoring is possible with suitable electrodes which have been calibrated. Such electrodes allow changes in the oxygen sample to be detected over short periods of time (2 sec) and their operation does not appreciably alter the concentration of dissolved oxygen. In the present study such an electrode system has been utilized to collect information on the time required for the reactions used in the Winkler system to proceed and of the extent to which the reactions proceed as a function of pH.

EXPERIMENTAL

Reagents

A.C.S. reagent grade chemicals were used to prepare the following solutions: 0·25*M* manganous sulphate; a solution 0·60*M* in sodium iodide and 1*M* in sodium hydroxide; 9*M* sulphuric acid; 0·10*M* sodium thiosulphate. Buffer solutions were prepared with pH values of 7·00 and 7·75 (based on phosphate), 8·10 [based on tris(hydroxymethyl)aminomethane], 8·50, 9·00 and 10·00 (based on borate).[3]

Procedure

A Sargent Model XV recording polarograph was used with a rotating platinum electrode and an S.C.E. for the measurement of the diffusion currents due to reduction of dissolved oxygen. All experiments were done at 25°. The operating voltage used was −0·35V and the current sensitivity 0·020 μA/in. Nitrogen was used as an inert atmosphere over the solution and, when needed, to purge oxygen from the solution to determine values on a "blank". The polarograph itself was standardized and the rotating platinum electrode cathodized by a method described by McNutt.[4]

The oxygen sensitivity of the system was determined by measuring the current obtained with an oxygen solution, the concentration of which was determined by the standard Winkler procedure. The results were obtained by first measuring the current with a standard oxygen solution and then running the reaction of Mn(II) and dissolved oxygen and comparing the currents obtained. The standard oxygen solution consisted of 50 ml of the appropriate buffer solution and 150 ml of distilled water of known oxygen concentration.

The electrode system was also calibrated by the Winkler method, in a manner very similar to that used in the experiments on pH dependence. Fifty ml of each buffer were mixed with 150 ml of distilled water containing dissolved oxygen and analysed in triplicate. These results were reproducible to ±0·5% or better. The oxygen content of the distilled water, established in this way, was used to calibrate the electrode system in the blank runs. The sample of analysed water was kept in a tightly stoppered bottle. Since the only variations in the concentration of oxygen under such conditions would be small ones due to variations in atmospheric pressure, the value established, $1{\cdot}225 \times 10^{-5}M$ oxygen, was used throughout the experiments. After standing for two weeks the oxygen solution was restandardized and found to have very nearly the same value ($1{\cdot}146 \times 10^{-5}M$, a decrease of 6%).

The observed current ranges for these solutions and the same solutions after deoxygenation were used to determine the oxygen calibration. After each such blank run the reaction vessel was cleaned and the same components added. To this second solution, under a nitrogen atmosphere, was now added 1 ml of 0·25*M* manganous sulphate. This resulted in a rapid change in the observed current to a new steady value and the current change was noted. Since the current is proportional to the concentration of dissolved oxygen,[2] comparison of the current change with the calibration run allowed an accurate estimate to be made of the oxygen consumption and the degree of completion of the reaction

$$\mathrm{Mn(II)} + \mathrm{O_2} \xrightarrow{\mathrm{OH^-}} \mathrm{MnO_2}$$

RESULTS AND DISCUSSION

The dependence of degree of completion of the reaction *vs.* pH is given in Fig. 1. The pH-dependence is certainly not surprising in view of the known dependence of the stability of Mn(II) on pH. This curve also provides dramatic evidence of the advantages of the rotating platinum electrode as an oxygen monitor. Its operating range is much broader and its response time is much shorter than those of the Winkler method. Offsetting these advantages are its lower accuracy and reproducibility and the irregular response of improperly cathodized rotating platinum electrodes.

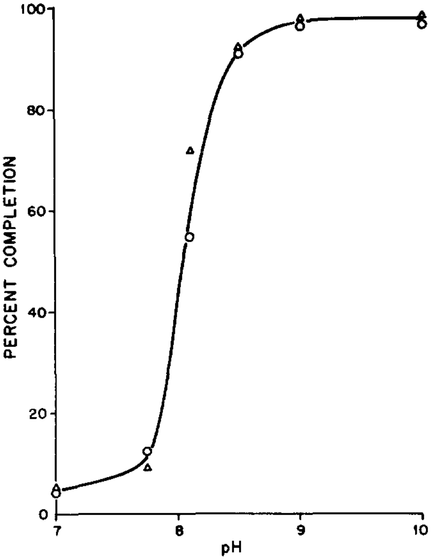

Fig. 1. The effect of pH on the percentage completion of the reaction between Mn(II) and dissolved oxygen in the Winkler analysis.

pH	7·00	7·75	8·10	8·50	9·00	10·00
% Completion (○)	4·2	12·5	55·0	91·2	97·1	97·2
(△)	5·2	9·1	72·1	92·1	98·3	98·6

A pH approaching 9 or more is clearly required for the complete consumption of the oxygen by the manganese. If the pH is too low when the manganous sulphate solution is added only part of the oxygen is consumed. In such a case the reaction does not go to completion until after the addition of the basic sodium iodide solution causes an increase in the pH.

The response time of the polarograph is about 3 sec for full-scale deflection. Since the time response of the system as a whole was determined in the course of each run it was apparent that these results might be useful in obtaining approximate information on the rate of the reaction. The estimated times ($t_{1/2}$) for the completion of half of the reaction are summarized below.

pH	7·00	7·75	8·10	8·50	9·00	10·00
$t_{1/2}$ *sec*	1·8	1·8	1·6	1·5	1·2	1·2

While the response time does vary somewhat, the response time of the instrument may well be the limiting factor. The results allow us to estimate only an upper bound for the half-life of the reaction of Mn(II) with dissolved oxygen and the reaction may be considerably more rapid. At any rate, we have shown that the reaction is sufficiently rapid for the error from incomplete reaction to be 0·1% or less if a total of as much as 20 sec is allowed for the reaction to proceed. The usual procedure will allow a much longer period for reaction than this

In conclusion we can state that the rotating platinum electrode is capable of monitoring reactions in which dissolved oxygen is consumed, such as those in the Winkler analysis. Its normal response time appears to be limited primarily by the speed of the recording device used. It is potentially capable of providing rate data for such reactions.

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Summary—The reactions in the Winkler determination of oxygen have been examined with a rotating platinum electrode and a recording polarograph. In this manner the extent of the reaction has been determined over the pH range 7–10; at a pH of 7 only about 5% of the dissolved oxygen reacts; at a pH of 9 or above the reaction is essentially quantitative. The reaction of dissolved oxygen with manganese(II) is quite rapid. The sluggish response of the polarograph recorder prevented an accurate determination of the rate, but the reaction half-times were about 2 sec or less over the pH range used.

Zusammenfassung—Die bei der Winkler-Bestimmung von Sauerstoff ablaufenden Reaktionen wurden mit einer rotierenden Platinelektrode und einem registrierenden Polarographen untersucht. Auf diese Weise wurde das Ausmaß der Reaktion im pH-Bereich 7–10 ermittelt. Bei pH 7 reagieren nur etwa 5% des gelösten Sauerstoffs; bei pH 9 und darüber ist die Reaktion praktisch quantitativ. Die Reaktion von gelöstem Sauerstoff mit Mangan(II) geht ziemlich rasch. Das langsame Ansprechen des Polarographenschreibers verhinderte eine genaue Bestimmung der Geschwindigkeit, jedoch betrugen die Halbwertszeiten der Reaktion im benutzten pH-Bereich etwa 2 sec oder weniger.

Résumé—On a examiné les réactions dans le dosage de Winkler de l'oxygène avec une électrode de platine tournante et un polarographe enregistreur. De cette manière, on a déterminé l'avancement de la réaction dans le domaine de pH 7–10; à un pH de 7, environ 5% seulement de l'oxygène dissous réagit; à un pH de 9 ou supérieur la réaction est essentiellement quantitative. La réaction de l'oxygène dissous avec le manganèse(II) est tout à fait rapide. La réponse lente de l'enregistreur du polarographe a empêché une détermination précise de la vitesse, mais les demi-temps de réaction sont d'environ 2 s ou moins dans le domaine de pH utilisé.

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A NOVEL METHOD FOR THE ESTIMATION OF ARSENIC(V) IN ORGANIC COMPOUNDS

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Arsenic(V) in organic compounds has been determined by digesting the compound with chloric acid, reducing with iodide to arsenic(III) and titrating iodometrically.[1] Another method involves (*a*) digestion with sodium sulphate and sulphuric acid, followed by titration with bromate, or (*b*) digestion with hydrogen peroxide and sulphuric acid, addition of hydrazine and titration with bromate, or (*c*) digestion with fuming nitric acid, then with sodium sulphate and concentrated sulphuric acid, and then with more conc. nitric acid, and titration with bromate.[2] The sample can be heated with sulphuric acid and hydrogen peroxide, then with hydrazine

In conclusion we can state that the rotating platinum electrode is capable of monitoring reactions in which dissolved oxygen is consumed, such as those in the Winkler analysis. Its normal response time appears to be limited primarily by the speed of the recording device used. It is potentially capable of providing rate data for such reactions.

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A NOVEL METHOD FOR THE ESTIMATION OF ARSENIC(V) IN ORGANIC COMPOUNDS

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Arsenic(V) in organic compounds has been determined by digesting the compound with chloric acid, reducing with iodide to arsenic(III) and titrating iodometrically.[1] Another method involves (*a*) digestion with sodium sulphate and sulphuric acid, followed by titration with bromate, or (*b*) digestion with hydrogen peroxide and sulphuric acid, addition of hydrazine and titration with bromate, or (*c*) digestion with fuming nitric acid, then with sodium sulphate and concentrated sulphuric acid, and then with more conc. nitric acid, and titration with bromate.[2] The sample can be heated with sulphuric acid and hydrogen peroxide, then with hydrazine sulphate; after addition of tartaric acid and potassium bromide, potassium bromate is used as titrant.[3] The sample can be treated with hydrogen peroxide and conc. sulphuric acid, hydrogen peroxide expelled, potassium iodide added and the iodine titrated with sodium thiosulphate.[4] The sample can be decomposed with hydrogen peroxide and sulphuric acid, arsenic reduced with hydrazine, and titrated with bromate in hydrochloric acid.[5] In another method the sample is heated with conc. chloric acid, and sodium hydroxide and then excess of hydrochloric acid is added, followed by potassium iodide, removal of free iodine with sodium sulphite, addition of sodium bicarbonate and titration of arsenic(III) with iodine, with starch as indicator.[6] The compound can be dissolved in conc. hydrochloric acid, the solution cooled, acetic acid, water and potassium iodide added and the iodine titrated with thiosulphate.[7] After digestion of sample with hydrogen peroxide and sulphuric acid, arsenic can be distilled as arsenic trichloride, then precipitated as sulphide, dissolved in alkali and titrated with permanganate.[8] After a similar decomposition, the arsenic can be precipitated as $MgNH_4AsO_4$.[9] The substance can be heated with water and ammonium persulphate till colourless, then oxalic acid is added and carbon dioxide expelled by heating; sulphuric acid and potassium iodide are added, iodine is expelled by boiling and any yellow colour destroyed with sodium thiosulphate. After dilution and addition of sodium carbonate and bicarbonate the arsenic is titrated with iodine solution. In view of these circuitous methods, it was thought profitable to devise some simple and satisfactory method for the determination of arsenic(V) in organic compounds.

EXPERIMENTAL

Reagents

Aqueous iodine solution (approximately 0·05*N*) containing 10 g of potassium iodide per litre was standardized with 0·1*N* sodium thiosulphate, with freshly prepared starch solution as indicator.

All reagents were of analytical grade. The samples tested are listed in Table 1.

Table 1

No. Compound	As, %		
	Theory	Starch end-point	Potentiometric end-point
1. Triphenylarsine oxide	23·29	23·1 23·4 23·2	—
2. 1,2-Ethylene-bis-diphenylarsine oxide	28·95	29·2 28·7 28·8	29·1
3. *p*-Chlorobenzaldehyde arsanilic acid	22·09	22·2 22·1 22·1	21·1
4. *o*-Chlorobenzaldehyde arsanilic acid	22·09	22·2 22·2 22·1	22·0
5. *m*-Nitrobenzaldehyde arsanilic acid	21.43	21·6 21·3 22·1	—
6. *o*-Nitrobenzaldehyde arsanilic acid	21·43	21·4 21·4 21·2	21·3
7. *o*-Carboxyphenylarsonic acid	30·49	30·8 30·4 30·3	30·3
8. *p*-Chlorophenylarsonic acid	31 71	31·4 31·9 31·9	—
9. *p*-Bromophenylarsonic acid	26·69	26·6 26·7 26·9	—
10. *p*-Tolylarsonic acid	34·72	35·0 34·7 34·9	—

Procedure

For compounds 1–7. A 10–15 mg sample was dissolved in a mixture of 30 ml of glacial acetic acid and 30 ml of ethyl alcohol in a 150-ml round-bottomed flask and the solution was heated to boiling. Then 2 g of zinc dust were slowly added to the continuously boiling mixture over a period of 15 min. The solution was cooled and decanted and the residual zinc washed with 10 ml of acetic acid, followed by 30 ml of water. The solution and washings were titrated with 0·05*N* iodine with starch as indicator added near the end-point, which is given by appearance of a light violet colour. Sometimes a light yellow colour results, which on dilution gives the light violet colour. Similar results were obtained when the compounds were dissolved in 50 ml of glacial acetic acid, reduced with 2 g of zinc dust during 20 min and then treated as before. A potentiometric end-point can also be used.

For compounds 8–10. A 10–20 mg sample was dissolved in 20 ml of glacial acetic acid and heated to boiling. Powdered zinc dust (2 g) was added and the mixture was heated for 5 min, cooled, the solution decanted, the residual zinc washed with 10 ml of glacial acetic acid and 10 ml of distilled water, and the solution and washings titrated with iodine as for compounds 1–7.

RESULTS AND DISCUSSION

Organic compounds containing arsenic(V) are usually insoluble in water but can be dissolved in acetic acid, or in a mixture of acetic acid and ethyl alcohol if the compound is not completely soluble in acetic acid. The arsenic(V) is reduced by the action of acetic acid and zinc. The arsenic(III) cannot be titrated in glacial acetic acid because of difficulty in the detection of the end-point, but addition of water removes the difficulty. The quantity of water added should be such that the solution to be titrated does not turn milky because of separation of organic species. Excellent results are obtained when the amount of arsenic(V) compound taken is 10–20 mg. This method is clean and quick.

Potassium chloride, bromide or iodide (10 mg) did not interfere. In the potentiometric titration, suitable for coloured solutions, a platinum electrode was coupled with a calomel electrode. The results obtained are given in the Table.

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Summary—A novel method for the determination of arsenic(V) in organic compounds has been developed by reducing combined arsenic(V) to arsenic(III) in aqueous acetic acid medium with zinc dust. In some cases, addition of ethyl alcohol is necessary to dissolve the compound and to keep the arsenic(III) compound in solution. The arsenic(III) is titrated with iodine and the end-point is detected visually with starch as indicator or potentiometrically.

Zusammenfassung—Ein neuartiges Verfahren zur Bestimmung von Arsen(V) in organischen Verbindungen wurde entwickelt. Gebundenes Arsen(V) wird dabei in wäßriger Essigsäure mit Zinkstaub zu Arsen(III) reduziert. In einigen Fällen ist eine Zugabe von Äthylalkohol

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notwendig, um die Verbindung zu lösen und die Arsen(III)-verbindung in Losung zu halten. Das Arsen(III) wird mit Jod (bei 30°) titriert und der Endpunkt visuell mit Starke als Indikator oder potentiometrisch nachgewiesen.

Résumé—On a élaboré une nouvelle méthode pour le dosage de l'arsenic (V) dans les composés organiques en réduisant l'arsenic (V) combiné en arsenic (III) en milieu acide acétique aqueux avec de la poudre de zinc. Dans quelques cas, l'addition d'éthanol est nécessaire pour dissoudre le composé et pour maintenir le comosé arsénié (III) en solution. L'arsenic (III) est titré par l'iode et le point final est détecté visuellement avec l'empois comme indicateur ou potentiométriquement

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INDIRECT POLAROGRAPHIC DETERMINATION OF TRIPOLYPHOSPHATE IONS IN THE PRESENCE OF OTHER POLYPHOSPHATES, WITH OCTYLTIN CHLORIDE

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No phosphate or polyphosphate anion is itself reducible at the dropping mercury electrode, but indirect methods for tripolyphosphate have been based on selective precipitation or complexation with a known excess of a polarographically active species. Precipitation methods are generally subject to interference from co-precipitation or suffer from incomplete precipitation, especially when only small concentrations are to be determined. A gravimetric method using tris(ethylenediamine)cobalt(III) in a pH 3·6 buffer as a precipitant for tripolyphosphate in the presence of pyrophosphate, has been published,[1,2] but radioactive labelling with ^{32}P has shown[3] that some co-precipitation occurs and that some tripolyphosphate remains in solution, even under carefully controlled precipitation conditions. Weiser[2] reported strong interference from sulphate ions, which decreased the completeness of precipitation. A recent investigation[4] has shown that tris(ethylenediamine)-cobalt(III) does not give complete precipitation at low concentrations ($\leq 10^{-2}M$) of tripolyphosphate ions.

Selective complexation by polyphosphates at low concentrations ($\leq 10^{-3}M$) has so far received surprisingly little attention for the determination of the polyphosphates. During a study of the effect of polyphosphates on the d.c. polarographic behaviour of some simple metal ions, Al-Sulimany and Townshend[4] developed a method for low concentrations of tripolyphosphate, based on the decreased height of the cadmium polarographic reduction wave. Selectivity was somewhat limited, but less than 5% of pyrophosphate and less than 50% of trimetaphosphate or tetrametaphosphate, relative to the tripolyphosphate, did not interfere in the analysis. Attempts to find metal ions which were more selective to individual polyphosphates were at that time unsuccessful. More recently, however, during an investigation of the polarographic behaviour of the n-octyltin chlorides, it was observed that buffer systems containing phosphate caused a complete disappearance of the reduction wave of mono-octyltin trichloride at pH > 3. This complexing effect has also been reported by other workers[6] for monoethyltin trichloride. Further experiments showed that polyphosphate ions had a similar effect. It has proved possible, by selection of suitable conditions, to devise a method for the determination of tripolyphosphate ions that is free from interference by much greater concentrations of other phosphate species. The development of this method is described in this paper.

The ability of organotin cations to form adducts with electron donors is well known.[5] The acceptor strength declines in the order $RSn^{3+} > R_2Sn^{2+} > R_3Sn^{+}$, and in general, organotin compounds with a single organic substituent form the most stable complexes. It was considered improbable, therefore, that the more highly substituted octyltin cations would respond more sensitively than mono-octyltin, and they were not investigated for this purpose.

EXPERIMENTAL

Apparatus

Polarograms were recorded with a Radiometer Polariter PO4 polarograph used in conjunction with a Drop Life Timer type D.L.T.1. An external standard calomel electrode was separated from the cell by a saturated potassium chloride bridge.

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Apparatus

Polarograms were recorded with a Radiometer Polariter PO4 polarograph used in conjunction with a Drop Life Timer type D.L.T.1. An external standard calomel electrode was separated from the cell by a saturated potassium chloride bridge.

Reagents

Mono-octyltin trichloride, purified by vacuum distillation, (b.p. 182–3°/29 mmHg) and sodium salts of the polyphosphates were provided by Albright and Wilson (Mfg.) Ltd., Oldbury, Worcs. Other chemicals used were of analytical reagent grade.

A stable solution of mono-octyltin trichloride ($6{\cdot}0 \times 10^{-4}M$) in perchloric/hydrochloric acid and 2-propanol can be prepared in bulk as follows. Transfer mono-octyltin trichloride (0·203 g) to a 1000-ml volumetric flask containing 2-propanol, 60% perchloric acid (130 ml) and concentrated hydrochloric acid (50 ml), and dilute to volume with 2-propanol.

Procedure for calibration and determination of tripolyphosphate ($<4 \times 10^{-3}M$)

Transfer 10 ml of the tripolyphosphate solution into a clean, dry polarographic cell. Add $0{\cdot}15M$ tetrametaphosphate solution (0·20 ml), followed by $6{\cdot}0 \times 10^{-4}M$ mono-octyltin trichloride solution (10 ml). Immediately, deaerate with nitrogen for 3 min, and allow to stand for a further minute with nitrogen passing over the solution. Record the polarogram, and measure the height of the wave having $E_{1/2} = -0{\cdot}45$ V *vs.* the S.C.E. Calibration should be carried out with 0–10 ml of $4 \times 10^{-3}M$ sodium tripolyphosphate solution and the volume of water required to bring the volume to 10 ml before addition of the octyltin solution.

A typical calibration curve is shown in Fig. 1.

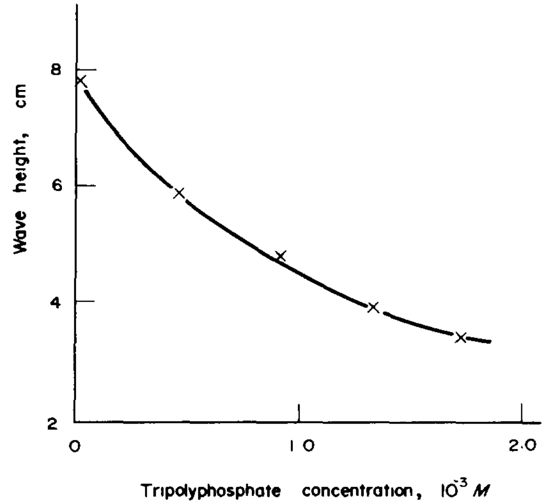

Fig. 1. Calibration graph for tripolyphosphate. Sensitivity 1·5 μA full-scale deflection. Drop-time 1·0 sec, blanking 30%.

RESULTS AND DISCUSSION

Mono-octyltin trichloride gives a single reduction wave in a 50% aqueous 2-propanol solution $1M$ in perchloric acid and $0{\cdot}25M$ in hydrochloric acid, $E_{1/2} = -0{\cdot}45$ V *vs.* S.C.E. The effects of orthophosphate and four polyphosphate ions on the height of the polarographic wave of mono-octyltin trichloride ($3{\cdot}2 \times 10^{-4}M$) in such an electrolyte are shown in Fig. 2. Orthophosphate ions have a negligible effect, but the polyphosphate ions all decrease the wave height, the order of effectiveness being tripoly > tetrameta > trimeta > pyrophosphate, The half-wave potential of the octyltin wave is unaffected, indicating that the wave measured is that of the uncomplexed octyltin ions. No wave corresponding to reduction of the complex is observed in the potential range before hydrogen ion discharge occurs.

The difference in the response to the various polyphosphate species is a complex function of pH and chloride ion concentration, as well as the stability of the octyltin–polyphosphate complex. The addition of hydrochloric acid allows the formation of competing complexes of the type $(OcSnCl_4)^-$. It was found that all the phosphates complex strongly with mono-octyltin ions in a medium of $2M$ perchloric acid and 2-propanol (1 : 1), and that no complexing by polyphosphates occurs in $2M$ hydrochloric acid and 2-propanol (1 : 1). In $0{\cdot}25M$ hydrochloric acid in 50% v/v 2-propanol, low concentrations of tripolyphosphate and tetrametaphosphate caused the complete disappearance of the octyltin wave. Optimal differentiation between tripolyphosphate and the other polyphosphate ions was achieved in 50% aqueous 2-propanol, $1M$ in perchloric acid and $0{\cdot}25M$ in hydrochloric acid, as depicted in Fig. 2.

Figure 2 also shows that concentrations of tetrametaphosphate ions above *ca.* $10^{-3}M$ have little further effect. If was found that if the supporting electrolyte was also $1{\cdot}5 \times 10^{-3}M$ in tetrametaphosphate, the effect of other polyphosphates was greatly reduced, whereas tripolyphosphate still gave an appreciable reduction in the octyltin wave height. Higher cell concentrations of tetrametaphosphate would further reduce polyphosphate interference, but at the expense of decreased sensitivity for tripolyphosphate.

Under the optimal conditions for the selective determination of tripolyphosphate, tolerance of the method to other phosphate anions was statistically determined. A standard 2^4 factorial design experiment[7] was set up with a high and a low level of each interfering species. At cell concentrations of tripolyphosphate of $2{\cdot}0 \times 10^{-4}$ and $8{\cdot}0 \times 10^{-4}M$, the presence of $1 \times 10^{-3}M$ ortho-, pyro-, or trimetaphosphate, and $5 \times 10^{-4}M$ tetrametaphosphate did not cause any significant reduction in wave height, though $10^{-3}M$ tetrametaphosphate did give a significant reduction.

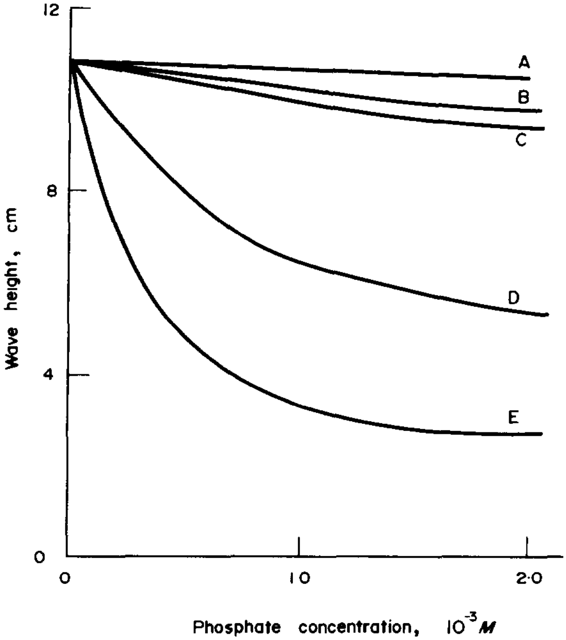

Fig. 2. Effect of phosphate ions on wave height of $3 \times 10^{-4}M$ mono-octyltin trichloride in 50% v/v aqueous 2-propanol, $1M$ in $HClO_4$ and $0{\cdot}25M$ in HCl. Instrument conditions as in Fig. 1. (*A*) orthophosphate, (*B*) pyro- (*C*) trimeta-, (*D*) tetrameta-, (*E*) tripolyphosphate.

Interference from sulphate ion is negligible. The presence of $10^{-2}M$ potassium sulphate had no effect. Magnesium (as sulphate, $4 \times 10^{-3}M$), and calcium (as chloride, $10^{-3}M$) could also be tolerated. Under the acidic conditions finally recommended, slow hydrolysis of the condensed phosphates does occur, but if the measurements are made without undue delay, this does not affect the reproducibility of the method.

The standard deviation based on seven determinations at a cell concentration of $8{\cdot}0 \times 10^{-4}M$ tripolyphosphate was found to be $4 \times 10^{-5}M$, giving (95% confidence limits) an error of $\pm 0{\cdot}94 \times 10^{-4}M$. Peak heights of approx. 60 mm were reproducible to within 1 mm and were found to decrease by about 3 mm if the solution was left for a further 10 min. Analysis at a higher pH, using $1{\cdot}0M$ acetic acid–$0{\cdot}5M$ potassium chloride solution mixed with 2-propanol (1 : 1), in an attempt to reduce the hydrolysis effect, was unsuccessful, since the necessary differentiation between pyro- and tripolyphosphate was not achieved.

Conclusion

The method described is simple, rapid and acceptably precise. It allows the determination of tripolyphosphate without interference from similar concentrations of other polyphosphates. Phosphate, sulphate, calcium and magnesium ions also do not interfere, so that the method is equally applicable to detergent preparations and effluent samples.

Acknowledgements—The authors thank Professor R. Belcher for his encouragement and valuable suggestions. They also thank the S.R.C. for the provision of an award (to S.S.) under the Co-operative Awards in Pure Science scheme, in conjunction with Albright and Wilson (Mfg) Ltd: the provision of organotin and polyphosphate samples by the latter is much appreciated.

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Summary—Tripolyphosphate ions form a soluble complex with mono-octyltin cations, thus reducing the polarographic wave height of the octyltin. This provides a method for the determination of 2×10^{-4}–$4 \times 10^{-3}M$ tripolyphosphate in the presence of $2 \times 10^{-3}M$ ortho-, pyro-, trimeta-, and $10^{-3}M$ tetrametaphosphate, together, or in any combination. The method is also insensitive to less than $2 \times 10^{-3}M$ magnesium or calcium and less than $10^{-2}M$ sulphate.

Zusammenfassung—Tripolyphosphat-Ionen bilden einen löslichen Komplex mit Monooktylzinn-Kationen und reduzieren dabei die Hohe der polarographischen Stufe des Oktylzinns. Dies bildet die Grundlage zur Bestimmung von $2{\cdot}10^{-4}$–$4{\cdot}10^{-3}$M Tripolyphosphat in Gegenwart von $2{\cdot}10^{-3}$M Ortho-, Pyro-, Trimeta- order 10^{-3}M Tetrametaphosphat zusammen oder in beliebiger Kombination. Das Verfahren ist auch unempfindlich gegen weniger als $2{\cdot}10^{-3}$M Magnesium oder Calcium und weniger als 10^{-2}M Sulfat.

Résumé—Les ions tripolyphosphate forment un complexe soluble avec les cations mono-octylétain, réduisant ainsi la hauteur de vague polarographique de l'octylétain. Ceci fournit une méthode pour le dosage de tripolyphosphate $2 \times 10^{-4} - 4 \times 10^{-3}$ *M* en la présence d'ortho-, pyro-, trimétaphosphate 2×10^{-3} *M* et de tétramétaphosphate 10^{-3} *M*, ensemble, ou selon n'importe quelle combinaison. La méthode est aussi insensible à moins de 2×10^{-3} *M* de magnésium ou de calcium et moins de 10^{-2} *M* de sulfate.

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FORMATION OF FERRICYANIDES—I*
SILVER(I), COPPER(II) AND CADMIUM(II)

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The analytical importance of potassium ferricyanide is not limited to the specific colours it gives with many cations; it can also yield stable complexes having different stoichiometry with cations having a given charge. It, in fact, can react with a metallic bivalent ion as follows:

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Summary—Tripolyphosphate ions form a soluble complex with mono-octyltin cations, thus reducing the polarographic wave height of the octyltin. This provides a method for the determination of 2×10^{-4}–$4 \times 10^{-3} M$ tripolyphosphate in the presence of $2 \times 10^{-3} M$ ortho-, pyro-, trimeta-, and $10^{-3} M$ tetrametaphosphate, together, or in any combination. The method is also insensitive to less than $2 \times 10^{-3} M$ magnesium or calcium and less than $10^{-2} M$ sulphate.

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SILVER(I), COPPER(II) AND CADMIUM(II)

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The analytical importance of potassium ferricyanide is not limited to the specific colours it gives with many cations; it can also yield stable complexes having different stoichiometry with cations having a given charge. It, in fact, can react with a metallic bivalent ion as follows:

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$$3M^{2+} + 2Fe(CN)_6^{3-} = M_3[Fe(CN)_6]_2 \quad (1)$$

$$mM^{2+} + pK^+ + qFe(CN)_6^{3-} = K_pM_m[Fe(CN)_6]_q \quad (2)$$

Thus the presence of the potassium ion leads to several possible complexes with variable K/M ratio In addition the composition of these complexes depends not only on the metal ion but also on the experimental conditions. We have therefore made a comparative conductometric and potentiometric study to establish which complexes are formed for the systems $AgNO_3$–$K_3Fe(CN)_6$, $CuSO_4$–$K_3Fe(CN)_6$, $CdSO_4$–$K_3Fe(CN)_6$.

These complexes have been studied earlier in aqueous and aqueous ethanolic (80 : 20) solution by means of thermometric,[1] potentiometric[2] or conductometric and thermometric measurements[3-5] and the complexes $Ag_3Fe(CN)_6$, $Cu_3[Fe(CN)_6]_2$ and $KCd_{10}[Fe(CN)_6]_7$ characterized, but the concentration range was very limited, being restricted to ~0·1*M*.

King[6] titrated $K_3Fe(CN)_6$ with $Cd(NO_3)_2$ solution and obtained a yellow precipitate which he deduced to be $Cd_3[Fe(CN)_6]_2$ on the basis of the Cd/Fe ratio.

To explain these differences we have investigated a wide concentration range with and without addition of potassium ions (0·15 and 0·5*M* final concentration) and with adjustment to constant ionic strength.

EXPERIMENTAL

Apparatus

The potentiometric cell for the silver and copper studies had a silver wire, a saturated calomel electrode and an agar–potassium nitrate bridge. From the equilibria (3) and (4) it is evident that the silver electrode

$$3Ag^+ + Fe(CN)_6^{3-} = Ag_3Fe(CN)_6 \quad (3)$$

$$mCu^{2+} + pK^+ + qFe(CN)_6^{3-} = K_pCu_m[Fe(CN)_6]_q \quad (4)$$

potential is related to the copper and potassium concentrations. A copper metal electrode was not used, because of its lower sensitivity, and an amalgam electrode was too easily oxidized. The titration error was negligible because the copper(II) concentration was always at least 1000 times that of silver.

As the cadmium electrode proved useless and an amalgam electrode was not practical the cadmium system was studied with a homemade oscillometer.[7]

Reagents

The silver nitrate solution was standardized oscillometrically with potassium chloride; the copper and cadmium solutions with EDTA.[8] Potassium ferricyanide solution was standardized according to Conde and Bellido[9] and kept in dark bottles. The stability of these solutions was checked periodically and no variation was found in 15 days for hexacyanoferrate(III) solution. Reagent purity was checked by means of blanks.

RESULTS

Reaction between Ag^+ *and* $Fe(CN)_6^{3-}$

The reddish-yellow powdery precipitate of $Ag_3Fe(CN)_6$ is the only product obtained, even in the presence of 0·5*M* potassium ion, over the concentration ranges $pAg^+ = 1-3$, $pFe(CN)_6^{3-} = 1-3·8$.

Use of 20% v/v aqueous ethanol as solvent medium gave a sharp equivalence point also corresponding to $Ag_3Fe(CN)_6$. This is in agreement with our earlier observation[10] for hexacyanoferrate(II) that the cations of heavy metals give only the simplest complex without formation of the mixed potassium salt.

The reactions all occurred immediately at room temperature.

Reaction between Cu^{2+} *and* $Fe(CN)_6^{3-}$

$Cu_3[Fe(CN)_6]_2$ is a yellow-brown powdery precipitate obtained in absence of extra potassium ions. $KCu_{10}[Fe(CN)_6]_7$ is formed in presence of 0·5*M* potassium nitrate and is soluble in ammonia. The potential drop at the equivalence point is about 50–60 mV in the titration of $Fe(CN)_6^{3-}$ with Cu(II) and 60–70 mV in the reverse titration.

The rate of reaction at room temperature is faster when Cu(II) is the titrand. The presence of an excess of potassium favours reaction (2), producing a mixed complex.

The concentration ranges studied were pCu^{2+} = 1·3–3·8 and $pFe(CN)_6^{3-}$ = 1·3–3·8.

Table 1 shows the results of a number of titrations. The average error is 0·2% and ferricyanide can be determined in this way in 0·5*M* potassium nitrate medium with a precision at least as good as that of other methods.

Table 1. Stoichiometry of the reaction between $K_3Fe(CN)_6$ and $CuSO_4$ at constant ionic strength, for $[K^+]$ = 0·5*M*

Titrand (100 ml)		Titrant				
mg $K_3Fe(CN)_6$	*μmole* $K_3Fe(CN)_6$	*mg* Cu(II)	*μmole* Cu(II)	Formula	Found, *mg*	Error, %
10·63	32·3	2·92	43·7	$KCu_{10}[Fe(CN)_6]_7$	10·59	−0·4
31·89	96·9	8·92	140	$KCu_{10}[Fe(CN)_6]_7$	32·02	+0·4
74·41	226·1	20·61	324	$KCu_{10}[Fe(CN)_6]_7$	74·73	−0·4
106·3	323	28·29	460	$KCu_{10}[Fe(CN)_6]_7$	106·3	0·0
106·9	324·6	35·48	558	$KCu_{10}[Fe(CN)_6]_7$	107·0	+0·1
534·3	1623	176·4	2276	$KCu_{10}[Fe(CN)_6]_7$	534·6	0·0
1068·7	3246	354	5570	$KCu_{10}[Fe(CN)_6]_7$	1068·6	0·0

Reaction between Cd^{2+} *and* $Fe(CN)_6^{3-}$

When cadmium(II) is titrated with ferricyanide in absence of additional potassium ions, yellow-brown $KCd_{10}[Fe(CN)_6]_7$ is formed over the concentration range pCd^{2+} = 1·0–1·8, yellow $Cd_3[Fe(CN)_6]_2$ is formed over the range pCd^{2+} = 2·1–3·7, and a mixture of the two over the intermediate range pCd^{2+} = 1·8–2·1. In the presence of 0·15*M* potassium nitrate or in the reverse titration under any conditions, only $KCd_{10}[Fe(CN)_6]_7$ is formed over the whole concentration ranges pCd^{2+} = 1–3·9, $pFe(CN)_6^{3-}$ = 1·2–3·7.

The error calculated on the basis of titration curves never exceeds 1% outside the region for formation of the mixture. Reaction rates are rather slow at room temperature.

When $K_3Fe(CN)_6$ is the titrand, enough potassium is present from the beginning of the titration for only $KCd_{10}[Fe(CN)_6]_7$ to be formed, whereas in the reverse titration additional potassium must be added for this to be the case.

K_{sp} *values and thermodynamic functions*

K_{sp} values for $KCu_{10}[Fe(CN)_6]_7$ were calculated from the conductivity of a saturated solution free from CO_2; for the other complexes they were calculated from the equivalence points of conductometric titration curves. For all complexes the measurements were made at 20°, 30° and 40°. Ionic mobilities at 30° and 40° were calculated by Walden's rule.[11] ΔG° values were obtained from $\Delta G^\circ = -RT \ln K_{sp}$, and ΔH° from the Gibbs-Helmholtz relation $\Delta H = -T^2\, \delta(\Delta G/T)/\delta T$. The results together with ΔS° values are summarized in Table 2.

Analysis of precipitates

Atomic-absorption spectrophotometric determination of the metal/iron ratio confirmed the combination ratios found for all the complexes.

Conclusions

A new "mixed" complex $KCu_{10}[Fe(CN)_6]_7$ was obtained in aqueous medium at constant ionic strength and $[K^+]$ = 0·5*M* and can be used for quantitative determination of $Fe(CN)_6^{3-}$.

Analysis of the $CdSO_4$–$K_3Fe(CN)_6$ system has cleared up the confusion about the concentration ranges over which the complexes are stable and explained the formation of $Cd_3[Fe(CN)_6]_2$ and $KCd_{10}[Fe(CN)_6]_7$ in the titration of Cd(II), and confirmed the correctness of Gaur and Bhattacharya's statement that $KCd_{10}[Fe(CN)_6]_7$ is formed in the titration of $K_3Fe(CN)_6$, in contradiction of King's work.[6]

Table 2. K_{sp}, ΔG°, ΔH° and ΔS° values

Formula	Temp., °C	Solubility, *mole/l.*	K_{sp}	ΔG°, *kcal/mole*	ΔH°, *kcal/mole*	ΔS°,* *kcal.mole.*$^{-1}$*deg*$^{-1}$
$Ag_3Fe(CN)_6$	20	$1\cdot2 \times 10^{-5}$	$5\cdot0 \times 10^{-19}$	$-24\cdot4$	$-9\cdot1$	$+0\cdot053$
	30	$1\cdot4 \times 10^{-5}$	$1\cdot3 \times 10^{-18}$	$-24\cdot7$	$-8\cdot66$	
	40	$1\cdot5 \times 10^{-5}$	$1\cdot4 \times 10^{-18}$	$-25\cdot5$	$-8\cdot92$	
$Cu_3[Fe(CN)_6]_2$	20	$3\cdot8 \times 10^{-6}$	$9\cdot0 \times 10^{-26}$	$-33\cdot4$	$-12\cdot9$	$-0\cdot07$
	30	$7\cdot0 \times 10^{-6}$	$1\cdot8 \times 10^{-24}$	$-32\cdot8$	$-11\cdot6$	
	40	$8\cdot2 \times 10^{-6}$	$4\cdot0 \times 10^{-24}$	$-31\cdot9$	$-10\cdot0$	
$KCu_{10}[Fe(CN)_6]_7$	20	$1\cdot2 \times 10^{-5}$	$2\cdot2 \times 10^{-77}$	$-102\cdot4$	-161	$-0\cdot20$
	30	$1\cdot4 \times 10^{-5}$	$5\cdot1 \times 10^{-72}$	$-98\cdot4$	-159	
	40	$1\cdot9 \times 10^{-5}$	$8\cdot5 \times 10^{-70}$	$-98\cdot4$	-161	
$Cd_3[Fe(CN)_6]_2$	20	$1\cdot2 \times 10^{-4}$	$3\cdot0 \times 10^{-18}$	$-23\cdot4$	$+140\cdot6$	$+0\cdot54$
	30	$1\cdot3 \times 10^{-4}$	$4\cdot5 \times 10^{-18}$	$-23\cdot9$	$+139\cdot6$	
	40	$1\cdot5 \times 10^{-4}$	$8\cdot2 \times 10^{-18}$	$-24\cdot3$	$+138\cdot3$	
$KCd_{10}[Fe(CN)_6]_7$	20	$1\cdot9 \times 10^{-5}$	$1\cdot0 \times 10^{-69}$	$-92\cdot2$	$-65\cdot8$	$+0\cdot09$
	30	$2\cdot2 \times 10^{-5}$	$1\cdot8 \times 10^{-68}$	$-93\cdot5$	$-66\cdot2$	
	40	$2\cdot5 \times 10^{-5}$	$2\cdot1 \times 10^{-66}$	$-93\cdot8$	$-65\cdot3$	

* Average value.

In agreement with previous observations on ferrocyanides[10], the presence of additional potassium favours the formation of the same complex whatever the direction of titration.

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Summary—With potassium ferricyanide copper(II) forms $KCu_{10}[Fe(CN)_6]_7$ quantitatively in $0{\cdot}5M$ potassium nitrate medium. Cadmium forms $Cd_3[Fe(CN)_6]_2$ if the ferricyanide is added to the cadmium solution in absence of extra potassium, and $KCd_{10}[Fe(CN)_6]_7$ if potassium is added first, or if the cadmium solution is added to the ferricyanide. Silver forms $Ag_3Fe(CN)_6$ only.

Zusammenfassung—Kupfer(II) bildet mit Kaliumferricyanid in 0·5M Kaliumnitratlösung quantitativ $KCu_{10}[Fe(CN)_6]_7$. Cadmium bildet $Cd_3[Fe(CN)_6]_2$, wenn man das Ferricyanid in Abwesenheit von weiterem Kalium zur Cadmiumlösung gibt, und $KCd_{10}[Fe(CN)_6]_7$, wenn man zuerst Kalium zugibt oder wenn die Cadmiumlösung zum Ferricyanid gegeben wird. Silber bildet nur $Ag_3Fe(CN)_6$

Résumé—Le cuivre (II) forme $KCu_{10}[Fe(CN)_6]_7$ avec le ferricyanure de potassium en milieu nitrate de potassium 0,5 *M*. Le cadmium forme $Cd_3[Fe(CN)_6]_2$ si le ferricyanure est ajouté à la solution de cadmium en l'absence de potassium supplémentaire, et $KCd_{10}[Fe(CN)_6]_7$ si le potassium est ajouté en premier, ou si la solution de cadmium est ajoutée au ferricyanure. L'argent ne forme que $Ag_3Fe(CN)_6$.

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THE USE OF FURFURAL THIOSEMICARBAZONE FOR THE GRAVIMETRIC DETERMINATION OF PALLADIUM

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Thiosemicarbazones have been used only occasionally as gravimetric reagents for palladium(II), although they form insoluble complexes with it. The thiosemicarbazone of *p*-ethylsulphonylbenzaldehyde has been used for this purpose with good results.[1] Complexes of palladium with some thiosemicarbazones have been isolated, and their infrared absorption spectra studied.[2]

In this paper, a procedure for the gravimetric determination of palladium(II) with furfural thiosemicarbazone is described. This compound forms an orange complex with palladium, insoluble in acid medium, and very easy to filter off. The optimum analytical conditions were determined.

EXPERIMENTAL

Reagents

Palladium solutions containing 5·795, 1·625 and 3·459 g/l. were standardized with dimethylglyoxime. More dilute solutions were prepared from these. All solvents and reagents were of analytical grade.

Preparation of the reagent

Furfural thiosemicarbazone was prepared by condensation of equimolar amounts of thiosemicarbazide and furfural.[3] The compound was recrystallized from ethanol. The infrared and ultraviolet spectra were recorded, and elemental analysis was made to confirm the synthesis (m.p. 145–147°; found: C 42·7%; H 4·1%; N 24·6%; calculated for $C_6H_7N_3OS$: C 42·70%; H 4·13%; N 24·60%).

An ethanolic solution (1·0%w/v) of the reagent was used in all subsequent work.

Qualitative tests

The reaction of furfural thiosemicarbazone with 40 cations, at concentrations up to 1000 ppm and at various pH values, was investigated. With Pd(II), an orange precipitate was produced. Cu(II) forms a green precipitate, and Ag(I), Hg(II) and Pt(IV) gave a weak yellow colour.

Precipitation of the palladium complex of furfural thiosemicarbazone

An aqueous solution of palladium chloride, containing 29·0 mg of palladium in 250–300 ml, was acidified with hydrochloric acid to between pH 3 and 4. A solution of furfural thiosemicarbazone was slowly added with constant stirring until a small excess was present. The precipitate was collected in a No. 3 porosity sintered-glass crucible, washed with about 100 ml of distilled water, and then dried at 60–80° to constant weight. (Found: C 32·5%; H 2·5%; N 19·0%. Calculated for $(C_6H_6N_3OS)_2Pd$: C 32·52%; H 2·71% N 18·97%.)

Thermal analysis

The thermogravimetric curve for the palladium-furfural thiosemicarbazone complex was recorded (Fig. 1). The complex was stable up to 180°; a sharp decrease occurs at 200°, and also at 450°. Suitable drying conditions for the complex were investigated. In all subsequent work, drying of the precipitate was always carried out at 60–120°.

Determination of the experimental conditions for precipitation

The effect of increasing the amount of furfural thiosemicarbazone was investigated with 32·5 mg of the palladium, pH between 3 and 5, and a final volume of 250 ml. Various volumes of the reagent were added. After 1 hr, the precipitate was collected and dried to constant weight. Table 1 gives the results, and shows that even when an appreciable excess of the reagent was added, no co-precipitation occurred.

The influence of various solvents for washing the precipitate were studied. Pure water was the best washing agent. Mixtures of ethanol–water (1 : 10 or 1 : 5) may also be used. Use of pure ethanol and acetone was unsuccessful.

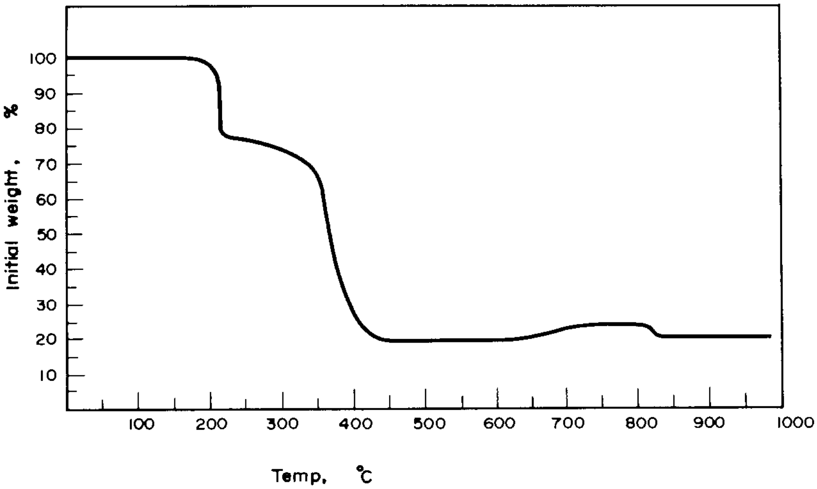

Fig. 1. Thermogravimetric curve of Pd-furfural thiosemicarbazone complex.

Table 1. Determination of the optimum amount of reagent

Reagent, *ml*	Pd taken, *mg*	Weight ppte, *mg*	Pd found, *mg*	Error, *mg*
5·0	32·5	5·5	1·3	−31·2
10·0	32·5	123·0	29·5	− 3·0
15·0	32·5	135·4	32·5	0·0
20·0	32·5	135·0	32·4	− 0·1
25·0	32·5	136·6	32·8	0·3
30·0	32·5	136·0	32·7	0·1

To determine the optimum pH for precipitation, the complex was precipitated from solutions at various pH values by using the method previously outlined. Table 2 gives the results. A pH between 2·0 and 6·0 was considered convenient, and all subsequent work was done in this pH range.

Recommended procedure for the determination of palladium

Take a sample solution containing 10–50 mg of palladium, dilute it to 200–250 ml, adjust the pH to 2·0–6·0, add 15–20 ml of 1% reagent solution (in ethanol) with constant stirring at room temperature. After 15–20 min, collect the precipitate in a weighed sintered-glass crucible, wash with 100–150 ml of distilled

Table 2. Influence of pH

pH	Pd taken, *mg*	Weight ppte, *mg*	Pd found, *mg*	Error, *mg*
0·5	29·0	51·5	12·4	−16·6
1·5	29·0	113·3	27·0	− 2·0
2·1	29·0	120·9	29·0	0·0
2·8	29·0	120·8	29·0	0·0
3·2	29·0	121·2	29·1	0·1
3·7	29·0	121·3	29·1	0·1
4·8	29·0	120·4	28·9	− 0·1
5·6	29·0	120·8	29·0	0·0
6·2	29·0	120·3	28·8	− 0·2
7·5	29·0	91·2	22·0	− 7·0
9·0	29·0	90·0	21·6	− 7·4

water, or 1 : 10 ethanol–water solution. Dry to constant weight at 60–120°. The weight of the precipitate, multiplied by 0·2402, gives the weight of palladium.

Determination of the error of the method

Table 3 gives results of recovery experiments. The standard deviation of a single measurements is 0·157 mg, and the standard deviation of the mean is ±0·032 mg. The error of the eight determinations is ±0·2%.

Table 3. Determination of the error of the method

Pd taken, *mg*	Weight ppte, *mg*	Pd found, *mg*	Error, *mg*
32·5	135·5	32·5	0·0
32·5	134·0	32·2	−0·3
32·5	135·6	32·6	0·1
32·5	135·5	32·5	0·0
32·5	135·2	32·5	0·0
32·5	136·0	32·7	0·2
32·5	135·3	32·5	0·0
32·5	134·4	32·3	−0·2

Interferences

Interference by foreign ions was investigated. Alkali metal salts were used for the solutions of the anions, and nitrates and chlorides for the solutions of the cations. In a few cases, sulphates and acetates were employed.

Up to at least 0·1 g of the following ions does not interfere; Co(II), Ni, Mn(II), Al, Zn, Fe(II), Ca, Sr, Ba, Ce(IV), Cd, La, Zr, Th, acetate, oxalate, fluoride and phosphate. The results obtained were all within the experimental error of the values obtained with palladium alone

Some ions were shown to interfere (Table 4).

Table 4. Interference of foreign ions

Pd taken, *mg*	Foreign ions, *mg*	Weight ppte, *mg*	Pd found, *mg*	Error, *mg*
34·6	100·0 Cu(II)	193·4	46·4	11·8
34·6	20·0 Pt(IV)	188·2	45·2	10·6
34·6	50·0 Hg(II)	147·6	35·4	0·8
34·6	100·0 Hg(II)	169·0	40·6	6·0
34·6	10·0 V(V)	153·5	36·9	2·3
34·6	100·0 V(V)	248·2	59·6	25·0
34·6	44·0 Au(III)	96·7	23·2	−11·4
34·6	10·0 Mo(VI)	155·3	37·3	2·7
34·6	20·0 Mo(VI)	175·9	42·2	7·6
34·6	10·0 W(VI)	154·8	37·2	2·6
34·6	100·0 W(VI)	244·5	58·7	24·1

DISCUSSION

Furfural thiosemicarbazone is a selective reagent for the determination of palladium(II). The compound is useful as a laboratory reagent, and there is no tendency for co-precipitation with the palladium complex. The precipitate formed is easy to filter off and stable, when dry, at temperatures up to 170–180°. The complex has a low solubility, and its large molecular weight gives appreciable increase in sensitivity compared with the classical reagents, such as dimethylglyoxime furfuraldoxime and thiophenaldoxime.

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Summary—The use of furfural thiosemicarbazone as a gravimetric reagent for palladium is described. The optimum analytical conditions for precipitation of the palladium complex and the effect of possible interferences have been investigated.

Zusammenfassung—Die Verwendung von Furfuralthiosemicarbazon als gravimetrisches Reagens für Palladium wird beschrieben. Die optimalen analytischen Bedingungen zur Fällung des Palladiumkomplexes und der Einfluß möglicher Storungen wurde untersucht.

Résumé—On décrit l'emploi de la thiosemicarbazone du furfural comme réactif gravimétrique pour le palladium. On a étudié les conditions analytiques optimales pour la précipitation du complexe du palladium et l'influence d'interférences possibles.

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EXTRACTIVE SPECTROPHOTOMETRY OF THE MOLYBDENUM (III) 1,10-PHENANTHROLINE THIOCYANATE AND 2,2′-BIPYRIDYL THIOCYANATE COMPLEXES*

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Komarowski and Poluektoff[1] observed that an acidic solution of molybdenum containing 2,2′-bipyridyl, when reduced with chlorostannous acid, gave a reddish violet colour. Moss *et al.*[2] later observed that the same reaction is given by 1,10-phenanthroline and tried to stabilize the colour of both complexes of reduced molybdenum, but were unsuccessful. They also observed that the phenanthroline reaction was the more sensitive but did not recommend the procedure, because of instability of the colour. Lazarev[3] stabilized the bipyridyl complex by reducing with chlorostannous acid in presence of tartaric acid, the molar absorptivity being $1{\cdot}8 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ at 520 nm. The phenanthroline complex was studied qualitatively by Rao *et al.*,[4] who also found the molar absorptivity to be $8{\cdot}82 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ at 565 nm.

It is now found that phenanthroline, bipyridyl and bathophenanthroline form stable complexes with molybdenum(III) in 1,2-dichloroethane in presence of chlorostannous acid and thiocyanate. An acidic solution of molybdenum containing thiocyanate and phenanthroline or bipyridyl is reduced with chlorostannous acid and the resultant precipitate extracted into 1,2-dichloroethane.

EXPERIMENTAL

Reagents

Standard molybdenum solution, 0.01%. Prepared by dissolving MoO_3 (1·5 g) in a few ml of dilute sodium hydroxide solution, diluting to about 100 ml, making slightly acidic with dilute hydrochloric acid and then diluting to 1000 ml. It was diluted to 0.001 and 0.0001% with 0.1*M* hydrochloric acid.

1,10-*Phenanthroline monohydrate solution*, 0·1%.

2,2′-*Bipyridyl solution*. 2,2′-Bipyridyl (1 g) dissolved in the minimum necessary amount of 6*M* hydrochloric acid and diluted to 1000 ml.

Bathophenanthroline (4,7-*diphenyl*-1,10-*phenanthroline*) *solution*, 0·1% *in ethanol*.

Potassium thiocyanate solution, 20%.

Chlorostannous acid solution, 5%. Stannous chloride (20 g) dissolved in 50 ml of concentrated hydrochloric acid and diluted to 400 ml. Metallic tin was added to prevent oxidation during storage.

All other reagents were analytical grade. Water and solvents were redistilled in glass apparatus.

Apparatus

Silver reductor. Prepared according to Vogel.[5]

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Résumé—On décrit l'emploi de la thiosemicarbazone du furfural comme réactif gravimétrique pour le palladium. On a étudié les conditions analytiques optimales pour la précipitation du complexe du palladium et l'influence d'interférences possibles.

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EXTRACTIVE SPECTROPHOTOMETRY OF THE MOLYBDENUM (III) 1,10-PHENANTHROLINE THIOCYANATE AND 2,2′-BIPYRIDYL THIOCYANATE COMPLEXES*

(*Received* 21 *June* 1972. *Accepted* 26 *August* 1972)

Komarowski and Poluektoff[1] observed that an acidic solution of molybdenum containing 2,2′-bipyridyl, when reduced with chlorostannous acid, gave a reddish violet colour. Moss *et al.*[2] later observed that the same reaction is given by 1,10-phenanthroline and tried to stabilize the colour of both complexes of reduced molybdenum, but were unsuccessful. They also observed that the phenanthroline reaction was the more sensitive but did not recommend the procedure, because of instability of the colour. Lazarev[3] stabilized the bipyridyl complex by reducing with chlorostannous acid in presence of tartaric acid, the molar absorptivity being $1\cdot8 \times 10^3$ l.mole^{-1}.cm^{-1} at 520 nm. The phenanthroline complex was studied qualitatively by Rao *et al.*,[4] who also found the molar absorptivity to be $8\cdot82 \times 10^3$ l.mole^{-1}.cm^{-1} at 565 nm.

It is now found that phenanthroline, bipyridyl and bathophenanthroline form stable complexes with molybdenum(III) in 1,2-dichloroethane in presence of chlorostannous acid and thiocyanate. An acidic solution of molybdenum containing thiocyanate and phenanthroline or bipyridyl is reduced with chlorostannous acid and the resultant precipitate extracted into 1,2-dichloroethane.

EXPERIMENTAL

Reagents

Standard molybdenum solution, 0.01%. Prepared by dissolving MoO$_3$ (1·5 g) in a few ml of dilute sodium hydroxide solution, diluting to about 100 ml, making slightly acidic with dilute hydrochloric acid and then diluting to 1000 ml. It was diluted to 0.001 and 0.0001% with 0.1*M* hydrochloric acid.

1,10-*Phenanthroline monohydrate solution*, 0·1%.

2,2′-*Bipyridyl solution*. 2,2′-Bipyridyl (1 g) dissolved in the minimum necessary amount of 6*M* hydrochloric acid and diluted to 1000 ml.

Bathophenanthroline (4,7-*diphenyl*-1,10-*phenanthroline*) *solution*, 0·1% *in ethanol*.

Potassium thiocyanate solution, 20%.

Chlorostannous acid solution, 5%. Stannous chloride (20 g) dissolved in 50 ml of concentrated hydrochloric acid and diluted to 400 ml. Metallic tin was added to prevent oxidation during storage.

All other reagents were analytical grade. Water and solvents were redistilled in glass apparatus.

Apparatus

Silver reductor. Prepared according to Vogel.[5]

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* Abstracted from a thesis presented by A. K. Bhadra to the University of Calcutta in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1970.

Procedure

To a solution containing 0·06 mg of molybdenum, 5 ml of phenanthroline or bipyridyl or bathophenanthroline solution, 5 ml of methanol and 2 ml of potassium thiocyanate solution were added. The pH was adjusted to 1·5 and the solution transferred into a separating-funnel, followed by 5 ml of chlorostannous acid. After 1 min, the solution was shaken with 15 ml of 1,2-dichloroethane for about 20 min. The extraction was repeated with 5 ml of 1,2-dichloroethane, with shaking for 3 min. The extracts were collected in a 25-ml flask and diluted to volume with 1,2-dichloroethane. Turbidity was removed by the addition of 0·5 g of anhydrous sodium sulphate. The absorbance of the phenanthroline and bipyridyl complexes was measured at 525 nm and that of the bathophenanthroline complex at 565 nm, against a reagent blank.

When 2,2′-bipyridyl is used, addition of methanol may be omitted. For calibration curves, a 5-10 min equilibration is enough.

RESULTS

The absorption spectra of the ternary complexes are shown in Fig. 1. The molar absorptivities *etc.* are given in Table 1.

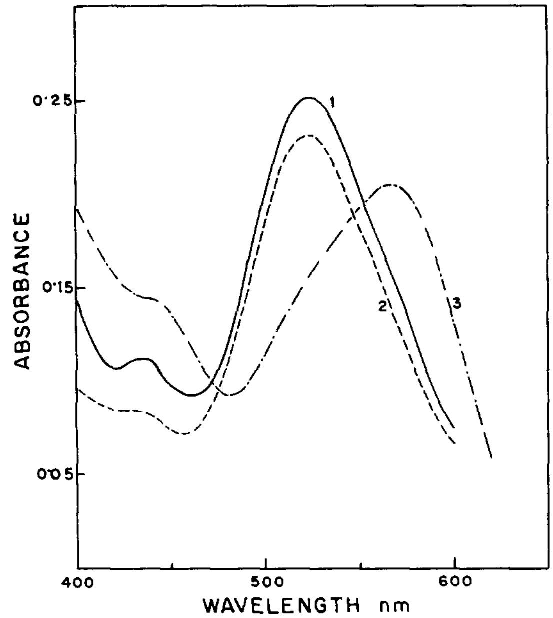

Fig. 1. Absorption spectra of the Mo(III)–1,10-phenanthroline thiocyanate (1), Mo(III)–2,2′-bipyridyl thiocyanate (2), and Mo–bathophenanthroline thiocyanate (3) complexes.

The optimum pH range of the aqueous solution before addition of chlorostannous acid is 1·2–6·5. If the pH is <1·2, the colour of the complexes decreases.

The optimum thiocyanate concentrations in the aqueous phase for the phenanthroline, bipyridyl and bathophenanthroline systems are 0.25–1, 0·25–2, and 0·25–2*M* respectively. Thiocyanate added in excess causes colourless precipitates insoluble in 1,2-dichloroethane.

Effect of methanol

Serious interferences due to phosphorus, tungsten, vanadium, silicon, aluminium *etc.* in the phenanthro-

Table 1. Characteristics of the extracts of the molybdenum(III) complexes

Complex	Solvent	λ_{max} *nm*	Molar absorptivity, *l*.mole^{-1}.cm^{-1}	Sandell sensitivity *μg/cm²*
Mo(III)–phen-thiocyanate	1,2-dichloroethane	525	$9{\cdot}52 \times 10^3$	0·010
Mo(III)–phen-thiocyanate	chloroform	525	$6{\cdot}46 \times 10^3$	0·014
Mo(III)–bipy-thiocyanate	1,2-dichloroethane	525	$8{\cdot}20 \times 10^3$	0·012
Mo(III)–bipy-thiocyanate	chloroform	525	$5{\cdot}88 \times 10^3$	0·016
Mo(III)–bathophen thiocyanate	1,2-dichloroethane	565	$8{\cdot}16 \times 10^3$	0·012

line system can be overcome by addition of methanol to the aqueous solution before addition of chlorostannous acid. The effect is not understood but the addition of methanol is necessary, as the method completely fails in presence of aluminium, tungsten, *etc.* in absence of methanol. With the bipyridyl system, addition of methanol is not necessary.

Two or three drops of the chlorostannous acid solution have been found to be sufficient for reduction of molybdenum. In order to reduce the interference of iron, 2–5 ml of chlorostannous acid solution were used in all cases. A large excess decreases the colour of the complexes.

Beer's law is obeyed over the concentration ranges 1–10 μg/ml, at 525 nm for the phenanthroline and bipyridyl systems, and at 565 nm for the bathophenanthroline complex.

Interference studies

To a solution containing 60 μg of molybdenum, the interfering ions were added, followed by 15 ml of phenanthroline or bipyridyl solution, 2 ml of thiocyanate solution, 5 ml of methanol and 2–3 ml of chlorostannous acid solution and the mixture was extracted with 1,2-dichloroethane, with shaking for about 20 min. A deviation of $<2\%$ was regarded as indicating no interference. The results are summarized in Table 2.

Table 2. Effect of various ions on the phenanthroline and bipyridyl ternary complexes.

Species	Added as	Tolerance limit, *mg*
Fe(III)	$FeNH_4(SO_4)_2{\cdot}12H_2O$	1·2
Al(III)	$Al_2(SO_4)_3{\cdot}18H_2O$	100
W(VI)	$Na_2WO_4{\cdot}2H_2O$	10.0
V(V)	V_2O_5	0·6
PO_4^{-3}	NaH_2PO_4	10.0
Silica	Added after fusion with sodium carbonate	10.0

Nature of the complexes

The oxidation state of molybdenum in the complexes was checked by comparing the complexes with those obtained by reaction of thiocyanate and phenanthroline or bipyridyl with molybdenum reduced to the tervalent state in 6*M* hydrochloric acid in a silver reductor at 60–80°.

Extraction took very much longer to complete (3–4 hr) than when the molybdenum was reduced in presence of the complexing agents. Only with reduction in 6*M* acid medium did the product have the same characteristics as that obtained by the recommended procedure. Reduction in 2 or 4*M* acid gave erratic results and incomplete complex formation. A similar check was not possible for the bathophenanthroline complex, on account of the severe interference from traces of iron(II) produced in the reduction step. No attempt was made to determine the stoichiometry of the complexes.

DISCUSSION

Because of its lower sensitivity and the serious interference from iron, the bathophenanthroline complex was not studied closely. The phenanthroline complex is poorly extracted in presence of interfering substances unless methanol is added before the extraction. The bipyridyl system is superior in this respect though somewhat less sensitive.

Several solvents were tried. In polar solvents, a pink red solution appears within a few minutes of shaking, but on standing the colour changes to yellow. The best solvent proved to be 1 2-dichloroethane .

The extraction is complete in a single pass with 1,2-dichloroethane. A 5-min equilibrium period is sufficient in absence of interfering elements but longer is needed in their presence. A blueish pink colour appears in the organic phase after shaking for a few seconds, and changes to reddish pink after 5–6 min shaking.

Binary complexes of molybdenum formed with phenanthroline, bipyridyl or bathophenanthroline in presence of chlorostannous acid are extractable into 1,2-dichloroethane, but are unstable. The phenanthroline and bipyridyl complexes have λ_{max} at 510–520 nm and the bathophenanthroline complex has λ_{max} at 540 nm. The molar absorptivities are $2{\cdot}72 \times 10^3$, $1{\cdot}8 \times 10^3$ and $3{\cdot}2 \times 10^3$ $1.mole^{-1}.cm^{-1}$ respectively. It is not known whether chlorostannous acid is responsible for the extraction of the molybdenum complexes as in the case of ferroin.[6]

The sequence of addition of reagents is important Colour development is extremely slow when a solution containing molybdenum and thiocyanate is shaken with 1,2-dichloroethane in presence of chlorostannous acid, followed by addition of phenanthroline, or bipyridyl, requiring an equilibration period of 3–4 hr. The yellow organic extract obtained by shaking for about 30 min, if left overnight in presence of the aqueous phase, changes to reddish pink with the correct absorbance. This probably indicates a rearrangement as suggested by Rao *et al.*[4]

We prefer the formula Mo(III)-1,10-phenanthroline$(SCN)_3$ to the MoO-1,10-phenanthroline$(SCN)_3$ suggested by Rao *et al.*,[4] as tervalent molybdenum is involved in the reaction.

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Summary—New extraction spectrophotometric methods for the determination of small amounts of molybdenum have been developed, using thiocyanate and 1,10-phenanthroline or 2,2′-bipyridyl as reagents in the presence of chlorostannous acid. Extracts of the ternary complexes of tervalent molybdenum in 1,2-dichloroethane obey Beer's law in the range 1–10 μg/ml at 525 nm. A 10-fold excess of iron and vanadium and 100-fold excess of tungsten, phosphorus and silicate do not interfere.

Zusammenfassung—Neue extraktions-spektrophotometrische Methoden zur Bestimmung kleiner Molybdänmengen wurden entwickelt; sie verwenden Thiocyanat und 1,10-Phenanthrolin oder 2,2′-Bipyridyl als Reagentien in Gegenwart von Chlorozinn(II)-säure. Extrakte der ternären Komplexe von dreiwertigem Molybdän in 1,2-Dichloräthan gehorchen bei 525 nm im Bereich 1–10 μg/ml dem Beerschen Gesetz. Ein 10-facher Überschuß von Eisen und Vanadium und 100-facher Überschuß von Wolfram, Phosphor und Silikat stören nicht.

Table 1. Results for gold in gold-doped germanium M

Sample No.	Expected by manufacturer, *ppM*	Neutron-activation analysis 1st detn. *ppM*	Neutron-activation analysis 2nd detn. *ppM*
14	~10*	—	24.1
39	~20	34·1	32·8
94	~20	34·6	37·0

* $\sim 5 \times 10^{14}$ atoms/cm^3.

Acknowledgement—I am grateful to Prof. J. Hoste for his interest in this work and to Miss J. Zels for her technical assistance. The financial support of the I.I.K.W (Interuniversity Institute for Nuclear Sciences) is gratefully acknowledged.

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Summary—Gold was determined in gold-doped germanium by neutron-activation analysis. The irradiated samples were dissolved in *aqua regia*, in the presence of gold carrier. The matrix activity was eliminated by distillation, and gold precipitated in the residue with hydroquinone. The gold fraction was essentially radiochemically pure. For a neutron dose of 5×10^{15}n/cm^2, a sensitivity of 1 ppM Au can be obtained, with a 2·4-g sample. The samples investigated contained from 24 to 36 ppM Au.

Zusammenfassung—Gold in golddosiertem Germanium wurde durch Neutronenaktivierungsanalyse bestimmt. Die bestrahlten Proben wurden in Gegenwart von Goldträger in Königswasser gelöst. Die Matrix-Aktivität wurde durch Destillation entfernt und Gold im Rückstand mit Hydrochinon gefällt. Die Goldfraktion war praktisch radiochemisch rein. Bei einer Neutronendosis von $5 \cdot 10^{15}$ n/cm^2 kann man eine Empfindlichkeit von 1 ppM Au in einer 2·4g-Probe erreichen. Die untersuchten Proben enthielten 24–36 ppM Au.

Résumé—On a dosé l'or dans le germanium dopé à l'or par analyse par activation de neutrons. Les échantillons irradiés ont éte dissous dans l'eau régale, en présence d'or entraîneur. L'activité de la matrice a été éliminée par distillation, et l'or précipité dans le résidue par-l'hydroquinone. Le fraction or était essentiellement radiochimiquement pure. Pour une dose de neutrons de 5×10^{15} n/cm^2, on peut obtenir une sensibilité de 1 ppM de Au avec un échantillon de 2·4 g. Les échantillons étudiés contenaient de 24 à 36 ppM de Au.

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ESTIMATION OF ALLYL ALCOHOL BY CHLORAMINE-T

(*Received* 4 *August* 1972. *Accepted* 18 *September* 1972)

Chloramine-T (CAT) has received considerable attention as a mild oxidant for several organic compounds[1,2,3]. Kinetic studies of oxidation reactions involving CAT have recently been reported.[4,5] During an investigation of the kinetics of oxidation of alcohols by CAT, it became necessary to establish the stoichiometry of the reaction. Attempts were made to oxidize several alcohols—isopropyl alcohol, methoxyethanol, glycol, 2,3-butanediol and allyl alcohol—with CAT. With the conditions employed in the present communication, the rate of oxidation was found to be low or almost negligible except for allyl alcohol. Allyl alcohol could be oxidized by CAT at all pH values with a two-electron change and the reaction was fastest and almost instantaneous in hydrochloric acid medium ($0{\cdot}5$–$1{\cdot}0M$). A direct titration of the alcohol with CAT with a visual end-point was not practicable and a back-titration procedure was developed. Allyl alcohol finds a number of industrial applications in the preparation of resins, plasticisers, pharmaceuticals and many organic compounds. A review of the literature shows that allyl alcohol can be estimated by titration with bromide-bromate mixture,[6] potassium dichromate[7] and mercuric acetate.[8] We have thoroughly investigated the oxidation of allyl alcohol by bromide–bromate mixture and found it to be very sluggish and less accurate. The present oxidation procedure with CAT gives a rapid and very accurate method of estimating allyl alcohol, compared with the methods involving other oxidants[7,8] and substantial amounts of the alcohol can be estimated by a proper adjustment of reaction conditions.

EXPERIMENTAL

Reagents

Allyl alcohol (Merck, corrected b.p. 97·1°, $n_{D(20°)} = 1{\cdot}412$) was used without further purification, but its purity was checked by determining the alcoholic hydroxyl group by phthalation with phthalic anhydride in pyridine.[9] The required quantity of the alcohol was accurately weighed and dissolved in the proper solvent to give an approximately $0{\cdot}2M$ solution. CAT was purified by the method of Morris *et al.*[10] An approximately $0{\cdot}1N$ solution was prepared and standardized by the iodometric method. All other reagents were of accepted grades of purity. Phosphate–citric acid buffers[11] were used for the pH range 2–8. Triply distilled water was used for preparing the solutions.

Preliminary studies

Known amounts of allyl alcohol solution in the proper solvent were added to a known excessive volume of CAT in an iodine flask placed in a thermostat at 30°. The reaction mixture was set aside for various intervals of time, with occasional shaking. Then the excess of CAT was determined by back-titration.

Table 1 gives a typical set of results for the extent of oxidation of allyl alcohol in 5 min by an excess of CAT. It is seen that oxidation is slow in media other than $0{\cdot}5$–$1{\cdot}0M$ hydrochloric acid. The rate of oxidation increases as the pH increases from 2·2 to 7·0, but then drastically decreases at pH above 7. However, the stoichiometry is unaffected in these media as the reaction goes to completion after 2–3 hr. The reaction is found stoichiometric and very rapid in $0{\cdot}5$–$1{\cdot}0M$ hydrochloric acid.

Recommended procedure

Prepare an aqueous solution of the allyl alcohol ($\sim 0{\cdot}1M$). Add an aliquot containing 0·1–2·5 mmole to a measured excessive (10–20%) volume of $0{\cdot}1N$ chloramine-T containing enough $2M$ hydrochloric acid to make the overall acid concentration $0{\cdot}5$–$1{\cdot}0M$. Shake the mixture and after a minute add 20 ml of 10% potassium iodide solution and 10 ml of $2N$ sulphuric acid and titrate with $0{\cdot}1N$ sodium thiosulphate. Run a blank with CAT solution alone. The amount (x mg) of allyl alcohol in the experimental solution is given by

$$x = 29y(V_1 - V_2)$$

where y is the normality of the thiosulphate, V_1 is the blank titration and V_2 the volume of thiosulphate used to titrate the excess of CAT after oxidation of the allyl alcohol.

Table 1. Extent of oxidation of allyl alcohol with chloramine-T

Medium	$\frac{\text{CAT used, mole}}{\text{Allyl alcohol taken, } \textit{mole}}$	Medium	$\frac{\text{CAT used, mole}}{\text{Allyl alcohol taken, } \textit{mole}}$
1·0*N* H_2SO_4	0·566	pH 2·2	0·887
0·5*N* H_2SO_4	0·544	pH 3·0	0·906
0·25*N* H_2SO_4	0·509	pH 4·2	0·918
0·125*N* H_2SO_4	0·429	pH 5·0	0·944
1·0*M* $HClO_4$	0·801	pH 6·2	0·944
0·5*M* $HClO_4$	0·601	pH 7·0	0·943
0·25*M* $HClO_4$	0·538	pH 8·0	0·877
0·125*M* $HClO_4$	0·488	pH 9·0	0·103
1·0*M* HCl	1·002	pH 10·0†	0·074
0·5*M* HCl	1·002	1·0 *M* NaOH	0·023
0·25*M* HCl	0·967	0·5*M* NaOH	0·023
0·125*M* HCl	0·960	0·25*M* NaOH	0·023

* Borax–HCl buffer

† Borax–NaOH buffer.

Allyl alcohol taken 0.28 mmole; CAT taken 1·93 mmole; time 5 min; temp. 30°C.

RESULTS AND DISCUSSION

Detailed investigation of the allyl alcohol system has brought out the following facts.

(*i*) The stoichiometry of the oxidation can be represented as

$$CH_2{=}CH{-}CH_2OH + RNClNa \longrightarrow CH_2{=}CH{-}CHO + RNH_2 + NaCl,$$

where $R{=}CH_3{-}C_6H_4SO_2$. The presence of allyl aldehyde (acrolein) in the reaction products can be demonstrated with the help of spot tests with sodium nitroprusside solution containing piperidine.[12]

(*ii*) Foreign ions such as K^+, Ba^{2+}, Zn^{2+}, NO_3^-, PO_4^{3-}, ClO_4^- and SO_4^{2-} have no influence on the rate of oxidation in hydrochloric acid medium.

(*iii*) Sodium chloride (up to 0·2 mole) has no effect on the rate of oxidation.

(*iv*) The stoichiometry is unaffected by a reversal of the order of addition of oxidant and allyl alcohol.

(*v*) The reaction rate is greatly retarded in sulphuric and perchloric acid media (*cf.* Table 1), although stoichiometric oxidation is complete within an hour.

The first step in the process of oxidation is thought to be the protonation of the alcohol:

$$CH_2{=}CHCH_2OH + H^+ \longrightarrow CH_2{=}CHCH_2OH_2^+$$

The protonated alcohol may form a highly solvated activated complex with the species present in larger concentration in acidified CAT solution.[13] It is likely that the Cl^- ion will have a greater stabilizing influence on the transition state than the perchlorate and sulphate ions, because of its comparatively smaller size. However, kinetic investigations of the oxidation are in progress which may throw light on the mechanism of oxidation.

Some typical results of analysis of allyl alcohol in aqueous solutions are given in Table 2. The values obtained are accurate within 0·5%.

Table 2

Allyl alcohol taken, *mg*	Allyl alcohol found, *mg*	Allyl alcohol taken, *mg*	Allyl alcohol found, *mg*
7·8	8·0	53·5	53·5
15·3	15·4	61·2	61·2
23·0	23·0	68·9	68·8
30·6	30·5	89·5	89·5
38·3	38·2	108·0	107·9
46·0	46·2	125·5	125·1

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Summary—A simple but rapid and accurate method for the estimation of allyl alcohol in aqueous solution has been developed, based on its oxidation with chloramine-T at room temperature, in 0·5–1·0*M* hydrochloric acid medium. The reaction involves a two-electron change. The effect of such variables such as pH of the medium, presence of foreign ions and perchloric or sulphuric acid on the rate of oxidation is discussed.

Zusammenfassung—Eine einfache, aber schnelle und genaue Methode zur Bestimmung von Allylalkohol in wäßriger Lösung wurde entwickelt. Sie beruht auf seiner Oxidation mit Chloramin-T bei Zimmertemperatur in 0·5–1·0 M Salzsäure. Bei der Reaktion werden zwei Elektronen umgesetzt. Der Einfluß von Variablen wie pH des Mediums, Anwesenheit von Fremdionen und Überchlor oder Schwefelsäure auf die Geschwindigkeit der Oxidation wird diskutiert.

Résumé—On a élaboré une méthode simple, mais rapide et précise, pour le dosage de l'alcool allylique en solution aqueuse, basée sur son oxydation par la chloramine-T à témpérature ambiante, en milieu acide chlorhydrique 0,5–1,0*M*. La réaction comprend un échange à deux électrons. On discute de l'influence de variables telles que le pH du milieu, la présence d'ions étrangers et d'acide perchlorique ou sulfurique sur la vitesse d'oxydation.

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PRECIPITATION OF CALCIUM OXALATE FROM HOMOGENEOUS SOLUTION BY CATION RELEASE

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Methods for precipitating calcium oxalate have been reviewed by Holth[1] and more recently and comprehensively by Bashar and Townshend.[2] The methods considered by the latter can be divided into three main groups: (*i*) pH change by urea hydrolysis;[3,4] (*ii*) precipitation from acetic acid medium;[5] (*iii*) hydrolysis of esters, such as dimethyl oxalate[6] and diethyl oxalate.[7] The principal criteria used for comparison of the various methods[2] were the ease and completeness of separation from magnesium and the particle-size of the precipitate. These authors concluded that a method involving the addition of urea to a hot clear solution and subsequent hydrolysis was the best.

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Summary—A simple but rapid and accurate method for the estimation of allyl alcohol in aqueous solution has been developed, based on its oxidation with chloramine-T at room temperature, in 0·5–1·0*M* hydrochloric acid medium. The reaction involves a two-electron change. The effect of such variables such as pH of the medium, presence of foreign ions and perchloric or sulphuric acid on the rate of oxidation is discussed.

Zusammenfassung—Eine einfache, aber schnelle und genaue Methode zur Bestimmung von Allylalkohol in wäßriger Lösung wurde entwickelt. Sie beruht auf seiner Oxidation mit Chloramin-T bei Zimmertemperatur in 0·5–1·0 M Salzsäure. Bei der Reaktion werden zwei Elektronen umgesetzt. Der Einfluß von Variablen wie pH des Mediums, Anwesenheit von Fremdionen und Überchlor oder Schwefelsäure auf die Geschwindigkeit der Oxidation wird diskutiert.

Résumé—On a élaboré une méthode simple, mais rapide et précise, pour le dosage de l'alcool allylique en solution aqueuse, basée sur son oxydation par la chloramine-T à témpérature ambiante, en milieu acide chlorhydrique 0,5–1,0*M*. La réaction comprend un échange à deux électrons. On discute de l'influence de variables telles que le pH du milieu, la présence d'ions étrangers et d'acide perchlorique ou sulfurique sur la vitesse d'oxydation.

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PRECIPITATION OF CALCIUM OXALATE FROM HOMOGENEOUS SOLUTION BY CATION RELEASE

(*Received* 17 *June* 1971. *Revised* 17 *April* 1972. *Accepted* 20 *September* 1972)

Methods for precipitating calcium oxalate have been reviewed by Holth[1] and more recently and comprehensively by Bashar and Townshend.[2] The methods considered by the latter can be divided into three main groups: (*i*) pH change by urea hydrolysis;[3,4] (*ii*) precipitation from acetic acid medium;[5] (*iii*) hydrolysis of esters, such as dimethyl oxalate[6] and diethyl oxalate.[7] The principal criteria used for comparison of the various methods[2] were the ease and completeness of separation from magnesium and the particle-size of the precipitate. These authors concluded that a method involving the addition of urea to a hot clear solution and subsequent hydrolysis was the best.

None of the methods described in the literature, however, gives partial or complete separation of calcium from other metals forming sparingly soluble oxalates, such as lead, copper, zinc, cadmium, mercury, which must therefore be absent during the estimation.

The general technique of precipitation from homogeneous solution by cation release has been reviewed by Cartwright *et al.*[8] whilst more recently various theoretical aspects of predicting the feasibility of such procedures have been studied.[9] The release of complexed cations by means of oxidation with hydrogen peroxide has been employed, for example, in the precipitation of ferric hydroxide,[10] bismuth phosphate[11] and manganese phosphate.[12]

Lead and silver[13] were successfully separated by complexing lead with EDTA whilst precipitating silver as chloride homogeneously by volatilization of ammonia. The effective stability constant of the silver/EDTA complex was lowered as the solution become progressively acid but the lead/EDTA complex remained sufficiently stable to prevent the preciptiation of lead chloride. The precipitation of calcium oxalate by cation release from the EDTA complex should allow at least partial separation of metal ions forming substantially stronger EDTA complexes than calcium does.

This paper describes the precipitation of calcium oxalate by releasing calcium from its EDTA complex by oxidation with hydrogen peroxide, into a solution containing excess of oxalate. The potential usefulness of the technique is exemplified by the separation of calcium from lead.

EXPERIMENTAL

Reagents

All reagents were of analytical grade.

Apparatus

To avoid providing sites for nucleation during precipitation, all experiments were carried out in clean, unscratched beakers; pH measurements were made to ±0·05 with a pH meter.

Establishment of procedure

A constant quantity of calcium (200 mg) was precipitated over a range of pH values between 6 and 10. Calcium chloride hexahydrate (1 g) was dissolved in distilled water (300 ml) and EDTA (1·86 g) was added so as to complex all the calcium. To the solution of the complex 40 ml of 5% ammonium oxalate solution were added and the pH was adjusted to the required level by addition of sodium hydroxide.

The reaction mixture was heated to boiling point and 50 ml of 100-vol hydrogen peroxide were slowly added; boiling was continued with occasional additions of distilled water to compensate for that lost by evaporation. After 60 min a further 15 ml of hydrogen peroxide were added and the solution was boiled for a further 15 min.

The solution was cooled and the precipitate filtered off, washed, and weighed after drying at 110° for 2 hr. The precipitate was confirmed to be calcium oxalate monohydrate by thermogravimetry.

The recovery as a function of pH is shown in Fig. 1, which shows that the optimum pH lies between 6 and 8. Below pH 6 spontaneous precipitation occurs on addition of the ammonium oxalate, whilst above pH 8 the calcium/EDTA complex is too strong to allow complete oxidation of the complex under the experimental conditions.

Variation in quantity of calcium

Experiments were carried out at pH 6–6·5 in which various quantities, nominally 50, 100 and 200 mg, of calcium were precipitated. The results obtained are summarized in Table 1, where it can be seen that the precipitation is quantitative. The reaction solutions were tested for completeness of precipitation by determining the remaining quantity of calcium by flame photometry. The maximum amount of residual calcium was <2ppm (equivalent to <0·6 mg in 300 ml).

Table 1. Precipitation of calcium oxalate—variation in amount of calcium

Calcium chloride, *g*	Calcium, *g*	Wt. of ppte, *g*	Ca found, *g*	Recovery, %
0·2500	0·0456	0·1695	0·0458	100·5
0·5020	0·0916	0·3366	0·0918	100·1
1·0020	0·1825	0·6720	0·1835	100·5

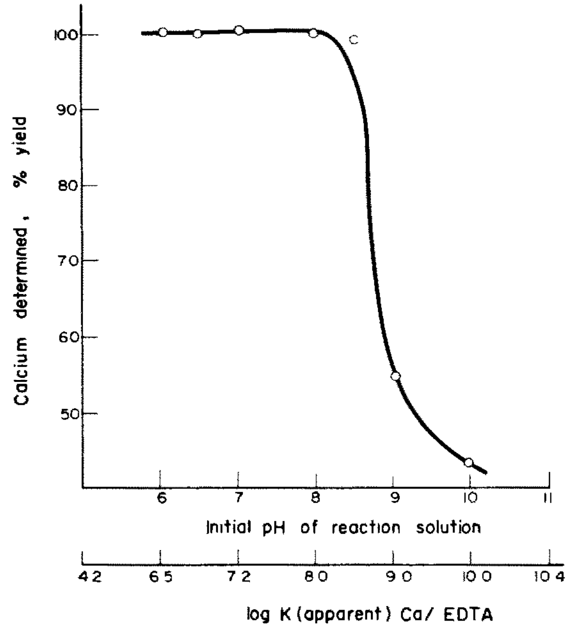

Fig. 1. Effect of initial pH on precipitation of calcium oxalate.

Crystal size

The crystals obtained were examined microscopically and the size of the precipitate particles was found to be 11–25 μm, mean 16 μm.

The urea-hydrolysis method yields larger crystals than the cation-release method but there is a limit beyond which increase in crystal size provides no further practical advantage. The precipitate obtained by the oxidative (cation-release) method settles quickly and is easily filterable.

Separation of calcium from lead

The potential usefulness of the cation-release technique is exemplified by separation of calcium from lead.

To a solution containing *ca.* 200 mg of calcium and *ca.* 100 mg of lead sufficient EDTA was added to complex both metals. The solution was adjusted to pH 8·8, in the presence of excess ammonium oxalate, and heated to boiling point; then 50 ml of 100-vol hydrogen peroxide were added. After 60 min of boiling a further 15 ml of peroxide were added and the solution was boiled for another 60 min, by which time the pH had dropped to about 7·8.

The reaction mixture was cooled and filtered, and the precipitate was washed, dried and weighed. The precipitate was dissolved and tested for lead with chromate. The precipitation of calcium was found to be quantitative and lead was found to be absent.

At similar pH values the calcium/EDTA complex is far more readily oxidized than the lead complex, as would be expected from their respective stability constants, $\log K_{\mathrm{CaY}} = 10{\cdot}7$, $\log K_{\mathrm{DbY}} = 18{\cdot}0$; the separation relies upon this difference in stability. It has been demonstrated that the calcium complex can be oxidized at pH 8 whereas the lead complex is not attacked at pH 6. Nevertheless in order to give the greatest margin of safety in the experimental procedure a higher pH was selected for the separation than when calcium alone was precipitated.

CONCLUSIONS

The homogeneous precipitation of calcium oxalate by cation release from the calcium/EDTA complex in the presence of oxalate is quantitative. The method also provides a means of separating calcium from lead and other metals forming sparingly soluble oxalates. Under the conditions of the experiments in which calcium and lead were separated the conditional stability constants of the calcium and lead/EDTA complexes were $\log K = 8{\cdot}8$ and $15{\cdot}5$, respectively. The fact that the reaction proceeds more quickly in the absence of lead is attributed to the difference in the pH used, 6·0–6·5 instead of pH 8.

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Summary—Calcium oxalate can be precipitated from homogeneous solution by oxidation of the calcium/EDTA complex with hydrogen peroxide in boiling solution, in the presence of oxalate ion, at pH 6–8. The method gives large crystals and enables calcium to be determined in the presence of lead, which remains complexed.

Zusammenfassung—Calciumoxalat kann durch Oxidation des Calcium-EDTA-Komplexes mit Wasserstoffperoxid in siedender Lösung bei pH 6–8 aus homogener Lösung gefällt werden. Das Verfahren liefert große Kristalle und erlaubt die Bestimmung von Calcium auch in Gegenwart von Blei, das komplex gebunden bleibt.

Résumé—On peut précipiter l'oxalate de calcium d'une solution homogène par oxydation du complexe calcium/EDTA, en la présence d'ion oxalate, par le peroxyde d'hydrogène en solution bouillante, à pH 6–8. La méthode donne de grands cristaux et rend possible la détermination du calcium en la présence de plomb, qui reste complexé.

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ANALYTICAL DATA

FORMATION OF FERROCYANIDES—III*
Fe(III), La(III) and Ce(III)

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The composition of the hexacyanoferrates(II) of tervalent metals is given by the general formulae $\mathrm{KMFe(CN)_6}$ and $\mathrm{M_4[Fe(CN)_6]_3}$.[1–6] The reaction between $\mathrm{K_4Fe(CN)_6}$ and La(III) or Ce(III) may be used for the direct or indirect determination of these two cations.[3–8] Our work[9–12] on the formation of hexacyanoferrates(II) therefore has been extended to Fe(III), La(III) and Ce(III).

The K_{sp} values as a function of ionic strength, temperature and solvent medium have also been evaluated.

EXPERIMENTAL

Potentiometric titrations were done with the cell

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Fe(CN)_6^{4-}} & \\ \mathrm{Fe(CN)_6^{3-}} & 10^{-6}M\end{matrix}\right\|\ \text{satd. } \mathrm{KNO_3}\ \Big\|\ \text{S.C.E.}$$

The $\mathrm{K_4Fe(CN)_6}$ solution was kept in dark bottles and standardized by potentiometric titration with Zn(II) solution under the analytical conditions for formation of $\mathrm{K_2Zn_3[Fe(CN)_6]_2}$.[9] The 0·01*M* nitric acid solutions of the nitrates of Fe(III), La(III) and Ce(III) were standardized gravimetrically, Fe(III) by means of ammonia and La(III) and Ce(III) by means of ammonium oxalate.[13].

RESULTS AND DISCUSSION

System $\mathrm{Fe(NO_3)_3}$–$\mathrm{K_4Fe(CN)_6}$–$\mathrm{H_2O}$

To avoid iron hydrolysis a 2*M* nitric acid medium was used. Higher acidity slows the reaction and causes dissociation of ferrocyanide and the precipitate, thus introducing uncontrollable variables.

Our results indicate that $\mathrm{Fe_4[Fe(CN)_6]_3}$ is formed irrespective of the direction of titration over the ranges pFe(III) = 1·7–3·76 and $\mathrm{pFe(CN)_6^{4-}}$ = 1·6–2·6. This formulation is in agreement with the infrared[14] and electronic[15] spectra. The potential drop at the equivalence point was 200–250 mV.

The precipitate, obtainable only at high Fe(III) concentrations, was spongy; only a blue colour was observed at low Fe(III) concentrations.

The same result was observed when 0·5*M* potassium nitrate medium was used.

System $\mathrm{La(NO_3)_3}$–$\mathrm{K_4Fe(CN)_6}$–$\mathrm{H_2O}$

Only the white $\mathrm{KLaFe(CN)_6}$ is obtained. The concentration ranges investigated were pLa(III) = 1·8–3·3 and $\mathrm{pFe(CN)_6^{4-}}$ = 1·95–3·96 respectively. The potential drop at the equivalence point was 70–90 mV, and 90–110 in 0·5*M* $\mathrm{KNO_3}$ medium. At room temperature the reaction is very slow; temperature of 70° was used. The product was found to be thermally stable.

System $\mathrm{Ce(NO_3)_3}$–$\mathrm{K_4Fe(CN)_6}$–$\mathrm{H_2O}$

This is similar to the lanthanum system but the potential drop at the equivalence point is about 10 mV greater and the reaction rate fast enough at room temperature. At 45° $\mathrm{KCeFe(CN)_6}$ undergoes rapid thermal decomposition but it is stable enough at 35° to permit determination of the K_{sp} value. The lowest concentrations titrated were pCe(III) = 3·23 and $\mathrm{pFe(CN)_6^{4-}}$ = 2·9.

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Table 1 summarizes the results of a number of titrations.

Table 1. Stoichiometry of the reactions between $Fe(CN)_6^{4-}$ and Fe(III), La(III), Ce(III).

Titrand (100 ml), *µmole*	Titrant, *µmole*	Formula	Found, *µmole*	Error, %
Fe(III)	$Fe(CN)_6^{4-}$			
71·5	54·4	$Fe_4[Fe(CN)_6]_3$	72·5	+1·4
142·9	106·8	$Fe_4[Fe(CN)_6]_3$	142·5	−0·3
448·5	330	$Fe_4[Fe(CN)_6]_3$	441·0	−1·6
$Fe(CN)_6^{4-}$	Fe(III)			
24·2	32·15	$Fe_4[Fe(CN)_6]_3$	24.11	−0·4
48·3	63·6	$Fe_4[Fe(CN)_6]_3$	47·7	−1·2
240·0	320·2	$Fe_4[Fe(CN)_6]_3$	240·0	0·0
La(III)	$Fe(CN)_6^{4-}$			
50·8	52·0	$KLaFe(CN)_6$	52·0	+2·3
101·6	101·2	$KLaFe(CN)_6$	101·2	−0·4
254·0	252·5	$KLaFe(CN)_6$	252·5	−0·6
$Fe(CN)_6^{4-}$	La(III)			
100·0	97·8	$KLaFe(CN)_6$	97·8	−2·2
175·0	172·7	$KLaFe(CN)_6$	172·7	−1·3
337·5	373·4	$KLaFe(CN)_6$	373·4	−0·4
Ce(III)	$Fe(CN)_6^{4-}$			
52·9	59·08	$KCeFe(CN)_6$	59·01	−1·4
299·6	249·1	$KCeFe(CN)_6$	294·1	−1·8
898·8	879·9	$KCeFe(CN)_6$	879·9	−2·1
$Fe(CN)_6^{4-}$	Ce(III)			
250·0	254·0	$KCeFe(CN)_6$	254·0	+1·6
500·0	494·3	$KCeFe(CN)_6$	494·3	−1·1

K_{sp} *values and thermodynamic properties*

K_{sp} values were obtained by means of measurements of the potential of a Pt electrode at constant temperature, at ionic strength from 0·22 to 0·66, obtained by addition of potassium nitrate.

The pK_{sp} values are linear functions of the ionic strength, slopes being as follows:

	T, °*C*	70	60	50	40
$KLaFe(CN)_6$	tan α	−1·93	−1·5	−1·95	−1·85

	T, °*C*	20	25	30
$KCeFe(CN)_6$	tan α	−1·90	−1·60	−1·88

Table 2 summarizes the thermodynamic values. $\Delta G°$ decreases linearly with temperature for both compounds. $\Delta H°$ and $\Delta S°$ being constant over the temperature range investigated.

Table 2. K_{sp} and thermodynamic data for $KLaFe(CN)_6$ and $KCeFe(CN)_6$ in H_2O.

Formula	*T*, °*C*	pK_{sp}	$\Delta G°$, *kcal/mole*	$\Delta H°$, *kcal/mole*	$\Delta S°$, *kcal. mole*$^{-1}$. *deg*$^{-1}$
$KLaFe(CN)_6$	70	8·8	−13 82	2·64	0·048
	60	8·7 ± 0·1	−13·25	2·73	
	50	8·7	−12·86	2·64	
	40	8·65	−12·38	2·64	
$KCeFe(CN)_6$	30	9·3	−12·90	4·07	0·056
	25	9·25	−12·62	4·07	
	20	9·2	−12·34	4·07	

Because interionic electrostatic effects may become significant on account of the high ionic charges, the influence of the dielectric constant was evaluated by means of measurements in aqueous ethanolic solutions. Linear dependence of pK_{sp} on ionic strength was again observed (Table 3).

Table 3. K_{sp} and thermodynamic data for $KLaFe(CN)_6$ and $KCeFe(CN)_6$ in H_2O–EtOH

Formula	H_2O : EtOH, *v/v*	*T*, *°C*	pK_{sp}	$\Delta G°$, *kcal/mole*	$\Delta H°$, *kcal/mole*	$\Delta S°$, *kcal. mole^{-1}. deg^{-1}*	$-\tan\alpha$
$KLaFe(CN)_6$	90 : 10	60	9·45	−14·39	2·26	0·050	2·82
		50	9·40	−13·89			2·46
	85 : 15	60	9·82	−14·95	14·35	0·088	3·18
		50	9·52	−14·07			1·98
	80 : 20	60	10·25	−15·61	19·35	0·105	3·70
		50	9·85	−14·56			2·66
	75 : 25	60	10·60	−16·14	24·34	0·122	3·94
		50	10·10	−14·92			2·40
$KCeFe(CN)_6$	90 : 10	30	10·25	−14·21	11·85	0·086	3·24
		25	10·10	−13·78			2·52
	85 : 15	30	10·75	−14·91	11·15	0·086	4·02
		25	10·62	−14·48			3·44
	80 : 20	30	11·08	−15·36	18·58	0·112	4·06
		25	10·85	−14·80			3·24
	75 : 25	30	11·50	−15·95	21·02	0·122	4·30
		25	11·25	−15·34			3·36

CONCLUSIONS

The analytical behaviour of the systems investigated is particularly simple, the same complex being always produced however the reaction is carried out. The reaction of Fe(III), La(III) or Ce(III) with $Fe(CN)_6^{4-}$ can be used for potentiometric determination of either the cations or the anion, if not too high an accuracy is required.

Addition of potassium nitrate has no quantitative effect on the reaction between $Fe(CN)_6^{4-}$ and La(III) or Ce(III) because it acts in two opposing ways: it lowers the solubility by the common ion effect, but at the same time K_{sp} increases with the increased ionic strength. The solubility of the La(III) and Ce(III) compounds is higher than that for similar complexes of bivalent metals.[10–12] The positive enthalpy change shows the prevalence of strong electrostatic repulsion effects. The formation of $KLaFe(CN)_6$ and $KCeFe(CN)_6$ is due to the favourable change in entropy.

With ethanolic media both the enthalpy and entropy changes are approximately linear functions of the ethanol concentration, but the slope for $T\Delta S°$ is greater than that for $\Delta H°$, so $\Delta G°$ becomes more negative with increasing ethanol concentration.

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Summary—Potassium ferrocyanide forms $Fe_4[Fe(CN)_6]_3$ with Fe(III), $KLaFe(CN)_6$ with La(III) and $KCeFe(CN)_6$ with Ce(III). The thermodynamic data for the two lanthanide compounds have been determined.

Zusammenfassung—Kaliumferrocyanid bildet mit Fe(III) $Fe_4[Fe(CN)_6]_3$, mit La(III)$KLaFe(CN)_6$ und mit Ce(III) $KCeFe(CN)_6$. Die thermodynamischen Daten für die beiden Lanthanidenverbindungen wurden ermittelt.

Résumé—Le ferrocyanure de potassium forme $Fe_4[Fe(CN)_6]_3$ avec Fe (III), $KLaFe(CN)_6$ avec La (III) et $KCeFe(CN)_6$ avec Ce (III). On a déterminé les données thermodynamiques pour les deux composés de lanthanides.

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DISTRIBUTION COEFFICIENTS OF Rb^+ ON ZIRCONIUM PHOSPHATE IN MIXED AQUEOUS-ORGANIC MEDIA

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The selectivity of cation-exchangers in mixed aqueous-organic solvents has been and is the subject of much study. Research has been nearly exclusively concerned with resin exchangers. To have a better understanding of the phenomena involved it seemed interesting to collect distribution coefficient data for cation-exchangers of a different type such as inorganic or cellulose ion-exchangers for non-complexed cations. This note summarizes the results obtained for the distribution of Rb^+ between zirconium phosphate and mixed solvents containing hydrochloric acid.

EXPERIMENTAL

Materials

Bio Rad ZP-1 cation-exchange crystals 50–100 mesh. All solvents were *pro analysi* products.

Procedure

The weight distribution coefficient, K_D, was determined at 25° after equilibration for 24 hr with ^{86}Rb. The hydrochloric acid concentration was kept constant at $0.85M$. Volume contraction effects were minimized by premixing of the solvent, hydrochloric acid and isotope solution before addition to the exchanger. The weight of zirconium phosphate was 200 mg, and 0·1–1 μg of rubidium was used.

RESULTS

The results are summarized in Table I. All values are the mean of at least two determinations. Reproducible results were obtained except in dimethylformamide in the 32–64% range.

An interpretation of the results is not possible at this stage. However, it can be noted here that the curves show in general the same trend on zirconium phosphate as on Dowex 50 resin except for dimethylsulphoxide, dimethylformamide and to a lesser extent, acetic acid.[1] For sulpholane no data on Dowex 50 are available.

12. *Idem*, — Atti IV° *Convegno Nazionale di Chimica Inorganicavenezia* 1971, in the press.
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Bio Rad ZP-1 cation-exchange crystals 50–100 mesh. All solvents were *pro analysi* products.

Procedure

The weight distribution coefficient, K_D, was determined at 25° after equilibration for 24 hr with ^{86}Rb. The hydrochloric acid concentration was kept constant at $0.85M$. Volume contraction effects were minimized by premixing of the solvent, hydrochloric acid and isotope solution before addition to the exchanger. The weight of zirconium phosphate was 200 mg, and 0·1–1 μg of rubidium was used.

RESULTS

The results are summarized in Table I. All values are the mean of at least two determinations. Reproducible results were obtained except in dimethylformamide in the 32–64% range.

An interpretation of the results is not possible at this stage. However, it can be noted here that the curves show in general the same trend on zirconium phosphate as on Dowex 50 resin except for dimethylsulphoxide, dimethylformamide and to a lesser extent, acetic acid.[1] For sulpholane no data on Dowex 50 are available.

Table 1. Distribution coefficient of Rb^+ on zirconium phosphate crystals in mixed aqueous-organic solvent, 0.85*M* in HCl.

							Solvent %, *v/v*					
Solvent	0	8	16	24	32	40	48	56	64	72	80	88
methanol	81	97	130	170	200	330	430	670	1050	1950	3100	3000
ethanol	81	120	140	190	300	370	590	1030	1550	3500	6800	$>10^4$
n-propanol	81	105	150	160	200	250	310	410	1200	1150	3600	$>10^4$
isopropyl alcohol	81	88	145	190	270	320	500	760	770	2300	6100	$>10^4$
t-butyl alcohol	81	95	130	180	210	250	340	530	800	1600	4300	7000
dimethylsulphoxide	81	69	60	58	50	50	40	50	48	29	19	19
N,*N*-dimethylformamide	81	55	65	65	56	63	54	67	—	68	77	37
tetrahydrofuran	81	110	160	220	250	420	450	600	920	1600	2100	4100
acetone	81	100	130	145	200	240	340	440	970	1050	1600	3000
dioxan	81	91	135	170	190	270	340	490	700	730	N.M.	N.M.
Methylcellosolve*	81	92	115	140	190	240	270	410	590	550	430	310
Propylcellosolve*	81	120	150	180	240	290	290	400	560	1000	1550	2100
acetic acid	81	84	87	67	70	52	50	46	43	36	34	46
sulpholane	81	96	96	120	127	126	—	—	170	—	200	193

* Registered trade-name.
N.M. = not completely miscible.

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Summary—The distribution coefficients have been determined for Rb^+ distributed between zirconium phosphate and 0·85*M* hydrochloric acid in aqueous solutions of methanol, ethanol, n-propanol, isopropyl alcohol, t-butyl alcohol, dimethylsulphoxide, dimethylformamide, tetrahydrofuran, acetone, dioxane, "Methylcellusolve", "Propylcellosolve", acetic acid and sulpholane, in 0–88% concentration.

Zusammenfassung—Die Verteilungskoeffizienten für die Verteilung von Rb^+ zwischen Zirkoniumphosphat und 0·85 M Salzsäure in wäßrigen Lösungen von Methanol, Äthanol, *n*-Propanol, Isopropylalkohol, *t*-Butylalkohol, Dimethylsulfoxid, Dimethylformamid, Tetrahydrofuran, Aceton, Dioxan, "Methylcellosolve", "Propylcellosolve", Essigsäure und Sulfolan bei Konzentrationen von 0–88% wurden ermittelt.

Resume—On a déterminé les coefficients de partage pour Rb^+ réparti entre le phosphate de zirconium et l'acide chlorhydrique 0,85 *M* en solutions aqueuses de méthanol, éthanol, *n*-propanol, isopropanol, t-butanol, diméthylsulfoxyde, diméthylformamide, tétrahydrofurane, acétone, dioxane, "Méthylcellosolve", "Propylcellosolve", acide acétique et sulfolane, en concentration 0–88%.

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POTENTIOMETRIC DETERMINATION OF STEPWISE STABILITY CONSTANTS OF ZIRCONIUM, THORIUM AND URANIUM CHELATES OF ASPARAGINE AND GLUTAMINE

(*Received* 18 *September* 1972. *Accepted* 4 *October* 1972)

In an earlier communication,[1] stepwise stability constants of the chelates of V(IV), Mo(VI) and W(VI) with asparagine and glutamine were reported. This paper gives the results of a similar study with Zr(IV), Th(IV) and U(VI).

RESULTS AND DISCUSSION

In all these systems precipitation occurs around pH 5–6. So $\bar{n}$ calculations were done only up to the beginning of precipitation. Under these conditions $\bar{n}$ approaches a value of 3 in the case of thorium, 2 for uranium, but approaches only 1.6 for zirconium. Thus K_1, K_2 and K_3 can be computed for thorium chelates, and only K_1 and K_2 for zirconium and uranium. For the zirconium chelates $K_1/K_2 \sim 10^{2\cdot6}$, so K_1 and K_2 were computed by the half-$\bar{n}$ method, and further confirmed by the correction term and successive approximation methods. For uranium $K_1/K_2 \sim 10^{0\cdot9}$, so the correction term and successive approximation methods were used. For thorium $K_1/K_2 \sim 10^{0\cdot7}$ and $K_2/K_3 \sim 10^{0\cdot5}$; so approximate constants were obtained by interpolation at half-$\bar{n}$ values and refined by successive approximation.

Table 1. Stability constants of zirconium(IV), uranium(VI) and thorium(IV) chelates formed with asparagine and glutamine (Temp. 25°C, $\mu = 0\cdot1M$ $NaClO_4$).

Metal ion	pH range for $\bar{n}$ calculations	Method	Asparagine			Glutamine		
			log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
Zr(IV)	2·6–5·5	Half-$\bar{n}$	8·80	6·25	—	8·75	6·10	—
		Correction term	8·76	6·28	—	8·75	6·09	—
		Successive approximation	8·80	6·25	—	8·75	6·10	—
U(VI)	4·0–6·0	Half-$\bar{n}$	6·95	6·00	—	6·85	6·00	—
		Correction term	6·73	6·19	—	6·62	6·22	—
		Successive approximation	6·79	6·16	—	6·63	6·22	—
Th(IV)	2·7–5·0	Half-$\bar{n}$	8·50	7·85	7·40	8·45	7·70	7·20
		Successive approximation	8·28	7·77	7·72	8·30	7·61	7·55

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Summary—The metal chelates of Zr(IV), Th(IV) and U(VI) with asparagine and glutamine have been studied potentiometrically. Stepwise stability constants in 0·1 *M* sodium perchlorate at 25° are as follows. *Asparaginate chelates*—log K_1 8·80, log K_2 6·25 for Zr, log K_1 6·79, log K_2 6·16 for U, log K_1 8·28, log K_2 7·77 and log K_3 7·72 for Th. *Glutaminate chelates*—log K_1 8·75, log K_2 6·10 for Zr, log K_1 6·63, log K_2 6·22 for U, log K_1 8·30, log K_2 7·61 and log K_3 7·55 for Th.

Zusammenfassung—Die Metallchelate von Zr(IV), Th(IV) und U(VI) mit Asparagin und Glutamin wurden potentiometrisch untersucht. Die stufenweisen Stabilitätskonstantenin 0·1 M Natriumperchlorat bei 25° ergaben sich wie folgt. *Asparaginate*: log K_1 8·80 und log K_2 6·25 für Zr, log K_1 6·79 und log K_2 6·16 für U, log K_1 8·28, log K_2 7·77 und log K_3 7·72 für Th. *Glutaminate*: log K_1 8·75 und log K_2 6·10 für Zr, log K_1 6·63 und log K_2 6·22 für U, log K_1 8·30, log K_2 7·61 und log K_3 7·55 für Th.

Résumé—On a étudié potentiométriquement les chélates métalliques de Zr (IV), Th (IV) et U (VI) avec l'asparagine et la glutamine. Les constantes de stabilité étagées en perchlorate de sodium 0,1 *M* à 25° sont les suivantes. *Chélates asparaginiques*—log K_1 8,80, log K_2, 6,25 pour Zr, log K_1 6,79, log K_2 6,16 pour U, log K_1 8,28, log K_2 7,77 et log K_3 7,72 pour Th. *Chélates glutaminiques*—log K_1 8,75, log K_2 6,10 pour Zr, log K_1 6,63, log K_2 6,22 pour U, et log $K_1 = 8{,}30$, log $K_2 = 7{,}61$ et log $K_3 = 7{,}55$ pour Th.

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SEPARATION AND QUANTITATIVE DETERMINATION OF THE CERIUM GROUP LANTHANIDES BY GAS–LIQUID CHROMATOGRAPHY

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Summary—A gas chromatographic method is reported for the separation and subsequent quantitative determination of the cerium group lanthanides. The lanthanides (RE) are synergistically extracted from aqueous solution with the polyfluorinated β-diketone 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD), as ligand, and di-n-butylsulphoxide, DBSO, as neutral donor. The composition of the extracted species is reported to be $RE(FHD)_3 \cdot 2DBSO$. Thermogravimetric analysis of the complexes is reported. Analytical curves were prepared and found to be usable over the range of 0·1–10 μg of metal. Individual lanthanides were determined with 99·0% recovery with a relative mean deviation of ±2·0%. Mixtures of lanthanides were analyzed with 101·2% recovery with a relative mean deviation of ±2·2%.

Considerable interest has been shown in the use of β-diketonates for gas chromatography of rare earths. Chelates of the rare earths with 2,2,6,6-tetramethyl-3,5-heptanedione[1] and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione[2] have been chromatographed. Rare earth chelates have also been prepared with 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione;[3,4] however, thermogravimetric analysis indicated decomposition of many of the complexes. In all these instances solid anhydrous chelates were prepared and dissolved in a suitable solvent before injection into the chromatograph. This type of preparation is unsuitable for quantitative formation of metal complexes in the organic phase.

Generally the chelates of the rare earths form hydrated complexes which are poorly extracted. Mitchell[5] has recently reported the successful extraction of lanthanides by using synergistic extraction systems of fluorinated β-diketones and various neutral donors. Butts and Banks[6] reported the use of these mixed-ligand systems for gas chromatography. Recently Sieck has completed a detailed study of several mixed-ligand systems.[7] Although the chelates of individual rare earths were chromatographed, separation of rare earth mixtures were not achieved and quantitative analysis were not reported. Earlier Burgett and Fritz[8] reported the successful gas chromatographic separation and quantitative determination of the yttrium group lanthanides as mixed-ligand complexes with 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD), and di-n-butylsulphoxide, DBSO.

This paper describes the preparation of volatile mixed-ligand complexes of the cerium group lanthanides by synergistic solvent extraction with H(FHD) and DBSO. These complexes are subsequently separated and quantitatively determined by gas chromatography. The solvent extraction effectively separates the lanthanides from major interferences and allows rapid preparation of the volatile species.

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EXPERIMENTAL

Instrumentation

A Hewlett–Packard Model 5756B gas chromatograph, equipped with a flame-ionization detector was used. A Hewlett–Packard Model 7128 A strip-chart recorder was used for development work, and a 1-mV Bristol recorder equipped with a Disc Integrator, Model 202, was used for the quantitative studies. Helium was used as the carrier gas, and stainless-steel tubing was used for all columns and the injection port liner. The following instrument operating conditions were used in the analyses: column, stainless steel, 20 × 0·25 in. o.d., packed with 6·46% Dexsil 300 GC (Analabs) on Chromosorb W (100/120 mesh); column temperature was held at 172° for 3 min then programmed to increase to 215° at 6°/min; helium flow was 50 ml/min, air pressure 33 psig, hydrogen pressure 8 psig, injection port temperature 280°, flame-ionization detector temperature 290°.

A DuPont Model 950 Thermogravimetric Analyzer was used to obtain all TG curves. A programmed heating rate (10°/min) was used with a nitrogen gas atmosphere with a flow-rate of 10 ml/min.

Reagents

The ligand 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione was prepared by a Claisen condensation of ethyl pentafluoropropionate with 3,3,4,4,4-pentafluoro-2-butanone as described previously.[8] Di-n-butylsulphoxide was obtained from Aldrich Chemical Company, and was used after recrystallization from low-boiling petroleum ether. Rare earth oxides of 99·9% purity were prepared by ion-exchange at this laboratory. All other chemicals were reagent grade or better.

Solvent extraction procedure

Rare earth stock solutions were prepared by dissolving the rare earth oxide in hot 1*M* hydrochloric acid, evaporating to near dryness and diluting to volume with pH 5·5 acetate buffer. The solutions were standardized by titration with EDTA, Xylenol Orange being used as the indicator.[9] The stock solutions were approximately 0·1*M* and appropriate dilutions were made to span the concentration range desired. Solvent extractions were performed in 15-ml screw-cap glass test-tubes. The inside lining of the screw tops was replaced with a Teflon disk to prevent any interaction with the plastic top. Shaking times of 30 min were used although equilibrium was established in 15 min, as determined by spectrophotometric analysis of the organic phase.

The samples were prepared by contacting 1·00 ml of the aqueous solution with 1·00 ml of cyclohexane containing β-diketone in an amount equivalent to three times the total metal concentration of the most concentrated sample, and neutral donor in an amount equivalent to twice the total metal concentration of the most concentrated sample. After equilibrium was established by shaking, the samples were washed with 1·0*M* sodium hydroxide to remove excess of H(FHD). Samples were withdrawn from the cyclohexane phase by syringe and injected into the gas chromatograph.

The composition of the extracted species was shown to be $RE(FHD)_3 \cdot 2DBSO$ by infrared analysis.[7] Here Re represents the rare earth metal, FHD represents the ligand anion and DBSO the donor di-n-butylsulphoxide. Analytical results for the mixed-ligand complexes are shown in Table 1.

Table 1. Analytical results for cerium group mixed-ligand complexes.

	Metal, %		Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$La(FHD)_3 \cdot 2DBSO$	10·01	10·1	32·03	32·1	2·83	2·8
$Ce(FHD)_3 \cdot 2DBSO$	10·09	10·1	32·00	32·0	2·83	2·8
$Nd(FHD)_3 \cdot 2DBSO$	10·35	10·4	31·91	31·0	2·82	2·8
$Sm(FHD)_3 \cdot 2DBSO$	10·75	10·8	31·76	31·7	2·81	2·0
$Eu(FHD)_3 \cdot 2DBSO$	10·85	10·8	31·73	31·7	2·81	2·0

Preparation of calibration curves

Standard solutions were prepared over the concentration range of approximately 0·1–15 μg of rare earth. In each case 3–5 separate 1·60-μl samples of the rare earth complexes were injected into the gas chromatograph and the average of the area under the peak, as determined by the disc integrator, was plotted *vs.* sample concentration. The calibration curves were obtained by using the flame-ionization detector and found to be invariant over a period of one month. Calibration curves for use in the determination of mixtures of rare earths were prepared by the same method as above, using stock solutions of rare earths in 1 : 1 ratio. This procedure was followed to correct for any peak overlap.

Gas chromatographic columns

No evidence of metal exchange, reaction and or decomposition of the metal chelates on the hot metal surface of the stainless-steel column was observed. The column packing was prepared by placing 5 g of dry solid support in a 2 × 10 in. cylindrical tube fitted with a glass frit. A solution of Dexsil 300 GC in 56 ml of benzene was poured into the tube and mixed with the support. The excess of solution was drained from the support through a stop-cock below the glass frit. Filtered air was passed through the packing while heat was applied by infrared lamps. After drying, the packing was placed in the stainless-steel columns and packed by vibrating the sides of the column. The packed columns were conditioned for 2 hr at 180° then overnight at 300° before use.

RESULTS AND DISCUSSION

Thermogravimetric studies

Thermogravimetric results for the mixed-ligand complexes of the cerium group lanthanides are shown in Fig. 1, and indicate complete volatilization without decomposition.

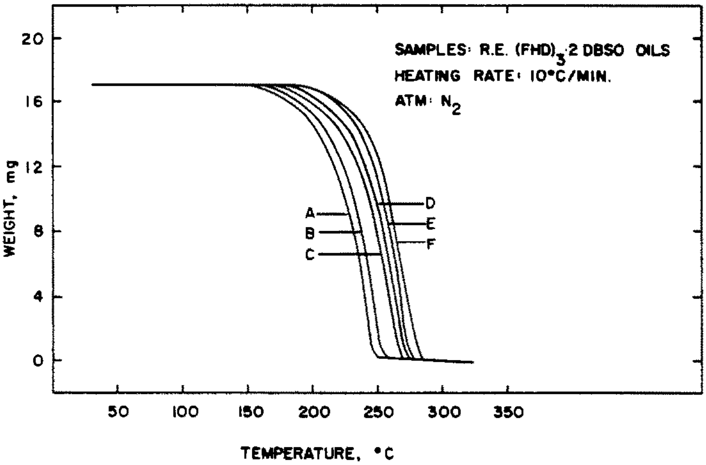

Fig. 1. TG curves for mixed-ligand complexes of the lanthanides with H(FHD) and DBSO. *A*–Eu(FHD)$_3$·2DBSO; *B*–Sm(FHD)$_3$·2DBSO; *C*–Nd(FHD)$_3$·2DBSO; *D*–Pr(FHD)$_3$·2DBSO; *E*–Ce(FHD)$_3$·2DBSO; *F*–La(FHD)$_3$·2DBSO.

Previously[1-5] complexes of several of these lanthanides have been found to decompose on volatilization. Examination of the temperature at the mid-point of weight loss shows significant differences in volatility for the mixed-ligand complexes with DBSO.

The heavier rare earths were found to be volatilized at lower temperature than their lighter neighbours. This difference in volatility can be correlated with the ionic radius of the tervalent lanthanides.[1]

Stationary phase

The selection of the liquid phase depends on two factors. The liquid must have high thermal stability so that column bleed at the temperatures required for elution of the rare earth complexes is avoided, and it must not interact irreversibly with the chelates being eluted.

Previously[8] we found the liquid phase Dexsil 300 GC useful in the gas chromatographic determination of mixed-ligand complexes. Columns prepared with Dexsil 300 GC as the liquid phase gave excellent results with the mixed-ligand complexes of the lanthanides. No prior conditioning of the columns by sample injection was required to obtain reproducible results. The mixed-ligand complexes were found to partition significantly into the Dexsil 300 GC, resulting in excellent separation of the lanthanides.

Separation of the lanthanides

All the lanthanides were found to be satisfactorily eluted from a 20 by 0.25 in. 6·46% Dexsil 300 GC column at 200°. To obtain separations it was necessary to employ various temperature programmes, *e.g.*, a 3-min hold at 172°, then a linear increase at 6°C/min. With this column and the appropriate temperature programme, excellent separations were achieved as shown in Fig. 2. The separation is complete and the peaks suitable for integration and quantitative analysis. Figure 3 illustrates the quantitative resolutions of a mixture of lanthanide metals having even atomic numbers, these being the lanthanides commonly existing in ores (on account of the alternating abundances); therefore analytical separations onthis basis are of practical utility. The peak shapes are very sharp for samples at the 0·2–20 μg metal level, but the peak is cigar-shaped at higher concentrations. This peak distortion is an indication of column overload and limits the concentration that can be used.

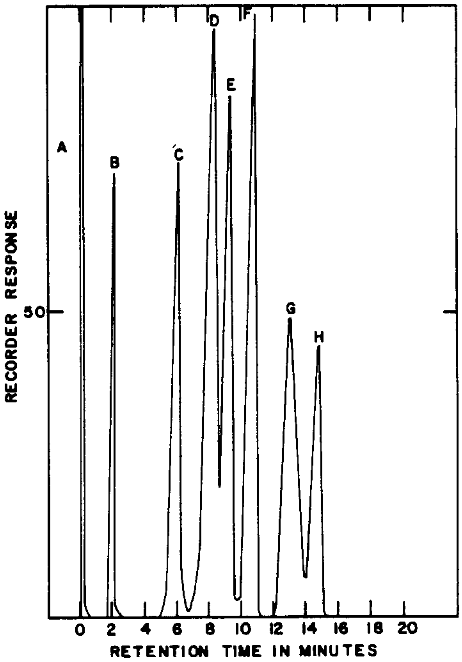

Fig. 2. Gas chromatogram of a mixture of FHD and DBSO mixed complexes of Yb, Er, Dy, Gd, Nd and Ce.
Column as described in text; 4-min hold at 172°C, temperature increase 4°/min.
A–Cycloxhexane H(FHD); *B*–DBSO; *C*–$Yb(FHD)_3 \cdot 2DBSO$; *D*–$Er(FHD)_3 \cdot 2DBSO$; *E*–$Dy(FHD)_3 \cdot 2DBSO$; *F*–$Gd(FHD)_3 \cdot 2DBSO$; *G*–$Nd(FHD)_3 \cdot 2DBSO$; *H*–$Ce(FHD)_3 \cdot 2DBSO$.

In all studies the composition of eluted species was verified by collection of eluates and subsequent infrared and fluorescence analysis. The complexes of each metal were found to be eluted without decomposition.

Quantitative studies

Calibration curves were prepared for the individual lanthanides. The curves were linear over the concentration range 0·2–15 μg of metal. Unknowns were prepared by the same

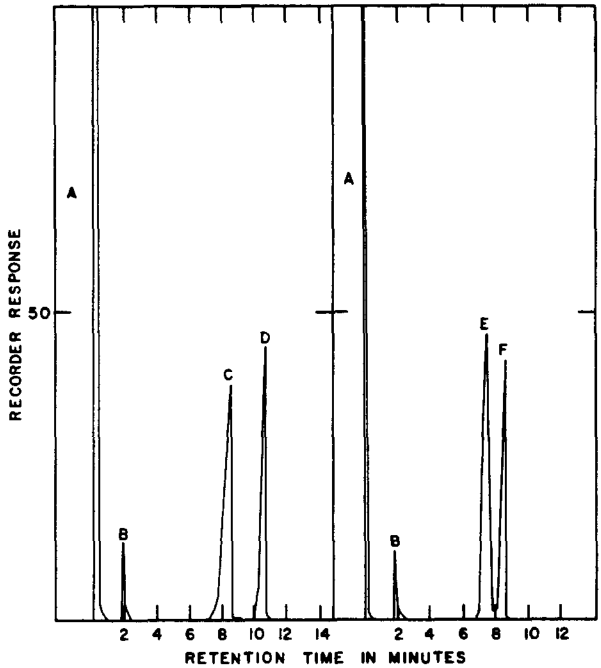

Fig. 3. Gas chromatogram of mixtures of several lanthanide mixed-ligand H(FHD)–DBSO complexes.
Column as in text; 3-min hold at 172°C.
Heating rate 6°/min.
A–Cyclohexane, H(HFD); *B*–DBSO; *C*–Eu(FHD)$_3$·2DBSO; *D*–La(FHD)$_3$·2DBSO.
Heating rate 10°/min.
E–Sm(FHD)$_3$·2DBSO; *F*–Ce–(FHD)$_3$·2DBSO.

extraction procedure as the standards. To eliminate excess of ligand from each extract, a few ml of 0·1*M* sodium hydroxide were added. The H(FHD) then forms the insoluble white sodium salt. Results for the determination of the individual lanthanides, by means of the analytical curves, are presented in Table 2. The individual lanthanides were determined

Table 2. Determination of the individual lanthanides as H(FHD)–DBSO mixed ligand complexes.

Rare earth	Taken, μg	Found, μg	Relative error, %
Eu	6·38	6·35	−0·5
	3·41	3·44	+0·9
Sm	5·87	5·80	−1·2
	4·44	4·35	−2·0
Pr	4·97	5.04	+1·4
	1·26	1·31	+4·0
Nd	3·24	3·20	−1·2
	5·72	5·66	−1·0
Ce	5·18	5·04	−2·7
	3·16	3·10	−1·9
La	4·46	4·08	−4·9
	6·47	6·30	−2·6

with 99·0% recovery with a relative mean deviation of ±2·0%.

The analytical curves do not extrapolate to zero but to 0·18 μg at zero response. This is undoubtedly a result of a finite loss of sample to the column material. Analyses of "unknown" solutions of rare earth mixtures are shown in Table 3. The lanthanides were determined with 101·2% recovery and a relative mean deviation of ±2·2%.

Table 3. Analysis of mixed-rare earth solutions *via* the H(FHD)–DBSO mixed-ligand complexes.

Mixture	Taken, *μg*	Found, *μg*	Relative error, %
Eu	10·10	10·10	0·0
Nd	7·05	7·39	+4·8
Sm	2·93	2·96	+1·0
Ce	2·79	2·76	−1·1

Detection limits were determined for all the rare earths tested. The detection limit was taken to be that amount of mixed-ligand complex necessary to give a chromatographic peak response equal to or greater than twice the background response. The detection limit observed was 0·20 μg of metal for each of the rare earths.

The response to the flame-ionization detector was found to vary from metal to metal, as shown in Table 4. The variation in response is probably caused by differences in the combustion of each metal. The extreme enhancement observed with the samarium complex limits the usefulness of the method for determining mixtures containing samarium. The detector readily becomes swamped and may not observe the lower signal from neighbouring metal chelates.

Table 4. Response factors for the flame-ionization detector.

Compound	Response factor 10^{-5} × *integration count/μg*
$La(FHD)_3 \cdot 2DBSO$	0·28
$Ce(FHD)_3 \cdot 2DBSO$	3·15
$Pr(FHD)_3 \cdot 2DBSO$	1·11
$Nd(FHD)_3 \cdot 2DBSO$	2·15
$Sm(FHD)_3 \cdot 2DBSO$	22·70
$Eu(FHD)_3 \cdot 2DBSO$	4·29

Calculated from slope of area *vs.* concentration plots.

Interferences

The extraction system was found to be useful in separating the lanthanides from calcium, scandium, iron(III), aluminium, uranyl and thorium. Calcium and scandium were not extracted at pH 5·5. Iron and uranium were extracted but were removed by washing the extract with 0·1*M* sodium hydroxide. Aluminum and thorium did not interfere with the determination of the lanthanides.

The yttrium group lanthanides also form complexes with the (FHD)–DBSO system and have been quantitatively determined.[8] The retention time of the yttrium group lanthanides is shorter than that of the cerium group rare earths and, as shown in Fig. 3, they offer no interference.

Yttrium is also extracted as the mixed-ligand complex, $Y(FHD)_3 \cdot 2DBSO$. The complex is thermally stable and can be chromatographed. The yttrium complex can be separated from all of the cerium group elements and quantitatively determined: its retention time is similar to that of holmium.

CONCLUSIONS

An efficient method for the determination of the lanthanides as the mixed-ligand complexes with H(FHD) and DBSO has been developed. This determination offers the first successful gas chromatographic separation and quantitative determination of the cerium group lanthanides. The synergistic extraction system renders the analysis virtually free from interferences and allows the first rapid preparation of volatile and thermally stable cerium group lanthanide chelates.

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Zusammenfassung—Eine gaschromatographische Methode zur Trennung und anschließenden quantitativen Bestimmung der Lanthaniden der Cergruppe wird angegeben. Die Lanthaniden (RE) werden aus wäßriger Lösung mit dem mehrfach fluorierten β-Diketon 1,1,1,2,2,6,6,7,7,7-Dekafluoro-3,5-heptandion H(FHD) als Ligand und Di-*n*-butylsulfoxid DBSO als neutralem Donor synergistisch extrahiert. Die Zusammensetzung der extrahierten Spezies wird als $RE(FHD)_3 \cdot 2DBSO$ angegeben. Die Ergebnisse der thermogravimetrischen Untersuchung der Komplexe werden mitgeteilt. Analytische Kurven wurden aufgezeichnet und im Bereich 0·1–10 μg Metall benutzbar genfunden. Einheitliche Lanthaniden wurden mit 99,0% Ausbeute und einer relativen Standardabweichung von ±2·0% bestimmt. Gemische von Lanthaniden wurden mit einer Ausbeute von 101·2% und einer relativen Standardabweichung von ±2·2% analysiert.

Résumé—On décrit une méthode chromatographique en phase gazeuse pour la séparation et le dosage quantitatif subséquent des lanthanides du groupe du cérium. On extrait les lantanides (RE) de manière synergique de la solution aqueuse avec la β-dicétone polyfluorée 1,1,1,2,2,6,6,-7,7,7-décafluoro 3,5-heptanedione, H(FHD), comme coordinat, et le di-*n*-butylsulfoxyde, DBSO, comme donneur neutre. La composition de l'espece extraite est donnée comme étant RE $(FHD)_3$, 2DBSO. On rapporte l'analyse thermogravimétrique des complexes. On a établi des courbes analytiques, et les a trouvées utilisables dans le domain 0,1–10 μg de métal. On a dosé les lanthanides individuels avec une récupération de 99,0% et un écart relatif moyen de ±2,0 %. On a analysé des mélanges de lanthanides avec une récupération de 101,2 % et un écart relatif moyen de ±2,2 %.

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COULOMETRIC TITRATION OF ACIDS IN ISOPROPANOL—II

ELECTRODE REACTIONS WITH LITHIUM CHLORIDE AND TETRAETHYLAMMONIUM BROMIDE AS SUPPORTING ELECTROLYTES

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Summary—Cathodic reactions in methanol and isopropanol have been investigated in the presence of both lithium chloride and tetraethylammonium bromide as supporting electrolytes. A side-reaction in lithium chloride medium leads to the formation of insoluble lithium hydroxide but base is generated stoichiometrically in tetraethylammonium bromide by reduction of solvent, oxygen and traces of water. Tetraethylammonium bromide is recommended as supporting electrolyte for the coulometric titration of acids in isopropanol.

The advantages of coulometric titration of acids in non-aqueous solvents have been well documented.[1] Because protolysis constants are lower in many non-aqueous solvents than in aqueous solutions, weak acids can be titrated in these media with much sharper end-points. Coulometric titrations in such media eliminate the preparation and standardization of the often expensive titrants necessary for volumetric titrations. Coulometric titration of acids has been accomplished in various solvents such as 70% aqueous isopropyl alcohol,[2] isopropyl alcohol,[3,4] isopropyl alcohol–methyl ethyl ketone (1:1 v/v)[3], acetone containing 0·5% methanol,[5] acetone[6,7] and t-butyl alcohol.[6,8] Several authors[2,9,10] have found it necessary to add water to the organic solvents in order to generate alkali with 100% current efficiency, but in general this is a disadvantage as it often reduces the sharpness of the end-point[3,5] and the solubility of the sample.

There are two difficulties with regard to the application of coulometric titrations in non-aqueous solvents. First the resistance of the solution is much higher than that of aqueous solutions, and most commercial constant-current generators, which are low-voltage sources, do not give constant currents under these conditions. In this situation, the analytical result is not obtained from a simple interpolation of the time for which a fixed current is passed. This may be overcome by current integration[3,5] or by the design of a suitable high-voltage constant-current source.[4] The second factor is that side-reactions often occur which may prevent the generation of titrant with 100% efficiency. However, most workers have been able to establish conditions under which a titration efficiency of 99% or better has been achieved in such solvents as acetone,[5,6] isopropyl alcohol[3] and t-butyl alcohol,[6] although in many cases solvent blanks are considerable.[6]

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In Part I,[4] a coulometric method was described for the determination of carbon in steel in which the carbon dioxide liberated by the high-temperature combustion of the sample is absorbed in isopropyl alcohol containing 3% ethanolamine and $0{\cdot}5M$ in tetraethylammonium bromide (TEAB) and titrated coulometrically. During the development of this procedure it was discovered that if lithium chloride was used as supporting electrolyte, the current efficiency was much lower than expected for isopropyl alcohol media and 100% current efficiency could only be restored by addition of substantial amounts of water. When subsequently lithium chloride was replaced by TEAB, 100% current efficiency was obtained. Recently, Rehioui and Johansson[11] have investigated the electrochemical behaviour of isopropyl alcohol at platinum electrodes and have concluded that the main cathodic reaction in a supporting electrolyte of $0{\cdot}5M$ sodium perchlorate is the generation of isopropoxide ions

$$2(CH_3)_2{-}C\begin{matrix}{}^{\diagup H}\\{}_{\diagdown OH}\end{matrix} + 2e \longrightarrow 2(CH_3)_2{-}C\begin{matrix}{}^{\diagup H}\\{}_{\diagdown O}\end{matrix} \quad H_2 \qquad (1)$$

However, these authors also observed the formation of a yellow deposit on the cathode,[3,11] the amount of the deposit being greatly increased when lithium perchlorate was used as supporting electrolyte.[11] The cathodic electrode reactions in methanol and isopropyl alcohol solutions of lithium chloride and tetraethylammonium bromide have been further investigated and the results are reported in this paper. As a result of these investigations TEAB is recommended as a supporting electrolyte for the coulometric titration of acids in isopropyl alcohol.

EXPERIMENTAL

Reagents

All reagents were of chemical reagent grade. The lithium chloride was dried at 100° to yield the anhydrous salt. The gases used (oxygen, nitrogen, air) were commercial materials used without further purification.

The tetraethylammonium bromide was recrystallized by dissolving 50 g in the minimum amount of isopropyl alcohol (*ca.* 150 ml) at 50–60° and adding 150 ml of acetone. The precipitated material was dried at 70° and stored in a desiccator to prevent absorption of water.

Apparatus

The electrodes used for coulometry were 1 × 1 cm pieces of platinum foil welded to platinum wire and sealed in soda-glass tubing. The electrodes used for amperometry were 22-gauge platinum wire sealed in soda-glass tubing with 2·5 cm left exposed. One of these was kept stationary and used as the anode, the other, the cathode, was rotated at 600 rpm by means of a Radiometer Rotating Platinum Electrode Assembly (type E70).

The reference electrode was in every case a saturated calomel electrode and all the voltages given in this paper are referred to the potential of this electrode. When the electrode was used for measuring the current/potential curves an additional salt bridge of $1M$ TEAB in the appropriate solvent was used to prevent water from contaminating the test solution.

The potentiostat used in the earlier experiments was a Heathkit three-electrode polarograph module (EUA-19-2). However this could not supply sufficient current, so a more powerful instrument was built, (Fig. 1), and currents were measured with an Avometer.

The coulometer was a modification of a valve circuit suggested by Glass and Moore[12] and supplied constant currents of 5–100 mA at voltages of up to 200 V. The switch which interrupted the current through the cell also controlled a clock which measured the time required to reach the end-point. With this instrument the current drifts slightly and it is necessary to monitor the current continuously with a potentiometer and standard resistance.

The coulometric titration vessel was an H-cell with sintered-glass discs separating the anode and cathode compartments (40 ml capacity) from the salt bridge which connected them. For the amperometric experiments a simple glass cup (40 ml capacity) was used, and no precautions were taken to avoid absorption of water during an experiment.

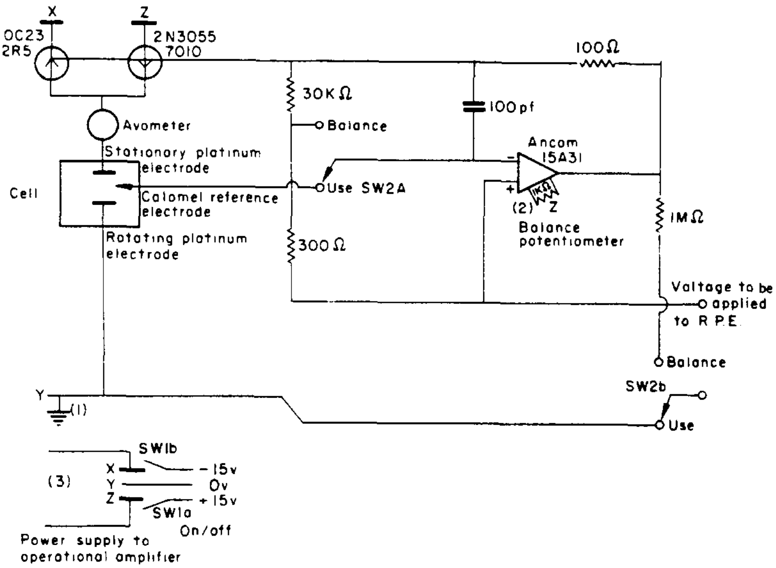

Fig. 1. Circuit diagram of high-current potentiostat.

Amperometry

The current/potential curve for solutions of lithium chloride in isopropyl alcohol was measured automatically with the Heathkit polarograph. Because equilibrium was reached very slowly, the initial potential was applied for one hour before the scan was started and the lowest possible scan-rate of 0·05 V/min was used. When lithium chloride in methanol was the electrolyte the measurements were taken manually with the high-current potentiostat, 10 min being allowed between voltage changes for the current to become steady. With tetraethylammonium bromide as the electrolyte in either solvent the electrode was cleaned between voltage changes by anodizing at +1·8 V for 1 min, and cathodizing at −1·8 V for 1 min; the potential was then applied and the current measured after 2 min. Measurements of the conductivity of the electrolyte suggest that the maximum error due to the voltage drop in solution between the reference and working electrodes would be 50 mV.

In investigation of the dependence of limiting-current on oxygen concentration, the oxygen concentration was measured by the Winkler method,[13] with omission of the permanganate/oxalate treatment used to destroy nitrite.

Coulometry

To reduce the resistance of the cell the anode compartment was filled with 1·0*M* tetraethylammonium bromide in methanol, the cathode compartment and salt bridge being filled with the solution being tested—either 0·1*M* lithium chloride in one of several alcohols or 0·5*M* tetraethylammonium bromide in isopropyl alcohol. If a potentiometric end-point was to be used, glass and calomel electrodes were inserted into the cathode compartment. If a spectrophotometric end-point was required 0·5 ml of 0·1% thymolphthalein in isopropyl alcohol was added to the cathode compartment which was placed in the cell compartment of an EEL Spectrotitrator. The solution was then preneutralized by passage of current until a selected e.m.f. or absorbance was reached. Known amounts of acid were added, and the titration completed by passing current until the same e.m.f. or absorbance was reached. The coulometric efficiency was calculated as 100 × acid added/acid found.

RESULTS AND DISCUSSION

Coulometric titrations in alcohols, with lithium chloride as supporting electrolyte

During investigations into the selection of the most suitable solvent medium for the coulometric determination of carbon in steel, coulometric titrations of benzoic acid were conducted in a range of alcohols as a check on the current efficiencies of the respective cathodic reactions. In these tests the electrodes were placed in separate compartments of a standard H-cell and the supporting electrolyte was $0{\cdot}1M$ lithium chloride. The end-point was detected visually with phenolphthalein as indicator. A current of 12·5 mA was used and with a 2-cm platinum cathode this gave a current density of 6·25 mA/cm^2. Results for the titration of 5 ml of 0·1% benzoic acid solution are given in Table 1 and show that although 100% current efficiency is obtained in methanol and ethanol under these conditions, the current efficiency drops considerably as the carbon chain of the solvent is increased in length or branched. This was considered unfortunate since the larger-chain alcohols are also those which have the smallest autoprotolysis constants, and are therefore more differentiating and better solvents for the titration of acids with a wide range of ionization constants. Addition of increasing amounts of water to the solvent medium increased the current efficiency of isopropyl alcohol but large amounts were required to obtain 100% current efficiency and such "semi-aqueous" media would suffer from the disadvantages mentioned above. Assuming the electrode reaction can be written generally as

Table 1. Coulometric current efficiencies for the titration of benzoic acid in various alcohols: $0{\cdot}1M$ lithium chloride as supporting electrolyte.
(Current density 6·25 mA/cm^2.)

	Current efficiency, %		
Alcohol	Water 0%	Water 15%	Water 30%
Methyl	100·0, 100·2, 100·0	—	—
Ethyl	100·1, 100·2, 100·1	—	—
n-Propyl	94·2, 93·3, 94·8	—	—
Isopropyl	61·2, 60·3, 60·8	95·0, 95·1	99·7, 100·0
n-Butyl	44·0, 44·0, 44·2	—	—

$$2\text{ROH} + 2e \longrightarrow 2\text{RO}^- + \text{H}_2 \qquad (2)$$

a low current efficiency indicates overconsumption of charge and therefore that another reaction is taking place which produces either no titrant or a smaller amount of titrant than the main reaction. To investigate these reactions a voltammetric study of two typical solvents in this series was undertaken.

Current/potential curves in methanol and isopropyl alcohol with lithium chloride as supporting electrolyte

Current–potential curves were measured in the cathodic region (from 0 to -3 V with respect to a saturated calomel electrode) for $0{\cdot}1M$ lithium chloride in isopropyl alcohol and for $1{\cdot}0M$ lithium chloride in methanol, a rotating platinum electrode being used. The results are illustrated in Fig. 2; methanol gives a sharp rise in current at about $-1{\cdot}5$ V (Curve A) corresponding to decomposition of the solvent, but isopropyl alcohol gives much smaller currents which increase more gradually (Curve B). For isopropyl alcohol medium the current was found to depend on the direction of the scan, higher currents being observed when the voltage was scanned from + to − than in the reverse direction (Curves B and C). This effect was much less noticeable with methanol as medium. Addition of water increased the currents obtained but the forward and reverse scans were still substantially different

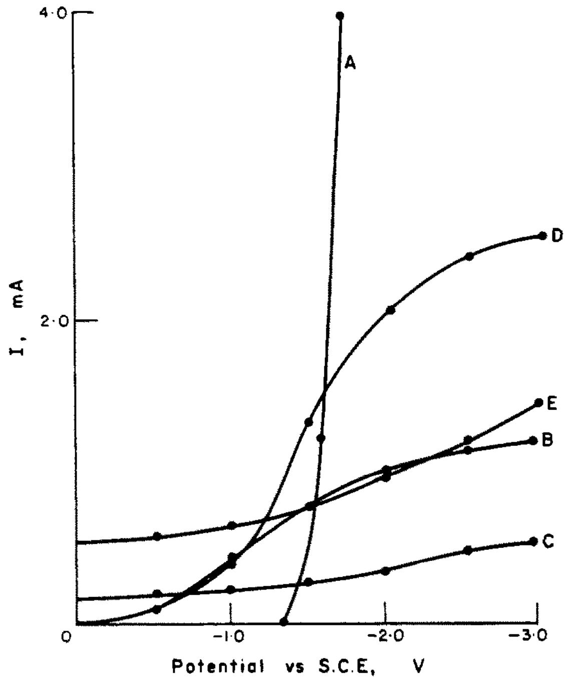

Fig. 2. Current/potential curves for methanol 1*M* in LiCl, and isopropyl alcohol 0·1*M* in LiCl. Rotating platinum electrode, automatic scan at a scan-rate of 0·05 V/min. Curve A, methanol forward and reverse scan. Curve B, isopropyl alcohol forward scan. Curve C, isopropyl alcohol reverse scan. Curve D, isopropyl alcohol/5% water, forward scan. Curve E, isopropyl alcohol/5% water, reverse scan. Solutions saturated with nitrogen.

(Curves D and E). Replacement of nitrogen with oxygen or air gave similar results but with the addition of an oxygen wave. For both solvents, under all conditions, the measured currents decreased steadily with time (Fig. 3*a*), the effect being worse in the presence of air or oxygen (Fig. 3*b*). Lower currents are therefore observed if the potential scan is carried out manually rather than automatically, although the shapes of the curves are similar.

The results can be interpreted by assuming that during electrolysis a deposit, similar to that observed by Rehioui and Johansson,[11] is formed on the cathode and causes a decrease in current as it increases in thickness. With isopropyl alcohol as solvent a white waxy deposit could in fact be observed on the cathode. The thickness of this deposit probably explains why very low currents (of the order of μA) are observed in isopropyl alcohol in the presence of lithium chloride whereas other solutions (see later) give much higher currents (of the order of mA). It would also explain why the currents are dependent on the direction of the scan since in scanning from 0 to −3 V the deposit will be building up whilst in the reverse scan a thick deposit will be formed initially.

The decay of current was also observed when methanol was used, even though no film was visible on the cathode. In this case there appeared to be three possible explanations for the decay of the current:

(*a*) the formation of an invisible film;

(*b*) the formation, during the electrolysis, of a substance that accumulates in solution and inhibits the cathodic reaction;

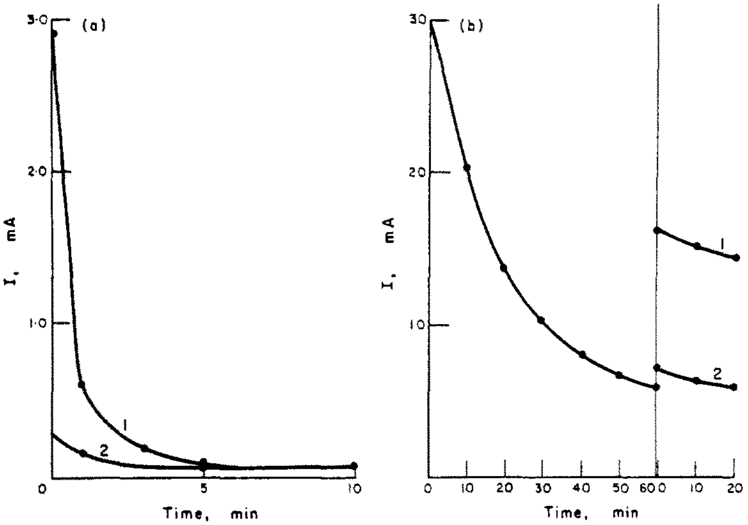

Fig. 3. (*a*) Change of potential with time for (1) methanol at −1 V *vs* S.C.E., (2) isopropyl alcohol at −3 V *vs*. S.C.E; solutions saturated with nitrogen. (*b*) Change of potential with time at −1 V *vs*. S.C.E. in methanol saturated with oxygen; after 60 minutes, (1) electrode removed, cleaned and replaced in the same solution, (2) electrode removed and placed in a new solution of the same composition.

(*c*) the slow growth of the diffusion layer to its equilibrium size accompanied by the decay of the current to a steady value.

To distinguish between these possibilities two tests were made. In the first, a potential of −1 V was applied to an electrode and the current allowed to decay to about one tenth of its initial value. The electrode was then withdrawn from the solution and, without any form of treatment, was placed in a fresh solution. The current then measured was almost identical to that obtained before the solutions were changed [Fig. 3*b*(2)]. This would only be expected in case (*a*) above. In the second test, the electrode was removed from the solution at the same point, cleaned in chromic acid and replaced in the same solution. The current was found to increase by a factor of 6 [Fig. 3*b*(1)] which would be expected in cases (*a*) and (*c*) above and not in case (*b*).

In both solvents, therefore, a deposit is formed on the cathode but the deposit is much thicker in isopropyl alcohol solutions. The deposit explains not only the unstable currents but also, if it is basic, the low current efficiencies. A large amount of deposit resulting from the electrolysis of an isopropyl alcohol/lithium chloride solution was dried and subjected to analysis. Microanalysis (Table 2) gave a very low carbon content, indicating that the substance was not organic, a conclusion supported by the infrared spectrum. This gave no peaks in the CH-stretch region but gave two sharp peaks at 3570 and 3680 cm^{-1}, which were also apparent in a spectrum of a sample of anhydrous lithium hydroxide. Other results suggest that both samples were partially hydrated.[14] An X-ray powder photograph of the deposit gave *d* spacings (2·96, 2·75, 2·66, 2·43 and 1·75 Å) and relative line intensities (60, 40, 100, 60, and 40 respectively) identical to those for $LiOH.H_2O$ but quite different from those for LiOH and LiCl[15]. The X-ray analysis took 5 hr to complete and it is likely that in this time sufficient water was absorbed to convert the sample completely into the hydrate. On titration with standard acid, the sample was found to contain the equivalent of 87% lithium hydroxide.

Table 2. Elemental microanalysis of cathodic deposits formed in isopropyl alcohol

	Supporting electrolyte	
	LiCl	TEAB
C, %	3·1	35·8
H, %	4·5	7·3
Cl, %	2·0	—
Br, %	—	21·0

Electrolysis of isopropyl alcohol in the presence of lithium chloride therefore results in the deposition of lithium hydroxide on the cathode, which reduces the current efficiency with respect to the generation of basic titrant.

Current/potential curves in methanol and isopropyl alcohol with tetraethylammonium bromide as supporting electrolyte

A satisfactory supporting electrolyte should have high solubility and conductivity in the solvent medium and ideally be unaffected by the passage of current. Several authors have used tetralkylammonium salts as supporting electrolytes in t-butyl alcohol[6,8] and acetone[7] and in this case the tetralkylammonium hydroxide formed by reduction of traces of water is assumed to be the generated titrant.[6] Several such salts were examined but most were not sufficiently soluble (*e.g.*, tetramethylammonium bromide, tetraethylammonium iodide, tetrapropylammonium iodide) in isopropyl alcohol to give the required high conductance. Two (tetrabutylammonium iodide and tetraethylammonium bromide) were sufficiently soluble, and of these tetraethylammonium bromide (TEAB) was chosen for voltammetric investigation because it had the higher solubility and conductance.

Currents measured when TEAB was used as supporting electrolyte were stable, changing only very slightly with time, and were independent of the direction of scan. Currents in methanol and isopropyl alcohol were of similar magnitude and no visible deposits were formed at the cathode. Use of TEAB therefore appeared to eliminate the difficulties encountered with lithium chloride.

The current/potential curves for $0{\cdot}1M$ TEAB in methanol showed a distinct wave due to oxygen. This is shown clearly in Fig. 4 by the increase in average limiting current in the region of $-1{\cdot}2$ V as the nitrogen atmosphere is successively replaced by air and oxygen. The limiting current was linearly related to the concentration of oxygen (determined by a modified Winkler method).[13] For example average limiting currents of 30·8, 14·6 and 1·8 mA/cm^2 were obtained for concentrations of oxygen determined as $7{\cdot}25 \times 10^{-3}M$ (oxygen-saturated solution), $3{\cdot}75 \times 10^{-3}M$ (air-saturated solution) and $1{\cdot}375 \times 10^{-3}M$ (nitrogen-saturated solution) respectively. As the methanol is diluted with water the limiting current decreases (Fig. 4) owing to the decreased solubility of oxygen in aqueous solutions. When the electrode was not rotated the wave disappeared, which confirms that it is not due to either methanol or water but is due to a solute of low concentration. In isopropyl alcohol the oxygen wave could not be resolved from the background current due to reduction of

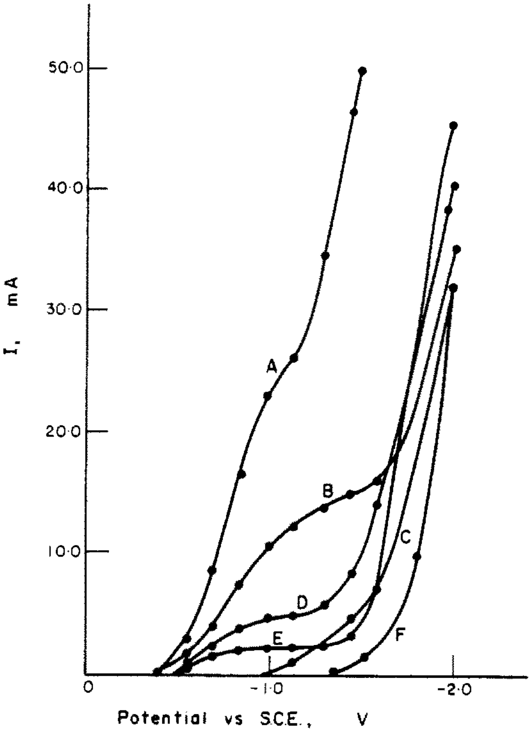

Fig. 4. Current/potential curves for methanol 0·2M in tetraethylammonium bromide. A, solution saturated with oxygen. B, solution saturated with air. C, solution saturated with nitrogen. D, methanol/20% water, air atmosphere. E, 100% water, air atmosphere. F, current/potential curve for methanol 1M in LiCl.

solvent, but the current was still dependent on the oxygen content (Fig. 5). For comparison of the relative currents, the curve obtained for 0·1M lithium chloride is included in Fig. 5.

In coulometry, the concentration of the supporting electrolyte governs the resistance of the cell and hence the voltage that the constant-current generator must deliver. The effect of TEAB concentration was investigated with methanol rather than isopropyl alcohol as medium, because of the better resolution of the oxygen wave. The limiting current for the oxygen wave decreased as the TEAB concentration was increased and this can be attributed to the increasing viscosity of the solution.[16]

Nature of the titrant generated in isopropyl alcohol with tetraethylammonium bromide as supporting electrolyte

Since TEAB appeared to be the most suitable supporting electrolyte for the coulometric titration of acids in isopropyl alcohol, the nature of the product of electrolysis in this medium was investigated. A solution of 0·1M TEAB in isopropyl alcohol was electrolysed for 5 hr and the products were precipitated with a solution of lithium bromide. Microanalysis of the precipitate suggested that it was a mixture of lithium isopropoxide and lithium bromide (Table 2) and the infrared spectrum showed the typical absorption pattern of the isopropyl group in the CH_3-stretch regions. The elemental analysis suggests that the precipitate is 65% lithium isopropoxide and 30% co-precipitated lithium bromide and is certainly different from the inorganic material formed in the presence of lithium chloride as supporting electrolyte.

Cathodic reactions

The results above allow a mechanism for the generation of base to be described. With lithium chloride as supporting electrolyte there are two products, a soluble base which reacts with acids (Table 1) and insoluble lithium hydroxide, the amount of the latter produced being much less in methanol than in isopropyl alcohol. The soluble base will be alkoxide ions produced by reaction (2). Lithium hydroxide may be produced by reduction of traces of water

$$2H_2O + 2e \longrightarrow 2OH^- + H_2 \tag{3}$$

or by reduction of dissolved oxygen

$$O_2 + 2ROH + 4e \longrightarrow 2OH^- + 2RO^- \tag{4}$$

where the hydroxyl ion reacts subsequently with the supporting electrolyte

$$Li^+ + OH^- \longrightarrow LiOH\downarrow \tag{5}$$

forming lithium hydroxide which is insoluble in both methanol and isopropyl alcohol. Reduction of isopropyl alcohol occurs at more negative potentials than that of methanol (Figs. 4 and 5) and allows reaction (3) to make a greater contribution to the overall current. At a potential of −2·5 V, a current of 100 mA is passed by water, 90 mA by methanol and

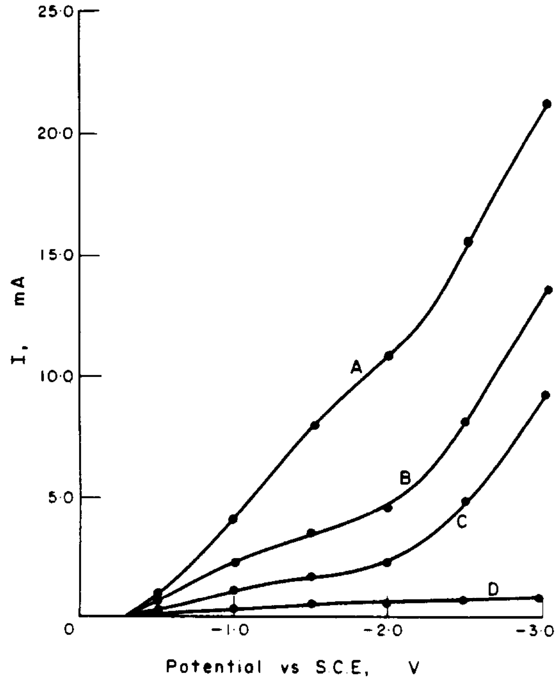

Fig. 5. Current/potential curves for isopropyl alcohol 0·2*M* in tetraethylammonium bromide. A, solution saturated with oxygen, B, solution saturated with air. C, solution saturated with nitrogen. D, curve for isopropyl alcohol 0·1*M* in LiCl, saturated with nitrogen.

2 mA by isopropyl alcohol. Thus if one Faraday is passed through an electrode immersed in an alcohol containing 0·1% water and the electrode is maintained at −2·5 V, then in the case of methanol 0·0011 equivalents of hydroxide ions will be generated or 0·1% of the total alkali. In the case of isopropyl alcohol, however, 0·048 equivalents or about 5% of the total alkali will be hydroxide. Despite the fact that this calculation applies strictly only to reversible systems, it is clear that in the case of isopropyl alcohol a much larger proportion of the alkali is generated as hydroxide ions and a much thicker deposit is formed. The film formed on the cathode in isopropyl alcohol essentially blocks the current and suppresses the appearance of any well-defined background wave. The reduction of the added water did not yield a wave which could be resolved from the background due to either solvent, which confirms the results of Rehioui and Johansson.[11]

Another possibility for the formation of lithium hydroxide is the reduction of lithium ions to lithium metal, a reaction which has a standard reduction potential of −3·0 V *vs.* S.C.E in water. The lithium formed would be expected to react rapidly with traces of water to form insoluble lithium hydroxide. Whilst the reduction potential of lithium will be different in the two solvents under consideration, this reaction appears a possibility in isopropyl alcohol. However, it seems unlikely that it could account for the formation of even a thin film in methanol as very high currents are passed in this solvent at potentials well below −2·0 V.

In TEAB, reactions (2), (3) and (4) would be expected to occur in both methanol and isopropyl alcohol and since tetraethylammonium hydroxide is soluble in these media, no film is formed on the electrode. In the coulometric determination of carbon,[4] oxygen is used to flush the carbon dioxide into the titration cell and reaction (4) could be expected to occur to a considerable extent. Since this produces the same number of equivalents of base per Faraday as reaction (2) the stoichiometry of the main reaction is not disturbed by this side-reaction. The analysis of the products of reduction in TEAB solutions did not reveal the formation of any hydroxide ion but small amounts would not be apparent in the analysis.

Coulometric titrations of acids in isopropyl alcohol

The only previous worker to use isopropyl alcohol for the coulometric titration of acids used sodium perchlorate as supporting electrolyte but also mentioned the use of tetraethylammonium iodide.[3] On the basis of the results in this paper, we would recommend the use of tetraethylammonium bromide and have recently described the determination of carbon in steel by use of such a system but with the addition of 3% ethanolamine to bring about efficient absorption of carbon dioxide.[4] To test the general application of this system, coulometric titrations of several other acids have been carried out.

In our laboratory, a constant-current generator, with a valve circuit basically similar to that described by Glass and Moore,[12] has been used. This delivers a large voltage (200 V, at 100 mA) suitable for titrations in non-aqueous solvents. Analytical results are then obtained by a simple calculation from the constant current and the time for which it is passed. A possible difficulty with such a system is that a large amount of heat is generated when a current is passed through such a large resistance. The resistance is located mainly in the sintered-glass partitions used to separate the anode and cathode compartments of the cell, and if the resistance is too high, the solution adjacent to these partitions will boil. This problem has been overcome (*a*) by using wide porous sinters and (*b*) by using the high-resistance isopropyl alcohol solution in the cathode compartment only, and methanol in the other compartments.

Initially large solvent blanks (approx. 1 meq/g) were encountered but these were traced to contamination of the TEAB by traces of a strong acid. Recrystallization of the TEAB reduced the blanks to 0·2 meq/g.

Coulometric titrations of *p*-nitrophenol, benzoic acid, ascorbic acid and phenol were carried out, with potentiometric end-point indication with a glass electrode–saturated calomel electrode couple. Titration efficiencies were always close to 100% even with phenol, although in this case the potential jump was small (70 mV). The precision was tested by titration of 5 mg of benzoic acid (10 determinations), a range of results from 5·148 to 4·958 mg being obtained, which yielded a standard deviation of 0·062 mg and a 95% confidence limit of 5·006 ± 0·049 mg for the mean. The proposed system therefore appears to be at least as satisfactory as other systems which have been proposed for the non-aqueous coulometric titration of acids.

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Zusammenfassung—Kathodische Reaktionen in Methanol und Isopropylalkohol wurden in Gegenwart von Lithiumchlorid und Tetraäthylammonium bromid als Leitsalzen untersucht. Im Lithiumchlorid-Medium führt eine Nebenreaktion zur Bildung von unlöslichem Lithiumhydroxid; mit Tetraäthylammoniumbromid wird durch Reduktion von Lösungsmittel, Sauerstoff und Wasserspuren stöchiometrisch Base gebildet. Zur coulometrischen Titration von Säuren in Isopropylalkohol wird Tetraäthylammoniumbromid als Leitsalz empfohlen.

Résumé—On a étudié les réactions cathodiques en méthanol et isopropanol en la présence à la fois de chlorure de lithium et de bromure de tétraéthylammonium comme électrolytes supports. Une réaction secondaire en milieu chlorure de lithium méne à la formation d'hydroxyde de lithium insoluble, mais la base est générée stoechiométriquement en bromure de tétraéthylammonium par réduction de solvant, d'oxygène et de traces d'eau. Le bromure de tétraéthylammonuim est recommandé comme support électrolyte pour le titrage coulométrique d'acides en isopropanol.

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SOME OBSERVATIONS ON THE REDOX BEHAVIOUR OF *N*-PHENYLANTHRANILIC ACID INDICATOR IN IRON(II) TITRATIONS

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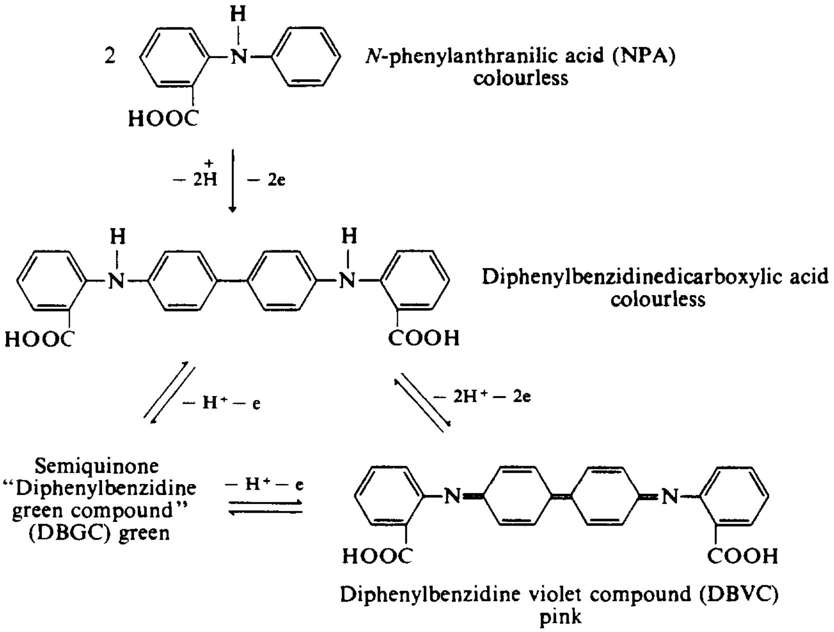
Summary—The optimum conditions for the successful use of *N*-phenylanthranilic acid as indicator in titrations of iron(II) with dichromate, cerium(IV) sulphate and vanadate have been established. The influence of iron(III) on the indicator action, and the nature of a green compound formed from the indicator in iron(II) titrations, have been investigated spectrophotometrically.

Syrokomskii and Stiepin[1] have studied the indicator properties of *N*-phenylanthranilic acid (NPA); that the indicator is superior to ferroin is implicit in their conclusions. As NPA is a derivative of diphenylamine, its oxidation mechanism is generally considered similar to that of the parent substance. The oxidation to the coloured compound can then be formulated as



Recently, however, Bishop and Hartshorn[2] have shown that the oxidation of the arylamine to the coloured compound is a single-step two-electron process with no detectable evidence for the formation of an intermediate, either of a benzidine or of a semiquinone, but they confirm that reduction of the oxidized arylamine stops at the benzidine stage.

Syrokomskii and Stiepin[1] report that the formal redox potential of the indicator system in 1*M* sulphuric acid is 1.08 V, but no working details of the Russian work are available. Lederer and Ward[3] claim to have confirmed this value, but they have made no allowance in their calculations for the irreversible step. In view of the behaviour of this indicator in the iron(II)–dichromate titration, the reported formal redox potential is considered high.[4] Belcher *et al.*[5] argue that the reported potential is incorrect in view of the redetermined value of the transition potential (0·89 V); further they do not expect such an abnormal rise in the redox potential of diphenylamine on the introduction of a carboxyl group. However the behaviour of the indicator in the iron(II)–dichromate titration cannot be used to assess the redox potential of the indicator system, in view of the peculiar behaviour of the dichromate/chromic system;[7,8] further, the transition potential of a one-colour indicator is dependent on the indicator concentration and the colour change does not depend on the ratio of the oxidized and reduced forms of the indicator as with a two-colour indicator.[9] The present author has failed to determine the redox potential of the system in 1*M* sulphuric acid from a potentiometric cerium(IV) sulphate titration of NPA alone or in combination with iron(II), at room temperature; the potentials from the beginning in the former system, and after the complete oxidation of iron(II) in the latter, were continuously drifting with time and were not reproducible even under carefully controlled experimental conditions. In the latter titration some of the indicator is oxidized along with the iron(II) and a bright greenish yellow colour is evident at a stage when the iron(II) end-point is imminent. The same colour is evident in the initial stages of the titration of NPA alone but only after a transient appearance of pink. It was thought that investigation into the cause of this colour formation might give some information on the failure of the potentiometric titrations.

Although Syrokomskii and Stiepin[1] claim that the indicator works well in the titration of iron(II) with cerium(IV), dichromate and vanadate, there are contradictory reports[1,4,5,6,10,11] on the behaviour of the indicator in the iron(II)–dichromate titration. Further, there is no detailed information on the limitations of the indicator in these titrations. In the present communication an attempt is made to define the working experimental conditions for these titrations more precisely and provide an explanation for the observed behaviour of the indicator.

EXPERIMENTAL

Reagents

Potassium dichromate, 0·05*N*. *Cerium(IV) sulphate*, 0·05*N*. Prepared by dissolving cerium(IV) ammonium sulphate in 1*N* sulphuric acid and standardized against arsenic trioxide according to the method of Gleu.[12]

Sodium vanadate, 0·05*N*. Prepared by treating the requisite amount of ammonium vanadate with a slight excess of sodium carbonate in solution, boiling until free from ammonia, then making up the solution to the desired volume. The solution is standardized against Mohr's salt by the procedure of Walden *et al.*[13]

Iron(II) ammonium sulphate, 0·05*N*. Prepared in 1*N* sulphuric acid from analytical-reagent grade material.

N-*Phenylanthranilic acid*, 0·005*M*.

Apparatus

The potentiometric assembly consisted of a Cambridge potentiometer and a suspension galvanometer. A bright platinum rod (*ca.* 0·2 mm in diameter) served as indicator electrode and a saturated calomel electrode as the reference electrode.

Investigation in visual titrations

Iron(II)–cerium(IV) sulphate. The indicator (2 drops per 50 ml of solution) has been found to function satisfactorily in this titration in 0·5–6·0*N* sulphuric acid medium. The colour change at the end-point is from a light greenish yellow to pink at lower acidities, and from an intense greenish yellow to pink at higher acidities. The colour change is not from colourless to pink as reported in the literature. The reduction of the oxidized indicator by iron(II) becomes somewhat slow towards the close of the titration in 4–6*N* sulphuric acid but there is little difficulty in locating the end-point. At still higher acid concentrations premature end-points have been obtained.

Iron(II)–dichromate. The indicator functions satisfactorily in 2–6*N* sulphuric acid medium in this titration; the titration is possible even at a lower acidity than 2*N* provided the titration mixture is 0·02*N* or more in iron(III). The colour change at the end-point is from greenish yellow to bright pink.

Iron(II)–vanadate. The indicator functions satisfactorily in 4–6*N* sulphuric acid medium in this titration but at the lower limit the colour change at the end-point requires a little time (5 sec) in view of the slowness of the indicator–oxidant reaction. This observation is contrary to an earlier report[14] that the working range of sulphuric acid is 4–13·5*N*. In titrations with >0·05*N* reagent the end-point is marked by the sharp appearance of the permanent bright blue-violet, the modification of the colour change being due to the blue colour of the vanadyl ion in solution. In titrations with 0·01*N* solutions, the end-point colour is pink owing to the smaller concentration of vanadyl ion; unlike the iron(II)–cerium(IV) case the greenish yellow colour is not evident during the titration, but with a higher concentration of the indicator the colour change is from greenish yellow to pink.

Influence of indicator concentration

With larger concentrations of the indicator, *e.g.*, 5–10 drops per 50 ml of titrand, the end-point colour is usually less permanent, turning to greenish yellow, and the colour change is less sharp. Besides resulting in the consumption of a considerable amount of oxidant before a sufficiently stable end-point colour is obtained, the use of a large concentration of indicator introduces an element of uncertainty in determining the exact equivalence point.

Influence of rate of titration and concentration of titrant

When the titrant is added more rapidly than usual, the intermediate greenish yellow colour is more intense, especially if 0·1*N* solutions are used rather than 0·01*N*. Nevertheless the colour change is always sharp provided a large concentration of the indicator is not used, but there is a slight variation in indicator correction when working with 0·01*N* solutions. In general the concentration of iron(III) at the end-point is without significant effect if the titrations are done at the usual speed. However, in titration of 5 ml of 0·01*N* iron(II) with 0·01*N* vanadate in 4*N* sulphuric acid medium, end-points premature by 2–2·5% have been obtained if 10 ml of 0·1*N* iron(III) are initially present in the titration mixture and about one min is allowed between drops towards the end.

Influence of acidity

Other conditions being the same, an increase in acidity has been found to facilitate the formation of the greenish yellow colour during the titration.

Spectrophotometric investigation

The effect of iron(III) on the oxidation of the indicator with dichromate is shown graphically in Fig. 1. The absorbance of the pink colour is plotted against time for reactions of (*i*) NPA with iron(III), (*ii*) NPA with dichromate, (*iii*) NPA with dichromate plus iron(III) in 2*N* sulphuric acid. The fall in absorbance after the maximum in (*iii*) may be due to instability of the oxidized form in 2*N* sulphuric acid.

The successful use of the indicator in titrations in 4–6*N* sulphuric acid is unexpected in view of the occurrence of the NPA–iron(III) reaction to a significant extent under experimental conditions similar to those prevailing just before the end-point. The influence of sulphuric acid concentration on the speed and extent of reaction are shown in Fig. 2, from measurements of the absorbance of the pink colour with respect to time. The absorbance reached a limiting value in 10–15 min. The presence of the reduced form of the indicator in the mixture at this stage was tested for by adding cerium(IV); the absorbance always increased on the addition of cerium(IV). By comparison of the limiting value with the maximum absorbance obtained with cerium(IV), the NPA–iron(III) reaction was found to be 28, 66 and 72% complete in 4, 6 and 8*N* sulphuric acid media respectively.

The greenish yellow compound (green form of NPA) in solution has been prepared by three different reactions: (*i*) by treating the pink oxidized form with a slight excess of iron(II), (*ii*) by treating the pink oxidized form with excess of NPA, and (*iii*) by allowing pink oxidized form to stand until all the pink colour is discharged. The species obtained in the three reactions yield the same pink oxidation product (with absorption maximum the same as for DBVC) on again being treated with cerium(IV) sulphate. It is observed that reaction (*i*) is quite rapid, reaction (*ii*) slow and reaction (*iii*) still slower. Further experiments have

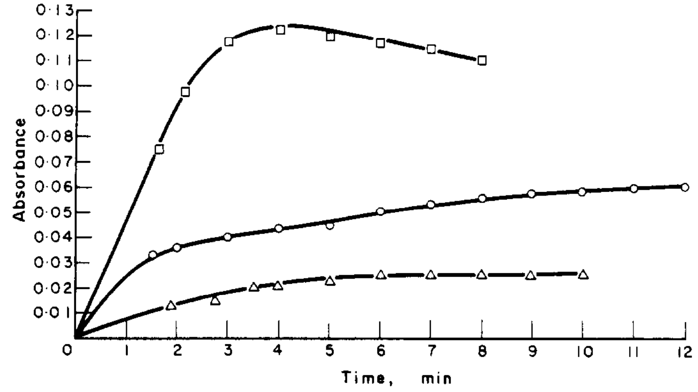


Fig. 1. Effect of iron(III) on the speed of oxidation of *N*-phenylanthranilic acid with dichromate. Overall acid concentration- $2N H_2SO_4$; absorbance at 530 nm

△ Solution $1 \times 10^{-5}M$ in NPA and $1 \times 10^{-2}M$ in iron(III)

○ Solution $1 \times 10^{-5}M$ in NPA and $1{\cdot}66 \times 10^{-5}M$ in potassium dichromate

□ Solution $1 \times 10^{-5}M$ in NPA, $1 \times 10^{-2}M$ in iron(III) and $1{\cdot}66 \times 10^{-5}M$ in potassium dichromate.

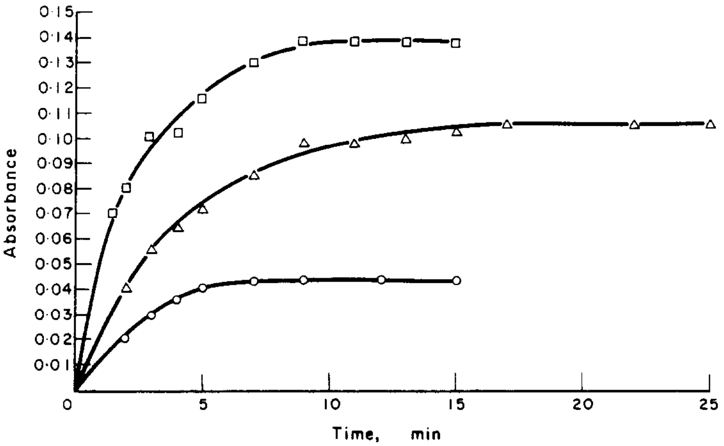


Fig. 2. Effect of sulphuric acid concentration on the speed and extent of oxidation of *N*-phenylanthranilic acid with iron(III)

Absorbance (at 530 nm) of a solution $1 \times 10^{-5}M$ in NPA and $2 \times 10^{-2}M$ in iron(III)

○ $4N$ H_2SO_4; △$6N$ H_2SO_4; □$8N$ H_2SO_4

revealed that the greenish yellow compound can be reduced quite rapidly to a colourless compound with a moderate excess of iron(II) but the reaction is retarded by the presence of a large excess of iron(III).

The pink oxidized form of NPA (DBVC) used in the preparation of the greenish yellow compound was obtained by adding the requisite amount of cerium(IV) sulphate. However, because of the lack of exact stoichiometry and the occurrence of side-reactions, a solution of known concentration of the greenish yellow compound could not be prepared. However, the solutions of the greenish yellow species obtained in the three reactions were suitably diluted to have nearly the same absorbance at one of the absorption peaks (430 nm). Figure 3 shows the absorption spectra. The three curves have peaks at 430 and 800 nm and are similar in shape, indicating the presence of the same species in the reaction products. The variation in absorbance at some wavelengths may be due to the products of side-reactions, especially in reaction (*iii*).

Potentiometric investigation

The potentials at which the indicator changes colour in a titration of iron(II) with cerium(IV) sulphate were determined as a function of acidity by the method of Belcher *et al.*,[15] and the other parameters studied were the

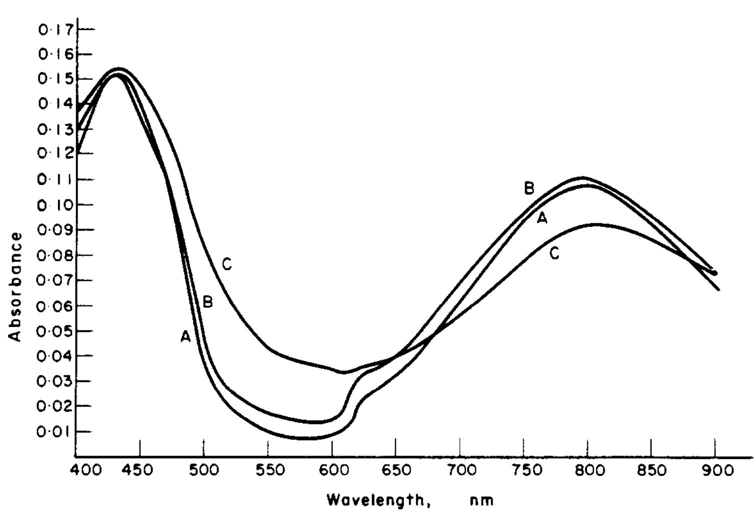


Fig. 3. Absorption spectra of DBGC in 6N H_2SO_4.
A; Prepared by reduction with Fe^{2+}; *B*, by treatment with NPA; *C*, by disproportionation.

stage of addition of the indicator in the titration and the indicator concentration. The results obtained are recorded in Table 1. In these experiments 5·0 ml of 0·01N iron(II) ammonium sulphate in about 45 ml of dilute sulphuric acid were titrated with 0·01N cerium(IV) sulphate. Towards the end 0·002N cerium(IV) sulphate was used instead of the 0·01N solution. When a perceptible colour had been obtained, 0·002N iron(II) ammonium sulphate was added to reverse the colour change. The amount of indicator used and the stage of addition of the indicator are indicated in the Table.

Table 1. Potential of colour change of NPA as a function of acidity

	Potential, V (*vs.* NHE, 28°C)			
$[H_2SO_4]$ N	2 drops added near the end-point*	1 drop added at the start of titration	2 drops added at the start of titration	5 drops added at the start of titration†
1·0	0·890	0·895	0·895	0·905
2·0	0·885	0·890	0·890	0·900
3·0	0·880	0·890	0·890	0·895
4·0	0·870	0·885	0·885	0·895
5·0	0·855	0·875	0·885	0·890
6·0	0·845	0·865	0·870	0·880
8·0§	0·795	0·835	0·845	0·865
10·0§	0·765‡	0·775	0·785	0·830

* Indicator added 0·5 ml before the true end-point.

† The greenish yellow colour modifies the colour change.

§ No colour reversal attempted, since colour change was difficult to assess.

‡ Indicator added 1·0 ml before the true end-point (otherwise the pink colour is obtained immediately on addition of the indicator).

It has been found that the colour-change potential is generally increased by a few mV after each reversal. In each case two or three reversals were performed and the average is recorded. The colour-change potential when the indicator is added at the start of the titration is generally higher than if the indicator is added towards the end; the colour change with a larger concentration of the indicator is generally observed at a higher potential. The dependence of the colour-change potential on these factors emphasizes the need for close observance of the experimental conditions for the recommended procedure.

Table 2.

$[H_2SO_4]$ N	Approximate equivalence potential range, (*vs.* NHE), V	Colour-change potential (*vs.* NHE), V*
1·0	0·825–0·855	—
2·0	0·825–0·875	—
3·0	0·830–0·890	—
4·0	0·830–0·920	0·885
5·0	0·840–0·930	0·865
6·0	0·845–0·940	0·855
7·0	0·860–0·960	0·835
8·0	0·865–0·975	0·805
10·0	0·895–1·005	0·770

* Titration of 5·0 ml of 0·01N iron(II) in 50 ml of titration solution, with 0·01N vanadate; 2 drops of indicator added at the start.

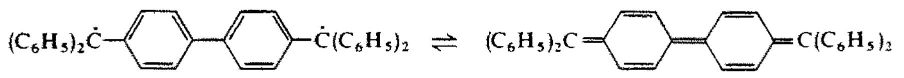
Table 2 records the influence of acidity on the equivalence-potential range of the iron(II)–vanadate titration and the colour-change potentials of the indicator. In 1–3N sulphuric acid medium the colour-change potentials are difficult to determine with this system, and are not reported.

The optimum acid range indicated by Table 2 agrees well with that found in the practical titrations recorded earlier. Although Table 2 indicates that the titration may be just possible in 3N acid [based on the value of the colour-change potential in iron(II)–cerium(IV) sulphate titration], this has been found not feasible in practice, probably owing to the slowness of indicator-oxidant reaction.

DISCUSSION

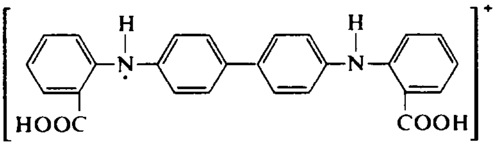
The oxidation of NPA to the pink product occurs in a single step with no detectable evidence for the formation of intermediates. This oxidation product rapidly decays to a green form which is also obtained from the former by reduction with iron(II) or treatment with the reduced form of the indicator. The green form is more stable than the pink oxidation product, but can be reduced by excess of iron(II) to a colourless product which is probably the benzidine form and can also be obtained[2] by zinc-dust reduction of the pink oxidation product. The benzidine and the green forms correspond to two stable oxidation states between NPA and the pink oxidation product.

Bishop and Hartshorn[2] have made the observation that the oxidation of the arylamine to the coloured form is an intermolecular reaction but no detailed mechanism was proposed. The evidence, however, is not in favour of Kolthoff and Sarver's theory.[16] Thiel[17] believes that a transient biradical of the type, $C_6H_5{-}N{=}C_6H_4\lessdot$ is the primary product, which condenses with another such radical to give a diquinonedi-imine; the latter is also obtained by a two-electron oxidation of the corresponding benzidine. Since this cannot have an intense colour the dimer may be expected to be in a triplet state (biradical), but the e.s.r. evidence is only qualitative. It is not unlikely that a favourable equilibrium exists for the ground-state (singlet) molecules in the mixture, if the energy of excitation to the triplet state is large enough; the analogous behaviour of Tchitchibabin's hydrocarbon with a related structure,



is noteworthy.[18]

The curious behaviour of the oxidized product of NPA to give on decay the green product instead of the expected colourless benzidine has been noted.[2] It may be speculated that this is due to disproportionation, but other evidence indicates that the green compound is a reduction product of the pink form. Its spectral behaviour in relation to the coloured oxidation product suggests that there is no gross difference in the structure of the two compounds. The green compound is most probably a free radical,



Diphenylbenzidine green compound
(DBGC)

stabilized by resonance.

The decomposition and further oxidation of the coloured product and products of decomposition, and the side-reactions of the coloured oxidation product with iron(II) and the unoxidized indicator, seem to be the cause of drifting and irreproducible potentials in the potentiometric titrations and hence do not permit even an approximate estimation of the formal potential of the indicator system.

Besides the induction effect of iron(II),[1] the catalytic effect of iron(III) on the oxidation of the indicator with dichromate is responsible for the indicator working better in the iron(II)–dichromate titration. In view of the observations that either the single-step two-electron oxidation took place or no oxidation occurred in the arylamine oxidation[2] and that iron(III) reacts with NPA to give the coloured product, the catalytic action of iron(III) may be explained in terms of the following steps:

$$\text{NPA} + \text{Fe(III)} \longrightarrow \text{DBVC} + \text{Fe(II)} \qquad (i)$$

$$\text{Fe(II)} + \text{Cr(VI)} \xrightleftharpoons{\text{fast}} \text{Fe(III)} + \text{Cr(V)} \qquad (ii)$$

$$\text{NPA} + \text{Cr(V)} \xrightarrow{\text{fast}} \text{DBVC} + \text{Cr(III)} \qquad (iii)$$

Step (*i*) should not be inferred to be slower than the indicator–dichromate reaction at the end-point, from the apparent rates observed (Fig. 1). In view of the curious mechanistic behaviour of the arylamine towards oxidants, step (*i*) is probably more complex, and iron(II) very much retards the reaction. In the presence of Cr(VI), the concentration of iron(II) in the iron(III) solution (probably in equilibrium with atmospheric oxygen) is decreased so that the reaction is faster than observed otherwise, and the rate continues to be fast till all the NPA is oxidized by the excess of dichromate used. Further, the overall oxidation of NPA proceeds both by steps (*i*) and (*iii*); this would not have been possible if the reduction of Cr(VI) with iron(II) were not stepwise.

The unexpectedly satisfactory behaviour of the indicator in iron(II) titrations in 4–6*N* sulphuric acid may be explained by the slow kinetics of the NPA–iron(III) reaction, with iron(II) tending to retard the forward reaction. At still higher acidities the hydrogen ion effect might over-ride the retarding effect of iron(II) and cause premature end-points in titrations. There is another possibility. Even though the oxidized form is obtained in perceptible concentration in a titration at a point with a slightly greater ratio of iron(II) to iron(III) than in a blank experiment, the analytical result is still within experimental error. The assumption is that equilibrium is reached faster in titrations than in blank experiments.

The differences in the colour-change potentials when the indicator is added towards the end and at the start of a titration, and when a larger amount of the indicator is used (Table 1) must be related to the formation of DBGC during titration. On this basis the lower colour-change potentials in iron(II)-vanadate titrations than in iron(II)-ceric sulphate titrations at corresponding acidities are indicative of less favourable conditions for the formation of DBGC in the former. The observation that the colour change is from nearly colourless to pink in the former but from greenish yellow to pink in the latter is in agreement with this conclusion. The premature end-point in the titration of iron(II) with 0·01*N* vanadate in the presence of a large excess of iron(III) and the absence of this effect in titrations with ceric sulphate and dichromate, can be explained in the same way. The influence of DBGC on the colour change may be due to its colour-masking ability or its different kinetic behaviour towards oxidants.

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Zusammenfassung—Die optimalen Bedingungen zur erfolgreichen Verwendung von *N*-Phenylanthranilsäure als Indikator bei Titrationen von Eisen(II) mit Dichromat, Cer(IV)sulfat und Vanadat wurden festgelegt. Der Einfluß von Eisen(III) auf die Indikatorwirkung und die Natur einer bei Eisen(II)-Titrationen vom Indikator gebildeten grünen Verbindung wurden spektrophotometrisch untersucht.

Résumé— On a établi les conditions optimales pour l'emploi satisfaisant de l'acide N-phénylanthranilique comme indicateur dans les titrages du fer (II) au bichromate, au sulfate de cérium (IV) et au vanadate. On a étudié spectrophotométriquement l'influence du fer (III) sur l'action de l'indicateur et la nature d'un composé vert formé à partir de l'indicateur dans les titrages de fer (II).

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DETERMINATION OF NANOGRAM AMOUNTS OF SULPHIDE BY RELEASE OF RADIOACTIVE IODIDE

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Summary—Two variants of a technique for determination of ng-amounts of sulphide ions in liquid samples are presented. They are based on the replacement of radioactively labelled iodide from silver iodide by sulphide. In the first variant, suitable for small sample volumes, the labelled silver iodide is fixed on a filter paper disc which is then shaken with the solution to be analysed until equilibrium is attained. In the second variant, suitable for sample volumes up to 300 ml, the sample solution is passed through a filter paper disc carrying labelled silver iodide or through a labelled silver iodide precipitate. The amount of sulphide is determined from the activity of the released radioiodide by comparison with standards which have been processed in the same way. The method is applicable to sulphide amounts greater than 5 ng and concentrations greater than 0.2 ppM. The interference by many common accompanying anions and cations has been investigated.

The determination of ng-amounts of sulphide is of interest, especially in two fields: (1) in biological and chemical systems (*e.g.*, in water supplies, in lake- and sea-water and sewage muds, or as an unpleasant air pollutant) where it must be determined separately from other possible forms of sulphur and (2) in various inorganic and organic materials in order to determine their total sulphur content by micro or trace techniques.

In general, the most frequently applied sensitive methods for the second purpose are those based on sulphide formation, *e.g.*, after hydrogenation or reductive decomposition methods in submicro organic elemental analysis[1–3] or in trace analysis.[4–7]

The chemical methods used in determining ng-amounts of sulphide are limited in their application by different types of interference: these methods include various spectrophotometric methods,[8–11] fluorimetric methods based on quenching of fluorescein mercury acetate,[12–14] catalytic methods based on the azide–iodide reaction[15] and reduction of silver with iron(II)[16] or the use of sulphide-sensitive electrodes.[2,3,17–19]

The displacement method—presented in two variants, one suitable for 1–5 ml samples, the other for up to about 300 ml—can bring certain advantages in some cases. It is similar to a simple technique proposed recently for the determination of other ions.[20,21]

The method is based on the replacement of radioactively labelled iodide from silver iodide, by sulphide ions:

$$2\,Ag^{131}I + S^{2-} \rightleftharpoons Ag_2S + 2\,{}^{131}I^- \qquad (1)$$

The labelled silver iodide is fixed on a filter paper disc. The disc is either shaken with the solution to be analysed (suitable only for small volumes) or the solution is passed through the disc until equilibrium for the reaction is attained. The unknown amount of sulphide is determined from the activity of the released radioiodide by using a calibration graph, or by comparison with a standard which has been processed in the same way.

In this replacement reaction, advantage is taken of the favourable molar and weight ratio between the sulphide to be determined and the iodide released, as well as of the great difference between the solubility products of silver iodide and silver sulphide ($K_{sp(AgI)} = 8 \times 10^{-17}$; $K_{sp(Ag_2S)} = 6 \times 10^{-50}$).[22] The exchange reaction is also favoured by the fact that the relatively small amount of silver iodide is distributed over a large surface area on a filter paper carrier, and the iodide released goes easily into aqueous solution.

EXPERIMENTAL

Reagents and materials

All reagents were of at least p.a. purity. Twice-distilled water (quartz apparatus) was used for preparing the solutions.

Radioiodide. Solutions of radioiodide were prepared from a carrier-free ^{131}I-solution and potassium iodide containing amounts of carrier between 0·01 and 1·00 mg of iodide per ml. The specific activities were between 0·025 and 4 mCi/mg of iodide.

Silver nitrate solutions. Solutions with silver concentrations of 0·02–0·5 mg/ml were used.

Filter paper. Discs were prepared from filter paper MN 2260 (Macherey, Nagel and Co., Düren).

Procedures

Preparation of the discs containing $Ag^{131}I$. In the "shaking" variant 3-μl portions of silver solution are placed on each of a series of filter paper discs 6 mm in diameter. The concentration of silver is chosen so that the activity of the disc is approximately halved in the replacement reaction. As a working rule, 1 μg of silver is suitable for 100 ng of sulphide. The discs are then immersed in a radioactively-labelled iodide solution which has a carrier concentration corresponding to the silver concentration and an appropriate specific activity, and are shaken for a few minutes. The discs are taken out from the solution and washed 5 times in 2*M* acetic acid, and then repeated with redistilled water, in order to remove excess of labelled iodide. The discs are dried with an infrared lamp. In the "flow-through" variant the preparation of the discs is similar, but the discs are 25 mm in diameter and 20 μl of silver solution are placed on each.

· The amount of carrier and the specific activity of the silver iodide are chosen according to the expected range of sulphide concentration in the solutions to be analysed. For example, if the sample solution contains a small amount of sulphide, the amount of silver iodide carrier on the discs should be small, and the specific activity must be high. Conversely, when more sulphide is present, the concentration of carrier must be higher, and the specific activity can be lower.

Shaking method (*variant 1*). Aqueous standard and sample solutions (which can be up to 0·1*M* in EDTA) are used. The most suitable pH value is 8·9 or slightly above. Aliquots of 1–4 ml of standard and sample solutions are transferred into glass ampoules ("Fiolax" Glass, Jenaer Glaswerke, Schott u. Gen., Mainz), each of which is then provided with a disc impregnated with labelled silver iodide. The ampoules are closed and shaken until equilibrium for the replacement reaction is attained. Under the optimal experimental conditions used by us 100 min of shaking are necessary. After the shaking is finished the discs are removed from the solutions, rinsed in distilled water, and dried. The unknown amount of sulphide ions can be determined either by measuring count-rates of equal fractions of the solutions containing the released iodide, or by measuring the loss of activity on the discs. When the activity released is a very small fraction of the original disc activity (*i.e.*, very small amounts of sulphide) it is better to measure the activity of the solution than the activity loss.

The γ-radiation from ^{131}I is counted with a well-type sodium iodide detector and a single-channel analyser. The blank test is carried out with water or with 0·1*M* EDTA at the same pH value as the sample and standard solutions. The complete procedure must be carried out in the absence of daylight.

Flow-through method (*variant 2*). In this variant a large excess of silver iodide must be present on the paper disc to obtain complete replacement of sulphide and in order for one disc to be used for the processing of many samples. For example, to analyse a series of samples each of which contains about 100 ng of sulphide, 100 μg of silver are used for the preparation of the labelled silver iodide. The prepared filter paper disc is then placed on a membrane filter (Sartorius, Göttingen) with a pore size of 0.15 μm, in a filter flask with an effective opening of 20 mm. Redistilled water (10 ml) is passed through the filter, under suction, until the specific activity had become constant (blank value). Then each of the standard and sample solutions is sucked through the filter twice at a rate of *ca.* 10 ml/min. The filter must either be washed with a few ml of redistilled water between samples or the first 4–5 ml of the filtrate from each new solution must be rejected. It is found convenient to run a standard after some sample solutions.

Instead of filter paper prepared with labelled silver iodide it is also possible to use a precipitate of labelled silver iodide uniformly distributed on a membrane filter, as follows. Add 1 ml of 10% nitric acid to *ca.* 15 ml of silver nitrate solution containing 20–100 μg of silver. Heat to near 100° and treat with a slight excess of iodide solution labelled with ^{131}I. Keep the mixture at that temperature for 15–20 min then filter off the silver iodide precipitate by suction through a membrane filter with a pore size of 0.6 μm. Wash the precipitate first with dilute acetic acid and then with 10-ml portions of water as described above.

RESULTS AND DISCUSSION

Shaking method

The rate of the iodide–sulphide replacement reaction is dependent on the experimental conditions. Figure 1 shows the time-dependence of the replacement, for two sets of shaking conditions. Obviously the shaking conditions must be constant for an experimental series.

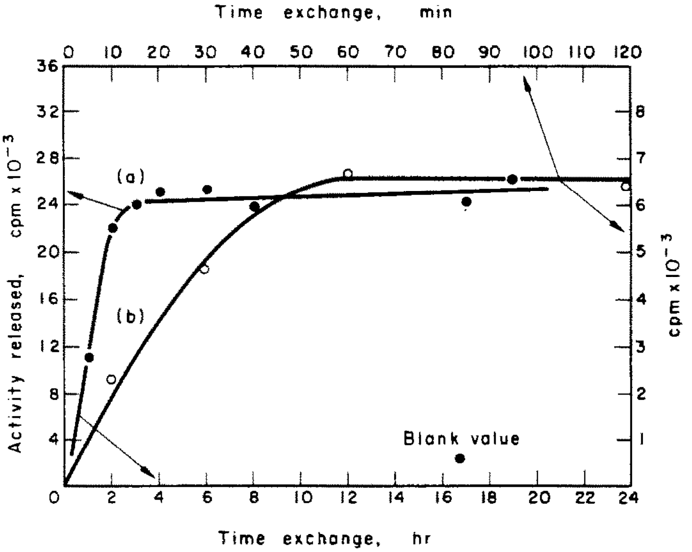

Fig. 1. Time dependence of the activity released for two different experimental conditions: (*a*) intensive shaking and water solution, (*b*) slower shaking and presence of EDTA

It has been known for a long time that sulphide solutions are unstable under normal conditions.[23] Generally, the stability of sulphide solutions is an important factor which must be taken into consideration, irrespective of the method used for the determination. In this variation, because of the relatively long shaking-time, the instability problem is of extraordinary importance. The main reason for the instability seems to be the volatility and oxidation of sulphide.

Sulphide becomes more unstable as its concentration decreases. Several substances have been proposed for stabilization of sulphide solutions. Bock and Puff[18] proposed ascorbic acid: hydrazine sulphate,[10] formaldehyde,[24] and other substances have also been used. It has been reported that in the sulphide concentration range 10^{-7}–$10^{-5}M$, the presence of oxygen does not affect the sulphide stability if the solutions are kept in darkness.[12]

In search for the best conditions, the influence of darkness, presence of hydrazine sulphate and ascorbic acid, and the effect of pH were investigated. Figure 2 shows the

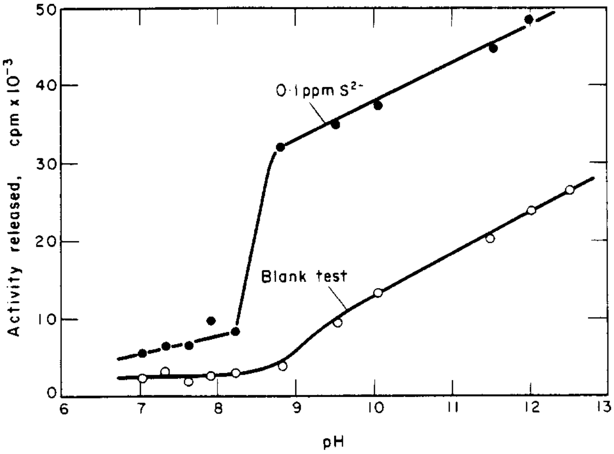

Fig. 2. Dependence of the activity released on pH: 0·1*M* EDTA, shaking method.

dependence of the released activity on the pH when the experiments are done in the absence of daylight. In the pH range 7–8.2 only a relatively small fraction of the sulphide takes part in the replacement, *i.e.*, the sulphide solution is not sufficiently stable for processing. The solutions begin to be stable enough at pH 8.9. Consequently, the determinations can be carried out at this pH and above. Increasing the pH also increases the blank value at about the same rate as the release reaction, so the activity released in the iodide–sulphide replacement stays practically constant.

The presence of ascorbic acid and hydrazine sulphate does not sufficiently stabilize sulphide solutions when they are processed in direct daylight: without any stabilizing agents only 53% of the sulphide taken was found; in the presence of ascorbic acid with a concentration[18] of 1 mg/ml, and of hydrazine sulphate with a concentration[10] of 20 μg/ml, 84% and 71%, respectively, of the sulphide taken was found. If the solutions are processed in the absence of daylight no stabilizing agents are necessary.

The applicability of the method was investigated for the determination of sulphide concentrations between 0 and 400 ng/ml. Since the calibration graphs are linear, the unknown amount of sulphide may be calculated by direct comparison with a standard, after application of the blank correction.

The limit of detection was found to be 5 ng of sulphide. The standard deviation was determined for five different concentrations of sulphide. It increases very rapidly as the amount of sulphide decreases below 50 ng (Fig. 3).

The interference of accompanying anions was investigated in more detail for a sulphide concentration of about 100 ng/ml. This sulphide concentration can be determined in the presence of at least 5000-fold amounts of SO_4^{2-}, F^- and Cl^-, 1000-fold amounts of Br^-, HCO_3^- and SCN^-, and 100-fold amounts of PO_4^{3-}, $S_2O_3^{2-}$ and I^-. Strong interference is caused by cyanide if present in much higher concentrations than sulphide. A CN^-/S^{2-} ratio of 1 can be tolerated.

Under normal conditions, cations forming sparingly-soluble sulphides would interfere. Consideration of stability constants shows that several complexants should work as masking agents for these cations. The majority of the elements forming sparingly-soluble sulphides form EDTA complexes with high stability constants and therefore EDTA can be used as masking agent. The masking agent must fulfil the following conditions however:

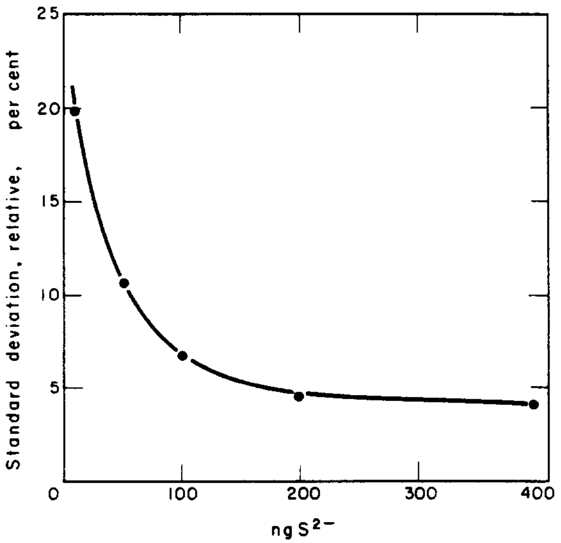

Fig. 3. Relative standard deviation as a function of amount of sulphide, for the shaking method.

(*i*) it should not attack the silver iodide, (*ii*) it should neither attack the sulphide in the solution nor disturb the exchange reaction, and (*iii*) it must allow the iodide released to be washed into the solution. A 0·1*M* EDTA medium was found to fulfil these conditions well.

At least the following excess of common cations is tolerable if the solution is made 0·1*M* in EDTA at a sulphide concentration of 100 ng/ml: 1000-fold Mn(II), Fe(III), Co(II), Ni(II), Zn(II) and Pb(II), 100-fold Tl(I), Cd(II), As(III), As(V) and Cu(II), and 10-fold Hg(II).

Sample volumes up to 5 ml can be used. However, the time necessary to attain equilibrium for the exchange reaction becomes longer with increasing sample volume.

Flow-through method

In the flow-through method much larger sample volumes can be used, up to 300 ml. However, the blank value must be determined with an approximately equal volume of water or EDTA solution.

In the flow-through method the sulphide solution is not subjected to so much stress as it is in the shaking method. This is why no special steps are necessary for preventing losses of sulphide. A relatively large pH range can be used, 5–10. Higher pH values are disadvantageous owing to the higher blank values. The experiments need not be carried out in the absence of direct daylight, but it is recommended to avoid direct daylight if a lot of samples taking a longer period of time are to be analysed. Some changes in the properties of the silver iodide on the filter paper can appear as a result of long exposure to direct daylight. If the experiments are to be interrupted, the filter paper disc or the precipitate must be kept wet.

The prepared filter paper discs gave a somewhat better reproducibility and limit of detection than did labelled silver iodide precipitate distributed on membrane filters. The relative standard deviation at a sulphide concentration of 4 ppM and sample volume 50 ml was found to be 2.5%. The limit of detection at this volume was determined to be 0·2 ppM or 10 ng absolute. The sample volume somewhat affects the blank value and thereby also the limit of detection: the limit of detection is dependent on sample volume. For example, the limit of detection is reduced by a factor of about 2, if 5-ml sample volumes are processed instead of 50-ml samples.

EDTA increases the blank value more in the flow-through method than in the shaking method. The tolerable EDTA concentration for the range of sulphide investigated is about $10^{-3}M$. The masking ability is then correspondingly lower, and reduces the tolerance limit for metals, *e.g.*, for Cu(II) and Pb(II) by a factor of about 4.

The replacement reaction is particularly advantageous if it is used in combination with X-ray fluorescence. Such a technique based on an enrichment of sulphide ions on a thin layer of silver chloride or iodide has been developed, including detailed studies of interference by accompanying ions.[25] It will be published later.

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Zusammenfassung—Eine Arbeitsvorschrift zur Bestimmung von ng-Mengen Sulfidionen in flüssigen Proben wird in zwei Varianten angegeben. Sie beruhen auf der Verdrängung von radioaktiv markiertem Jodid aus Silberjodid durch Sulfid. Bei der ersten Variante, die sich für kleine Probenvolumina eignet, wird das markierte Silberjodid auf einer Filtrierpapierscheibe aufgezogen; diese Scheibe wird dann mit der zu analysierenden Lösung geschüttelt, bis das Gleichgewicht erreicht ist. Bei der zweiten Variante, die sich für Probenvolumina bis zu 300 ml eignet, wird die Probenlösung durch eine Filtrierpapierscheibe geführt, die markiertes Silberjodid enthält, oder durch eine Fällung aus markiertem Silberjodid. Die Sulfidmenge ermittelt man durch Vergleich der Aktivität des freigesetzten Radiojodids mit auf die selbe Weise behandelten Standards. Die Methode läßt sich auf Sulfidmengen über 5 ng und Konzentrationen über 2 ppM anwenden. Die Störung durch viele gängige begleitende Anionen und Kationen wurde untersucht.

Résumé—On présente deux variantes d'une technique pour le dosage de quantités de l'ordre du ng d'ions sulfure dans des échantillons liquides. Elles sont basées sur le remplacement de l'iodure marqué radioactivement de l'iodure d'argent par le sulfure. Dans la première variante, convenable pour de petits volumes d'échantillon, l'iodure d'argent marqué est fixé sur un disque de papier filtre qui est alors agité avec la solution à analyser jusqu'à ce que l'équilibre soit atteint. Dans la seconde variante, convenant à des volumes d'échantillon jusqu'à 300 ml, la solution d'échantillon est passée à travers un précipité d'iodure d'argent marqué. La quantité de sulfure est déterminée à partir de l'activité du radioiodure libéré par comparaison à des étalons qui ont été traités de la meme manière. La méthode est applicable à des quantités de sulfure supérieures à ng et à des concentrations supérieures à 0,2 p.p.M. On a étudié l'interférence de nombreux anions et cations accompagnateurs communs.

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ELECTRONIC ABSORPTION AND FLUORESCENCE OF 9-ANTHRALDEHYDE AND ITS CONJUGATE CATION

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Summary—The appearance or lack of vibrational structure in the ^1L_a and ^1L_b absorption bands of the neutral species and cation derived from 9-anthraldehyde is explained in terms of adherence to or violation of the Franck-Condon principle. The lack of vibrational structure is attributed to the motions of the aldehyde group during the course of electronic transition, a process which destroys vibration quantization in the Franck-Condon excited state. The appearance of well-defined vibrational structure in the ^1L_a band of the cation establishes that intramolecular charge-transfer alone, without accompanying vibrational or solvent relaxation which is contemporaneous with electronic transition, is not responsible for the lack of structure in most intramolecular charge-transfer transitions. The previously reported fluorescence of 9-anthraldehyde in hydroxylic solvents is found to be in error and is likely to originate from an impurity produced by photo-reduction. The actual fluorescence of 9-anthraldehyde is at much lower frequency than previously reported.

The application of fluorescence spectroscopy to chemical analysis is somewhat restricted by the limited number of organic molecules, of analytical interest, which fluoresce. This problem can be substantially reduced in importance by the preparation of fluorescent derivatives of non-fluorescing analytes. One of the most widely employed of such techniques entails the condensation of a molecule containing a fluorophore and a reactive functional group with the molecule of analytical interest. Normally, in such reactions an excess of reactant is added to the reaction medium, with the result that the native fluorescence of the reactant may constitute an interference with the measurement of the fluorescent derivative. Under this circumstance it would be useful to carry out a variation of the chemical composition of the reaction medium (*e.g.*, pH or Hammett acidity) in order to select the solution conditions under which minimal overlap occurs between the emissions of the reactant and its condensation product with the analyte. Similar arguments are also applicable to the absorption spectrophotometric analyses of condensation products of reactive chromophores with analytes which do not absorb in the near ultraviolet or visible regions of the electromagnetic spectrum.

9-Anthraldehyde appears to be a particularly interesting reagent for such reactions because of the highly fluorogenic and chromophoric properties of the anthracene ring and the diverse and highly reactive chemistry of the aldehyde group. Aromatic aldehydes are generally known to be very weak bases in their ground electronic states and moderately weak bases in their lowest electronically excited singlet states. These factors determine the spectral regions in which the aromatic aldehydes absorb and fluoresce, respectively, in solutions of varying acidity. Consequently, it was felt that the intelligent application of 9-anthraldehyde as an analytical reagent, in aqueous solutions, demanded consideration of the acidity dependence of its molecular electronic spectra.

9-Anthraldehyde has been reported to fluoresce in hydroxylic solvents but not in aprotic media.[1] This has been attributed to the lowest excited singlet state being of the n,π^* type in aprotic solvents. However, in hydroxylic solvents, hydrogen-bonding of the solvent with the non-bonded electron pairs of the carbonyl group raises the energy of the n,π^* state while the polarizing effect of hydrogen-bonding and the gross dielectric properties of the activating solvent lower the energy of the lowest $^1\pi,\pi^*$ state to the point where it becomes the lowest excited singlet state, favouring fluorescence over intersystem crossing as a means of deactivation of the lowest excited singlet state.[1]

The basic properties of 9-anthraldehyde have been investigated by Culbertson and Pettit[2] who found that in the ground electronic state this compound is considerably more basic than benzaldehyde or the naphthaldehydes. This result was attributed to the stabilization of the cation by greater delocalization of positive charge, over the anthracene ring, than is possible in the smaller ring aldehyde cations. A recent calculation of the dissociation constant of the 9-anthraldehyde cation in the lowest excited singlet state, employing the Förster cycle[3] and the averages of the absorption and fluorescence maxima of the neutral molecule and the cation as the spectroscopic *O-O* bands, indicated that 9-anthraldehyde was far more basic (11 orders of magnitude) in the lowest excited singlet state than any other aromatic aldehyde yet investigated.[4] On the basis of the differences in sizes of the aromatic rings in 9-anthraldehyde and other aromatic aldehydes, we had difficulty in rationalizing the differences in excited state basicity suggested in the previous study[4] and therefore decided to reinvestigate the electronic spectra and titration behaviour of 9-anthraldehyde.

EXPERIMENTAL

9-Anthraldehyde was recrystallized from 95% ethanol. Reagent grade sulphuric acid and distilled demineralized water were employed as the solvents in these studies.

Absorption spectra were taken on a Beckman DB-GT spectrophotometer. Fluorescence measurements were performed on a Perkin–Elmer MPF-2A fluorescence spectrophotometer with monochromators calibrated against the xenon line-emission spectrum and output corrected for instrumental response by means of a Rhodamine-B quantum counter.

Approximately $10^{-3}M$ 9-anthraldehyde was prepared in 95% ethanol immediately before mixing 0.1 ml with 10.0 ml of buffer or acid solution. Only these freshly prepared 9-anthraldehyde solutions in ethanol were used for spectral study.

RESULTS AND DISCUSSION

The electronic spectral features of 9-anthraldehyde and its conjugate cation are summarized in Table 1. The variations of the absorption and fluorescence spectra of 9-anthraldehyde with pH and Hammett acidity[5] are shown in Figs. 1 and 2.

The absorption spectrum of the neutral molecule shows that the ^1L_a band is unstructured while the ^1L_b band which is observed on the short wave-length side of the ^1L_a band is highly structured. However, remarkably, the ^1L_a band of the cation is structured while the ^1L_b band of the cation is diffuse. It is assumed that the ^1L_a band is the lowest frequency absorption band in both the cation and neutral molecule because aldehyde substitution in the 9-position mixes charge-transfer character into the short-axis polarized $^1L_a \leftarrow {}^1A$ transition of anthracene, lowering the energy of the $^1L_a \leftarrow {}^1A$ transition of anthracene (which is the lowest energy absorption in unsubstituted anthracene) to a greater degree than the $^1L_b \leftarrow {}^1A$ transition. The lack of vibrational structure in an electronic absorption spectral band is the result of the loss of vibrational quantization in the Franck-Condon excited state to which transition takes place and is often observed in intramolecular charge-transfer transitions, especially in fluid polar solvents and when exocyclic functional groups are better conjugated with an aromatic ring in the excited state than in the ground state. The loss of

Table 1. Electronic absorption ($\bar{\nu}_{1L_a}$ and $\bar{\nu}_{1L_b}$) and fluorescence ($\bar{\nu}_f$) maxima of 9-anthraldehyde and its conjugate cation. Diffuse spectral bands are represented by the band maximum ($\bar{\nu}$ max). Structured spectral bands are represented by the *O-O* vibronic bands ($\bar{\nu}_{(0-0)}$) and by the second vibronic feature ($\bar{\nu}$ (2nd band)). Frequencies are reported in cm^{-1} × 10^{-4}.

Temperature, *K*	Neutral molecule (pH 4)			Cation (H_0 − 6·9)		
	$\bar{\nu}_{1L_b}$	$\bar{\nu}_{1L_a}$	$\bar{\nu}_f$	$\bar{\nu}_{1L_b}$	$\bar{\nu}_{1L_a}$	$\bar{\nu}_f$
			In aqueous media			
298	2·69(*O-O*) 2·83(2nd band)	2·45(max)	1·96(max)	2·45(max)	1·88(*O-O*) 1·98(2nd band)	1·78(max)
77			2·15(*O-O*) 2·04(2nd band)			1·83(max)
			In n-hexane			
298	2·69(*O-O*) 2·84(2nd band)	2·52(max)	—*			
			In n-hexane + trifluoroacetic acid (1 %)†			
298	2.65(*O-O*) 2.80(2nd band)	2·35(max)	—	—	—	1·88(max)

* No fluorescence was observed from the neutral molecule in hexane.

† The absorption in n-hexane + trifluoroacetic acid is due to the hydrogen-bonded neutral molecule; the fluorescence is from the cation.

vibrational quantization in the Franck-Condon excited state may be attributed to solvent relaxation processes and functional group rehybridization occurring at a rate which is only slightly slower than the rate of the electronic absorption. The transient thermal relaxation processes alter the vibronic sublevels of the Franck-Condon excited state while the electronic transition is occurring, with the result that a continuum of vibronic transitions comprises the absorption band, giving the band its diffuse appearance. Thus the assumption of total separability of electronic and nuclear motions, upon which the Franck-Condon principle is based, is sometimes only approximate. The appearance of vibrational structure in the ^1L_b band of 9-anthraldehyde and in the ^1L_a band of its cation indicate that these transitions are well described by the Franck-Condon principle. However, the lack of vibrational structure in the ^1L_a band of the neutral molecule and in the ^1L_b band of the cation suggests that the

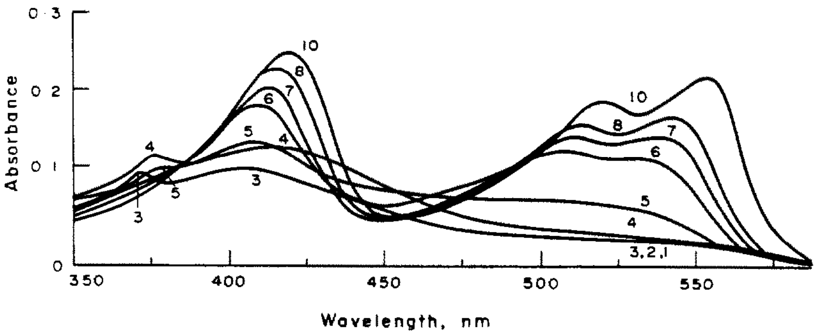

Fig. 1. Electronic absorption spectra of 1 × 10^{-5} *M* 9-anthraldehyde in sulphuric acid. (1) $H_0 = -0·7$, (2) $H_0 = -1·6$, (3) $H_0 = -2·5$, (4) $H_0 = -3·4$, (5) $H_0 = -4·7$, (6) $H_0 = -5·8$, (7) $H_0 = -6·9$, (8) $H_0 = -8·0$, (10) $H_0 = -10·0$.

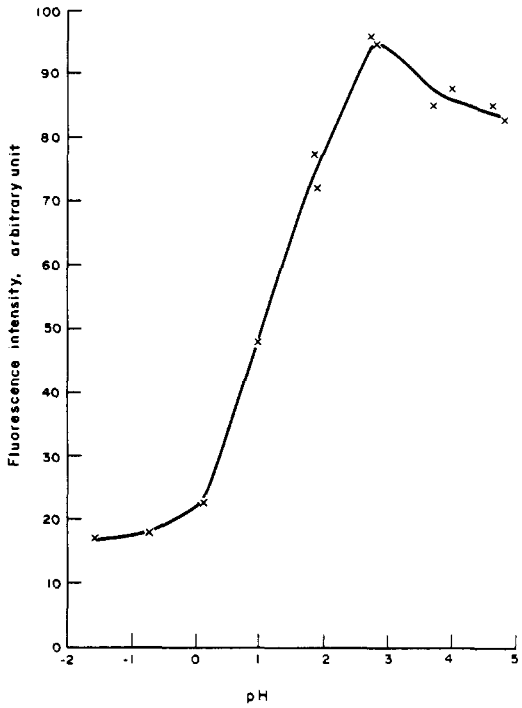

Fig. 2. Fluorimetric pH titration curve for $10^{-5}M$ 9-anthraldehyde. Fluorescence intensity was monitored at 510 nm.

Franck-Condon principle is only approximate for these transitions. The appearance of blurred vibrational structure in the ^1L_a band of the neutral molecule is observed in hexane solutions and indicates that the loss of vibrational structure in water is, at least in part, related to changes in solvent interaction accompanying electronic transition. It was considered that the loss of structure in the ^1L_a band of the neutral molecule might be the result of rotation of the aldehyde group from an out-of-plane conformation, into coplanarity with the anthracene ring during the absorption process. Perpendicularity between the carboxyl group and the anthracene ring has been observed in the ground state of 9-anthroic acid[6]. However, in 9-anthraldehyde the fluorescence of the neutral molecule in rigid media at 77 K is not similar to that of anthracene as would be expected if conjugation between the aldehyde group and the ring was prevented by freezing the molecule into the ground-state conformation. Rather, the fluorescence of 9-anthraldehyde at $2{\cdot}15 \times 10^4 \mathrm{cm}^{-1}$, at 77 K, is indicative of strong conjugation and coplanarity in the ground-state. In the cation derived from 9-anthraldehyde, there is no question that the protonated aldehyde group is coplanar (conjugated) with the anthracene ring in the ground-state as well as the excited state, because the fluorescence of the cation in rigid sulphuric acid at 77 K occurs at $1.83 \times 10^4 \mathrm{cm}^{-1}$ which is much too low a frequency for fluorescence from an unconjugated anthracene derivative. The reason for loss of structure in the ^1L_b band of the cation is not certain, because solvent effects on the cation absorption spectra could not be evaluated, as the ground-state cation could not be formed in non-polar, non-hydrogen-bonding media. However, that the ^1L_a band of the cation is structured indicates that neither rapid solvent nor intramolecular conformational relaxation occurs during the course of the $^1L_a \leftarrow {}^1A$

transition. Because of the low frequency of the ^1L_a band in the 9-anthraldehyde cation, it cannot be disputed that the $^1L_a \leftarrow {}^1A$ transition in this species has a great deal of charge-transfer character. It is thus apparent that lack of vibrational structure in intramolecular charge-transfer transitions, although common, is not general.

Absorptiometric titration of 9-anthraldehyde with sulphuric acid employing the corrected Hammett acidity scale of Jorgensen and Hartter[5] yielded $pK_a = -5{\cdot}1$ for the 9-anthraldehyde cation. The pK_a of $-4{\cdot}81$ previously reported[2] was based upon Hammett's original H_0 function.[7]

In aqueous solutions 9-anthraldehyde exhibited a diffuse fluorescence band with maximum at $1{\cdot}96 \times 10^4$ cm^{-1}. In acidic media the emission was still diffuse, but considerably weaker and had its maximum at $1{\cdot}78 \times 10^4$ cm^{-1}. The former fluorescence is assigned to the $^1L_a \rightarrow {}^1A$ transition of the neutral molecule and the latter to the $^1L_a \rightarrow {}^1A$ transition of the cation. The fluorescence of the neutral molecule in ethanol was previously reported[4] to occur at $2{\cdot}54 \times 10^4$ cm^{-1} which is considerably higher in frequency than the emission observed in the present work in water. However, our studies with a freshly recrystallized sample of 9-anthraldehyde in ethanol yielded an emission maximum at $2{\cdot}08 \times 10^4$ cm^{-1}. On standing for several hours in ethanol (or water) our 9-anthraldehyde solutions developed a fluorescence at the frequency reported by the previous investigators[4] and the low frequency fluorescence diminished appreciably in intensity. Moreover, the appearance of the high-frequency emission was enhanced in the presence of light. It is likely that 9-anthraldehyde undergoes photo-reduction in hydroxylic solvents to the arylmethylcarbinol, a process which is often observed in arylaldehydes. Thus the fluorescence maximum of 9-anthraldehyde reported by the previous investigators was probably that of an impurity.

Fluorimetric titration of the 9-anthraldehyde yielded a midpoint for the interconversion between the cation and neutral molecule at pH 1·3. This value is assigned to the dissociation constant of the cation in the ^1L_a state (pK_a^*) and indicates that 9-anthraldehyde is only 6 orders of magnitude more basic in the ^1L_a state than in the ground-state, rather than 17 orders as suggested by the previous investigators.[4] If pK_a^* is calculated by the Förster cycle method,[3] employing the averages of absorption and fluorescence maxima determined in the present work to represent the spectroscopic *O-O* bands of the ^1L_a transitions in cation and neutral molecules, a value of 1·8 is obtained for pK_a^*, which is in fair agreement with the value obtained by fluorimetric titrimetry. If the shift in the absorption spectra alone upon protonation is employed to calculate pK_a^*, a value of 6·9 is obtained, and a value of $-1{\cdot}3$ if the shift in the fluorescence spectra alone is employed. The inaccuracy of the value calculated from the absorption shift can be attributed to unequal excited state thermal relaxation energies for cation and neutral molecule (the Stokes shift for the cation is 2000 cm^{-1} and that for the neutral molecule is 4900 cm^{-1}) which are not reflected in the absorption spectra.[8] The inaccuracy of the pK_a^* value calculated from the fluorescence shift can be primarily attributed to the differences in vibrational composition of the ground states of the cation and neutral molecule as reflected by the differences in half-band widths of the fluorescences (1600 cm^{-1} for the cation and 2900 cm^{-1} for the neutral molecule). Because the errors in the estimation of pK_a^* from absorption shifts alone and from fluorescence shifts alone arise from different sources, the averaging of absorption and fluorescence spectra does not truly give the position of the *O-O* bands of the ^1L_a bands of cation and neutral molecule and the better agreement of the pK_a^* value calculated from the shift of the averaged absorption and fluorescence spectra with that determined from the fluorimetric titration appears to be fortuitous.

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Zusammenfassung—Das Auftreten oder Nichtauftreten von Schwingungsstruktur in den ^1L_a- und ^1L_b-Absorptionsbanden der neutralen Spezies und des Kations von 9-Anthraldehyd wird im Sinne einer Befolgung oder Nichtbefolgung des Franck-Condon-Prinzips erklärt. Das Fehlen von Schwingungsstruktur wird den Bewegungen der Aldehydgruppe im Verlauf des Elektronenübergangs zugeschrieben, einem Prozeß, der die Schwingungsquantisierung im angeregten Franck-Condon-Zustand zerstort. Das Auftreten von wohldefinierter Schwingungsstruktur in der ^1L_a-Bande des Kations weist nach, daß die intramolekulare Ladungsübertragung allein, ohne Schwingungs- oder Lösungsmittelrelaxation, die gleichzeitig mit dem Elektronenübergang ablauft, nicht für das Fehlen von Struktur in den meisten intramolekularen Ladungsübertragungs-Übergängen verantwortlich zu machen ist. Die früher mitgeteilte Fluoreszenz von 9-Anthraldehyd in hydroxylhaltigen Lösungsmitteln ist offenbar nicht reell; wahrscheinlich rührt sie von einer durch Photoreduktion erzeugten Verunreinigung her. Die tatsächliche Fluoreszenz von 9-Anthraldehyd liegt bei viel niedrigerer Frequenz, als früher angegeben wurde.

Résumé—On explique l'apparition ou le défaut de structure de vibration dans les bandes d'absorption ^1L_a et ^1L_b de l'espèce neutre et du cation dérivés du 9-anthraldéhyde par rapport au fair que le principe de Franck-Condon est respecté ou pas. Le défaut de structure de vibration est attribué aux mouvements du groupe aldéhyde durant le temps de la transition électronique, un processus qui détruit la quantification de vibration dans l'état excité de Franck-Condon. L'apparition d'une structure de vibration bien définie dans la bande ^1L_a du cation établit que le transfert de charge intramoléculaire seul, sans relaxation de vibration ou de solvant simultanée, qui est contemporaine de la transition électronique, n'est pas responsable de l'absence de structure dans la plupart des transitions de transfert de charge intramoléculaires. On a trouvé que la fluorescence du 9-anthraldéhyde rapportée antérieurement dans des solvants hydroxylés doit être erronée et doit provenir vraisemblablement d'une impureté produite par photoréduction. La fluorescence réelle du 9-anthraldéhyde est à une fréquence beaucoup plus faible qu'il n'a été rapporté antérieurement.

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THE ADSORPTION OF SILVER ON POTASSIUM CYANOCOBALT(II)FERRATE(II)

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Summary—A procedure is described for recovering silver from industrial sewage (mining and photo-industry *etc*) with the aid of the ion-exchanger potassium cyanocobalt(II)ferrate(II) (KCFC). Silver is easily removed by simple mixing with KCFC, even from solutions containing less than 1 g of silver per ton of solution. The process is performed at room temperature at $pH < 7$. There is no interference from a 600-fold amount of Ca, Cu(II), Zn, Cd, Pb, and Fe(II). Pure silver may be obtained by dissolution of the ion-exchanger in potassium cyanide solution, subsequent precipitation as sulphide, and roasting, or by melting it out of the ion-exchanger after heat treatment in a high-frequency furnace. With 1 kg of KCFC, 1·25 kg of silver may be extracted from solution. The process is simple and economic.

Potassium cyanocobaltferrate was first used for the selective adsorption of caesium from radioactive sewage.[1] Since then several papers have dealt with the capacity of this salt and its ammonium homologue for ion-exchange of trace amounts of several elements at varying pH-values and in the presence of an excess of foreign ions.[2–4] To our knowledge, however, there have been no experimental investigations of the ion-exchange behaviour of KCFC towards the coinage metals, which might be expected to interact with it, because they form 18-electron type ions which are strongly polarizing, and hence should form more stable cyanocobaltferrates than the alkali metals, which give the stability series[5] $Li < Na < K < Rb < Cs$. If this were indeed the case, the effect might be used to recover noble metals from highly diluted waste solutions, which would be of great economic interest.

EXPERIMENTAL

Reagents

The KCFC used was either a commercial product (LOBA-Chemie Wien or Bio-Rad Laboratories) or prepared[1] from 0·5*M* $K_4Fe(CN)_6 \cdot 3H_2O$ and 0·3*M* $Co(NO_3)_2 \cdot 6H_2O$. No differences in the chemical behaviour of the products have been found.

Radioactive tracer

^{110m}Ag ($t_{1/2} = 253$ days; 0·66 and 0·88 MeV gamma-rays) was obtained by irradiation of 27·5 mg of metallic silver for 10 days in the drum equipment of the deuterium-moderated tank reactor FRJ-2, type DIDO, of the Nuclear Research Centre, Jülich, at a neutron flux of 7×10^{12} n/cm^2/sec. The isotope (induced activity 1·13 mCi) was dissolved, diluted and added to the silver salt solutions as tracer.

Apparatus

"Eppendorf-Microliter-System" microlitre pipettes, centrifuge, vessels, heating block, rotary mixer, *etc*, were used; other vessels were made of Teflon or polypropylene.

Procedures

Batch procedures were used for all ion-exchange tests. The capacity of KCFC for silver was determined by shaking about 100 mg of KCFC for 20 min each time with three consecutive 1-ml portions of 10% silver nitrate solution, centrifuging, discarding the supernatant liquid and washing the KCFC with 0·5-ml portions of water. Analogously 400 mg of KCFC and 20 ml of solution were used to determine the dependence of the capacity of KCFC on the concentration of silver and acidity in pure silver salt solutions and simulated waste solutions. The silver remaining in the solution after the ion-exchange process were determined either radiometrically with ^{110m}Ag as tracer or by atomic absorption. Potassium, cobalt and iron exchanged for silver were determined by atomic absorption only.

RESULTS AND DISCUSSION

Capacity of KCFC for silver

Table 1 shows the results for the capacity determination mentioned above. As shown in Table 1, 100 mg of KCFC adsorb a total of 121·3 ± 0·5 mg of silver from three charges. It can be estimated that a fourth charge would exchange about 5% of its silver, so the maximum capacity is estimated to be 1·243 g of Ag per g of KCFC or 11·53 meq of Ag per g of KCFC (containing 4·13 meq of K).

Effect of silver concentration

The recovery of silver from residues is usually considered economic only when the minimum silver content is 100 ppm in silver ores, waste and sludge, and 15–30 ppm in ores of other metals. Therefore the efficiency of recovery of silver from highly dilute solutions was investigated by shaking 400 mg of KCFC with 10^{-1}–$10^{-5}M$ silver for 20 min. The results (averages of three concordant determinations) are compiled in Table 2.

Silver can evidently be recovered quickly and economically even from solutions con-

Table 1. Exchange of silver on KCFC

Sample no.	Charge* no.	Residual activity, *cpm*	Residual amount of silver, %	Silver exchanged by 100 mg of KCFC		
				%	*mg*	*mg* (total)
I	1	6,259	4·5	95·5	60·7	
	2	52,520	37·4	62·6	39·8	
	3	97,153	67·4	32·6	20·7	121·2
II	1	7,254	5·2	94·8	60·3	
	2	48,422	34·4	65·6	41·6	
	3	99,693	69·1	30·9	19·6	121·5
III	1	9,312	6·6	93·4	59·3	
	2	54,170	38·5	61·5	39·0	
	3	95,533	66·3	33·7	21·4	119·7
IV	1	5,745	4·1	95·9	60·9	
	2	50,865	36·2	63·8	40·5	
	3	98,976	68·6	31·4	19·9	121·3
V	1	5,194	3·7	96·3	61·2	
	2	43,105	30·7	69·3	44·0	
	3	104,203	72·3	27·7	17·6	122·8

* Count-rate of silver solutions before exchange: 1 and 2—140,572 cpm; 3—144,025 cpm.

Table 2. Adsorption of silver by KCFC as a function of the concentration of silver salt

Charge no.	$[AgNO_3]$, *ppm*	Silver added, *mg*	Silver adsorbed	
			mg	%
1	$1{\cdot}08 \times 10^4$	215·7	211·9	98·2
2	$1{\cdot}08 \times 10^3$	21·57	21·5	99·5
3	108	2·157	2·02	93·8
4	10·8	0·2157	0·145	67·0
5	1·08	0·0216	0·0145	67·0

taining silver well below the level hitherto regarded as economic for recovery. Even in the 1–10 ppm range, 67% of the silver is recovered in a single step, and the KCFC used may be used again for further exchange.

Effect of foreign ions

A series of simulated "waste solutions" was prepared, $10^{-3}M$ in each of the following: silver, calcium, copper(II), zinc, cadmium, lead, and iron(II) nitrates. A similar series was made with $0{\cdot}1M$ concentrations of the foreign ions. Portions of KCFC (100 mg) were shaken for 20 min with 1 ml of each "waste solution" adjusted to be neutral or strongly acidic. The KCFC was well washed with water and the amount of silver left in the solution determined radiometrically. The results are compiled in Table 3.

The exchange of silver is practically unaffected by variation of the conditions over the ranges given, even by a 100-fold excess of copper and zinc, which may be contrasted with the report[2] that zinc is 95% exchanged on KCFC over a wide range of pH.

Equivalence of exchange

It was stated above that 11·53 meq of silver are exchanged by 1 g of KCFC containing 4·13 meq of potassium. Hence some other ion besides potassium must take part in the exchange, and it was found that with increasing concentration of silver solution an increasing amount of cobalt is liberated from KCFC and exchanged for silver. If sufficiently concentrated silver solution is used, the KCFC crystal will be destroyed and all the potassium and cobalt take part in the ion-exchange process, 11·53 meq of silver being adsorbed per g of KCFC and 4·13 meq of potassium and 6·95 meq of cobalt being exchanged. However if the ratio of exchangeable potassium to silver available exceeds 10 there is negligible exchange of cobalt. Thus with very dilute silver solutions the KCFC crystal structure remains intact and the KCFC may be used repeatedly. Table 4 shows the results.

Table 3. Exchange of silver by KCFC from "waste solutions"

Charge no.	Foreign ion concentration, *M*	Acidity	Silver exchanged, %
1	10^{-3}	neutral	94
2	10^{-3}	pH 1·7	98
3	0·1	neutral	100
4	0·1	pH 1·7	100

Table 4. Equivalence ratios for the adsorption of silver by KCFC
(20 ml of silver solution, 400 mg of KCFC)

Charge no.	Ag added, *meq*	Ag adsorbed, *meq*	K released, *meq*	Co released, *meq*	K_{rel}/Ag_{ads}	Co_{rel}/Ag_{ads}
1	2·0	1·96	1·53	$2·23 \times 10^{-1}$	0·78	0·11
2	$2·0 \times 10^{-1}$	$1·99 \times 10^{-1}$	$1·81 \times 10^{-1}$	$7·40 \times 10^{-3}$	0·9	0·038
3	$2·0 \times 10^{-2}$	$1·88 \times 10^{-2}$	$1·88 \times 10^{-2}$	0	1·00	0
4	$2·0 \times 10^{-3}$	$1·34 \times 10^{-3}$	$1·40 \times 10^{-3}$	0	1·04	0
5	$2·0 \times 10^{-4}$	$1·34 \times 10^{-4}$	$1·40 \times 10^{-4}$	0	1·04	0

Recovery of silver from KCFC

The silver adsorbed on KCFC may be recovered in high purity by one of the following methods.

(*a*) The dry KCFC (1 g) is heated in a solution of 2 g of potassium cyanide in 5 ml of water at 40–60° until a yellow-brown, clear solution is obtained. This solution is diluted with 3–5 ml of water and cooled and a solution of 5 g of $Na_2S \cdot 9H_2O$ in 5 ml of water is added. The mixture is heated for 10 min at 60–80° and filtered hot. The precipitated silver sulphide is washed well with water and ignited at 800–900°. The silver recovered contains $<1\%$ of cobalt.

(*b*) The KCFC is transferred to a silica vessel, which is either wrapped in a sheet of tantalum or immersed in a bath of gold, and heated at 1500° in a high-frequency furnace. Crystals of silver are deposited and pure silver will drop off. If the silver solidifies on the KCFC, it may be separated by a vibrator or ultrasonic device.

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Zusammenfassung—Es wird ein Verfahren zur Entsilberung von industriellen Abwässern (Bergbau, Fotoindustrie u.a.m.) mit Hilfe des Kationenaustauschkristalls KCFC beschrieben. Auch aus Lösungen, die 1 g Silber und weniger pro Tonne Lösung enthalten, wird Silber durch KCFC entfernt. Fremdionen wie Ca, Cu, Zn, Cd, Pb, Fe(II) stören selbst in 600-fachem Überschuß weder im sauren, noch im neutralen Bereich. Reines Silber kann u.a. durch Erhitzen im Hochfrequenzofen aus dem Ionenaustauschkristall herausgeschmolzen werden. 1 Kilogramm KCFC vermag etwa 1,25 Kilogramm Silber aus Lösungen anzureichern. Die quantitativen Austauschverhältnisse werden untersucht und es wird gezeigt, daß von einer bestimmten Silberkonzentration an neben Kalium auch Kobalt aus dem KCFC verdrängt wird.

Résumé—On décrit une technique pour la récupération de l'argent d'eaux résiduaires industrielles (industrie minière et industrie de la photo, etc. . . .) à l'aide de l'échangeur d'ions cyanocobalt (II) ferrate (II) de potassium (KCFC). L'argent est aisément éliminé par simple mélange avec le KCFC, même de solutions contenant moins de 1 g d'argent par tonne de solution. L'opération

est réalisée à température ambiante à pH < 7. Des quantités 600 fois supérieures de Ca, Cu (II), Zn, Cd, Pb et Fe (II) n'apportent pas d'interférence. On peut obtenir l'argent pur par dissolution de l'échangeur d'ions dans une solution de cyanure de potassium, précipitation subséquente à l'état de sulfure, et calcination, ou par séparation par fusion de l'échangeur d'ions après traitement thermique dans un four haute fréquence. Avec 1 kg de KCFC, on peut extraire 1,25 kg d'argent de la solution. Le procédé est simple et économique.

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SHORT COMMUNICATIONS

MICROTITRIMETRIC DETERMINATION OF URANIUM IN TRIBUTYLPHOSPHATE (30%)-n-DODECANE-NITRIC ACID MEDIUM IN THE PRESENCE OF EXCESS OF IRON, MAGNESIUM AND ALUMINIUM

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Countercurrent extraction is one of the main methods of uranium recovery in reprocessing spent nuclear fuels or in refining uranium from its concentrates. Tributylphosphate[1] has been in common use as an extraction solvent either in reprocessing (*e.g.*, Purex process) or in research. To follow the course of countercurrent extraction from the loss of uranium in the aqueous phase only, as is done in equilibrium extraction studies, has been shown, according to our experience with mixer-settlers, to be insufficient. It is known from the literature that conventional redox determinations of uranium are subject to interference from organic matter. Nitric acid also seriously interferes.[2,3] Recently, Cherry[4] has worked out a method of amperometric determination of uranium (procedure range 2–200 mg of U) in a solution containing nitric acid or tributylphosphate.

The aim of our study was to work out a method (based on our earlier work[3]) of direct microdetermination of uranium in the aqueous as well as the organic phase from extraction of uranium with tributylphosphate (30%) in n-dodecane from solutions containing nitric acid (0–6*M*) and excess of iron, magnesium and aluminium. It was found experimentally that uranium could be simultaneously stripped from the organic phase and reduced to uranium(IV) by treatment by iron(II). A similar micro-method for uranium determination in the presence of fission products is being developed.

EXPERIMENTAL

Reagents and apparatus are those described before.[2,3] The procedure is suitable for both aqueous and organic phases containing 0·1–3·0 mg of uranium and 0–6*M* in nitric acid, and is that described previously[3] with the following modifications.

1. Rinse out the micropipette with at least 100 μl of acetone; this volume is not counted in the 500 μl of the procedure (this is necessary in analysing the organic phase).
2. After adding iron(II) continue the procedure within 5 min. Stir so that an emulsion may form.
3. Before the dilution a thin layer of TBP will protect U(IV) against aerial oxidation for about 2 hr. It is possible to protect samples of the aqueous phase with 100 μl of TBP in a similar way.
4. In the titration samples of the organic phase the TBP layer should remain intact. An emulsion retards the colour change.

DISCUSSION AND RESULTS

Stripping

The conditions of the procedure make quantitative stripping of uranium from the organic phase possible, as can be seen from the results given in Table 1.

Destruction of nitrite

Destruction of nitrous acid or nitrites in aqueous uranium solutions was discussed in detail earlier.[3] It is known from the literature that nitrous acid is preferentially[5] extracted into TBP and accumulates there,[6] in contrast to sulphamic acid[5] or hydrazine[6] which are not extracted. The reaction of sulphamic acid with nitrites (to destroy the nitrites) proceeds slowly at the interface.[5]

Formation of a temporary emulsion by efficient stirring at the stage of destroying excess of iron(II) (so that the interface is continuously enlarged and renewed) successfully eliminates nitrites from the TBP phase, as experimentally proved.

Yellow colour in the organic phase

A yellow colour was observed to be formed in organic phases prepared with use of nitric acid intentionally exposed to direct daylight (*cf.* Schmid[7]) for half a year. The intensity and induction period of the yellow colour were found to be proportional to the concentration of nitric acid present; the first directly, the second inversely.

When an acid mixture of 4*M* nitric acid/0·1*M* sulphamic kept in a dark bottle for a year and a half was used in preparation of the organic phases the yellow colour did not occur within two days.

The yellow colour mentioned may be due to a complex [TBP . HNO_2].[8]

Table 1. Microdetermination of uranium in organic phase by titration with 0·05*N* $K_2Cr_2O_7$

$[HNO_3]$, *M*	Uranium, μg taken	Uranium, μg found
0·0	2400	2385
0·3		2384
1·2		2384
0·0	1200	1200
0·3		1198
1·2		1198
0·0	600	600
0·3		602
1·2		601
0·0	240	243
0·3		245
1·2		245
0·0	120	124
0·3		123
1·2		123

Table 2. Effect of aqueous phase on microdetermination of uranium

Medium	Uranium, μg taken	Uranium, μg found
W	2400	2398
AP		2396
W	1200	1198
AP		1200
W	600	597
AP		598
W	240	242
AP		244
W	120	122
AP		123

W : aqueous solution of uranium, $[HNO_3]$ about 0·5*M*
AP : TBP(30%) in n-dodecane dissolved in water

Stability of uranium solutions

Dilute uranium solutions acidified to be about 0·5*M* in nitric acid proved to be stable for about a month. At lower acidities low results for uranium were obtained, probably owing to hydrolysis to hydroxy-complexes.[9]

Effect of TBP

In analysis of organic and/or especially aqueous phases (containing traces of dissolved TBP) the reaction mixture, which is green after the Fe(II) addition, starts to turn yellow or brown within 5 min. This indicates a spontaneous oxidation of Fe(II) not observed in analysis of aqueous samples,[3] where the reaction mixture remained green and only became yellow if $[HNO_3]$ was about 9*M* and then only after a much longer time had elapsed.[3] To prevent possible oxidation of U(IV) it is recommended to continue the procedure within 5 min of adding the Fe(II) (see Table 2).

Effect of other ions

Nitric acid present in either phase (0–6*M* in the aqueous, 0–1·2*M* in the organic) does not interfere. Neither the mineralization of organic matter nor the preliminary stripping required in conventional methods is needed. Excess of iron, magnesium and aluminium does not interfere in the aqueous phase, and is not extracted into the organic phase.

Accuracy and precision

Amounts of 0·6–2·4 mg of uranium can be determined with an error less than ±1% both in the aqueous (Tables 3, 4) and organic phase (Table 1). Twelve replicate determinations of an aqueous phase containing 2400 μg of uranium in the presence of 2·4 mg of magnesium and 2·7 mg of aluminium gave an average of 2395 ± 4 μg, the mean relative deviation being ±0·2%. As in the previous method[3] no blank correction was found necessary.

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Table 3. Microdetermination of uranium in aqueous phase in the presence of nitric acid, excess of magnesium and aluminium, by titration with 0·05N $K_2Cr_2O_7$

$[HNO_3]$, M	U taken, μg	Mg, μg	Al, μg	U found, μg
0·0	2400	2430	2698	2395
3·0				2397
6·0				2394
0·0	1200	2430	2698	1202
3·0				1206
6·0				1210
0·0	600	2430	2698	597
3·0				599
6·0				599
0·0	240	2430	2698	243
3·0				244
6·0				243
0·0	120	2430	2698	123
3·0				123
6·0				123

Table 4. Microdetermination of uranium in aqueous phase in the presence of iron, magnesium and aluminium by titration with 0·05N $K_2Cr_2O_7$

$[HNO_3]$, M	U taken, μg	Fe, μg	Mg, μg	Al, μg	U found, μg
0·0*	2400				2389
0·0		5583	2430	2698	2385
3·0					2383
6·0					2383

* Aqueous solution of uranium, for comparison.

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Summary—A method is described for microdetermination of uranium in aqueous phases containing nitric acid, iron, magnesium, aluminium and traces of TBP, and in organic phases containing TBP, n-dodecane and nitric acid. Treatment of the organic phase strips the uranium, reduces it to U(IV), and destroys any nitrite present.

Zusammenfassung—Ein Verfahren zur Mikrobestimmung von Uran in Salpetersäure, Eisen, Magnesium, Aluminium und Spuren TBP enthaltenden wäßrigen Phasen und in TBP, *n*-Dodekan und Salpetersäure enthaltenden organischen Phasen wird beschrieben. Eine Behandlung der organischen Phase extrahiert das Uran zurück, reduziert es zu Uran(IV) und zerstört alles vorhandene Nitrit.

Résumé—On décrit une méthode pour le microdosage de l'uranium en phases aqueuses contenant de l'acide nitrique, du fer, du magnésium, de l'aluminium et des traces de TBP, et en phase organique contenant du TBP, du *n*-dodécane et de l'acide nitrique. Le traitement de la phase organique sépare l'uranium, le réduit en U(IV), et détruit tout nitrite présent.

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INDIRECT ATOMIC-ABSORPTION DETERMINATION OF BORON BY SOLVENT EXTRACTION AS TRIS(1,10-PHENANTHROLINE)CADMIUM TETRAFLUOROBORATE

(*Received* 26 *June* 1972, *Accepted* 23 *October* 1972)

Indirect determination of non-metals by means of atomic-absorption spectrophotometry of a metal ion complexed with a compound of the non-metal is well known. A colorimetric method for the determination of boron by solvent extraction as Tris(1,10-phenanthroline)iron(II) tetrafluoroborate has been reported,[1] and applied to the analysis of tap-water.[2] In atomic-absorption spectrophotometry (AAS), the sensitivity for cadmium is 5–10 times that for iron,[3,4] so for an AAS method we have used Tris(1,10-phenanthroline)cadmium(II) as counter-cation instead of Tris(1,10-phenanthroline)iron(II), and extraction into nitrobenzene. The cadmium atomic absorption at 228·8 nm is a linear function of boron concentration in the aqueous phase over the range of 0·01–0·5 ppm. The sensitivity for boron is apparently about 1000 times that of the direct atomic-absorption method. Certain metal ions interfere because of their reaction with phenanthroline and fluoride. Boron in steel has been determined at ppM levels.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard boron solution, 0·025M. Boric acid (0·7726 g) was dissolved in an appropriate amount of water and the solution diluted to 500 ml. This solution was diluted 100-fold to $2\cdot5 \times 10^{-4}M$ before use.

Tris(1,10-phenanthroline)cadmium solution, 0·005M. Cadmium sulphate, $3CdSO_4\cdot8H_2O$ (1·28 g) and 1,10-phenanthroline, $C_{12}H_8N_2\cdot H_2O$ (3·17 g) were dissolved in 100 ml of 0·001N sulphuric acid and the solution diluted to 1000 ml.

Ammonium hydrogen fluoride solution, 1·25M.

Buffer solution. Potassium dihydrogen phosphate (0·25M) and disodium hydrogen phosphate (0·25M) were mixed in appropriate ratio.

Nitrobenzene. Purified by distillation under reduced pressure and equilibrated with water before use.

Apparatus

Methyl borate was distilled in a quartz still.

Procedure

Mix 1 ml of 1·25M ammonium hydrogen fluoride and 0–5 ml of the $2\cdot5 \times 10^{-4}M$ boric acid in a 50-ml polyethylene test-tube. Place the tube in a water-bath (80°) for about 20 min and then cool the tube to room temperature. Transfer the mixture into a 125-ml polyethylene separatory-funnel. Add 5 ml of Tris(1,10-phenanthroline)cadmium solution, 5 ml of phosphate buffer solution (pH 5), dilute to 25 ml with water and add 5·0 ml of nitrobenzene. Shake the funnel vigorously for 3 min with a mechanical shaker. Allow to stand for about 15 min. Transfer the organic layer to a test-tube containing 1 g of anhydrous sodium sulphate to eliminate traces of water in the extract. Measure the absorbance of cadmium at 228·8 nm against a reagent blank, under optimum operating conditions of the atomic-absorption instrument, using an air–acetylene flame.

Zusammenfassung—Ein Verfahren zur Mikrobestimmung von Uran in Salpetersäure, Eisen, Magnesium, Aluminium und Spuren TBP enthaltenden wäßrigen Phasen und in TBP, *n*-Dodekan und Salpetersäure enthaltenden organischen Phasen wird beschrieben. Eine Behandlung der organischen Phase extrahiert das Uran zurück, reduziert es zu Uran(IV) und zerstört alles vorhandene Nitrit.

Résumé—On décrit une méthode pour le microdosage de l'uranium en phases aqueuses contenant de l'acide nitrique, du fer, du magnésium, de l'aluminium et des traces de TBP, et en phase organique contenant du TBP, du *n*-dodécane et de l'acide nitrique. Le traitement de la phase organique sépare l'uranium, le réduit en U(IV), et détruit tout nitrite présent.

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EXPERIMENTAL

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Ammonium hydrogen fluoride solution, 1·25*M*.

Buffer solution. Potassium dihydrogen phosphate (0·25*M*) and disodium hydrogen phosphate (0·25*M*) were mixed in appropriate ratio.

Nitrobenzene. Purified by distillation under reduced pressure and equilibrated with water before use.

Apparatus

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Procedure

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Procedure for steel analysis

Place a 0·5–1·0 g of sample containing not more than 0·05% of boron, in a quartz beaker. Dissolve the sample with a mixture of 15 ml of hydrochloric acid, 5 ml of nitric acid and 5 ml of phosphoric acid with heating on a hot-plate. To remove chloride and nitrate add 10 ml of sulphuric acid and evaporate nearly to dryness. Let cool, dissolve the residue, and dilute to a standard volume with water, keeping the boron concentration below 10 ppm. Take a 5-ml aliquot in a 100-ml quartz flask, and add 3 ml of sulphuric acid and 10 ml of methyl alcohol. Distil the methyl borate by heating the flask on a water-bath (80°). Introduce the first distillate (10 ml) into 0·1*M* sodium hydroxide solution (5 ml) in a marked polyethylene tube cooled with water. Transfer the solution into a 100-ml quartz beaker, rinsing in with a small amount of methyl alcohol. Evaporate the solution nearly to dryness on a water bath (50 ± 5°). Cool the residue and dissolve it with 2·8 ml of 0·1*N* sulphuric acid and dilute to 25 ml with water. Take an aliquot (5 ml) in a polyethylene separatory-funnel and continue according to the general procedure described above.

RESULTS AND DISCUSSION

The extraction was maximal when the fluoride concentration was $5\text{–}6 \times 10^{-2}M$, indicating that at least a 1300-fold molar excess of fluoride is necessary for the complete formation of tetrafluoroborate in the aqueous phase. The complexation reaction should be continued for 15–20 min at a temperature above 70°.

At least a 5-fold molar excess of Tris(1,10-phenanthroline)cadmium is required for maximum extraction of the tetrafluoroborate.

With a single extraction, a pH range of 4·3–6·0 was found to give a plateau on the absorption *vs.* pH graph. In acidic solutions the cadmium complex may decompose, and in alkaline medium hydroxotrifluoroborate (BF_3OH^-) may be formed, which is not suitable for this extraction system. No appreciable effect on the absorption was caused by changing the phosphate buffer concentration over the range 0·04–0·12*M*.

The shaking time for the extraction was varied from 0·5 to 10 min, and it was found that 2 min sufficed.

Beer's law is obeyed up to 0·5 ppm of boron and the sensitivity for 1% absorption was 0·005 ppm of boron, about the same as that of cadmium, as determined by using bis(acetylacetonato)cadmium nitrobenzene solutions. For 10 solutions, each containing 0·4 ppm of boron, the mean absorbance was 0·227, with relative standard deviation of 1·5%. Normal room temperature fluctuations (15–25°) had no effect on the absorption.

Table 1. Effect of diverse ions.

Ion	[Ion]/[Boron]	Relative error, %	Ion	[Ion]/[Boron]	Relative error, %
Be^{2+}	10	+ 3	Fe^{3+}	10	− 12
Mg^{2+}	10	0	Co^{2+}	1	− 9
Ca^{2+}	10	+ 9	Ni^{2+}	1	− 15
Zr^{4+}	10	− 8	Cu^{2+}	1	− 18
Al^{3+}	10	+ 29	Zn^{2+}	1	− 13
Ga^{3+}	10	0	Cl^-	10	+ 10
Tl^{3+}	10	0	NO_3^-	10	+ 7
Mn^{2+}	1	− 3	SiO_3^{2-}	10	0
Fe^{2+}	1	− 12			

Boron: 8.1 μg/25 ml.

Table 2. Analysis of steel samples.

Sample	Boron, %	
	Curcumin method	Proposed method
A	0·0055	0·0053 0·0053 0·0053
B	0·0021	0·0019 0·0021 0·0018
C	0·0092	0·0102 0·0103 0·0101

Large amounts of sulphate, phosphate, acetate and silicate do not interfere. Chloride and nitrate give a positive error when present in tenfold molar amount relative to borate, but both can easily be eliminated by evaporation from sulphuric acid medium. As seen in Table 1, presence of transition elements cations causes negative errors because of consumption of phenanthroline.

To check the reliability of the proposed method, steel was chosen as a matrix. Recovery tests were successfully made with a certain amount of boron added to boron-free standard steel samples. Boron must be separated from the matrix because of the interference of iron, and this can be done by the conventional distillation of methyl borate.[5-7] Samples were also analysed by spectrophotometry with curcumin.[6] The results are shown in Table 2. It is seen that both sets of results are in satisfactory agreement.

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Summary—An indirect atomic-absorption method for boron has been developed. Boric acid is converted into tetrafluoroborate and extracted into nitrobenzene with Tris(1,10-phenanthroline)cadmium(II). The cadmium in the extract is determined by its atomic-absorption at 228·8 nm. A fivefold molar excess of the cadmium chelate is necessary for the extraction from pH 4·3–6·0 medium. The sensitivity for boron is thus made about the same as that of cadmium, 0·005 ppm. Metal ions that react with fluoride or phenanthroline interfere. A procedure is described for determination of boron in steel.

Zusammenfassung—Ein indirektes Atomabsorptionsverfahren zur Bestimmung von Bor wurde entwickelt. Borsäure wird in Tetrafluoroborat überführt und mit Tris(1,10-phenanthrolin)-cadmium(II) in Nitrobenzol extrahiert. Das Cadmium im Extrakt wird durch seine Atomabsorption bei 228·8 nm bestimmt. Zur Extraktion aus einem Medium mit pH 4·3–6·0 ist ein fünffacher molarer Überschuß des Cadmiumchelats notwendig. So wird die Empfindlichkeit für Bor etwa dieselbe wie die für Cadmium, 0·005 ppm. Metallionen, die mit Fluorid oder Phenanthrolin reagieren, stören. Eine Arbeitsvorschrift für die Bestimmung von Bor in Stahl wird angegeben.

Résumé—On a élaboré une méthode d'absorption atomique indirecte pour le bore. L'acide borique est converti en tétrafluoroborate et extrait en nitrobenzène par le Tris(1,10-phénanthroline)cadmium(II). On détermine le cadmium dans l'extrait par son absorption atomique à 228,8 nm. Un excès molaire quintuple du chélate de cadmium est nécessaire pour l'extraction d'un milieu de pH 4,3–6,0. La sensibilité pour le bore est ainsi rendue à peu près la même que celle du cadmium, 0,005 p.p.m. Les ions métalliques qui réagissent avec le fluorure ou la phénanthroline gênent. On décrit une technique pour le dosage du bore dans l'acier.

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SULPHONATED AZO-DYES AS EXTRACTIVE METALLOCHROMIC REAGENTS

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The metallochromic properties of azo-dyestuffs, particularly those containing *o,o*′-dihydroxy groups, are well known and many of these reagents have found application in the complexometric titration of metals.[1] Examples of their use for the spectrophotometric determination of metals have also appeared,[2] but in general these reactions are non-selective. Selectivity or specificity may be achieved by the use of appropriate masking agents. Furthermore, in some instances the use of an azo-dye as a spectrophotometric reagent is prevented by similarity in the colours, and consequently, in the absorption spectrum of the metal complex and the reagent itself. For practical purposes it is convenient if the molecule contains at least one sulphonic acid group to make the reagent soluble in water. If more than one sulphonic acid group is present, the tendency of the reagent to form extractable ion-association complexes is reduced.

With the hope of improving the selectivity and sensitivity of such reactions we, as well as previous workers in the Laboratory,[3] have investigated the possibility of extracting the metal complexes of a number of representative sulphonated *o,o*′-dihydroxyazo-dyes into chloroform as the ion-association complexes formed with a quaternary ammonium cation. In the present work the pH range between 1·0 and 12·0 was investigated. In acid solution (~ < pH 1) dissociation of sulphonic acid groups is suppressed and it is probable that the reagents and their metal complexes will be extracted even in the absence of a large cation.

The number of possible substitutions of azo-dyes is very large, but *o,o*′-dihydroxy mono-azo dyes may be classified conveniently according to the number of aromatic rings present and further, for the naphthyl series, by the position of the azo-substitution. Thus, the parent compounds are

I 2,2′-azodiphenol
II 2-(2′-hydroxy-1′-naphthylazo)phenol
III 2-(1′-hydroxy-2′-naphthylazo)phenol
IV 2,2′-dihydroxy-1,1′-azonaphthalene
V 1,2′-dihydroxy-2,1′-azonaphthalene
VI 1,1′-dihydroxy-2,2′-azonaphthalene

Some readily available monosulphonated derivatives of I–V were investigated, *viz.*

		Colour Index No.	*Commercial name*
A	5-Cl,4′-OH,3-SO_3H-I	Mordant Red 72	Lumogallion
B	5-SO_3Na-II	15670	Acid Alizarin Violet (N)
C	5-CH_3,4′-SO_3H-II	—	Calmagite
D	5-OH,5-SO_3Na-III	16500	Chrome Fast Black PV
E	4-SO_3H-IV	15705	Calcon, Eriochrome Blue Black R
F	4-SO_3H-V	14640	Eriochrome Blue Black B
G	6-NO_2,4-SO_3H-V	14645	Eriochrome Black T

Two closely related reagents

H	5-Cl,8′-OH,3′,6′-SO_3Na-III	16680	Eriochrome Blue SE
I	2-(2′-Hydroxy-1′-naphthylazo)-3-methyl-5-phenyl-1-hydroxylpyrazole-4-sulphonic acid	18760	Eriochrome Red B

were also examined.

Systematic classification of dyes with two azo linkages is more complicated, but three examples of this class which have found application in spectrophotometric analysis were also studied.

K	Acid Alizarin Black SN	21725
L	Fast Sulphon Black F	26990
M	Calcichrome	

EXPERIMENTAL

Reagents

Acetate (pH 1·1–5·2), phosphate (6·1) and borate (7·5–12·0) buffers were prepared to cover the pH range 1–12 and their ionic strength was adjusted to 0·3 with sodium perchlorate.

Metal ion solutions (0·1*M*) were prepared, from the perchlorates where possible.

Dye solutions nominally $4 \times 10^{-4}M$ were prepared by dissolving the theoretical amounts of the solids in distilled water. No attempts were made to purify the commercial products.

Solutions of the quaternary ammonium salts (0·1*M*) were prepared by dissolving Aliquat 336 (methyltricaprylylammonium chloride) (General Mills, Chemical Division, Kankakee, Illinois) or tetrahexylammonium iodide in chloroform. The latter solution was converted into the perchlorate form by shaking three times with an equal volume of 10% sodium perchlorate solution.

Procedure

Qualitative tests were made of the reaction of a given reagent with 20 selected metal ions, *viz.* Al, Bi(III), Ca, Cd, Co(II), Cu(II), Fe(III), La, Mg, Mn(II), Mo(VI), Ni(II), Pb(II), Pd(II), Sn(IV), U(VI), V(IV), W(VI), Zn and Zr(IV) at each of eleven pH values by addition of one drop of 0.1*M* metal ion solution to a test-tube containing 1 ml of $4 \times 10^{-4}M$ reagent solution and 3 ml of the appropriate buffer solution. After thorough mixing, a few minutes were allowed for reaction before the colour was noted. One ml of quaternary ammonium salt solution (0·05 or 0·1*M*) was added, the mixture was agitated vigorously for a few seconds and, after settling, the colour of each phase was noted.

Reactions giving interesting colour changes were carried out semiquantitatively (again with an excess of metal ion over reagent) and the spectrum of the metal complex as well as of the reagent alone was plotted in the visible region for the aqueous phase or for the organic phase after extraction, as appropriate. Reactions appearing to have analytical possibilities, *i.e.*, giving a large shift in absorption maximum and an intensely coloured metal complex, were then further investigated by preparing a Beer's law plot to test the sensitivity under the reaction conditions used.

RESULTS

It will be appreciated that in qualitative tests the recognition of a potentially useful reaction is very subjective. The further characterization of a given reaction in terms of sensitivity and selectivity is necessary to achieve objectivity. The present survey has, however, confirmed previous workers' findings that *o,o′*-dihydroxyazo dyes react with many metal ions in aqueous solution under various pH conditions, *e.g.*, Mo(VI) with almost every reagent in acid solution; Cu(II) with reagents *B*, *F* and *K* at pH 1–4; Zr(IV) with *A*, *B* and *H* at pH 1–4; Fe(III) with *A*, *B*, *D*, *F*, *H*, and *J* at pH 1–5; V(IV) with *B*, *D*, *F*, *G*, *H*, *J*, *K* and *M* at pH 3–6; U(VI) with *F*, *G*, *H*, and *K* at pH 4–5; several transition metals and La(III) with *K* and *L* at around pH 7; Ca and Mg with *B*, *C*, *D*, *F*, *H*, and *M* in alkaline solution.

In several instances these reactions are best suited to spectrophotometric application by measurement of the decrease in absorbance at a given wavelength upon complex formation and have already been used in this manner.[4,5]

The formation of an extractable species depends upon neutralization of the negative charge of the metal complex by ion-association with one or more quaternary ammonium cations. At low pH only the sulphonic acid groups are dissociated, the hydroxyl groups ionize successively as the pH is increased. Thus at higher pH more quaternary ammonium ions are needed to achieve neutralization of charge. The reactions of the *o,o′*-dihydroxyazo dyes after extraction are summarized in Table 1 in which each reagent is represented by the letters assigned to it above. Entries appear for all conditions under which there was a significant difference between the colour of the organic phase with a metal present and that for the reagent alone. No extractable complexes were formed by reagents *L* and *M*, indicating that the presence of three or more sulphonic acid groups prevented charge-neutralization under these experimental conditions. Bi(III), Ca, Cd, La(III), Mg, Pb(II) and Zn formed no extractable complexes coloured differently from the reagent.

These tests were done with an excess of metal over reagent so that in some instances, although complex formation occurred, the reaction would not be applicable to spectrophotometric analysis. Several reactions, however, did appear to be worthy of consideration for spectrophotometry and a rapid examination was made to obtain an estimate of the sensitivity of a number of these without rigorous optimization of conditions. These results are shown in Table 2. The reaction of aluminium with Calmagite at pH 8·6 has been studied more thoroughly as a spectrophotometric method.[6]

Conclusion

The investigations described herein have shown that several monosubstituted *o,o′*-dihydroxyazo dyes form coloured metal complexes which are extractable into chloroform as ion-association complexes with a quaternary ammonium cation. These reactions may offer advantages in selectivity and sensitivity over existing spectrophotometric methods based on metal-azo-dye complexation.

Table 1

Metal ion	pH 1·1	2·0	3·0	4·2	5·2	6·1	7·5	8·6	10·0	11·1	12·0
Al(III)	*D, K*		*E*					*B, C*	*B, C*	*B, C*	*B, C*
Co(II)			*E, F*	*E, F, G*	*B, C, E, F, G, J*	*B, C, E, F, J*	*B, C, F, J*	*B, C, J*	*C, J, K*	*J, K*	
Cu(II)	*A, B, D, F, G, H, K*	*E*	*E, J*	*E*	*E*				*C*	*C*	
Fe(III)	*D, F, H, J, K*	*E, F, J*	*E, F, J*	*E, K*							
Mn(II)							*J*	*J*			
Mo(VI)	*A, B, C, D, E, F, G, K*	*B, C, E, F, G, K*	*B, C, E, F, G, K*	*B, C, E, F, G, K*	*B, C, E, F, G, K*	*F*					
Ni(II)								*C*	*C*	*C*	
Pd(II)	*A, B, E, K*	*B, C, E*	*B, C*	*C, F*	*C, F*	*C*	*C*	*C*	*C*	*C*	*C, F*
Sn(IV)							*K*				
U(VI)		*K*	*K*	*G*	*E, F, G*	*F*	*F, J*	*C, J*	*C*	*C*	
V(IV)	*A, K*	*K*	*F, K*	*E, F, G, J, K*	*E, F, G, J, K*	*C, E, F, J*	*C, J*	*C*			
W(VI)	*A, B, D, E, F, K*	*B, E, F*	*E, F*								
Zr(IV)	*F, H*			*K*	*K*						

Table 2

Metal	Reagent	pH	Wavelength, *nm*	ε, *l.mole*$^{-1}\cdot$*cm*$^{-1}$
Mo(VI)	*B*	1·1	570	$6{\cdot}5 \times 10^3$
Mo(VI)	*C*	1·1	575	$6{\cdot}0 \times 10^3$
Mo(VI)	*K*	1·1	610	$12{\cdot}0 \times 10^3$
W(VI)	*B*	1·1	570	$7{\cdot}0 \times 10^3$
Cu(II)	*B*	1·1	570	$5{\cdot}5 \times 10^3$
Pd(II)	*B*	1·1	570	$5{\cdot}5 \times 10^3$
Fe(III)	*K*	1·1	610	$18{\cdot}0 \times 10^3$
Co(II)	*C*	4·2	580	$8{\cdot}0 \times 10^3$
Co(II)	*B*	5·2	570	$24{\cdot}0 \times 10^3$
Co(II)	*B*	8·6	570	$25{\cdot}0 \times 10^3$
Al(III)	*B*	8·6	570	$29{\cdot}0 \times 10^3$
Al(III)	*C*	8·6	580	$40{\cdot}0 \times 10^3$

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6. C. Woodward and H. Freiser, *Talanta*, 1968, **15**, 321.

Summary—A survey has been made of analytically useful extractable ion-pair complexes that are formed by the use of a series of metallochromic indicator-metal complexes in conjunction with quaternary ammonium ions. The reagents were *o,o'*-dihydroxyazo dyes and azo-oxines.

Zusammenfassung—Es wird eine Übersicht über analytisch nützliche extrahierbare Ionenpaarkomplexe gegeben, die aus einer Reihe von Metallfarbindikator-Metall-Komplexen mit quartären Ammoniumionen gebildet werden. Die Reagentien waren *o*, *o'*-Dihydroxyazofarbstoffe und Azooxine.

Résumé—On a effectué une étude de complexes paires d'ions extractibles, analytiquement utiles, qui sont formés par l'emploi d'une série de complexes indicateur métallochrome-métal conjointement à des ions ammonium quaternaires. Les réactifs sont des colorants *o*, *o'*-dihydroxyazo et des azo-oxines.

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N-(2-ACETYL-1,3-INDANDIONE-1-HYDRAZONE)TRIALKYLAMMONIUM IODIDES AS A NEW GROUP OF REAGENTS FOR THE CARBONYL GROUP

(*Received* 8 *September* 1972. *Accepted* 23 *October* 1972)

Braun and Mosher[1] introduced 2-diphenylacetyl-1,3-indandione-1-hydrazone as a reagent for characterization of carbonyl compounds. Aldehydes and ketones react with the hydrazone to give fluorescent azines having sharp and well spaced melting points. Brandt and Cheronis[2] showed that concentrations of these azines as low as $10^{-9}M$ could be detected spectrophotometrically. Mosher, Bechara and Pozomek[3] indicated the use of the reagent and its analogues for identification of various classes of organic compounds such as amines, alcohols, anhydrides, hydrazines and ortho-esters. The potential usefulness of these reagents appears to be due to the 2-acetyl-1,3-indandione nucleus.

The present paper deals with the investigation of quarternary ammonium derivatives of these reagents,[4] which have been found to react with aldehydes, ketones and keto-acids, but not with alcohols, amines and non-keto carboxylic acids.

EXPERIMENTAL

Preparation of 2-acetyl-1,3-indandione

2-Acetyl-1,3-indandione was obtained by Claisen condensation of dimethyl phthalate with acetone in the presence of sodium methoxide according to the method reported by Kilgore.[5]

Preparation of N-*(2-acetyl-1,3-indandione)trialkylammonium iodides*

2-Acetyl-1,3-indanadione was quaternized with an appropriate tertiary amine and iodine in methanolic medium.[4] The compounds prepared were the trimethyl (m.p. 221–223°), triethyl (m.p. 131–132°), tripropyl (210° dec.) and tributyl (m.p. 52–53°) derivatives.

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Zusammenfassung—Es wird eine Übersicht über analytisch nützliche extrahierbare Ionenpaarkomplexe gegeben, die aus einer Reihe von Metallfarbindikator-Metall-Komplexen mit quartären Ammoniumionen gebildet werden. Die Reagentien waren *o*, *o'*-Dihydroxyazofarbstoffe und Azooxine.

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Table 1. Colour and absorption maxima of various monohydrazone reagents with carbonyl compounds

Compound	Trimethylammonium*		Triethylammonium		Tripropylammonium		Tributylammonium	
	Colour	λ_{max}, *nm*	Colour	λ_{max}, *nm*	Colour	λ_{max} *nm*	Colour	λ , *nm*
Reagent	Yellow	354	Very light yellow	330	Yellow	333	None	335 338
Acetaldehyde	Intense yellow-orange	320 360	Yellow	312 335	Dark tea	315 350	Yellow	330 358
Benzaldehyde	Intense yellow	330 371	Tea	330 350	Reddish brown	335 370	Deep yellow	350 370
Salicylaldehyde	Light red	328 380	Yellow-light red	318 352	Deep yellow	320 365	Light orange-flesh	330 360
Propionaldehyde	Light red	334 373	Very light orange	325 345	Light orange	320 348	Light yellow	325 348
Acetophenone	Deep yellow	332 345	Yellow–tead	335 348	Brown	338 362	Intense yellow	320 363
Cyclohexanone	Dark tea	335 362	Tea	337 382	Orange	345 360	Yellow	315 361
Cyclopentanone	Deep yellow	325 390	Yellow	325 334	Yellow–orange	320 352	Yellow	317 365
Ethyl methyl ketone	Dark yellow	330 385	Light yellow	325 333	Tea	319 350	Yellow	327 355
Benzyl methyl ketone	Orange	330 358	Light yellow	327 368	Dark yellowish red	318 360	Deep yellowish red	348 360
Vanillin	Deep red	460	Deep yellow	345 380	Deep yellow	348 373	Deep lemon yellow	345 370
Acetone	Orange	322 351	Yellow	349 365	Yellow	320	Deep yellow	329
Pyruvic acid	Deep reddish brown	330 349	Deep yellow–dark red	385	Deep yellow	347	Deep yellow	345
p-Dimethylamino benzaldehyde	Dark brown	355 385	Dark red	348 387	Dark reddish yellow	346	Blood red	335 349

* Only the alkyl substituent of the *N*-(2-acetyl-1,3-indandione-1-hydrazone)trialkylammonium iodide is indicated here.

Preparation of monohydrazones

N-(2-Acetyl-1,3-indandione)trialkylammonium iodide (2.0 g), hydrazine hydrate (80% solution in alcohol, 2 ml) and methanol (20 ml) were heated in a 100-ml round-bottomed flask on a water-bath for 5 min, allowed to cool, and left overnight. A light yellow product separated which was recrystallized from absolute alcohol. The hydrazones were hygroscopic. The m.p. values were 101–102°, 170–177° dec., 185–187° dec., and 89–90° for the trimethyl, triethyl, tripropyl and tributyl derivatives respectively.

Colour reaction with carbonyl compounds

These hydrazones react with several carbonyl compounds in ethanolic medium to give coloured azines. The colour produced varies from light yellow to reddish-yellow depending upon the reagent and the carbonyl compound. Unlike the monohydrazone of 2-diphenylacetyl-1,3-indandione, these compounds do not react with amino, anhydride, carboxylic or hydroxy groups. The colour reaction takes place easily on the addition of a small quantity of carbonyl compound to an ethanolic solution of the hydrazone. The individual carbonyl compound may be characterized by its characteristic λ_{max} in ethanolic medium (Table 1).

The carbonyl group was successfully detected in the presence of isopropyl alcohol, isobutyl alcohol, n-pentanol, dimethylamine, aniline, methylaniline and butyric acid.

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Summary—Monohydrazones of *N*-(2-acetyl-1,3-indandione)trialkylammonium iodides have been synthesized and used as reagents for the carbonyl group. Aldehydes, ketones, keto-acids and cyclic ketones react with these compounds, producing a yellow colour. Carbonyl compounds can be identified by the absorption spectrum of their derivatives with these reagents.

Zusammenfassung—Monohydrazone von *N*-(2-Acetyl-1,3-indandion)-trialkylammoniumjodiden wurden synthetisiert und als Reagentien für die Carbonylgruppe verwendet. Aldehyde, Ketone, Ketosäuren und cyclische Ketone reagieren mit diesen Verbindungen und bringen eine gelbe Farbe hervor. Durch das Absorptionsspektrum ihrer Derivate mit diesen Reagentien können Carbonylverbindungen identifiziert werden.

Résumé—On a synthétisé les monohydrazones d'iodures de N-(2-acétyl 1,3-indandione)trialkylammonium et les a utilisées comme réactifs du groupe carbonyle. Les aldéhydes, cétones, céto-acides et cétones cycliques réagissent avec ces composés, produisant une coloration jaune. Les composés carbonylés peuvent être identifiés par le spectre d'absorption de leurs dérivés avec ces réactifs.

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SULPHOLANE AS COLOUR-ENHANCING AND STABILIZING AGENT FOR SILICOMOLYBDIC ACID

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Sulpholane (*i.e.*, tetrahydrothiophene-1,1-dioxide) produces a significant enhancement of colour when added to a solution containing the thiocyanaoto-complex of cobalt.[1] In tests of the effect of the solvent on solutions of other metals and complexes a pronounced deepening of the colour of silicomolybdic acid was noticed and the possibility of an analytical application of this enhancement was investigated.

The yellow colour developed when solutions of silicate and molybdate ions are mixed was first described by Jolles and Neurath[2] in 1898. Since then many procedures have been described, making use of the reaction in the determination of silica. Quite contradictory results and statements are found in the literature. An explanation for this situation was provided by Strickland[3] in 1952 when he discovered that two silicomolybdic acids exist which he called the α and β forms. Because the two forms differ (among other things) in their absorptivities, doubtful analytical results are obtained unless care is taken that only one of the acids is formed during colour development. Of analytical significance was the contribution by Chalmers and Sinclair[4] who recommended the addition of acetone when preparing the solution to be subjected to the photometric measurement. Acetone (some other polar organic solvents have the same effect, but to a lesser degree) enhances the colour and stabilizes the β-form. This form is of greater analytical interest because it has the higher absorbance over most of the absorption spectrum and allows operation in more acidic solutions. Without stabilization the β-form converts into the α-form at a rate that depends on the pH and the composition of the solution and that is generally difficult to control. Recently Halász *et al.*[5,6,6] have studied heteropoly acids containing molybdenum and critically evaluated the various parameters influencing their formation, stability, interaction *etc.* and also made analytical recommendations.

Sulpholane-containing systems

In the present studies, acetone, the best enhancer so far known, was replaced by sulpholane, which proved superior in several ways. The enhancement is greater than with acetone as can be seen from Fig. 1. Sulpholane is less volatile and thus the possibility of error due to volume changes caused by evaporation is diminished. Sulpholane does not give a turbidity when test solutions are made strongly acidic. This is in contrast to the acetone-containing solutions. The formation of the turbidity has not been reported by previous authors. Sulpholane also stabilizes the β-form and to a higher degree than acetone. For solutions containing acetone Chalmers and Sinclair[4] reported a rate of fading of 0·4% per hour. In the case of sulpholane no change in absorbance was noticed over a period of four days.

The absorption spectra of silicomolybdic acid in both forms in the presence of sulpholane are essentially identical in shape to those in the absence of the solvent, but show higher absorptivities. For either form the highest sensitivity would result from photometric measurements at the peak wavelengths between 300 and 320 nm. Unfortunately, the absorptivity of free molybdate is also considerable in that region and thus leads to an extremely high blank value. Therefore, it is preferred to use wavelengths of about 400 nm where the molybdate does not absorb at all.

As can be seen from Fig. 1 the amount of sulpholane added should be at least 20% v/v to ensure maximum colour development. While no influence on the colour is observed when more solvent is present, a practical limit exists at 40%. Beyond that concentration the molybdate forms a yellow complex with sulpholane and again a detrimentally large blank results.

The β-molybdic acid-sulpholane entity was found to be stable within the "pH" range 0·1–1·8. It should be noted that pH is set within quotation marks to indicate that not the true proton activity is intended but rather the reading on a pH-meter when a glass and calomel electrode combination is dipped into the sulpholane-containing solution. Below pH 0·1 the formation of the complex is incomplete. Above pH 1·8 the conversion into the α-acid is increasingly rapid and at pH 3 almost instantaneous. Once formed, the α-acid persists and no reconversion to the β-acid takes place upon acidification.

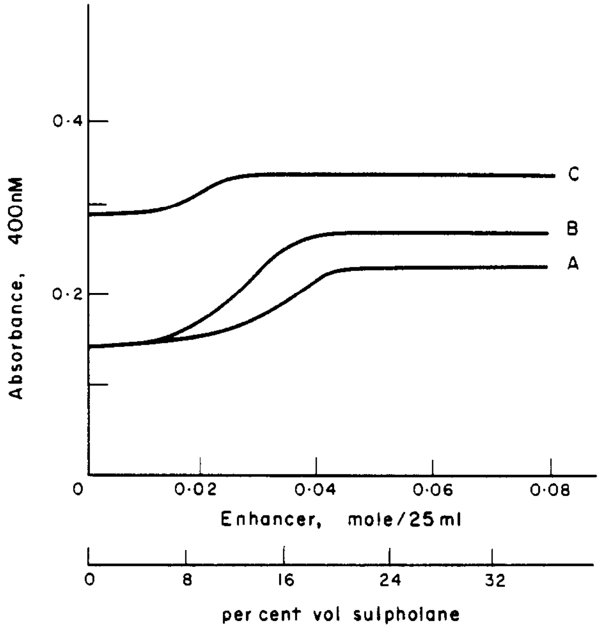

Fig. 1. Enhancement due to acetone and sulpholane.
(A) α-Acid with acetone; (B) α-acid with sulpholane; (C) β-acid with sulpholane.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade or better. Demineralized distilled water was used exclusively. Sulpholane was obtained in distilled form from J. T. Baker: Eastman Practical Grade material was employed after purification by distilling at 118–120° at 1·5 mmHg.

The silicate standard solution was prepared by dissolving sodium matasilicate in demineralized water to yield a $6{\cdot}25 \times 10^{-3}$ *M* solution.

All solutions were stored in polyethylene bottles.

Procedure

Place the roughly neutralized sample solution containing up to 0·4 mg of SiO_2 in a 25-ml volumetric flask and add 4 ml of 0·3*M* perchloric acid, 5 ml of liquefied sulpholane and 5 ml of 0·05*M* ammonium molybdate. Dilute to the mark with distilled water and mix. Allow to stand for 15 min and measure the absorbance at 400 nm *vs.* a reagent blank. Obtain the result in the usual manner from a calibration curve established under identical conditions.

Remarks

The sample solution should be freshly neutralized from the alkaline side in order to avoid polymerization of the silicate, which would lead to erroneous results. The final acidity of the solution should be between "pH" 0·1 and 1·8. The amount of sulpholane can be larger, up to 10 ml. Sulpholane is solid at room temperature and must be liquefied. It may be kept in a warm place to prevent solidification or may be employed as a concentrated aqueous solution.

RESULTS

Some results obtained with this procedure are shown in Table 1. Interference studies have not been made to any extensive degree. Arsenate and phosphate interfere and must be absent. Because of the similarity of the action of sulpholane and acetone it is quite probable that the procedures developed for the latter solvent can be applied with little or no modifications to the sulpholane method.

Table 1. Results of silicon determinations by the sulpholane-β-silicomolybdic acid method

Silica, μg		Silica, μg	
Taken	Found	Taken	Found
55.7	54.0	155	158
73·8	71·7	203	206
94·2	96·3	222	217
111	110	295	292
148	144	369	371

Standard deviation ± 3·1 μg SiO_2

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Summary—Addition of between 20 and 40% v/v sulpholane gives a colour enhancement of silicomolybdic acid better than that achieved with acetone. The β-silicomolybdic acid is stabilized, and solutions yielding a pH-meter reading of 0·1–1·8 give the best results. The photometric measurement is made at about 400 nm. Another advantage of sulpholane is its much lower volatility.

Zusammenfassung—Die Zugabe von 20–40 Vol-% Sulfolan verstärkt die Färbung von Silikomolybdänsäure in höherem Ausmaß, als man es mit Aceton erreicht. Die β-Silikomolybdänsäure wird stabilisiert: Lösungen, für die man am pH-Meter 0·1–1·8 abliest, geben die besten Ergebnisse. Die photometrische Messung wird bei etwa 400 nm ausgeführt. Ein weiterer Vorteil von Sulfolan ist seine viel geringere Flüchtigkeit.

Résumé—L'addition de quantités comprises entre 20 et 40 % (v/v) de sulfolane donne une exaltation de coloration de l'acide silicomolybdique meilleure que celle obtenue avec l'acetone. L'acide β-silicomolybdique est stabilisé, et les solutions donnant une lecture au pH mètre de 0,1–1,8 donnent les meilleurs résultats. La mesure photométrique est effectuée à environ 400 nm. Un autre avantage du sulfolane est sa volatilité beaucoup plus faible.

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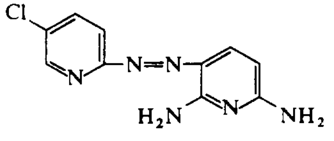
o-AMINO HETEROCYCLIC AZO-DYES AS ANALYTICAL REAGENTS—II

SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 3-[(5-CHLORO-2-PYRIDYL)AZO]-2,6-DIAMINOPYRIDINE

(*Received* 23 *December* 1971. *Revised* 26 *October* 1972. *Accepted* 15 *November* 1972)

In a search for new sensitive and selective reagents, a thorough study of some of the azo compounds containing halogen-substituted pyridine has been made.[1–4] It was found that one of these compounds, 3-[(5-chloro-2-pyridyl)azo]-2,6-diaminopyridine (5-Cl-PADAPy, **I**), formed a deep blue water-soluble complex with cobalt(II), and a highly selective determination of microgram amounts of cobalt is possible under the conditions established. Recently, Talipov *et al.*[5] determined cobalt with 3-(2-pyridylazo)-2,6-diaminopyridine photometrically.



I

EXPERIMENTAL

Reagents

5-Cl-PADAPy solution. An ethanolic 0·1% w/v solution was prepared from the pure material (see below). The solution is stable for several months if stored in an amber glass bottle.

Cobalt(II) solution. A stock chloride solution was prepared from 99·99% pure cobalt metal.

Buffer solution. Hydrochloric acid (0·2*M*)-potassium chloride (0·2*M*), acetic acid (0·2*M*)-sodium acetate (0·2*M*), boric acid (0·2*M*)-potassium chloride (0·2*M*)-sodium hydroxide (0·2*M*) and borax (0·2*M*)-sodium hydroxide (0·1*M*) mixtures.

Solutions (1 + 1 dilution) were made from high-purity sulphuric, hydrochloric, nitric, perchloric and phosphoric acid.

All other reagents were made from high-purity materials or purified reagents, and were prepared with redistilled water.

Preparation of reagent

Diazotization. Freshly prepared isopentyl nitrite (5·46 g) was added to a solution containing 6 g of 5-chloro-2-aminopyridine and 2·4 g of sodium amide in 80 ml of absolute alcohol, refluxed for 2 hr and cooled.

Coupling. 2,6-Diaminopyridine (5·1 g) was dissolved in 10 ml of ethanol and added to the diazonium salt solution at 5°, and carbon dioxide was passed through the solution continuously. The mixture was let cool overnight and the precipitated reddish brown crystals were filtered off, washed with water, dissolved in hot ethanol, recrystallized from aqueous solution, and sublimed at about 200°. Purified materials for physicochemical determinations can be obtained by sublimation in vacuo. Analysis: calculated C 48·30%, N 33·80%, H 3·65%; found C 48·5%, N 33·7%, H 3·8%.

Protonation behaviour of the reagent

The reagent is sparingly soluble in water, but soluble in various organic solvents including ethanol, acetone and dioxan, as well as in strongly acid solution. Five species, H_4L^{4+}, H_3L^{3+}, H_2L^{2+}, HL^+, and L are involved in the protonation equilibria. The proton-dissociation constants have values of $pK_{a3} = 1{\cdot}3$ for the *p*-amino group and $pK_{a4} = 5{\cdot}9$ for the *o*-amino group. The pK_{a1} and pK_{a2} values for the pyridine and 2,6-diaminopyridine heterocyclic nitrogen atoms may exist at about $H_0 = -2{\cdot}5$, but could not be distinguished by the spectrophotometric method.

Colour reaction with metals

The coloured complexes are easily prepared by adding a few drops of a solution of 5-Cl-PADAPy in ethanol to solutions of heavy metals. The ions that give a colour with the reagent are listed in Table 1. Ions that do not give a detectable colour at room temperature include silver, aluminium, beryllium, bismuth, cadmium, calcium, chromium(III), mercury(II), manganese(II), nickel (at pH 4), lead, thorium, tungsten, yttrium, zinc, zirconium, titanium. When mineral acid is added to the solution containing metal complexes, only the cobalt complex is stable, and therefore the selectivity for cobalt is excellent.

Table 1. Colour reaction of metals with 5-Cl-PADAPy

Ion	Colour			
	pH 5	H_2SO_4 added	pH 10	H_2SO_4 added
Reagent	Orange	Orange red	Orange	Orange red
Co^{2+}	Green	Bluish purple	Green	Blue
Cu^{2+}	Purple	nil*	Purple	nil*
Fe^{3+}	Brown	Red brown	Brown	Red brown
Ni^{2+}	nil	nil	Red purple	nil*

* This means reversion to the colour of the reagent.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the reagent and its cobalt complex in aqueous solution at pH 5·0 (initial conditions of colour development) are shown in Fig. 1. When hydrochloric acid is added to the sample solution, the cobalt complex may be changed into a different species, which is suitable for determination of cobalt. The spectra of the reagent and its complex in 1·2*M* hydrochloric acid are shown in Fig. 2.

Optimum pH

The effect of initial pH on colour development was studied by developing the colour in a series of solutions varying in pH from 1·5 to 12 and then measuring the absorbance after the acidity had been increased to 1·2*M* (hydrochloric acid). The absorbance increased steeply in the pH range 2–3, but no change in absorbance was observed over the pH range 3·5–12. In practice the initial pH should be as low as possible because nickel does not react appreciably with the reagent at pH 3·5–5. Subsequent studies were carried out at an initial pH of 5·0.

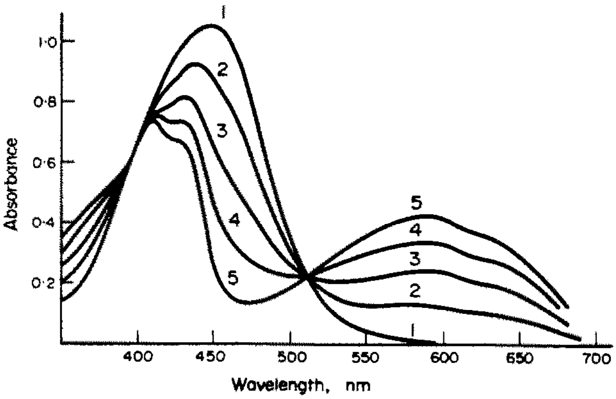


Fig. 1. Absorbance curves of 5-Cl-PADAPy and its cobalt complex in aqueous solution at pH 5·0 with $4 \times 10^{-5}M$ 5-Cl-PADAPy.

Concentration of Co: (1) nil; (2) $0{\cdot}5 \times 10^{-5}M$; (3) $1 \times 10^{-5}M$; (4) $1{\cdot}5 \times 10^{-5}M$; (5) $4 \times 10^{-5}M$

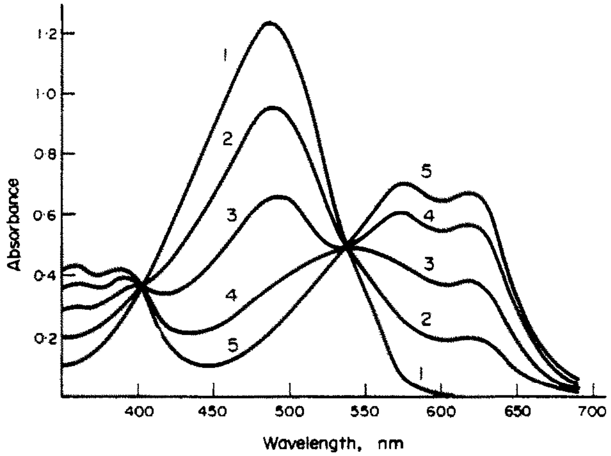
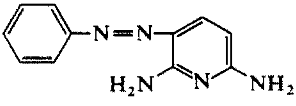


Fig. 2. Absorbance curves of 5-Cl-PADAPy and its cobalt complex in 1·2*M* hydrochloric acid solution. Concentrations of 5-Cl-PADAPy and cobalt as for Fig. 1.

Cobalt and 5-Cl-PADAPy in an acid medium did not form any complexes; under these conditions, the ligand was protonated on the nitrogen atoms and amino groups. In complex formation the pyridine nitrogen atom plays a very important role: benzeneazodiaminopyridine (II) does not react with cobalt under any conditions.



II

However, the complex formed at pH 3·5-12 could be changed into another species of higher absorptivity, by addition of mineral acid. The effects of acidity and type of acid were studied. No change in absorbance was observed over the range 2-10 ml of added (1 + 1) hydrochloric, sulphuric, nitric, perchloric or phosphoric acid. Subsequent studies were carried out with addition of 5 ml of hydrochloric acid (1 + 1).

Reaction conditions

The absorbances of a series of solutions containing 20 μg of cobalt and 0·1–2·0 ml of 0·1% dye solution were measured. It was found that 0·5 ml of dye solution sufficed to complex up to 20 μg of cobalt. For qualitative detection of cobalt, the excess of reagent can be destroyed by the addition of hydrogen peroxide and heating at about 50–60° on a water-bath. Then the colour of the cobalt complex can be detected more easily by eye.

The minimum time for complete colour development was found to be 1–2 min at room temperature. The absorbance was then stable for at least a week. The calibration graph proved to be linear over the range 0·1–1·2 ppm of cobalt. The effective molar absorptivity for the cobalt complex was $3·6 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ at 620 nm.

Effect of foreign ions

Numerous cations and anions were examined by applying the method to fixed amounts of cobalt in the presence of increasing quantities of the ion being studied (Tables 2 and 3). It is evident that many have no effect at the levels studied. Among the cations, interference was caused only by iron(III) and large amounts of copper. Iron(III), about 20 mg, can be masked by the addition of 2 ml of 6% hydrogen peroxide, which interferes appreciably in the formation of the iron complex. Fortunately, hydrogen peroxide does not attack the reagent at room temperature, so 5-Cl-PADAPy can be used for determining microamounts of cobalt in many industrial and natural materials without separation.

Table 2. Effect of foreign cations on determination of 20·0 μg of Co

Metal	Amount added, *mg*	Co found, *μg*	Error, *μg*	Metal	Amount added, *mg*	Co found, *μg*	Error, *μg*
Al^{3+}	2	20·0	±0·0	Mg^{2+}	2	19·9	−0·2
	4	19·8	−0·2		4	19·7	−0·3
Bi^{3+}	2	20·0	±0·0	Mn^{2+}	2	20·2	+0·2
	4	19·8	−0·2		4	21·0	+1·0
Cd^{2+}	2	19·4	−0·6	Ni^{2+}	2	20·2	+0·2
	4	19·7	−0·3		4	21·2	+1·2
Cu^{2+}	0·05	20·4	+0·4	Pb^{2+}	2	20·0	±0·0
Cr^{6+}	2·5	20·4	+0·4		4	20·0	±0·0
	5	20·9	+0·9	Th^{4+}	2	20·0	±0·0
Cr^{3+}	0·1	20·8	+0·8		4	20·0	±0·0
	1	20·9	+0·9	Ti^{4+}	1	20·1	+0·1
Fe^{2+}	0·2	19·6	−0·4		2	20·3	+0·3
	0·4	19·0	−1·0	W^{6+}	2	20·6	+0·6
Fe^{3+}	5*	20·2	+0·2		4	24·1	+4·1
	10*	20·3	+0·3	Y^{3+}	2	20·1	+0·1
	15*	19·9	−0·1		4	19·7	−0·3
	20*	20·5	+0·5	Zn^{2+}	2	20·2	+0·2
	0·01	23·6	+3·6		4	19·8	−0·2
Hg^{2+}	2	19·8	−0·2	Zr^{4+}	2	20·2	+0·2
La^{3+}	2	20·0	±0·0		4	20·0	±0·0
	4	19.7	−0·3				

* 2 ml of 6% H_2O_2 added.

Table 3. Effect of anions (20 μg of cobalt)

Salt	Amount added, *g*	Co found, *μg*	Error, *μg*	Salt	Amount added, *g*	Co found, *μg*	Error, *μg*
K_2SO_4	1	20·0	±0·0	K_2CO_3	1	18·7	−1·3
KNO_3	1	20·0	±0·0	$NaClO_4$	1	19·2	−0·8
KCl	1	20·0	±0·0	NaCl	1	20·0	±0·0
KBr	1	19·7	−0·3	$NH_4H_2PO_4$	1	19·8	−0·2
KI	1	16·6	−3·4	Tartaric acid	1	19·7	−0·3

Nature of the cobalt complex

The empirical formulae of the complexes were studied by the continuous-variation and mole-ratio methods. The curves obtained indicate the formation of a complex 1 : 3 metal : ligand ratio at pH 5 and in 1·2*M* hydrochloric acid. However, it is difficult to see how the three ligands can be co-ordinated to cobalt, on account of the structure of the reagent. A further critical study of the reaction is therefore planned. The present communication discusses only the analytical conditions.

Recommended procedure for the determination of cobalt

Into a 25-ml volumetric flask transfer a suitable aliquot of sample solution containing up to 25–30 μg of cobalt, and add 1·0 ml of ethanolic 0·1% reagent solution. Adjust to pH 5 with 5 ml of buffer solution and mix. Then add 5 ml of hydrochloric acid (1 + 1), dilute to volume and mix. Measure the absorbance of the cobalt complex at 620 nm against a reagent blank. Obtain the concentration of cobalt from a standard calibration curve obtained under identical conditions.

Table 4. Determination of cobalt in some alloys

Alloy	Composition, %	Cobalt found, %
For electric resistors	Ni, 73·07	17·20
	Co, 17·16	17·19
Konel	Ti, 8·8	17·21
	Si, 0·5	—
	Al, 0·26	17·20
For glass fusion	Ni, 30·0	25·3
	Co, 25·0	25·1
EMK	Cr, 8·0	25·3
	Fe, 37·0	—
		25·2

Determination of cobalt in some alloys

A sample (0·1 g) of alloy was dissolved in the usual way and cobalt determined on an aliquot of the solution. Some results are shown in Table 4.

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Summary—Cobalt(II) and 3-[(5-chloro-2-pyridyl)azo]-2,6-diaminopyridine (5-Cl-PADAPy) in slightly acid, neutral or alkaline media form a blue complex which is very stable even in the presence of mineral acids. The complex has two absorption maxima, at 575 and 620 nm, in 1·2*M* hydrochlororic acid. The system conforms to Beer's law; the optimal range for a 1-cm cell is 0·2–1·2 ppm cobalt. Milligram amounts of common anions and cations do not interfere. The molar absorptivity is $3·69 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ at 620 nm.

Zusammenfassung—Kobalt(II) und 3-[(5-Chlor-2-pyridyl)azo]-2,6-diaminopyridin (5-Cl-PADAPy) bilden in schwach sauren, neutralen oder alkalischen Medien einen blauen Komplex, der selbst in Gegenwart von Mineralsäuren sehr stabil ist. Der Komplex hat in 1·2 M Salzsäure zwei Absorptionsmaxima bei 575 und 620 nm. Das System gehorcht dem Beerschen Gesetz. Der beste Konzentrationsbereich für eine 1 cm-Zelle ist 0·2–1·2 ppm Kobalt. Milligrammengen gängiger Anionen und Kationen stören nicht. Der molare Extinktionskoeffizient beträgt bei 620 nm $3·69 . 10^4$ $\text{l mol}^{-1}\text{cm}^{-1}$.

Résumé—Le cobalt (II) et la 3-[(5-chloro 2-pyridyl) azo] 2,6-diaminopyridine (5-Cl-PADAPy) en milieux légèrement acide, neutre ou alcalin forment un complexe bleu qui est très stable même en la présence d'acides minéraux. Le complexe a deux maximums d'absorption, à 575 et 620 nm, en acide chlorhydrique 1,2*M*. Le système suit la loi de Beer; le domaine optimal pour une cellule de 1 cm est de 0,2–1,2 p.p.m. de cobalt. Des quantités d'anions et de cations communs de l'ordre du mgr n'interfèrent pas. Le coefficient d'absorption molaire est de $3,69 \times 10^4$ $\text{l.mole}^{-1} . \text{cm}^{-1}$ à 620 nm.

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ANALYTICAL DATA

METAL COMPLEXATION WITH 2-HYDROXY-6-METHYLPYRIDINE-3-CARBOXYLIC ACID

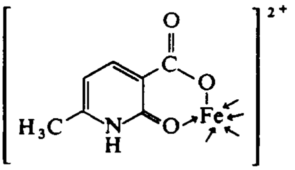
(*Received* 21 *April* 1972. *Revised* 1 *September* 1972. *Accepted* 20 *September* 1972)

In continuation of studies on metal complexation with hydroxypyridines,[1–4] 2-hydroxy-6-methylpyridine-3-carboxylic acid (HMPC) is examined as a ligand for use in determination of iron(III).

EXPERIMENTAL

Spectral investigations

The ligand solution is colourless and shows maximum absorption at 235 and 315 nm (ε 6·7 × 10^3 and 9·6 × 10^3 $l.mole^{-1}.cm^{-1}$). When it is added to iron(III) solution, a yellow colour is developed instantaneously, having λ_{max} = 410 nm, independent of the metal : ligand ratio, so only one complex is formed. The absorbance is independent of the acid concentration in the range 0·5–2·0*M* perchloric acid. For subsequent analytical work, 1*M* perchloric acid was chosen as the medium and an 80-fold molar excess of HMPC was found necessary for full colour development. Beer's law is obeyed up to an Fe(III) concentration of 16 μg/ml, the molar absorptivity being 5·0 × 10^3 $l.mole^{-1}cm^{-1}$. The complex was shown to be 1 : 1 by the continuous variation and the logarithmic[5] methods. The apparent stability constant of the complex is calculated to be 0·9 × 10^3 in 1*M* perchloric acid medium, at 25°. In view of the dominant lactam structure of hydroxypyridines[3,6] the structure (I) may be suggested for the complex, assuming that the remaining co-ordination sites around iron are occupied by water molecules or by anions. Iron(II) does not give a yellow colour with HMPC in 0·5–2·0*M* perchloric acid medium.



(I)

Interferences

The amounts of foreign ions (in μg/ml) tolerated in estimation of 2·5 μg/ml of Fe(III) in 1*M* perchloric acid medium are: 250 of NO_2^-, NO_3^-, Cl^-, Br^-, SO_4^{2-} or BO_3^{3-}; 150 of UO_2^{2+}; 100 of CH_3COO^-, F^-, citrate, tartrate, PO_4^{3-}, Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Ti(IV), Zr, V(V), As(III), Sb(III), Mn(II), Ru or thiourea; 50 of Ce(III), Mo(VI) or Ir; 35 of W(VI); 10 of $C_2O_4^{2-}$, EDTA or Pt(IV); 5 of Rh. As the Ru and Ir solutions are coloured, these metals are included in the blank when they are present. Mo and W can be masked by addition of 100 μg of citrate per ml. I^-, $S_2O_3^{2-}$ and Cr(III) interfere, but iodide can be oxidized to iodine with hydrogen peroxide and extracted into chloroform, and chromium can be oxidized to perchromic acid with peroxide and extracted into pentanol.

Procedure

A drop of test solution (in 2*M* perchloric acid) is placed on a spot-plate followed by a drop of the reagent solution ($10^{-2}M$ in water). An immediate yellow colour shows the presence of iron(III).

The limits of identification and dilution are 0·8 μg/ml and 1 : 50,000 respectively.

Stability constants of bivalent metal complexes with HMPC

The method of Bjerrum and Calvin as modified by Irving and Rossotti[7] was used to obtain values of $\bar{n}$ and pL which were plotted to obtain the formation curves of the metal complexes. The values of log K_1 and log K_2 were calculated by the correction-term method of Irving and Rossotti.[8] From the results (Table 1) it is seen that the order of stability of the bivalent transition metal complexes with HMPC is as follows:

$$\mathrm{Cu} > \mathrm{Zn} > \mathrm{Fe} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Mn}$$

Table 1. Stability constants of bivalent metal complexes with HMPC

Cation	log K_1	log K_2
Cu(II)	4·59	3·62
Zn(II)	3·90	2·81
Fe(II)	3·61	2·54
Ni(II)	3·46	2·50
Co(II)	3·42	2·40
Mn(II)	3·24	2·21

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Summary—Metal complexation with 2-hydroxy-6-methylpyridine-3-carboxylic acid has been studied. The ligand finds use in detection and determination of iron (III). The order of stability constants of the bivalent transition metal complexes is Cu > Zn > Fe > Ni > Co > Mn.

Zusammenfassung—Die Komplexbildung von Metallen mit 2-Hydroxy-6-methylpyridin-3-carbonsäure wurde untersucht. Der Ligand findet Verwendung beim Nachweis und bei der Bestimmung von Eisen(III). Die Reihenfolge der Stabilitätskonstanten der Komplexe mit zweiwertigen Übergangsmetallen ist Cu > Zn > Fe > Ni > Co > Mn.

Résumé—On a étudié la complexation des métaux avec l'acide 2-hydroxy 6-méthylpyridine 3-carboxylique. Le coordinat trouve son emploi dans la détection et la détermination du fer (III). L'ordre des constantes de stabilité des complexes des métaux de transition bivalents est Cu > Zn > Fe > Ni > Co > Mn.

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APPLICATION OF INDIRECT METHODS IN ANALYSIS BY ATOMIC-ABSORPTION SPECTROMETRY

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Summary—The use of indirect methods for the determination by atomic-absorption spectrometry of those elements not normally amenable to sensitive determination by this technique is reviewed. The available indirect methods are classified into five general types of procedure; specific reported procedures for the determination of metals, non-metals and some compounds are discussed.

Atomic-absorption spectrometry (AAS) may be used directly for the determination of 68 elements. The sensitivity attainable in these direct methods, defined as that concentration of the element in solution which produces 1% absorption at a given wavelength, is high for many of these elements (0·01–5 μg/ml). This sensitivity value is determined principally by the oscillator strength of the atomic line employed, the degree of atomization in the atom cell used and on the efficiency of the nebulization process by which the solution is introduced into the cell; the value for a particular element in a given solution does not vary greatly between instruments when commercially available apparatus is employed. The detection limit realizable for an element in AAS depends on the signal : noise ratio under particular analytical conditions and is considerably better than the 1% absorption sensitivity for most elements; this value, however, does vary with the instrumental assembly employed and the particular analyses undertaken.

A considerable number of elements may not be determined directly by atomic-absorption spectrometry with conventional instrumentation, or may be determined only with low sensitivity (> 5 μg/ml for 1% absorption) so that they are not readily determined at trace levels in solution. Thus, for example, the elements F, Cl, Br, I, S, P, O and N exhibit their principal resonance lines in the vacuum ultraviolet (Table 1) and are not directly determinable by AAS with conventional equipment. A second large group of elements for which direct AAS is difficult includes those elements for which, although

Table 1. Elements with main resonance lines at $\lambda < 200$ *nm*

Element	Line, *nm*	Element	Line, *nm*
F	95·5, 95·2	P	178·8, 178·3, 177·5
Cl	138·0, 134·7	S	182·6, 182·1, 180·7
Br	157·6, 148·9	As	197·3, 193·8, 189·0
I	183·0	Se	196·1
C	165·7, 156·1	Hg	184·9

Table 2. Summary of available indirect AAS methods for elements (Periodic Table)

H																	He
Li	Be											B	C	**N**	O	**F**	Ne
Na	Mg											**Al**	**Si**	**P**	**S**	**Cl**	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	**Ge**	**As**	**Se**	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Tc	**I**	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	**Hg**	**Tl**	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw		

☐ Not determinable by AAS with conventional equipment

☐ Determinable by indirect AAS procedures their resonance lines lie in an accessible region of the spectrum, it is extremely difficult to form and maintain a significant atomic population in flame and non-flame cells. This group includes Th and Ce, for which no report of direct determination by AAS with appreciable sensitivity has been made, and in decreasing order of difficulty the elements U, B, W, Ta, La, Nb, Zr, Re, Lu, Hf, Hg, Gd, Ir, Pr, Nd, Sm and Tb. In addition the attainable sensitivity for several other elements that are frequently to be determined may be inadequate for their determination at the trace levels commonly encountered in samples to be analysed; these include As, Ge, Ti, V, Se and Te.

In order to extend the range of application of AAS, and to increase the attainable sensitivity for those elements where it is inadequate for trace analysis, much attention has been devoted to the development of indirect methods of analysis for many of those elements listed above. In addition some work has been reported for the application of indirect methods to permit the determination of organic species by AAS. The information on indirect AAS methods is scattered in the literature; an opportunity is taken in this paper to review these methods and comment on their application in analysis.

GENERAL CONSIDERATIONS

One of the principal advantages of direct methods of analysis by AAS is the high selectivity for particular elements in dilute solution. The success of indirect methods of analysis by AAS, and their applicability to practical analyses, depends on the degree to which the selectivity for the determination of the species concerned can be retained *via* the chemical reaction utilized before the final flame absorbance measurement. Even in those methods where some loss of selectivity is experienced owing to the nature of the initial chemical reaction employed, the ability to increase the sensitivity, or to achieve the AAS determination at all, is frequently of considerable value.

Several distinct types of procedure may be employed in indirect determinations by AAS. In each of these the species to be determined is made to undergo a reaction with one or more other ions and the concentration of the reaction product or of the unreacted excess of added reagent (which are directly and inversely proportional, respectively, to the concentration of the analyte species in the sample) is measured. The following specific types of procedure may be employed.

1. Measurement of the suppression or enhancement of the atomic-absorption signal for a given element by its reaction in the flame with the species to be determined.
2. Precipitation of the ion or compound to be determined by a second ion which is determined by AAS in the precipitate or filtrate.
3. Formation of an ion-association or chelate complex between an organic compound or an anion to be determined and a metal or metal complex; the metal is then determined by AAS after extraction with an organic solvent.
4. Formation of a binary or ternary heteropoly acid species between the analyte ion and other ions (one of which is usually molybdate), and determination of its concentration by AAS after separation of the complex by solvent extraction.
5. Application of the reducing (or oxidizing) properties of the analyte species to yield an equivalent concentration of the lower (or higher) oxidation state of a metallic ion, only one oxidation state of which forms an extractable chelate complex, which may be determined by AAS.

This review could be arranged under these five headings, and this approach has been adopted in earlier brief reviews of indirect AAS methods.[1,2] As the analytical chemist is most frequently interested in the determination of a particular element or group of elements, however, this review has been written with classification by the element determined.

METALS

Only rarely are the metallic elements not directly determinable by AAS; with the exception of thorium the indirect methods reported have therefore been concerned only to provide increased sensitivity in their determination.

Aluminium

An indirect AAS method for aluminium has recently been reported.[3] The sensitivity obtained in the determination of iron by AAS is low in the fuel-rich air–acetylene flame. An enhancement of the absorbance for iron is observed in the presence of small amounts of aluminium when this fuel-rich flame is employed. The enhancement by aluminium of the absorbance produced on nebulization of a 25-μg/ml iron solution is linear with respect to the aluminium content of the solution in the range 0·25–1·2 μg/ml.

The sensitivity obtained in the determination of aluminium by this method may be varied by the nebulization of different concentrations of iron; in this way with a 25-μg/ml iron solution the most sensitive working range for aluminium was found to be 0·01–0·09 μg/ml. Aluminium was also observed to enhance the absorbance of the elements cobalt, nickel and chromium in the flame employed. Titanium, calcium and zirconium at the same concentration levels as aluminium interfere with its determination. At concentrations equivalent to the iron concentration nickel and chromium interfere. The method is useful only for relatively pure aluminium solutions or analyses in which a separation procedure is included.

Germanium

The indirect determination of germanium by AAS, based on the formation of molybdogermanic acid (MGA) in which the molybdenum : germanium combining ratio is 12 : 1, has been described by Jakubiec and Boltz.[4] After its formation in hydrochloric acid solution at pH 1·5, the MGA complex is extracted with a mixture of 1-pentanol and diethyl ether (1 : 4 v/v). The complex is then back-extracted and decomposed by shaking the organic layer with an ammoniacal buffer at pH 9·3. The resulting molybdate is measured by AAS at 313·2 nm in an air–acetylene flame. A sensitivity for germanium of 0·05 μg/ml was reported with conformity to Beer's law in the range 0–1·6 μg/ml. No interference was found for 500 μg/ml of Ca, Co, K, Mg, Mn, Na, Ni, Zn, acetate, chloride, perchlorate, nitrate or sulphate ions in the determination of 1·5 μg/ml of germanium. The maximum permissible concentrations of foreign ions for non-interference in the determination of 1·5 μg/ml of germanium were established as: Al, Cd, Cr(III), Cu, Mo(VI) 500 μg/ml; Pb 50 μg/ml; Fe(II), Fe(III), Ti(IV), Cr(VI), W(VI) 10 μg/ml; As(III), As(V), P(V) and Si interfered at any concentration.

Mercury

Mercury(II) may be converted into its anionic bromo-complex and extracted into 1,2-dichloroethane as an ion-association complex with the zinc 2,2-bipyridyl chelate cation. Yamamoto *et al.*[5] have reported the determination of the zinc content of the extract, which is equivalent to the mercury present in the sample, by AAS in an air–acetylene flame.

The extraction was found to be quantitative between pH 3·5 and 5·5 and a linear calibration graph was obtained for 0·8–4·0 μg/ml of mercury in the initial aqueous phase with a sensitivity (for 1% Zn absorption) of 0·04 μg/ml of mercury. The following maximum permissible concentrations of foreign ions for non-interference with the determination of 2 μg/ml of mercury were established: Cu, 0·1 μg/ml; Co, I$^-$ 5 μg/ml; Cd, 15 μg/ml; Fe, 20 μg/ml; Pb, 200 μg/ml; Cl$^-$, 400 μg/ml.

Niobium

Kirkbright *et al.*[6] have utilized the formation of the ternary complex between niobium, phosphate and molybdate as the basis of an indirect method for the determination of niobium. The method is of the general type illustrated schematically in Fig. 1. As the molybdoniobophosphoric acid (MNPA) cannot be formed in aqueous solution without the simultaneous formation of molybdophosphoric acid (MPA) a prior selective extraction of MPA is required. Both MPA and MNPA are formed in 0·5*M* hydrochloric acid solution. The MPA may then be extracted with isobutyl acetate before extraction of MNPA into a single portion of n-butanol. The molybdenum associated with the niobium in the MNPA is then determined by direct AAS in the n-butanol phase which has been washed with dilute hydrochloric acid. A sensitivity of 0·015 μg/ml of niobium was reported, compared to a sensitivity by conventional direct AAS determination of 20 μg/ml for 1% absorption at the 334·4 nm line (Table 3); the calibration curve obtained was linear in the range 0·22–2·2 μg/ml of niobium. Out of twenty-seven ions studied for their interference with the determination of 1·30 μg/ml of niobium at the 30–700-fold weight ratio level, only As(V), Ge, Si, Ti, V(V) and Cr(VI) interfered. The method is sensitive because of the amplification accruing *via* the 11 : 1 combining ratio of molybdenum to niobium in MNPA and the "organic solvent effect" in the nebulizer of the flame spectrometer.

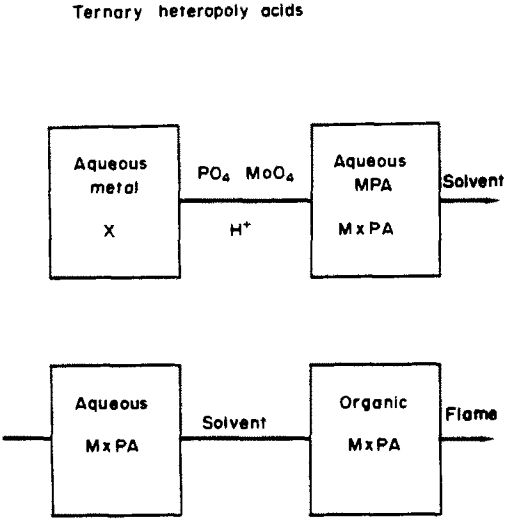

Fig. 1. General scheme for indirect determination of elements by AAS *via* formation of ternary heteropoly acids.

Table 3. Indirect AAS methods based on formation of molybdo-heteropoly compounds

Element	Sensitivity*		Range, indirect	Ref.
	Indirect	Direct†	μg/ml	
P	0·003	250	0·04–2	44
As	0·025	0·25	0·2 –2	17
Ge	0·05	2·5	0–1·6	4
Si	0·008	2·0	0·08–1·2	39
V	0·011	1·5	0·2 –2	15
Nb	0·015	20	0·22–2·2	6
Th	0·063	—	1–6	8
Ti	0·013	2·0	0·3 –3	11

* Sensitivity-concentration in μg/ml for 1% absorption.
† From Perkin–Elmer Methods Book.

Thallium

Molybdophosphoric acid (MPA) has been used as a precipitant for thallium; the molybdate obtained by dissolution of the precipitate may be determined by AAS at 313·2 nm in an air–acetylene flame.[7] Thallium(I) is precipitated with MPA as $Tl_2HPMo_{12}O_{40}$ from 0·5*M* perchloric acid medium. The precipitate is centrifuged, washed with perchloric acid and dissolved in 0·1*M* sodium hydroxide solution. The molybdate equivalent to a definite amount of thallium is then determined. The optimum concentration range was found to be 2–20 μg/ml of thallium. The effect of other ions was not examined but as the method may also be used for the determination of ammonium by co-precipitation, this ion may thus interfere, as would other heavy metals which precipitate as molybdophosphates. As thallium can be determined by AAS in an air–acetylene flame with a sensitivity for 1% absorption of *ca.* 0·5 μg/ml at the 276·8 nm line it is doubtful whether, in view of the decreased selectivity, this method represents any advance on the direct method.

Thorium

Thorium may be determined indirectly by a method similar to that used for niobium.[8] Molybdothorophosphoric acid (MThPA) is formed in 0·15*M* hydrochloric acid in the presence of excess of MPA. The latter is then selectively extracted into isobutyl acetate and discarded. MThPA is extracted with n-butanol which is washed with butanol-saturated dilute hydrochloric acid. Although Kirkbright *et al.* claim to extract MThPA as such it is probable that only the MPA associated with the ternary complex was actually extracted; treatment with n-butanol has been shown to break down MThPA into thorium and MPA.[9,10] Eleven molybdenum atoms are associated with one thorium atom in the complex and the molybdenum is measured by AAS at 313·2 nm in a nitrous oxide–acetylene flame. A linear calibration curve was obtained for 1–6 μg/ml of thorium in the initial aqueous solution with a sensitivity of 0·063 μg/ml of thorium for 1% absorption. Only Zr, Fe(III), Si, As(V), Ti and Nb interfered seriously and required removal or masking.

Titanium

Titanium may be determined *via* its ternary heteropoly complex, molybdotitanophosphoric acid (MTPA).[11] The dissolution of the sample in hydrofluoric acid before the addition of phosphate, molybdate and acid requires the addition of aluminium to mask the excess of fluoride ion, which otherwise interferes in the determination. The excess of MPA is selectively extracted with chloroform : n-butanol (4 : 1 v/v) after formation of MTPA in 0·5M hydrochloric acid. The MTPA is extracted with n-butanol which is then washed with butanol-saturated dilute hydrochloric acid before nebulization into a nitrous oxide–acetylene flame. Eleven molybdenum atoms are associated with two titanium atoms in the complex and the molybdenum is measured by AAS at 313·2 nm. A linear calibration curve was obtained for 0·3–3 μg ml of titanium in the initial aqueous solution, corresponding to a sensitivity (for 1% Mo absorption) of 0·013 μg/ml of titanium. Interference was observed from As(V), Ge, Zr, Ta and Nb.

Ottaway *et al.*[12] have used the enhancement by titanium of the atomic-absorption signal of iron in a fuel-rich air–acetylene flame to determine titanium in the range 0·01–10 μg/ml. The iron is nebulized as ferric sulphate in $10^{-3}M$ sulphuric acid. Chloride, calcium, aluminium and zirconium also give enhancements at similar concentrations. A method based on the suppression of the absorbance of strontium by titanium in the presence of oxalate ions when nebulized into a stoichiometric air–acetylene flame has been used to determine titanium in the range 1–10 μg/ml.[13] The suppression is thought to be due to compound formation by strontium with titanium and oxalate. A solution $2 \times 10^{-4}M$ in strontium and containing 100 μg/ml of oxalate, 10% by volume of hydrochloric acid, and the titanium is nebulized into an air–acetylene flame. If the strontium concentration is increased higher ranges may be covered; these can, however, equally well be determined directly with a nitrous oxide–acetylene flame. A sensitivity of 0·15 μg/ml of titanium was recorded. Slight negative interference is experienced with EDTA, whereas Mn(II), Cu, Mg, Ca, Sn(IV) and Ni present at 200 μg/ml produce a small positive interference with 2 μg/ml of titanium. Al, Zr, H^+, Cr(III), PO_4^{3-} and F^- all interfere and therefore the method has limited applicability but does allow determination of titanium in the presence of high hydrochloric acid concentrations. Titanium causes similar depressions in the absorbances of calcium and barium in the presence of oxalate but methods based on these effects are less sensitive.

Vanadium

Vanadium(V) has been determined indirectly by AAS *via* the formation of molybdovanadophosphoric acid (MVPA).[14,15] In the method of Jakubiec and Boltz[14] a mixed phosphate and molybdate reagent is added to an aliquot of the sample at pH 1·5–2·0. The excess of MPA is extracted with diethyl ether, and the MVPA complex is then extracted with an n-pentanol : diethyl ether mixture (1 : 4 v/v). The organic layer is washed with dilute hydrochloric acid, and the MVPA is decomposed by back-extraction into an ammonia–ammonium chloride buffer solution. The molybdate content of this solution, which is equivalent to the vanadium, is then determined in a reducing air–acetylene flame with a sensitivity for vanadium of 0·05 μg/ml for 1% absorption. The following ions caused interference in the determination of 2·17 μg/ml of vanadium at the levels indicated: Cr(III), NO_3^-, SO_4^{2-} 250 μg/ml; Cd, $C_2H_3O_2^-$, Cr(VI) 100 μg/ml; As(V); Sn(IV) 50 μg/ml; Ti, Si, W(VI) 10 μg/ml; Fe(III) 5 μg/ml; Fe(II) interfered at any concentration.

A method has been developed which does not require back-extraction of MVPA from the organic solvent.[15] Phosphate and molybdate are added separately to the vanadium(V) solution to form MVPA in a 0·4*M* nitric acid medium. An n-butanol : chloroform mixture (1 : 4 v/v) is used to extract the MPA selectively and has the advantage of forming the denser phase so that it is readily separated and discarded without the need for transfer of the sample solution. MVPA is extracted with n-butanol, which is then washed with butanol-saturated dilute acid and nebulized into a fuel-rich nitrous oxide–acetylene flame. Eleven molybdenum atoms are associated with each vanadium atom in the complex and the molybdenum is measured at 313·2 nm. A sensitivity (for 1% Mo absorption) of 0·011 μg/ml of vanadium was obtained with a linear calibration from 0·2 to 2·0 μg/ml. Interference with the determination of 0·8 μg/ml of vanadium was experienced from F^-(16 μg/ml) As(V), Sn(IV) (8 μg/ml); Cr(VI) (2·4 μg/ml); Zr (0·8 μg/ml); Ti and Si interfered at any concentration. A scheme has been recommended to improve the selectivity of the procedure in the presence of ions which form binary or ternary heteropolymolybdates. These ions are removed as their corresponding heteropoly acids before formation and extraction of MVPA. This is possible as vanadium exists both as V(IV) and V(V) and only V(V) forms the ternary heteropoly acid. Vanadium in aluminium has been determined with reasonable results.

NON-METALS

Most of the published work which deals with indirect methods of analysis by AAS has been concerned with the determination of the non-metallic elements and other anionic species which cannot be determined directly because of the difficulties described earlier.

Arsenic

The reported indirect AAS methods for arsenic are all based on the formation of the binary heteropoly acid, molybdoarsenic acid (MAA). Danchik and Boltz[16] used bromine water to ensure that arsenic was present as As(V) before its reaction with molybdate at pH 1·8. The MAA was extracted with methyl isobutyl ketone (MIBK) which after being washed with dilute hydrochloric acid was shaken with a basic buffer solution to decompose and back-extract the MAA. The molybdenum associated with the arsenic was measured by AAS at 313·2 nm in an air–acetylene flame in the basic aqueous phase. A sensitivity of 0·07 μg/ml was achieved. MAA formed at pH 0·9 has been selectively extracted into an ethyl acetate : butanol : isopentyl acetate mixture (1 : 1 : 2 v/v) in the absence of PMA.[17] A sensitivity of 0·025 μg/ml was reported for measurement of the associated molybdenum in a nitrous oxide–acetylene flame. The effect of 40-fold weight ratios of 40 ions was studied, none of which was found to interfere. Arsenic has been determined with a sensitivity of 1 μg/ml in urine.[18] In this procedure the MAA was formed at pH 1, MPA was extracted with isobutyl acetate and the pH was then increased to 2 before extraction of MAA with cyclohexane.

By judicious choice of the extraction system arsenic may be determined with high sensitivity and good selectivity *via* its heteropoly acid species with molybdate.

Fluorine

The presence of fluoride ion depresses the absorbance produced at 285·2 nm for magnesium in an air–coal gas flame; this effect may be utilized as the basis of an indirect AAS method.[19] The change in absorbance of the magnesium at 285·2 nm was reported to be proportional to the fluoride concentration over the range 0·2–20 μg/ml of fluoride. When the concentration ratio of magnesium to fluoride in the sample solution reached 1 : 2 a constant absorbance was obtained. The method is subject to some interference, principally from phosphate and sulphate. Aluminium, oxalate and acetate also interfered at greater than 1000-fold molar ratio to fluoride. An alternative, but less sensitive, technique based on the enhancement of zirconium absorbance by fluoride in a nitrous oxide–acetylene flame at 360·1 nm has been reported to allow the determination of fluoride in aqueous solution with a high degree of freedom from interference over the range 5–200 μg/ml.[19] Phosphate again interferes, but the similar enhancement observed for titanium absorption at 364·3 nm can be used for fluoride determinations in the range 40–400 μg/ml in the presence of phosphate.[19] These indirect AAS methods for fluoride are considerably more rapid than the classical methods.

Chlorine

All the indirect AAS methods for the determination of chloride ion have been based on its reaction with silver nitrate. Either the excess of silver in the supernatant liquid is measured by AAS at 328 nm after removal of the silver chloride precipitate,[20–24] or the precipitate is redissolved in ammonia solution and the silver content of the ammoniacal solution is measured.[25,26,27] Chloride has been determined in serum,[20] plant liquors,[21] wine,[22] and polyvinyl chloride[23] by the first technique. A variation of this method involves the addition of a range of silver ion concentrations to aliquots of the sample containing chloride. After filtration the excess of silver in each filtrate is measured by AAS; a graph of absorbance *vs.* silver concentration should then show a point of inflection at the concentration of silver equivalent to the chloride content of the original solution.

The first reported determination of chloride by AAS was based on precipitation of silver chloride, dissolution of the precipitate in ammonia solution and the determination of the silver in the resulting solution.[27] This method has been applied to the determination of chloride in titanium metal with an air–hydrogen flame[25] and to the determination of chlorine in selenium.[26]

Perchlorate

Perchlorate forms a complex with copper(I) and neocuproin (2,9-dimethyl-1,10-phenanthroline) corresponding to the composition $Cu(neocuproin)_2ClO_4$; this species is extractable into ethyl acetate. When the copper is determined by AAS at 324·7 nm the method may be applied to the determination of 12·5–125 μg of perchlorate with a sensitivity of 0·025 μg/ml.[28] In the determination of 3 μg/ml of perchlorate by this method Collinson and Boltz[28] observed interference when nitrate, ammonia, magnesium or aluminium were present at concentrations greater than 10 μg/ml.

Iodine

Iodine has been determined by AAS, by use of a cadmium hollow-cathode lamp.[29,30] The method is based on solvent extraction into nitrobenzene of the ion-association complex formed between Tris(1,10-phenanthroline)Cd(II) and iodide at pH 5; subsequent AAS determination of the cadmium content of the extract may then be made at 228·8 nm in an air–acetylene flame. The effect of a number of diverse anions upon the determination of $2 \times 10^{-5}M$ iodide has been studied. Interference was experienced at concentrations greater than the molar ratios relative to cadmium indicated for the following ions: IO_4^- (0·02); ClO_3^-, ClO_4^- (0·03); NO_2^-, NO_3^- (0·1); Br^- (0·2); Cl^-, BrO_3^- (2); CN^-(10); IO_3^- (100); F^-, CO_3^{2-}, $B_4O_7^{2-}$ (1000). Christian and Feldman[31] have described the determination of iodide by utilization of its reducing action on a metal ion, coupled with extraction of the remaining oxidized form into an organic solvent and its estimation by AAS. Thus, for example, iodide reduces chromium(VI) in acid medium and the excess of chromium(VI) may be extracted from 3*M* hydrochloric acid into MIBK. The absorbance of chromium(III) in the aqueous layer increases linearly and the absorbance of the unreacted chromium(VI) in the MIBK decreases linearly with increasing amounts of iodide. The reaction is slow and does not go to completion in dilute solutions. Interferences have not been studied but most reducing species *e.g.*, Fe^{2+} would probably have a similar effect and thus interfere.

Selenium(IV) is reduced by iodide to elemental selenium in acid solution. When iodide is allowed to react with excess of selenium(IV) and the solution is filtered through a Millipore filter, the decrease in absorbance of the filtrate is proportional to the iodide ion concentration of the original sample solution.[31] Again, reducing species would be expected to interfere, though no results were reported for the effects of other ions.

Iodate

Iodate oxidizes iron(II) to iron(III) in acid medium; the iron(III) may be extracted into diethyl ether from 9*M* hydrochloric acid solution. The absorbance of iron in the ether phase is then proportional to the iodate concentration. The solutions must be deaerated to prevent aerial oxidation. As with the reduction method for iodine, this method lacks specificity and is only useful when no other oxidizing species are present.

Nitrogen compounds

Ammonia. Bond and Willis[32] have used the enhancement of zirconium absorbance in a nitrous oxide–acetylene flame at 360·1 nm by nitrogen-containing compounds for the determination of ammonia. For ammonia, the magnitude of this enhancement was found to be proportional to the concentration of the base in the range 1×10^{-4} to $5 \times 10^{-3}M$ and was used for its determination in the absence of phosphate and certain nitrogen-containing compounds. In the presence of interfering species, prior separation of the ammonia by distillation is required. The method has been applied to the determination of ammonia in biological systems.[32]

Danchik, Boltz and Hargis[7] have shown the co-precipitation of ammonium molybdophosphate with a known amount of thallium molydophosphate and subsequent dissolution of the precipitate to provide the basis for an indirect AAS method for the determination of ammonia. The molybdate obtained by dissolution of the precipitate, which is equivalent to a known amount of thallium and ammonia, is determined at 313·2 nm in an air–acetylene flame. Molybdophosphoric acid is used as precipitant in 0·5*M* perchloric acid. The method is unselective, as many heavy metals are precipitated as phosphomolybdates.

Cyanide. Cyanide may be determined *via* the equivalent silver associated with it in the $Ag(CN)_2^-$ complex.[33] Pieces of metallic silver are added to the solution containing the cyanide to be determined and the mixture is then shaken for 1 hr. The dissolved silver is determined by AAS to produce a rectilinear calibration graph for up to 3 μg/ml of cyanide ion. No inteference is experienced from Br^-, I^-, SCN^- or SO_4^{2-} ions but $S_2O_3^{2-}$ enhances the signal. Danchik and Boltz[34] report two methods for the indirect determination of cyanide. The first is based on the formation and extraction of the dicyano-bis(1,10-phenanthroline)Fe(II) complex. The complex is extracted into chloroform, which is then evaporated, and the residue is dissolved in ethanol. The associated iron is determined by AAS in an air–acetylene flame at 248·3 nm. A sensitivity of 0·06 μg/ml of cyanide has been obtained by this method, the calibration graph being linear up to 5 μg/ml. Precipitation of silver cyanide and measurement of the excess of silver in the supernatant solution by AAS in an air–acetylene flame at 328·1 nm forms the basis of a second method. A working range of 0·3–2·5 μg/ml of cyanide has been obtained with a sensitivity of 0·03 μg/ml. No study has been made of the effect of other ions.

Thiocyanate. Thiocyanate forms dithiocyanatodipyridine copper(II) complex, $Cu_2(Py)_2(SCN)_2$, which is extractable with chloroform. The copper equivalent to the thiocyanate is determined at 324·7 nm. A sensitivity of 0·2 μg/ml of thiocyanate has been reported with an optimum concentration range of 7–18 μg/ml.[35] The sensitivity may be improved to 0·05 μg/ml by evaporating the chloroform solution almost to dryness and diluting with ethyl acetate. The optimum concentration range is then between 0·5 and 2·0 μg/ml.

Nitrate. A small amount of nitrate ion is extractable into MIBK when neocuproin (2,9-dimethyl-1,10-phenanthroline) is contained in the organic phase and copper(I) ions are present in the aqueous phase. The copper associated with the nitrate ions in the complex, $Cu(I)(neocuproin)_2NO_3$, is measured in an air–acetylene flame at 324·7 nm.[36,37] Beer's law is obeyed in the range $1–7 \times 10^{-5}M$ nitrate in the aqueous phase. Nitrite and nitro-groups in organic compounds have also been determined *via* formation of the ion-pair with the Cu(I) neocuproin complex after their oxidation to nitrate with ceric sulphate or potassium permanganate.[38] The complex may be extracted into MIBK before measurement of the associated copper. Prior reduction of nitrite and nitro groups to amino groups by sulphamic acid permits determination of nitrate in the presence of such groups.

Phosphorus

Orthophosphate has been determined indirectly, mainly *via* the formation of molybdophosphoric acid (MPA) in the presence of molybdate in acid solution. The general procedure most frequently employed is illustrated in Fig. 2. Molybdate (ammonium or sodium salt) is added to the sample solution containing orthophosphate and the acidity is adjusted to its optimum value. The solution is mixed and allowed to stand for 5–10 min to ensure complete formation of MPA. The MPA is then extracted into an organic solvent which is either washed with dilute acid[39,40] to remove molybdate transferred to the organic layer, or with citrate solution to complex the excess of molybdate.[43,44] The molybdate associated with the phosphate in the complex is measured by AAS at 313·2 nm in an air–acetylene[40–46] or a nitrous oxide–acetylene flame.[17,39,47] Kumamaru *et al.*[47] employed 0·5*M* hydrochloric acid to form MPA and performed the extraction with n-butyl acetate to obtain a linear calibration graph up to 0·35 $\mu g/ml^{-1}$ of phosphorous. A general method for the determination of inorganic phosphate, using 2-octanol as a solvent,[44] has been applied to the determination of phosphate in fresh and sea water and in blood, serum, bone, biological tissues and enzyme-containing reaction mixtures.[45] 2-Octanol was chosen as solvent after examination of n-butanol, isobutyl alcohol, 1-hexanol, 1-heptanol, 1-octanol and 2-octanol.[45] Phosphate

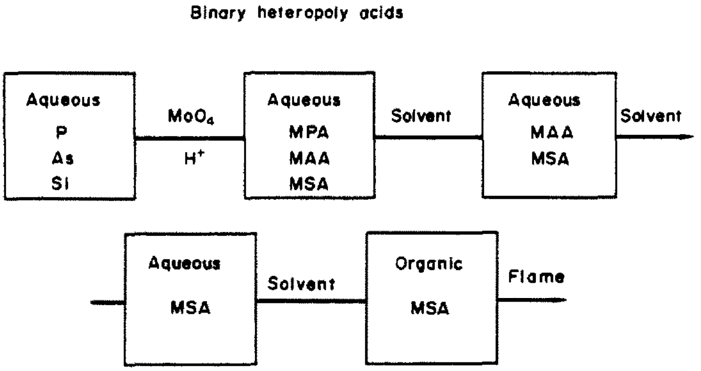

Fig. 2. General scheme for indirect determination of elements by AAS *via* formation of binary heteropoly acid species with molybdate.

has been determined in urine, the MPA being formed in 0·37*M* hydrochloric acid and extracted into isobutyl acetate.[41] Linden *et al.*[42] have determined phosphorus in milk products and blood serum *via* MPA, using perchloric acid medium and MIBK as solvent, for the range 100–200 μg of phosphorus. The results obtained agreed with those established colorimetrically. Phosphate has been determined in small (0·2 ml) samples of plasma.[43] The MPA is formed at pH 1·9 in a DL-α-alanine-hydrochloric acid buffer and is extracted with MIBK. The authors claim to extract MPA with an Mo : P ratio of 15 : 1. No evidence concerning the establishment of this apparently anomolous combining ratio is given. The procedure is applicable to the determination of between 5 and 200 μg/ml of phosphorus.

Several schemes have been devised for the sequential determination of phosphorus, arsenic and silicon,[17] phosphorus and arsenic,[18] and phosphorus and silicon[39,40] (Fig. 2). All are based on the ability to extract MPA selectively. Thus MPA has been selectively extracted with isobutyl acetate after formation at pH 0·7 in nitric acid medium, to result in a final sensitivity of 0·01 μg/ml of phosphorus.[17] Devoto[18] used isobutyl acetate to extract MPA formed at pH 1 in an ammonium nitrate–nitric acid medium. Isobutyl acetate has also been used by Kirkbright *et al.*[39] to selectively extract MPA formed at an acidity of 0·96*M* in hydrochloric acid in a single portion of solution containing phosphate and silicate, before formation of molybdosilicic acid (MSA). A sensitivity of 0·0068 μg/ml of phosphorus and a rectilinear calibration from 0·08 to 1 μg/ml of phosphorus was obtained by measuring the associated molybdate in the organic phase at 313·2 nm in a nitrous oxide–acetylene flame. Only W(VI) is reported as interfering out of 26 ions examined. MPA formed at pH 1·3 has also been extracted from 1·2*M* hydrochloric acid medium with diethyl ether.[40] After washing with dilute hydrochloric acid, the organic layer may be shaken with an ammoniacal buffer and the molybdate released measured in the aqueous phase by AAS in an air–acetylene flame. The optimum concentration range reported is 0·05–1·3 μg/ml of phosphorus. The use of isobutyl acetate coupled with the formation of MPA produces an extremely selective method for the determination of phosphorus by indirect AAS.

Phosphorus has been determined by several workers using the direct chemical interference of phosphate on a metal species in a flame to produce a depression of the absorption, which is a function of the phosphate concentration.[31,48,49] Orthophosphate up to $2{\cdot}5 \times 10^{-4}M$ added to $5 \times 10^{-4}M$ calcium solution produces a marked depression in the absorbance obtained for calcium at 427·7 nm with a total consumption burner.[31] The limiting concentration of phosphate may be increased by increasing the calcium concentration. Singhal and Banerjee have determined phosphorus in rock phosphate by depression of both calcium[49] and strontium[48] absorbance. In both cases the powdered rock phosphate is treated with a cation-exchange resin (H^+-form) before addition of calcium or strontium solution. A modification of the quinolinium molybdophosphate method has been proposed whereby total phosphorus is determined indirectly by the AAS measurement of molybdenum.[50] The familiar and well-tried gravimetric method is followed to the stage where the quinolinium molybdophosphate is formed. The precipitate is then dissolved in ammonia solution and the molybdenum determined by AAS at 313·2 nm. The method has been applied to the phosphorus analysis of Magruder collaborative fertiliser samples.[50]

Selenium

Selenium is difficult to determine directly with high sensitivity by AAS in a flame because of strong absorption of the resonance radiation at 196 nm by the flame and optical components of the spectrometer. An indirect method has been described based on two selective reactions of selenite with 2,3-diaminonaphthalene (DAN) and palladium(II) to form the complex $Pd(DANSe)_2Cl_2$.[51] When excess of DAN is added to a solution of selenite at pH 1·5–2·5 the following reaction occurs:

$$\text{I} \quad C_{10}H_6(NH_2)_2 + SeO_3^{2-} + 2H_3O^+ \longrightarrow \underset{\text{(DANSe)}}{C_{10}H_6N_2Se} + 5H_2O$$

In the presence of palladium chloride three further reactions are possible:

$$\text{II} \quad 2\ \text{DANSe} + PdCl_2 \xrightarrow{\text{pH} \leq 6} Pd(DANSe)_2Cl_2\text{(purple)}$$

$$\text{III} \quad 2\ \text{DANSe} + 2PdCl_2 \xrightarrow{\text{pH} \leq 6} Pd_2(DANSe)_2Cl_4\text{(green)}$$

$$\text{IV} \quad \text{DAN} + PdCl_2 \xrightarrow{\text{pH } 0\text{–}12} \text{white polymeric complex.}$$

Whether it is reaction II or III that occurs depends on the pH, relative concentration of reagents and also on the solvent used for the DANSe. Reaction IV always occurs and thus DANSe is removed from excess of DAN by extraction with chloroform. With chloroform as solvent the complex from reaction III is formed. The optimum calibration is from 0·05 to 1 μg/ml of selenium. A sensitivity of 0·017 μg/ml has been obtained. A study of the effect of 60-fold molar ratios of 50 ions on the determination of 0·5 μg/ml of selenium showed that only Fe(III), Sn(IV) and Ce(IV) interfered.

Silicon

Most indirect methods for silicon are based on the formation of molybdosilicic acid (MSA).[17,39,40,52] In one case MSA is formed at pH 1·3, extracted with a 1-pentanol : diethyl ether mixture (1 : 5 v/v) from 2*M* hydrochloric acid medium and decomposed by back-extraction into a 0·1*M* ammonia solution.[52] A known excess of lead(II) ion is then added to the aqueous solution to precipitate the molybdate as lead molybdate in amount equivalent to the amount of silicon present. The lead remaining in solution may be measured by AAS at 217·1 nm in an air–acetylene flame. An optimum concentration range of 0·005–0·07 μg/ml of silicon has been reported.[52] No interference is experienced from 500 μg/ml of Al^{3+}, NH_4^+, Fe^{3+}, Mg^{2+}, Cl^-, NO_3^-, ClO_4^-, SO_4^{2-} in the determination of 0·02 μg/ml of silicon. Silicon has also been determined sequentially with phosphorus[39,40] and arsenic[17] by using their respective molybdoheteropoly acids (Fig. 2). Kirkbright *et al.*[39] first investigated the determination of silicon by this means. Phosphorus is determined as phosphate by forming MPA in 0·96*M* hydrochloric acid medium and selectively extracting it into isobutyl acetate. The silicon in the same aliquot of solution is determined after the MPA extraction by adjusting the acidity of the solution to 0·15*M* hydrochloric acid with 4*M* ammonia solution to allow efficient formation of MSA. The MSA may then be extracted into n-butanol and the twelve molybdenum atoms associated with each silicon atom determined by AAS at 313·2 nm in a nitrous oxide–acetylene flame. A sensitivity of 0·008 μg/ml of silicon and an optimum concentration of 0·08–1 μg/ml of silicon are obtainable. The presence of a 100-fold weight ratio of 24 ions caused no interference in the determination of 12 μg of silicon; only arsenic(V) and germanium(IV) interfere by formation of their respective heteropoly acids. Hurford and Boltz[40] have described a similar sequential procedure. The MSA is formed at pH 1·3 after the MPA has been extracted and is then extracted from 2*M* hydrochloric acid medium with a 1-pentanol : diethyl ether mixture (1 : 5 v/v). After washing with dilute hydrochloric acid the organic layer is shaken with basic buffer solution which extracts and decomposes the MSA. In this method the molybdenum is then measured in an air–acetylene flame. A calibration range of 0·05–1·1 μg/ml is obtained. MSA formed at pH 0·7 may be separated from large amounts of MPA and molybdoarsenic acid by extraction into MIBK in the presence of citrate.[17] A sensitivity of 0·01 μg/ml of silicon is obtained, the optimum concentration range being from 0·1 to 1 μg/ml. Of 40 ions tested only germanium(IV) interfered with the determination of silicon.

Silicate has been determined in waste waters by atomic-absorption inhibition titration.[53] The method is based on the strong inhibition by silicate of the magnesium absorbance produced in an air–hydrogen flame. The absorbance is measured continuously while the nebulized solution is titrated; this procedure contrasts with the usual direct suppression methods when discrete sample solutions are nebulized. The sample at pH 3–4 is passed through a cation-exchange resin (H^+-form) to remove magnesium and other interfering cations. The eluate from the column is titrated with standard magnesium solution and the titrated solution simultaneously nebulized into an air–hydrogen flame. The end point is detected by a sharp increase in the magnesium absorption signal at 285·2 nm. High accuracy and precision is obtained with a limit of detection of 0·1 μg/ml of silica. The removal of cations by ion-exchange ensures the selectivity of the method.

Sulphur

The first reported indirect AAS method for sulphur is based on the precipitation of barium sulphate on addition of excess of barium chloride to the sample solution. In this method the precipitate is dissolved in a solution of disodium EDTA and the resulting barium concentration is determined at 553·5 nm in an air–acetylene flame.[64] Lanthanum is added to prevent phosphate interference. The method has been used to estimate sulphur in urine, faeces and biological tissues after oxidation by one of several techniques. In a procedure which avoids the necessity to dissolve the barium sulphate precipitate a known excess of barium is added to the sample solution, and the excess is determined after the precipitation of barium sulphate.[55,56] A 0·02M hydrochloric acid medium is used to minimize loss of selectivity through co-precipitation of other ions. The error caused by the partial dissolution of the precipitated barium sulphate and the incomplete reaction is overcome by calibration against standard sulphate solutions treated in a similar manner. The method has been applied to the determination of sulphate in textiles.[56] A similar method has been applied to the determination of water-soluble sulphate in acidic sulphate soils.[57] Calcium and phosphate above 30 and 10 μg/ml respectively interfere with the determination of 50 μg/ml of sulphate. A sensitivity of 1·5 μg/ml of sulphur has been reported for a method which involves precipitation of sulphate with barium chloride, centrifugation and measurement of the excess of barium.[58] An improvement in sensitivity is claimed to be achieved by reduction of the concentration or volume of the barium chloride solution added. The method has been applied to determination of sulphur in samples from deep mine waste water which have a high cation and sulphate concentration, and in the percolate from pyrite-bearing coalmine spoils. Good correlation has been reported between the results of the indirect AAS method and standard methods.

Sulphur in soils derived from volcanic ash is extracted with potassium dihydrogen phosphate solution; the extracted sulphur is transformed into suphate ions, and the organic matter destroyed with 30% hydrogen peroxide solution and sulphate precipitated with 15% barium chloride solution. The barium sulphate may be dissolved in a solution of EDTA (diammonium salt), and the barium measured by AAS in the presence of 1500 μg/ml of sodium ions to suppress barium ionization, to give a sensitivity (1% absorption) of 0·8 μg/ml of sulphur.[59]

Sulphur dioxide, after its preliminary conversion into sulphate with hydrogen peroxide, has been determined after precipitation and centrifugation of lead sulphate. The excess of lead remaining in the supernatant liquid may be measured at 283·3 nm in an air–acetylene flame. Ethanol is added to make the solution 25% with respect to ethanol and thus aid the precipitation of lead sulphate. A concentration range of 2–20 μg/ml of sulphur dioxide was recommended.[60] Interference is experienced above the levels shown for the determination of 5 μg/ml of sulphur dioxide with the following ions Fe(III), PO_4^{3-} (0 μg/ml); Ba, Al (10 μg/ml); EDTA (20 μg/ml), $CH_3CO_2^-$ (250 μg/ml). Sulphite or sulphur dioxide have been measured by AAS, with utilization of the high stability of the $Hg(SO_3)_2^{2-}$ complex.[61] Addition of sulphite ions to a suspension of mercury(II) oxide leads to dissolution of the oxide and formation of the soluble complex. The amount of oxide dissolved is proportional to the increase in absorbance at 253·7 nm observed for mercury in the supernatant fluid, and is then indicative of sulphite concentration. An optimum concentration range of 12–84 μg/ml of sulphite ions (10–77 μg/ml of sulphur dioxide) with a sensitivity of 13 μg/ml of sulphite has been reported. The reaction is not specific and iodide, thiosulphate and thiocyanate interfere.

Sulphate has been determined by atomic-absorption inhibition titration.[62] The test solution containing 0·05–1 mg of sulphate is titrated at a constant delivery rate with standard magnesium chloride solution. The titrated solution is simultaneously nebulized into an air–hydrogen flame. The magnesium absorbance is inhibited until the magnesium to sulphate concentration ratio approaches unity. Thereafter the graph representing increasing magnesium content becomes rectilinear and extrapolation to the base-line is used to locate the end-point. Interfering cations such as those of the alkaline earths metals are removed by passing the solution at pH 3–4 through a cation-exchanger (H^+-form). Silicate and phosphate interfere with the method.

ORGANIC COMPOUNDS

No systematic study of the determination of organic compounds by AAS appears to have been undertaken. Of the methods reported some are extremely specific and rely on the formation of a particular complex and its subsequent extraction,[63–66] while others utilize a more general reaction which can be applied for the determination of a range of compounds.[17,67]

2-Hydroxynaphthoic acid has been determined indirectly through the selective extraction of Tris(1,10-phenanthroline)Ni(II)–2-hydroxynaphthoate into nitrobenzene.[66] Measurement of the nickel concentration by AAS in an air–acetylene flame as a function of the 2-hydroxynaphthoic acid concentration initially present in the aqueous phase leads to a calibration which is linear in the range from 8×10^{-5} to $4 \times 10^{-4} M$ 2-hydroxynaphthoic acid. No interference is experienced from 2-naphthol.

Phthalic acid is extractable into MIBK as the ion-pair formed between bis(neocuproin) Cu(I) and the univalent anion of phthalic acid. The copper extracted is determined by AAS in an air–acetylene flame at 324·7 nm. The absorbance of the extract gives a linear relationship with the phthalic acid concentration initially present in the aqueous phase in the range 4×10^{-6} to $4 \times 10^{-5} M$.[63,64] Isophthalic and terephthalic acid do not interfere if present in amounts equimolar with the phthalic acid.

A similar method has been employed for the determination of pentachlorophenol.[65] The basis of the method is the solvent extraction into nitrobenzene of the ion-pair formed between Tris(1,10 phenanthroline)Fe(III) and the pentachlorophenol anion. The iron is subsequently determined in the extract by AAS at 248·3 nm in an air–acetylene flame. A concentration range up to $3 \times 10^{-4} M$ in pentachorophenol was studied.

Vitamin B_{12} contains one atom of cobalt per molecule. On dissolution of the vitamin the cobalt may be determined by AAS at 242·5 nm. The method has formed the basis for the determination of vitamin B_{12} in pharmaceutical dosage forms.[68,69]

Christian and Feldman[17] have determined several organic compounds by a variety of methods. Glucose oxidase and ribonuclease may be determined by their depressive effect on the absorbance of calcium. The upper concentration can be increased by raising the calcium concentration. Glucose below $10^{-6} M$ is found to produce a marked decrease in the absorbance obtained for calcium, but above that concentration it produces an increase, up to a limiting concentration of $10^{-5} M$. Glucose in the range 10^{-6} to $5 \times 10^{-5} M$ was also found to give a linear enhancement in the calcium absorbance which had been depressed by the addition of a constant amount of sulphate to the solution. Ammonium pyrrolidine dithiocarbamate (APDC) has been determined by measurement of the equivalent amount of copper or cobalt with which it complexes; the complex is extracted into MIBK at pH 3. With 1 ml of 1% metal ion solution a concentration of $10^{-5} M$ APDC may be determined. Similarly oxine is determinable *via* extraction of its copper complex into MIBK or ethyl acetate from an ammonium acetate buffer at pH 6·5 and subsequent AAS measurement of the copper. With 1 ml of $10^{-4} M$ copper solution a concentration of $2 \times 10^{-5} M$ oxine is determinable. EDTA may be determined through its action as a masking agent for the copper oxinate chelate. The decrease in absorbance of the extracted copper is proportional to the concentration of EDTA in the initial aqueous phase.

Sugar in plant materials has been determined by measurement of unreduced copper.[70] Copper is reduced in alkaline solution by the reducing sugars to form insoluble copper(I) oxide. The copper(I) oxide is centrifuged from solution and the unreduced copper(II) in solution is measured by AAS. The concentration of sugar in test solutions is determined from standard graphs prepared from known amounts of sugar.

Several organic compounds have been determined by precipitation of their silver compounds and measurement by AAS of the concentration of the excess of silver left in solution.[67] Thus iodoform, theobromine, sodium salicylate, mercaptobenzothiazole and xanthate have all been determined in this way.[67]

Non-ionic surfactants may be determined indirectly by AAS.[71,72] In one method the surfactant is precipitated as the MPA–Ba complex and the molybdenum in the supernatant liquid is assayed by AAS.[71] The molybdenum concentration is related to the quantity of surfactant by an empirical factor which must be determined for each batch and multicomponent system, as the precipitate is non-stoichiometric. A somewhat better method which does not require the introduction of an empirical factor has been developed.[72] The basis is the extraction of a cobaltithiocyanate–surfactant adduct from aqueous solution into benzene, and measurement of the associated cobalt in the benzene by AAS. Pollution levels of non-ionic surfactants in the Atlantic have been estimated in this way with a precision better than 10%.

CONCLUSION

As shown in Table 2, indirect AAS methods have been reported for the determination of inorganic cations and anions in solution as well as for the organic species described above. Tables 3 and 4 illustrate that the sensitivities obtainable are usually clearly superior to those in the corresponding direct AAS determinations, where these are possible; with careful choice of experimental conditions many of the indirect methods reported exhibit sufficient selectivity for the analyte species, to be applicable for practical analyses. Although several workers have described the direct determination of elements such as carbon,[73] phosphorus,[73,74] sulphur and iodine[74] in non-flame cells, and sulphur[75] and iodine[76] in the inert gas-separated nitrous oxide–acetylene flame, using the resonance lines of these elements in the vacuum ultraviolet, these procedures require modified or specialized instrumentation and have not yet found widespread application.

Table 4. Indirect methods based on miscellaneous procedures

Element	Sensitivity*		Range, indirect, *μg/ml*	Ref.
	Indirect	Direct		
Al		1·3	0·01–10	3
Hg	0·04	11	0·8 –4	5
Tl		0·45	2 –20	7
Se	0·017	2	0·05–1	51
F^-		—	0·2 –20	19
Cl^-		—	0 –0·4	25
ClO_4^-	0·025	—	0·5 –5	28
I^-		—	0·5 –5	30
CN^-	0·03	—	0·3 –2·5	34
SCN^-	0·2	—	7 –18	35

* See footnotes to Table 3.

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Zusammenfassung—Es wird eine Übersicht gegeben üben die Verwendung indirekter Methoden bei der Bestimmung jener Elemente durch Atomabsorptionsspektrometrie, die einer empfindlichen Bestimmung mit dieser Methode normalerweise nicht zugänglich sind. Die verfügbaren indirekten Methoden werden in fünf allgemeine Typen von Arbeitsvorschriften unterteilt; bekannte spezielle Arbeitsvorschriften zur Bestimmung von Metallen, Nichtmetallen und einigen organischen Verbindungen werden diskutiert.

Resumé—On passe en revue l'emploi des méthodes indirectes pour le dosage par spectroscopie d'absorption atomique des éléments qui ne sont pas normalement susceptibles d'être dosés de manière sensible par cette technique. Les méthodes indirectes disponibles sont classées en cinq types généraux de techniques; on discute de techniques spécifiques données pour le dosage de métaux, de non-métaux et de quelques composés organiques.

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ARSENAZO III AS METALLOCHROMIC INDICATOR FOR COMPLEXOMETRIC DETERMINATION OF CALCIUM IN SLIGHTLY ALKALINE MEDIUM

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Summary—Arsenazo III is proposed as metallochromic indicator for calcium in slightly alkaline medium. The visual titration with EDTA was performed at pH 8 and 40 μg–12 mg of calcium were determined. The interference of some ions was considered and it was found that phosphate does not interfere appreciably. Spectrophotometric detection of the end-point was used for titration of calcium in the presence of magnesium at pH 9. For the estimation of the titration error, the conditional stability constants of the calcium–arsenazo III complex were found.

Most complexometric titrations of calcium are performed in a strongly alkaline medium suitable for the colour change of the indicators used and where the interference by magnesium can be avoided by precipitation of the hydroxide. The indicator described in this paper was selected and studied for the complexometric titration of calcium in slightly alkaline medium.

In our previous work[1] it was shown that calcium and arsenazo III form a blue 1 : 1 complex, the absorbance being maximal at pH 9. These data and the acid–base equilibria of arzenazo III serve as the basis for the present investigation. Some simple considerations show that the visual complexometric titration of calcium is possible at pH 8 with arsenazo III as metallochromic indicator. This is confirmed by the results obtained. The method is sensitive and calcium is determined in amounts from 40 μg to 12 mg. Interference of other ions has been studied, and phosphate in particular was found not to interfere.

In order to increase the sensitivity and selectivity of the method spectrophotometric end-point detection was used, which permits the determination of calcium in the presence of magnesium. For calculation of the titration error the conditional metal–indicator stability constant was determined.

EXPERIMENTAL

Reagents

Calcium chloride solution. A 0·1M solution was prepared by dissolving calcium carbonate in hydrochloric acid. A $10^{-2}M$ solution was prepared by dilution and standardized complexometrically with Thymolphthalexone and Calcon as indicators. Solutions of lower concentration were prepared by dilution.

EDTA and EGTA. 10^{-1} *and* $10^{-2}M$ Prepared according to the recommended methods[2] and standardized complexometrically with standard calcium solution.

Arsenazo III solution, $10^{-4}M$ Standardized by spectrophotometric titration with thorium nitrate solution at 600 nm and pH 3. An aqueous 0·1% w/v solution of arsenazo III was used as indicator

Buffer solutions. Boric acid (0·1M) and sodium hydroxide (0·1M) solutions were used to prepare buffer solutions[3] of pH 8–9.

All other reagents used were analytical-reagent grade.

RESULTS AND DISCUSSION

According to Buděšínský[4] arsenazo III [3,6-bis(2′-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid] is decabasic when doubly protonated ($H_{10}L^{2+}$). The dissociation of the groups responsible for the colour change of the arsenazo III solution is important. The dissociation of the sulphonic acid groups (the forms H_8L, H_7L^-) and of the first arsonic acid group protons (the forms H_6L^{2-}, H_5L^{3-}) causes a very small colour effect. The solution is red with $\lambda_{max} = 540$ nm. The dissociation of the next arsonic group protons (the forms H_4L^{4-}, H_3L^{5-}) already causes a bathochromic effect and the colour of the solution changes to wine-red and then violet. The acidity of the hydroxyl groups on the naphthalene ring is strongly affected by the field effect, which increases the bathochromic effect. As a result a blue colour appears.

The acid–base equilibria for the last four steps according to Buděšínský[4] are as follows:

$$\underset{\text{red}}{H_4L^{4-}} \xrightleftharpoons{pK_7\ 6\cdot27} \underset{\text{wine-red}}{H_3L^{5-}} \xrightleftharpoons{pK_8\ 9\cdot05} \underset{\text{violet}}{H_2L^{6-}} \xrightleftharpoons{pK_9\ 11\cdot98} \underset{\text{blue}}{HL^{7-}} \xrightleftharpoons{pK_{10}\ 15\cdot1} \underset{\text{pure blue}}{L^{8-}}$$

Since the calcium–arsenazo III complex is blue it is obvious that the form H_3L^{5-} of arsenazo III is the most important for the complexometric determination of calcium. The following colour-change reaction is proposed:

$$\underset{\text{wine-red}}{H_3I^{5-} + Ca^{2+}} \rightleftharpoons \underset{\text{blue}}{CaH_2I^{4-}} + H^+$$

To define the conditions for existence of H_3L^{5-} in aqueous solution, we have calculated the distribution curves of ionic forms of arsenazo III at pH > 5. The results are shown in Fig. 1. It can be seen that the pH range 7–8 is the most suitable for the use of arsenazo III as a metal-ion indicator in the visual titration of calcium.

For complexometric titration the conditional metal-titrant stability constants are also important. The value of $K_{MY'}$ determines the minimum pH-value for the effective titration of metal ions. It can be calculated that for the Ca–EDTA titration this minimum pH-value is 7·5 for $10^{-2}M$ calcium. This value could also be found from the curve given by Reilley and Schmid.[5]

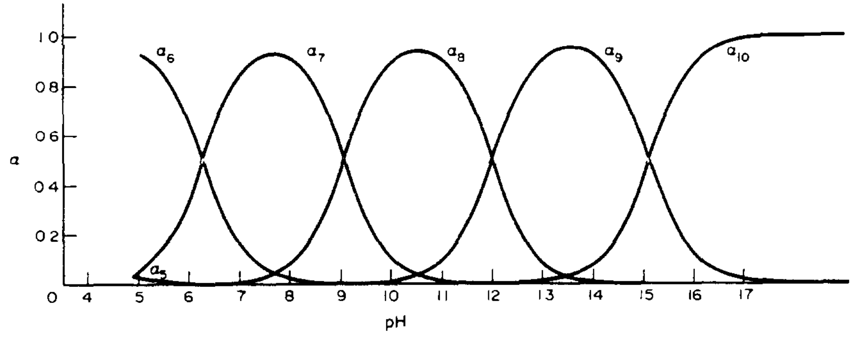

Fig. 1. Fraction of arsenazo III present in various ionic forms. α_5, as H_5L^{3-}; α_6 as H_4L^{4-}; α_7, as H_3L^{5-}; α_8, as H_2L^{6-}; α_9, as HL^{7-}; α_{10} as L^{8-}.

These considerations show that the visual titration of calcium with arsenazo III could be carried out at pH ~ 8.

Visual titration at pH 8

Place the test solutions containing 40 µg–12 mg of calcium in 50-ml glass beakers, add 5–15 ml of buffer at pH 8·1 ± 0·1 and 2 drops of 0·1% arsenazo III solution. An intense blue colour appears. Titrate with standard EDTA solution, stirring magnetically. The end-point is indicated by the colour change from blue to wine-red and is observed within a 2-drop interval (*ca* 0·03 ml). For samples containing >4 mg of calcium, sodium hydroxide must be added towards the end of the titration to maintain the pH at 8, because of the low buffer capacity. Table 1 shows some results.

Table 1. Complexometric titration of calcium

Calcium taken, *µg*	EDTA, *M*	No. of titns	Titration values Average observed, *ml*	Theoretical, *ml*
40	1.25×10^{-3}	8	0·826 ± 0·005	0·806
81	1.25×10^{-3}	7	1·615 ± 0·005	1·611
121	1.25×10^{-3}	7	2·40 ± 0·01	2·417
202	5.00×10^{-3}	7	1·02 ± 0·005	1·007
404	5.00×10^{-3}	7	2·03 ± 0·00	2·014
807	1.25×10^{-2}	6	1·60 ± 0·005	1·611
1210	1.25×10^{-2}	7	2·41 ± 0·005	2·417
4040	9.38×10^{-2}	3	1·080 ± 0·000	1·074
12.12×10^{3}	9.38×10^{-2}	4	3·21 ± 0·00	3·222

Interference of foreign ions

Solutions with 202 and 404 µg of calcium were investigated. Because of the more favourable difference in the conditional constants for the calcium and magnesium complexes, EGTA was used as titrant. Even so, positive errors were obtained at Ca : Mg ratios <4 : 1. The interference of Al(III), Fe(III) and Ti(IV) was eliminated by masking with 10 ml of 20% triethanolamine solution.

It was found that 0·44 mg of oxalate, 4·5 mg of tartrate and 80 mg of phosphate did not interfere in titration of 200 µg of calcium. In titration of >200 µg of calcium, addition of 80 mg of phosphate caused a slight precipitate, but this disappeared in the course of the titration if this was done slowly. For a sample of 2 mg of calcium 140 mg of phosphate did not interfere and the addition of 10 mg of phosphate did not precipitate calcium at all. The results are given in Table 2.

Spectrophotometric titration

Introduce the solution to be titrated into a 30-ml cell, add 1–1·5 ml of $10^{-4}M$ arsenazo III and 5–15 ml of buffer solution at pH 9·0 ± 0·2. Stir the mixture and measure the absorbance at 650nm after each addition of titrant. Plot the graph in the usual way.

Typical results are given in Tables 3 and 4.

The results in Tables 1 and 3 indicate that the proposed method has good sensitivity and accuracy. The method was applied to a wide concentration range of calcium, including concentrations that are usually determined spectrophotometrically. It was also found (Table 2) that phosphate does not interfere considerably.

Table 2. Interference of ions
(For 202 μg of Ca the theoretical consumption of $1·41 \times 10^{-3} M$ EGTA is 0·357 ml and for 404 μg it is 0·714 ml; 3 or 4 titrations were done in each case)

Calcium taken, μg	Diverse ions	Concentration tested (upper limit), *mg*	Average $5 \times 10^{-3} M$ EDTA or $1·41 \times 10^{-3} M$ EGTA consumed, *ml*	
			EDTA	EGTA
202	Mg(II)	0·050	—	0·375 ± 0·010
404	Mg(II)	0·135	—	0·740 ± 0·010
404	Fe(III)	0·45	2·03 ± 0·02	—
404	Ti(IV)	0·88	2·02 ± 0·015	—
404	Al(III)	4·0	2·01 ± 0·005	—
202	$C_2O_4^{2-}$	0·44	0·995 ± 0·015	—
202	$C_4H_4O_6^{2-}$	4·5	1·010 ± 0·01	—
202	PO_4^{3-}	80	1·005 ± 0·005	—

Table 3. Spectrophotometric complexometric titration of calcium with arsenazo III as indicator

Calcium taken, μg	EDTA, *M*	No. of titns	EDTA consumed	
			Average observed, *ml*	Theoretical, *ml*
20	$1·25 \times 10^{-3}$	3	0·402 ± 0·005	0·403
202	$5·00 \times 10^{-3}$	3	1·005 ± 0·000	1·007
4040	$9·38 \times 10^{-2}$	4	1·080 ± 0·005	1·074
8080	$9·38 \times 10^{-2}$	2	2·14 ± 0·00	2·148
$12·12 \times 10^3$	$9·38 \times 10^{-2}$	3	3·195 ± 0·005	3·222

Table 4. Spectrophotometric complexometric titration of calcium in the presence of magnesium

Calcium taken, μg	Magnesium taken, *mg*	EGTA, *M*	No. of titns.	EGTA consumed	
				Average observed, *ml*	Theoretical, *ml*
202	1·25	$1·41 \times 10^{-2}$	3	0·365 ± 0·020	0·357
404	5·0	$1·41 \times 10^{-2}$	4	0·710 ± 0·005	0·714
2020	1·5	$1·41 \times 10^{-1}$	3	0·350 ± 0·010	0·357
4040	7·5	$1·41 \times 10^{-1}$	3	0·730 ± 0·000	0·714

For titration of calcium in the presence of magnesium (Table 4) the lowest Ca : Mg ratio for accurate results was established experimentally for each amount of calcium. This ratio depends mainly on the magnitude of the break in the titration curve. In the experiments shown in Table 4 the absorbance jump was at least 0·100.

The use of arsenazo III as metallochromic indicator in complexometric titration of calcium requires the estimation of the precision in the determination of ΔpM or the titration error. For this purpose the conditional stability constant of calcium–arsenazo III complex was determined.

Determination of the conditional stability constant

The graphical method of Frank and Oswald[6] was used to determine the conditional stability constant of calcium–arsenazo III complex (MI) at pH 8 and $\mu = 0{\cdot}1$ From this value, however, we could not calculate the conditional constant at pH 9 using only the value of $\alpha_{I(H)}$ of arsenazo III. For this purpose the value of $\alpha_{MI(H)}$ is also necessary.[7]

Since we did not have this information, the value of the constant at pH 9 was determined directly by the same method. The values found were as follows.

For pH 8, $\log K_{CaI} = 4{\cdot}9 \pm 0{\cdot}2$ (graphically $\log K_{CaI} = 4{\cdot}8$)

For pH 9, $\log K_{CaI} = 5{\cdot}3 \pm 0{\cdot}2$ (graphically $\log K_{CaI} = 5{\cdot}3$)

These values were used for the calculation of the titration error by means of the following equation.[2]

$$\text{Titration error, \%} = \frac{460\,.\,\Delta pM}{([M]_t\,.\,K_{M'Y'})^{1/2}} \tag{1}$$

When $10^{-2}M$ calcium is titrated with EDTA at pH 8 the error can be easily calculated. We have:

$$\log K_{CaY'} = 8{\cdot}4;\ \log K_{CaI} = 4{\cdot}9;\ pM_{eq} = 5{\cdot}2;\ \Delta pM = 0{\cdot}3$$

Then the error = 0·09 ~ 0·1%.

For the titration of $10^{-3}M$ calcium, ΔpM is 0·8 and the error calculated is 0·7% although the use of the error equation is less correct for these conditions. The same error was obtained from Ringbom's diagram.[8]

When the spectrophotometric method was used an error at about ±0·1 pM unit was obtained, even for the titration of $10^{-3}M$ calcium.

The sensitivity of photometric pM measurement was estimated by Ringbom's method.[8] The expression used was:

$$\frac{\Delta pM}{\Delta T} = -\frac{0{\cdot}188(1 + [M]K_{MI})}{(A - A_{MI}^{max})T[M]K_{MI}} \tag{2}$$

where T is the transmittance, [M] the metal concentration at the end-point and A the absorbance of the solution at the end-point.

For this calculation the titration data (Table 5) for 5 ml of $1{\cdot}007 \times 10^{-3}M$ calcium

Table 5.

EDTA added, *ml*	Absorbance at 650 *nm*	EDTA added, *ml*	Absorbance at 650 *nm*
0	0·508	2·185	0·168
0·940	0·480	2·200	0·114
1·800	0·461	2·230	0·099
2·073	0·436	2·250	0·094
2·120	0·414	2 395	0·084
2·170	0·283		

Addition of 1 drop of $0{\cdot}1M$ EDTA gave $A_I^{max} = 0{\cdot}080$.

Addition of 1 drop of $\sim 1M$ Ca^{2+} gave $A_{MI}^{max} = 0{\cdot}510$.

titrated with $2{\cdot}31 \times 10^{-3}M$ EDTA at pH 8·8, in the presence of 1·5 ml of $9{\cdot}81 \times 10^{-5}M$ arsenazo III were used.

It is necessary also to use the following data: $\log K_{\mathrm{CaY}} = 9$, $[\mathrm{CaY}]_{\mathrm{eq}} \sim 10^{-3{\cdot}5^{-}}M$, $\log K_{\mathrm{CaI'}} = 5{\cdot}3$, $V_{\mathrm{total}} = 18{\cdot}9$ ml.

The calculations gave $\mathrm{pCa}_{\mathrm{eq}} = 6{\cdot}28$; $[\mathrm{Ca}]_{\mathrm{eq}} \,.\, K_{\mathrm{CaI'}} = 0{\cdot}105$.

The absorbance at the end-point was calculated from the equation

$$A_{\mathrm{eq}} = \frac{(A_{\mathrm{I}}^{\max} + A_{\mathrm{MI}}^{\max} \,.\, [\mathrm{M}]_{\mathrm{eq}} \,.\, K_{\mathrm{MI}})}{1 + [\mathrm{M}]_{\mathrm{eq}} \,.\, K_{\mathrm{MI}}} \tag{3}$$

A_{eq} found was 0·121. By interpolation in the data from Table 5 the value $V_{\mathrm{eq}} = 2{\cdot}198$ ml was found.

According to equation (2) $\Delta\mathrm{pCa} = 0{\cdot}067 \sim 0{\cdot}07$. For this value of ΔpCa and $\log C_{\mathrm{Ca}} \,.\, K_{\mathrm{CaY'}} = 5{\cdot}43$ the titration error is ~0·07% from Ringbom's diagram.

The indicator correction was also calculated from the equation:

$$[\mathrm{MI}]_{\mathrm{eq}} = \frac{C_{\mathrm{ind}}(A_{\mathrm{eq}} - A_{\mathrm{I}}^{\max})}{A_{\mathrm{MI}}^{\max} - A_{\mathrm{I}}^{\max}} \tag{4}$$

and found to be $[\mathrm{MI}]_{\mathrm{eq}} = 7{\cdot}4 \times 10^{-7}M$. The volume of EDTA solution corresponding to this correction was 0·006 ml. Then the volume of EDTA used at the equivalence point was 2·204 ml, corresponding to 204 μg of calcium. The same result could be obtained by graphical extrapolation, which is therefore equally valid and more convenient.

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Zusammenfassung—Arsenazo III wird als Metallfarbindikator für Calcium in schwach alkalischem Medium vorgeschlagen. Die visuelle Titration mit EDTA wurde bei pH 8 ausgeführt und 40 μg-12 mg Calcium bestimmt. Die Störung durch einige Ionen wurde in Betracht gezogen; es wurde gefunden, daß Phosphat nicht nennenswert stört. Zur Titration von Calcium in Gegenwart von Magnesium wurde der Endpunkt bei pH 9 spektrophotometrisch nachgewiesen. Zur Abschätzung des Titrationsfehlers wurden die Stabilitätskonstanten des Calcium-Arsenazo III-Komplexes unter den betreffenden Bedingungen ermittelt.

Résumé—On propose l'Arsenazo III comme indicateur métallochrome pour le calcium en milieu légèrement alcalin. Le titrage visuel avec l'EDTA a été réalisé à pH 8 et l'on a dosé 40 μg-12 mg de calcium. On a considéré l'interférence de quelques ions et l'on a trouvé que le phosphate ne gêne pas de manière appréciable. On a utilisé la détection spectrophotométrique du point final pour le titrage du calcium en la présence de magnésium à pH 9. Pour l'estimation de l'erreur de titrage, on a trouvé les constantes de stabilité conditionnelles du complexe calcium-arsenazo III.

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ULTRAMICRO ATOMIC-ABSORPTION SPECTROSCOPY WITH A TUNGSTEN-FILAMENT ATOM-RESERVOIR

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Summary—The detection and measurement of traces of zinc, lead, copper and silver by atomic-absorption spectroscopy with a tungsten-filament atom-reservoir (TFAR), hollow-cathode lamps and limited-field viewing is described. The performance of this atom cell is compared with that of the carbon-filament atom-reservoir for determination of lead. Greater sensitivity and fewer matrix effects are observed with the TFAR system. The lifetime of the tungsten filament is almost indefinite.

The development of ultramicro techniques of atomic-absorption and atomic-fluorescence spectroscopy with a carbon-filament atom-reservoir (CFAR) has been described in several papers from this laboratory[1-11] these techniques have been applied to several practical problems.[10-13] The advantages include the ability to handle very small samples (1–5 μl), high absolute sensitivity and low background signals. Matrix effects, which arise chiefly in the vapour phase above the surface of the filament and almost exclusively from elements that atomize at similar temperatures to the analyte element,[3,4] may be reduced by limited-field viewing close to the surface of the filament before condensation reactions set in to reduce the atomic population of the analyte element.[6,7]

A recent paper by Takeuchi *et al.*[14] describes the determination of Al, Cr, Cu, Fe, Mg and Mn by flameless atomic-absorption measurements, using a tantalum strip which is electrically heated in an enclosed argon atmosphere, and somewhat similar to the original CFAR unit of West and Williams.[1]

Earlier, Donega and Burgess[15] described an absorption chamber which consisted of a tantalum or tungsten sample boat heated electrically in an enclosed inert atmosphere maintained at any desired pressure, usually in the range 1–300 torr. The boat was supported in a 50 mm i.d. quartz tube with quartz windows at each end.

In this communication we describe the determination of traces of Ag, Cu, Pb and Zn by use of an unenclosed tungsten-filament atom-reservoir (TFAR), reporting detection limits, sensitivity and matrix effects, and comparing the relative performance of TFAR and CFAR units on the same apparatus.

EXPERIMENTAL

Apparatus

Atomic-absorption measurements were made with a Jobin-Yvon "Delta" atomic-absorption spectrometer. An Alder and West[3] type of atom-reservoir unit was mounted on the base plate which normally holds the burner unit. The carbon filament normally used in the CFAR was replaced by a cylindrical tungsten filament 60 mm long and 2·2 mm in dia., that had been ground to produce a 1-mm deep recess (~ 2 mm wide) at its centre, in which the 1-μl samples could be located. The presence of the notch also ensured that this position where the sample located was also the hottest point when the filament was electrically heated. The burner-height adjustment mechanism of the spectrometer also allowed the position of the filament to be adjusted in a vertical plane with respect to the beam of the hollow-cathode lamp along the optical axis of the spectrometer. The beam of incident radiation from the hollow-cathode lamp was modulated mechanically at 125 Hz and focused by a system of two silica lenses to form a sharp image *ca* 3 mm in dia. over the centre of the filament. A 20-mm dia. collimator tube was placed centrally in the light-path as close as possible to the tungsten filament. The tube carried a 0·5 or 1-mm horizontal slit at the end nearest to the filament. A third lens placed between the TFAR and the monochromator focused the light onto the entrance slit. The output from the amplifier was presented to the input of a Smith's Instruments "Servoscribe" chart recorder. The gas flow and electrical supplies to the TFAR were as described previously for CFAR units.[3]

Reagents

All reagents were of analytical grade. Water was distilled in glass apparatus and then treated with a cation-exchange resin in the H^+ form. The water thus purified was found to contain no measurable amount of the elements examined. Volumetric flasks used to prepare or contain metal solutions more dilute than 100 ppm were previously treated with a silicone preparation, "Repelcote," as were the Drummond micropipettes used to place the 1-μl samples on the filament. Standard solutions containing less than 100 ppm of the cations were freshly prepared before use to minimize losses due to surface adsorption effects.

Measurement technique

The following sequence was found to give the best sensitivity, detection limit and reproducibility of measurement of atomic-absorption signals with the TFAR unit.

The monochromator was tuned to receive the resonance line of the element being studied and the filament shielding-gas (argon or nitrogen) was allowed to flow at the optimum flow-rate. The aqueous sample (1 μl) was placed in the recess in the filament by means of a Drummond micropipette. The following time-cycle was then followed: the filament was switched on at low power (1·5V), to evaporate the water from the sample slowly without loss due to sputtering. The current was switched off and the voltage was increased to that determined to be optimum for the particular element; the filament current was then turned on again to atomize the sample. This took approximately 2·5 sec, and the absorption peak was recorded on the chart paper, for subsequent measurement. This cycle was repeated at 75-sec intervals. This sequence allowed sufficient time for the filament to cool down before application of the next sample solution. No memory effects were detected for any of the elements studied, at the ppm concentrations usually used in atomic-absorption measurements.

RESULTS AND DISCUSSION

The response times of the amplifier of the Jobin-Yvon Delta spectrometer and the Servoscribe recorder are the usual for a flame spectrometer, but are relatively slow for transient signal measurements. The net result is that as the applied voltage is increased, the peak height increases to a maximum and then decreases with further increase of voltage, because the temperature rise-time of the filament, and therefore, the speed of atomization, increases with increase of voltage until the rate of generation of free atoms exceeds the capability of the electronic circuitry to respond to it. This behaviour is shown in Fig. 1 for fixed amounts of the four elements studied. The absorbance–voltage peak varies from one element to another, depending on the atomization temperature, but also to a limited extent on the amount or concentration of the element.

Figure 2 shows that as the silver atoms come off the filament more quickly at higher voltages they pass out of the light beam before the detection system can fully respond to them. This is evident from curves (*b*) and (*c*) but more particularly from (*a*) where larger amounts of silver are involved and where self-condensation may further lower the population of absorbing atoms. The effect of collimation is shown by curves (*b*) and (*c*). At higher voltages the limited sampling area produced by collimation is filled with a denser atomic population producing a higher signal, but at voltages, <*ca*. 5V, the collimated signals are weaker because atomization is insufficiently fast to fill the sampling area.

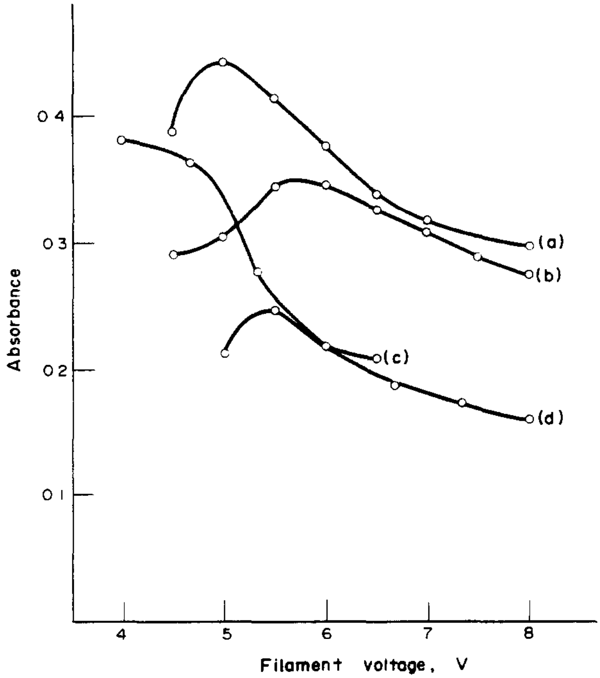

Fig. 1. Variation of absorbance with tungsten filament voltage. (*a*) = 1 ng of lead: (*b*) = 0·5 ng of copper. (*c*) = 0·2 ng of silver; (*d*) = 0·01 ng of zinc.

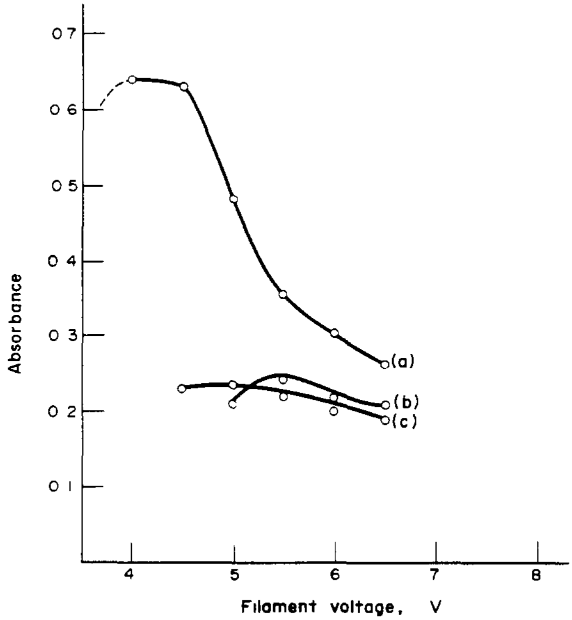

Fig 2 Variation of absorbance with concentration of analyte and with collimation. (*a*) = 1 ng of silver, no collimation. (*b*) = 0·2 ng of silver: 0·5-mm slit and collimation. (*c*) = 0·2 ng of silver, no collimation.

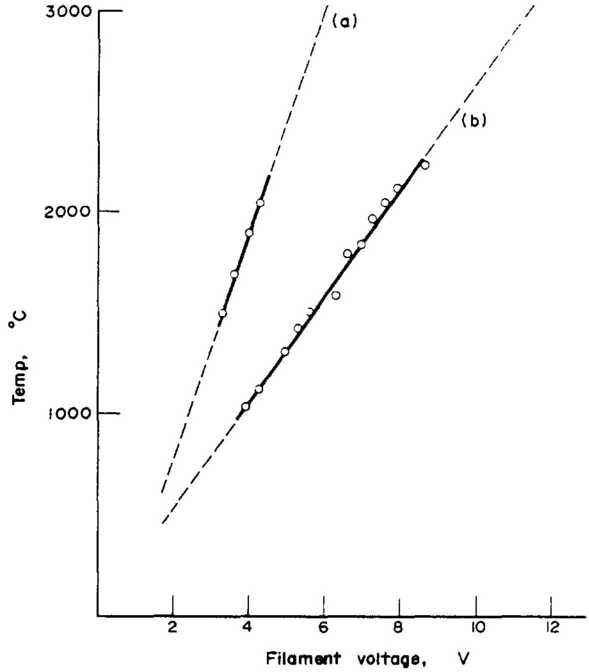

Fig. 3. Equilibrium temperatures.
(*a*) = 2·2-mm tungsten filament; (*b*) = 2-mm carbon filament.

A tungsten filament has a much lower resistance than a carbon filament so requires a considerably lower voltage to reach the same temperature. Figure 3 shows temperature–voltage curves for TFAR and CFAR units (2·2 and 2 mm in dia.), for equilibrium temperatures as measured by an optical pyrometer.

Effect of shielding-gas flow-rate on signal

Figure 4 shows the effect of the shielding-gas flow-rate on the absorbance for the elements examined. Although it is possible to choose an optimum flow-rate in each case, it is clear that small fluctuations have very little effect on the absorption signal. When nitrogen and argon were used immediately after each other, each at its optimum flow-rate, there was no difference between the absorption signals obtained. Some optimized operating parameters for this apparatus are given in Table 1.

Table 1. Operating parameters for AAS of Zn, Pb, Cu, Ag with TFAR

Element	λ, *nm*	Lamp operating Current, *mA*	Monochromator entry slit, *mm*	Filament voltage, *V*	Gas flow-rate, *l./min*
Zn	213·8	4	0·5	4·5	Ar (1·6)
Pb	217·0	6	1·0	5·0	Ar (2), N_2 (3·2)
Cu	324·7	6	0·05	5·5	N_2 (3·2)
Ag	328·1	10	0·04	5·5	N_2 (3·7)

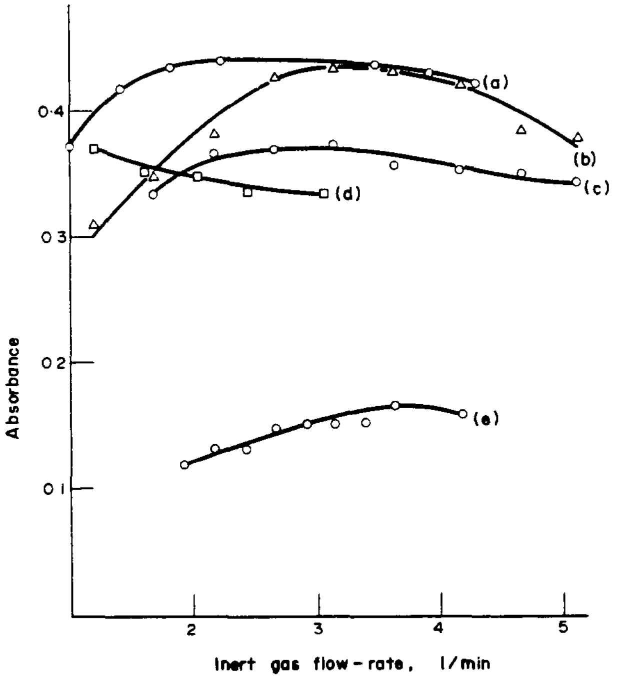

Fig. 4. Variation of absorbance with inert gas flow-rate.
(*a*) = 1 ng of lead (argon); (*b*) = 1 ng of copper (nitrogen); (*c*) = 1 ng of lead (nitrogen); (*d*) = 0·01 ng of zinc (argon); (*e*) = 0·2 ng of silver (nitrogen).

Detection limits and sensitivity

Detection limits (signal : noise = 2 : 1) and sensitivity (1% absorbance) for the TFAR under optimized conditions are quoted in Table 2. Figure 5 shows typical calibration curves for the four elements studied. The non-linearity in some of these curves may be partly, if not entirely, associated with the slow response rate of the amplifier/recorder system (~0·8 sec full-scale recorder deflection) with respect to the more transient signals (~0·05 sec half-peak width). Better sensitivities could obviously be achieved with more rapid-response electronics, and more particularly, with integration.

Comparison with CFAR

The performances of the two filament materials were compared by using each in turn with lead as the test element. At the optimum voltages, which were found to be 5V for tungsten and 6V for carbon, the absorbances shown in Table 3 were obtained for 1 ppm of lead at corresponding filament positions for both materials.

Table 2 Detection limits and sensitivities for TFAR

Element line, *nm*	Detection limit, *ppm*	*pg*	Sensitivity (1% absorption) *ppm*	*pg*
Zn 213·8	0·00028	0·28	0·00078	0·78
Pb 217·0	0·02	20	0·014	14
Cu 324·7	0·006	6	0·0075	7·5
Ag 328·1	0·006	6	0·0044	4·4

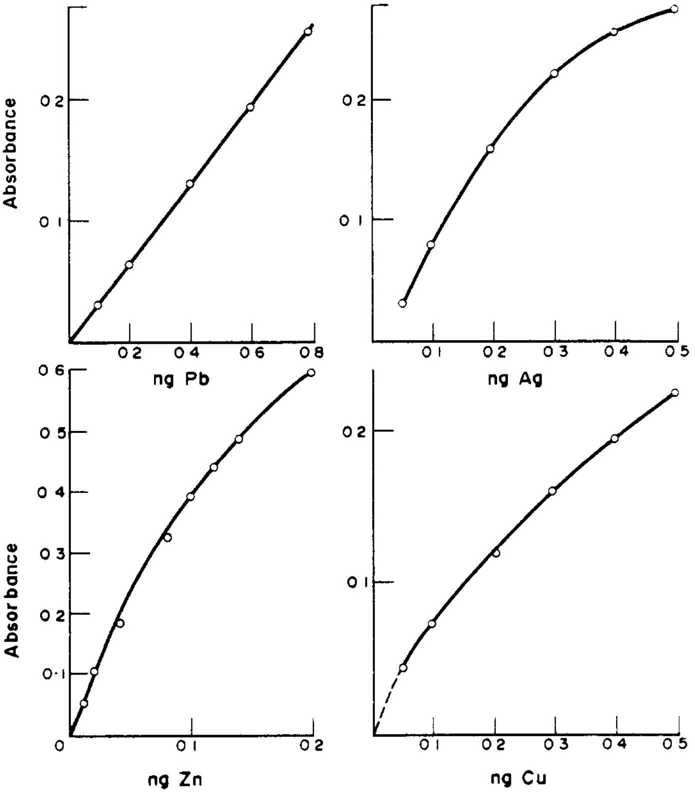

Fig. 5. Analytical calibration graphs.

For positions from *a* to *e* the filament height increased in 1/6-mm steps. Position *b* corresponded to grazing incidence of the light beam. At position *e* the depression in the filament lay within the horizontal optical plane.

It can be seen from Table 3 that the signal from the tungsten filament was about 50% higher than that from the carbon filament at the highest filament position. At higher positions the noise on the base-line was intolerable owing to radiation from the filament in the light path. The reproducibilities were comparable for each filament. Standard deviations were generally less than 2% of the signal.

Table 3. Absorbance for 1 ng of lead at 217 nm

Filament height position	CFAR absorbance	TFAR absorbance
a	0·17	0·22
*b**	0·24	0·28
c	0·26	0·36
d	0·27	0·41
e†	0·27	0·41

* Grazing incidence.

† Totally in light path. Signal very noisy if filament higher than this.

Table 4. Comparison of potential interferences in determination of lead (1 ppm) with TFAR and CFAR cells

Interfering element, 1 *mg*	% Suppression, CFAR	% Suppression, TFAR
Ag^+	20	0
Bi^{3+}	45	0
Co^{2+}	35	29
K^+	30	0
Na^+	12	0
HCl	30	0

As well as improving sensitivity, the TFAR seemed to remove matrix effects or reduce them very considerably. Table 4 shows the effect on the absorbance of 1 ppm of lead of 1000 ppm of six interferents which cause problems with the CFAR technique. All measurements were made at the highest possible filament position.

Since the tungsten filament is stronger, its lifetime is much longer than that of a carbon filament; the latter has to be changed every 100–200 shots, depending on the voltage used, and often fractures from thermal shock, whereas a tungsten filament will last indefinitely if treated correctly. Electrical contact is improved because the tungsten filament can be clamped to the electrodes much more tightly.

Because of the lower electrical resistance, higher currents flow in the TFAR than in the CFAR. Figure 6 shows a plot of current *vs.* voltage in the transformer primary. However, the same power supply has been used successfully for both atom cells throughout this work. The use of a tungsten filament does not, therefore, necessitate the use of more expensive apparatus for handling and switching current.

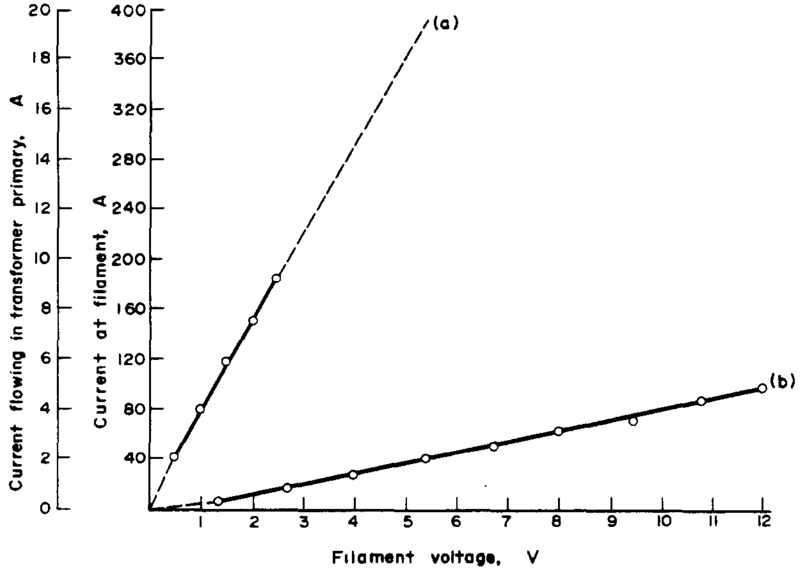

Fig. 6. Filament current/voltage characteristics.
(*a*) – 2·2-mm tungsten; (*b*) – 2-mm carbon.

Table 5. Comparison of interferences for copper, with TFAR and CFAR

Interfering element, *M*	Ratio (M : Cu) *w/w*	% Suppression TFAR, 0·5 *ppm* Cu	% Suppression CFAR[6] 1 *ppm* Cu	% Suppression CFAR[6] 0·5 *ppm* Cu
Ca^{2+}	1000	0	25	0
Cr^{3+}	1000	0	50	20
Fe^{2+}	1000	10	55	10
K^{+}	1000	12	25	0
Mn^{2+}	1000	0	60	40
H_2SO_4	5000	0	not reported	—
HCl	5000	20	not reported	—

Further interference studies

Table 5 shows the effect of various interferents on the absorbance for 0·5 ppm of copper with the TFAR, and that previously reported for the CFAR.[6] With the CFAR some of the interferences could be reduced by using a smaller concentration of analyte. It seems, therefore, that the absolute amount of interferent is the determining factor rather than its ratio to the amount of analyte. This is consistent with the interferences occurring in the gas phase.[4]

The TFAR may be seen, therefore, as a very useful alternative to the CFAR for use in analytical spectroscopy. At least for the elements examined so far it possesses all the good characteristics of the CFAR and complements these with many of its own, *viz.* its very long lifetime, much lower tendency to show matrix effects, and somewhat greater sensitivity.

The behaviour of other elements will be reported at a later stage when it may be possible to comment more definitely on the reasons for increased sensitivity and greater freedom from matrix interferences. It appears possible that the increased sensitivity may be due to the fact that added solutions do not penetrate to any appreciable extent within a tungsten filament as they do in a carbon filament. Thus the sample, when dried out, exists in a more concentrated form on the surface and therefore produces a denser cloud of atomic species upon atomization. It is more difficult to account yet for the apparent lower susceptibility to matrix effects. This may possibly be due to the greater heat dissipation of the TFAR and its greater ability to transfer heat to the atoms in the gas phase and thus minimize the condensation phenomena which give rise to matrix effects in filament atom-reservoir spectroscopy, but this is the subject of further investigation.

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Zusammenfassung—Nachweis und Messung von Spuren Zink, Blei, Kupfer und Silber durch Atomabsorptionsspektrometrie mit einem Wolframfaden-Atomreservoir (TFAR), Hohlkathodenlampen und Ausnutzung eines begrenzten Gesichtsfeldes wird beschrieben. Das Verhalten dieser Atomzelle wird mit dem des Kohlefaden-Atomreservoirs zur Bleibestimmung verglichen. Mit dem TFAR-System beobachtet man größere. Empfindlichkeit und geringere Matrixeffekte. Die Lebensdauer des Wolframfadens ist fast unbegrenzt.

Résumé—On décrit la détection et la mesure de traces de zinc, plomb, cuivre et argent par spectroscopie d'absorption atomique avec un réservoir d'atomes à filament de tungstène (TFAR), des lampes à cathode creuse et une visée à champ limité. On compare la performance de cette cellule d'atomes à celle du réservoir d'atomes à filament de carbone pour le dosage du plomb. On observe une plus grande sensibilité et moins d'effets de matrice avec le système TFAR. La durée de vie du filament de tungstène est presque indéfinie.

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RAPID DESTRUCTION OF PLANT MATERIAL WITH CONCENTRATED NITRIC ACID VAPOUR (VAPOUR PHASE OXIDATION)

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Summary—Concentrated nitric acid vapour is used in a simple rapid method for the destruction of organic matter in plant tissue before analysis for trace elements. About 90% of the organic matter is destroyed by the nitric acid vapour within 5-6 min and destruction is then completed by the addition of perchloric acid. The method gives zero or low blank values and has comparable precision and accuracy to conventional acid digestion methods.

Analysis of biological materials for metallic elements generally requires prior treatment of the material in order to destroy the organic matter present. Some direct wet extraction procedures have been reported[1-4] but these are either too slow, not quantitative, or suffer from other disadvantages. The most commonly used methods for destruction of the organic material are acid digestion and dry ashing. Acid digestion involves heating the organic material in the presence of concentrated oxidizing acids. It is often time-consuming and can have the problem of high blank values because of the quantities of reagents that need to be added. Dry ashing destroys the organic matter by heating the material at 400-700° in a muffle furnace, where atmospheric oxygen is used as the oxidizing agent. It is not only time-consuming but some elements can be lost.

There are a number of variations of the acid digestion procedure, involving, for example, different acid mixtures and preparations of acids, addition of hydrogen peroxide, *etc.* Smith *et al.*[5] list six acid digestion procedures for the destruction of human tissue. The Analytical Methods Committee of the Society of Analytical Chemistry[6] recommend four different methods of carrying out the initial stages of the decomposition, involving various acid mixtures, depending on the reactivity of the material. The Committee state that their methods of destruction are suitable for most organic materials, including dyestuffs, medicinal compounds, rubber chemicals, synthetic polymers, biological material and foodstuffs. Harrison and Andre[7] have added sodium molybdate as a catalyst to the nitric/perchloric/sulphuric acid digestion mixture in order to shorten the time required for complete destruction of the organic material. Gorsuch,[8] in a very thorough investigation, has discussed the relative merits of both wet and dry oxidation procedures for a large number of elements.

Gorsuch[9] has also commented on the potential of destroying organic matter in an atmosphere of nitric acid vapour. Rinkis[10] has used a stream of nitric acid vapour to complete the oxidation of carbonized plant samples. We have examined a similar system as a means of destroying the organic matter present in plant material without any prior treatment. It was found that "vapour phase oxidation" (VPO) with nitric acid was extremely efficient, destroying up to 90% of the organic material in 5–6 min. At this stage an addition of perchloric acid ensured speedy and complete oxidation. Moreover, the presence of nitric acid during the final perchloric acid oxidation eliminated any explosion hazard. The method gave very low blank values for impurity elements.

Comparison of the relative standard deviation and accuracy obtained by use of VPO with that for destruction by nitric/perchloric acid in a Kjeldahl flask (hereafter called the Kjeldahl digestion or procedure) showed that the two methods had comparable precision and accuracy. At the same time the VPO procedure has the same advantages as the Kjeldahl digestion, when compared with dry ashing. These are:[11] the low temperature required, the freedom from loss of trace elements by retention on solid material in the system, and the simplicity and low cost of the equipment used.

EXPERIMENTAL

Apparatus and reagents

Nitric acid vapour was generated by dropping concentrated (sp. gr. 1·4) nitric acid into a reservoir of 100 ml of nitric/sulphuric acid mixture (1 : 1) at 152°. The nitric acid vapour distils at 122°. This corresponds to a vapour consisting of 67% nitric acid.[12] The distillation temperature remains constant throughout the entire vapour phase oxidation.

The all-glass apparatus used is illustrated in Fig. 1. The 1 : 1 nitric/sulphuric mixture was contained in a 250-ml round-bottomed flask heated by an electrical heating mantle. The flask was fitted with two "Quickfit" joints, one carrying a dropping funnel containing the concentrated nitric acid, the other a "Quickfit" splash-head. A "gas-finger" was fitted to the other end of the splash-head and this introduced the nitric acid vapour onto the sample being digested, which was contained in a "Quickfit" tube with side-arm, mated to the gas-finger. The gas-finger extended 5·5 cm into this reaction tube. A "Quickfit" pouring lip was attached to the reaction test tube for quantitative transfer of the digest solution to the volumetric flask.

During the entire digestion period the tube was heated by an infrared heating lamp. This prevented excessive condensation of the vapour before it reached the sample to be digested.

The side-arm of the reaction tube allowed excess of nitric acid vapour to escape. The reaction tube was 14 cm long and 4·5 mm o.d., fitted with a B19 joint.

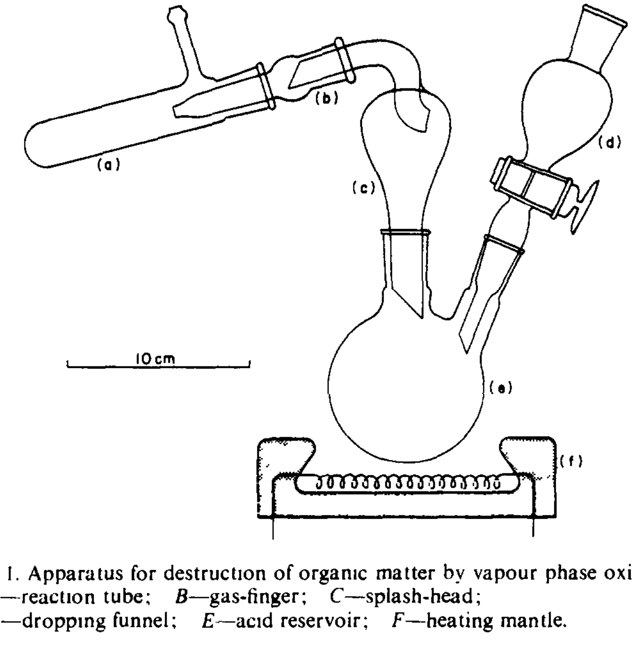

Fig. 1. Apparatus for destruction of organic matter by vapour phase oxidation.
A—reaction tube; *B*—gas-finger; *C*—splash-head;
D—dropping funnel; *E*—acid reservoir; *F*—heating mantle.

The perchloric acid digestion was carried out by removing the reaction tube from the gas-finger, adding the perchloric acid, and placing the tube in a cylindrical furnace at 280°. The furnace was constructed by winding alternate layers of 3·84 ohm/m nichrome resistance wire and asbestos tape around a Pyrex cylinder to give a final resistance of 15–16 ohm. The furnace was connected to a 32-V step-down transformer operated from a 240-V mains supply and the temperature adjusted by a Variac voltage controller connected in series.

The powdered plant samples were pelleted before digestion, to prevent charring of the material during the initial stages of the nitric acid vapour oxidation. Charring occurred with powdered samples because of a combination of two factors: the large surface area of the powdered plant material and the rapid oxidation by the nitric acid vapour and the accompanying large heat of reaction. Pelleting the plant material reduced the surface area available for reaction with the nitric acid vapour

The gas-finger was positioned so that it did not come in contact with any froth produced during the nitric acid digestion. Consequently it could be used for successive samples, and there has so far been no evidence of cross-contamination.

The rate at which nitric acid was dropped onto the nitric/sulphuric reservoir was optimized at 5–6 ml/min. A slower rate does not give a sufficient flow of nitric vapour to digest the sample in 5 min. A faster rate does not markedly increase the digestion time and can be wasteful of nitric acid.

Doubly distilled demineralized water was used throughout. Analytical-reagent grade nitric and sulphuric acids were used for VPO. Doubly distilled analytical grade nitric acid was used for the Kjeldahl digestions. Analytical grade perchloric acid (70–72%) was used for both procedures. All glassware was cleaned in a 1 : 1 mixture of analytical grade nitric and sulphuric acids, left standing overnight, and finally rinsed with distilled water.

Procedure

Plant samples were washed[13] and "biologically killed" immediately following collection from the field, by heating in a forced-draught air-oven at 60° for 24 hr. The plants could then be stored until required. Before analysis the plant was powdered to pass a 40-mesh nylon sieve, with a 5-in. Christy Norris Junior Laboratory Mill. As the working surfaces of this mill are constructed of a special alloy steel, slight metallic contamination of the plant sample resulted. However, as subsamples for both the VPO and Kjeldahl methods were obtained from the same sample, the contamination from this and the subsequent mixing would have been much the same for both procedures. The powdered material was then rolled in a stoppered glass container for 6–8 hr to ensure homogeneity. Homogeneity was tested by dry-ashing 0·5-g samples of the powder and weighing the ash. For the VPO method the powdered sample was compressed at 14×10^5 kg/m^2 by means of a hydraulic press, into a pellet 1·5 cm in dia. and 4 mm thick. The plant powder was analysed directly by the acid Kjeldahl method. The dry weight of both pellet and powder was obtained after heating at 98° for 24 hr. Lack of contamination from the press is evidenced by the good agreement between the VPO and Kjeldahl results.

A few drops of doubly distilled kerosene[11] were added to each pellet after it was placed in the reaction tube. This was to ensure that excessive frothing did not occur during the initial nitric acid digestion period.

After the nitric acid digestion, 2 ml of perchloric acid were added and the sample was heated to perchloric acid fumes, indicating that oxidation of the organic matter was completed. The reaction tube contents were then washed into a 25-ml standard flask with doubly distilled water and the sample made up to volume and analysed by atomic absorption.

RESULTS AND DISCUSSION

The procedure described offers an alternative to the Kjeldahl digestion and has the advantages of zero or extremely low blank values and a shorter digestion period. Low blanks were obtained because distilled nitric acid vapour was the main oxidant. Analytical reagent grade nitric acid gave zero blank values for all metals studied, but it was necessary to doubly distil the acid for use directly in the Kjeldahl method.

Perchloric acid was added directly to the sample in the VPO and Kjeldahl procedures and analytical grade acid was found to be satisfactory for both.

A feature of the VPO method is the significant reduction in time required for complete destruction of the organic material. The conventional Kjeldahl procedure with 10 ml of nitric acid for 0·5 g of plant sample usually requires 30–45 min of moderate heating before the nitric acid has oxidized most of the sample and perchloric acid can safely be added, but with the VPO method the main oxidation is complete within 5–6 min.

Further time is saved during the final stage of digestion with heating to fumes of perchloric acid, because there are only 3–4 ml of nitric acid in the reaction tube to be evaporated instead of the 10 ml in the Kjeldahl procedure.

The total digestion times are therefore: VPO 30–45 min; Kjeldahl 60–90 min. However, for the VPO method an individual furnace is needed for each reaction tube, but this need not be a disadvantage, as three furnaces can be run from one 32-V transformer. Using only five furnaces, a total period of 2 hr was necessary to have 10 samples digested by VPO and ready for analysis.

One of the advantages of the Kjeldahl method is the refluxing of the acids within the long neck of the flask, which ensures that all the material present in the flask is digested. Although this reflux action does not occur to the same extent in the reaction tube, of the sides of the tube were still effectively washed, partly by reflux when in the furnace, and partly by condensation of nitric acid vapour during the digestion stage.

It can be seen from the results listed in Tables 1–3 that the precision and accuracy of the results obtained by the VPO method compare favourably with those of results obtained by the Kjeldahl procedure.

The precision of the VPO procedure is illustrated in Tables 2 and 3. Those cases in which the relative standard deviation (RSD) is greater than 8% are generally attributable to the low concentrations of the metal found in the plant. This is well illustrated by comparison of the RSD for copper in *Eucalyptus blakelyi* and *Lycimum feracissimum* (Table 3). Both determinations have nearly equal standard deviations but the large difference in copper concentration results in different RSD values.

Rapid methods have been described for the destruction of organic matter by use of mixtures of sulphuric acid and 50% hydrogen peroxide[17–19] or of sulphuric and perchloric acids and sodium molybdate.[7,20] Digestion times of 10 min or less have been claimed for destruction of plant materials, and although VPO cannot match this rate for large samples, it does offer the advantage that the final solutions are relatively free from interfering substances. Sulphuric acid methods suffer from the disadvantage that sulphate ions interfere in atomic-absorption spectrometry[7,11] and that precipitation of alkaline earth metal sulphates can also carry down iron, lead and manganese.[8,11] The use of sodium molybdate is clearly unsuitable if sodium or molybdenum is to be determined, and the high salt content arising from its use may cause some solubility products to be exceeded, with attendant risk of loss by precipitation.

Table 1 Analysis of standard reference materials after vapour phase oxidation

	Mn, *ppm**	Cu, *ppm*	Fe, *ppm*	Zn, *ppm*
(a) N.B.S. Standard Reference Material 1571 [Orchard leaves][14]				
Published	91 ± 4	12 ± 1[12 ± 2][15]	300 ± 20[278 ± 43][15]	25 ± 3[28 ± 3][15]
Vapour Phase Oxidation	96·8 ± 3·6†	13·1 ± 0·6	272 ± 16	23·5 ± 1·8
(b) Kale[16]				
Published	14·9 ± 1·8	4·81 ± 0·74	119·5 ± 19·5	31·88 ± 4·82
Vapour Phase Oxidation	14·9 ± 0·8†	6·4 ± 0·6	119·3 ± 8·4	32·4 ± 2·3

* Results are given as parts per million in the dried plant material.

† The indicated limits are equal to 2 standard deviations for three replicate analyses.

Table 2. Analysis of various plant species after vapour phase oxidation, and comparison with acid Kjeldahl digestion (AKD)

	Acacia doratoxylon		*Acacia melanoxylon*		*Anacardiacae Schinus molle*	
	VPO	AKD	VPO	AKD	VPO	AKD
Zinc						
Mean, *ppm**	27·6	27·2	123·3	129·8	173·8	173·7
SD, *ppm*†	1·3	1·9	3·3	4·2	3·5	2·0
RSD, %§	4·7	6·8	3·1	3·2	2·03	1·2
Copper						
Mean, *ppm*	52·1	74·0	10·5	10·0	28·1	23·1
SD, *ppm*	3·9	19·6	1·1	0·9	5·3	1·9
RSD, %	7·6	26·5	12·9	9·1	18·8	8·1
Manganese						
Mean, *ppm*	12·0	12·5	145·0	147·8	313·2	309·6
SD, *ppm*	0·52	2·0	2·4	3·7	6·1	2·6
RSD, %	4·3	16·2	1·2	2·5	2·0	0·8
Iron						
Mean, *ppm*	160·7	161·6	59·1	64·8	358·4	322·0
SD, *ppm*	14·5	7·9	4·7	5·1	7·7	6·5
RSD, %	9·0	4·9	12·5	7·9	2·2	2·0

	Eucalyptus manniferra		*Eucalyptus blakelyi*		*Lycimum feracissimum*	
	VPO	AKD	VPO	AKD	VPO	AKD
Zinc						
Mean, *ppm*	26·5	27·2	21·3	23·4	71·9	72·7
SD, *ppm*	1·5	1·1	0·6	1·7	1·1	2·7
RSD, %	5·5	4·2	2·6	7·4	1·5	4·3
Copper						
Mean, *ppm*	6·4	6·1	9·4	8·9	84·6	84·2
SD, *ppm*	0·95	1·4	1·9	2·3	1·6	3·6
RSD, %	11·7	22·3	19·7	25·6	1·9	5·4
Manganese						
Mean, *ppm*	335·5	366·3	664·6	615·2	69·8	68·2
SD, *ppm*	9·4	7·4	10·8	10·4	1·3	2·8
RSD, %	2·8	2·0	1·6	1·7	1·9	3·1
Iron						
Mean, *ppm*	115·0	121·3	88·3	98·6		
SD, *ppm*	49·1	49·6	10·8	15·0		
RSD, %	42·7	40·9	12·2	15·2		

Results were derived from 15 separate determinations.

* Results are given as parts per million in the dried plant material.

† Standard deviation.

§ Relative standard deviation.

Table 3. Analysis of *Lycium feracissimum* after vapour phase oxidation

	1	2	3	4	5	6	7	8
Zinc								
Mean, *ppm**	70·9	70·4	71·0	68·4	69·1	70·0	71·9	72·0
SD, *ppm*	3·5	4·1	4·0	5·0	2·7	3·6	1·1	1·7
RSD, %	5·6	6·7	5·7	7·3	4·0	5·1	1·5	2·4
Manganese								
Mean, *ppm*	63·2	62·9	67·0	66·4	66·8	67·7	69·8	67·9
SD, *ppm*	2·6	4·4	1·4	2·2	2.1	2·2	1·3	1·6
RSD, %	3·1	5·2	2·1	3·3	3·2	3·2	1·9	2·3
Copper								
Mean, *ppm*	81·3	81·9	85·0	84·5	91·7	90·1	84·6	84·4
SD, *ppm*	1·7	1·9	3·1	3·8	3·1	2·1	1·6	0·7
RSD, %	2·7	2·9	3·6	4·5	3·3	2·3	1·9	0·9

Each mean involved of 10 separate determinations giving a total of 80 determinations for each element.

* Results are given as parts per million in the dried plant material.

VPO clearly has potential as a means of rapid destruction of organic material when the blank value must be practically zero. Thus Sanui[21] has described an apparatus for oxidizing biological samples with activated oxygen, in which rat liver cell microsomes can be ashed, with a negligible blank. The ashing time required, however, can be anything from 2 to 30 hr depending on the nature of the sample and how much of it is exposed to the oxygen. VPO should reduce the ashing time considerably and give comparable blanks.

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Zusammenfassung—In einer einfachen Schnellmethode zur Zerstörung von organischem Material in Pflanzengewebe vor der Analyse auf Spurenelemente wird der Dampf von konzentrierter Salpetersäure verwendet. Innerhalb 5–6 min werden etwa 90% der organischen Substanz durch den Salpetersäuredampf zerstört; der Abbau wird dann durch die Zugabe von Überchlorsäure zu Ende geführt. Die Methode gibt gar keine oder niedrige Blindwerte und bietet vergleichbare Genauigkeit und Richtigkeit wie übliche Methoden des Säureaufschlusses.

Résumé—On utilise la vapeur d'acide nitrique concentré dans une méthode simple et rapide pour la destruction de la matière organique dans les tissus végétaux avant analyse d'éléments à l'état de traces. Environ 90% de la matière organique sont détruits par la vapeur d'acide nitrique en 5–6 mn et la destruction est alors complétée par l'addition d'acide perchlorique. La méthode donne des valeurs de témoin nulles ou faibles et a une précision et une fidélité comparables aux méthodes de digestion acide habituelles.

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AUTOMATIC CONTROL OF THE ION-ILLUMINATION ANGLE IN A SPARK-SOURCE MASS SPECTROMETER

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Summary—Automatic adjustment of only the spark-gap width in a spark-source mass spectrometer does not ensure that optimum conditions of electrode geometry are maintained with respect to the ion-optics system A device has been developed which simultaneously maintains a constant gap width and also a more constant z-axis ion-illumination angle. This is the first development to utilize ion-optics parameters to adjust the sparking electrodes automatically. The system maintains the electrodes in an optimum configuration such that higher and more constant instrument sensitivity is maintained automatically. In addition, a significant improvement in the precision of instrumental response is demonstrated. It appears that relative isotopic abundances can be determined directly by the spark-source method which are comparable to those obtained in some cases by surface ionization or by electron bombardment. Results are given that support this contention.

The spark-source mass spectrometer is an extremely useful analytical tool because of its ability to provide semiquantitative assays for essentially all elements with very high detection sensitivity. Significant improvements[1] continue to be made in the overall technique. One of these improvements was the development of a method of maintaining, automatically, a spark *via* continuous adjustment of the spark-gap width[2] which was originally described at the 1969 ASTM Committee E14 on Mass Spectrometry conference in Dallas, Texas.[3] Others have since developed different techniques for automatic gap-width control.[4]

This paper describes a new ion-source development in which a constant spark-gap width or voltage is maintained simultaneously with a more constant z-axis ion-illumination angle for the ion-optics system. This is the first development to utilize ion-optics parameters to adjust the sparking electrodes automatically. Exploratory experiments indicate that ion-illumination angle control along with spark-gap control provides significant improvement in the maintenance of optimum spark-electrode geometry. The enhancement of instrument sensitivity and measuring precision with this improved ion source will be illustrated.

Basis for operation

Gap sensing. The spark gap is energized by a variable width pulse (3·2–320 μsec) at a 1-MHz alternating high voltage (10–80 kV). The repetition rate of the pulse is also variable (1·0 Hz–3·2 kHz). An electromagnetically coupled pick-up circuit senses the magnitude of the spark-gap voltage, rectifies the signal, and provides a d.c. output voltage which is proportional to the spark-gap width. This d.c. voltage is then used as a reference for automatic adjustment of the gap width *via* an electromechanical balancing system.

Ion-illumination angle sensing. Ions produced in the spark source possess an energy spread of several thousand eV[5] and in this laboratory they are accelerated typically through 24 kV. The magnitude of the refocusing that occurs during ion acceleration is not well known. However, it has been qualitatively established that the ion beam enters the ion-optics system in a manner highly dependent upon the actual location of the spark relative to the bulk shape of the sparking electrodes, the gap width, and the co-ordinates of the ion-optics system.[5]

Ordinarily, spark-electrode shape and gap geometry can be chosen initially for full illumination of the object slit. Although the spark gap can then be automatically maintained, the spark location may soon become less than ideal and may even become "hidden" from the ion-optics system by the electrodes themselves, owing to the erosion of one or both of the electrodes.

Figure 1 is a schematic representation of the x and z axes of the ion-optics system (*i.e.*, the x-axis is axial with the ion beam; the y-axis is along the focusing plane perpendicular to the plane of the figure; the z-axis is parallel to the magnetic field lines). The spark-source electrodes (SS) are shown in an "end-on" configuration in order to give the best concept of the axis in which gap control is maintained. However, the actual configuration of the electrodes with respect to the ion-optics x, y, and z axes is shown in Fig. 2 as a perspective drawing. Further descriptions of the electrodes as well as other instrumental conditions are given in Table 1.

As illustrated in Figs. 1 and 2, the gap-width adjustment is along the z-axis of the instrument's optical system. The conventional means of gap-width adjustment in spark instruments is normally along the y-axis.[6] The particular axis utilized for gap-width control is not always identified in the literature.[4] No attempt is made here to quantify or to argue the relative merits of gap-width adjustment along either axis. However, we would point out that the configuration shown in Figs. 1 and 2 should provide for more

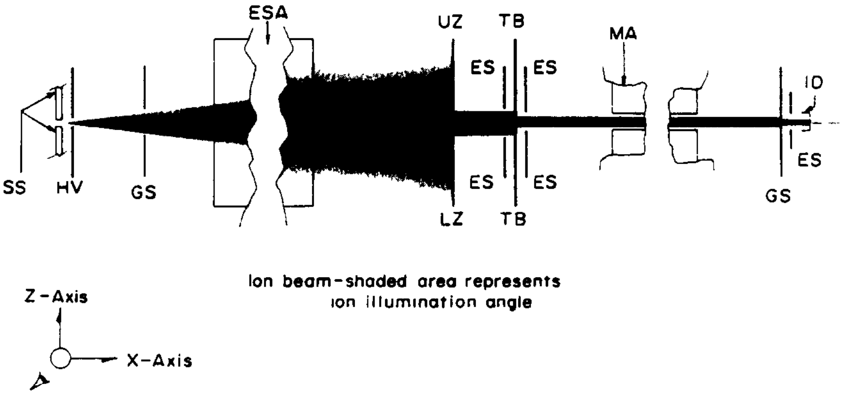

Fig. 1. Schematic diagram of ion-illumination of z-axis beam limiting plates. SS = spark electrodes. HV = high-voltage accelerating plate. GS = grounded slit. ESA = cylindrical electrostatic analyser. LZ = lower z-limit plate. UZ = upper z-limit plate. ES = secondary electron suppressor. TB = total beam monitor. MA = magnetic analyser. ID = ion detector at image. Basic instrument is a Nuclide Corporation model Graf II-2 spark-source mass spectrometer.

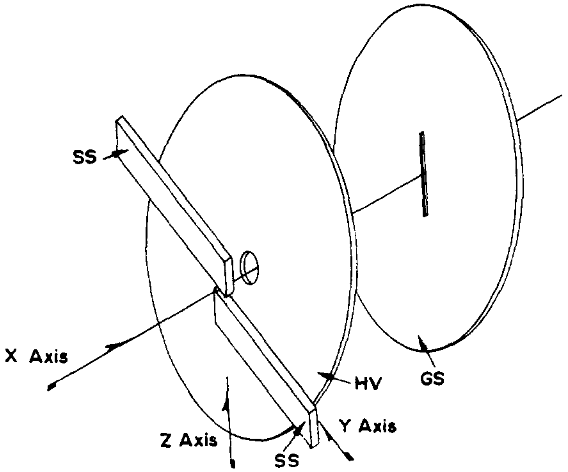

Fig. 2. Perspective view of spark-source electrode configuration relative to the ion-optics axes.

uniform ion-illumination of the y-plane along the particular z-plane of interest, the plane centred within the magnetic field.

Manual adjustment of one electrode along the x-axis is frequently employed to maintain illumination of the object slit. However, a definite effect on the ion beam takes place as one electrode is moved along the x-axis relative to the other electrode. Figure 3 illustrates this effect by means of plots of two parameters which are of interest. The abscissa for both plots is the position (x-axis) of one electrode relative to the other. The

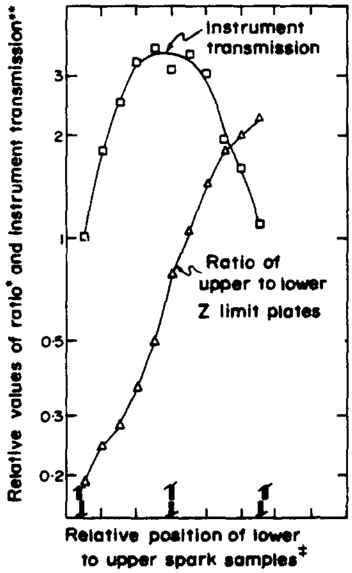

Fig. 3. Plot of data illustrating effect of altered z-axis ion-illumination angle as a function of electrode geometry.

* = ratio of ion currents to upper and lower z-limit plates. ** = relative level of ion current at image. ‡ = extreme and median positions of electrodes indicated above abscissa. Total x-axis translation of lower sample ~ 1·4 mm or ~0·2 mm per division indicated.

ordinate represents the ratio of the ion signal on the upper z-axis limiting plate UZ to the ion signal on the lower z-axis limiting plate, LZ. The relationship between this ratio and the x-axis position of the lower electrode is indicated by triangles. The data clearly demonstrates that the ion-beam density is translated along the z-axis in a monotonic manner, relative to the electrode positions indicated above the abscissa on the figure. This function may be described qualitatively as the "z-axis ion-illumination angle effect." The ion-current ratio of the UZ to the LZ plates will be identified hereafter in this text as the "illumination angle setting."

The second function, plotted as squares on Fig. 2, is really of greater practical interest. The ordinate is now simply relative values of ion current measured at the image in the instrument, normalized to the data point at the leftmost side of the figure ($\equiv$ unity). This second plot indicates that the transmission of ions to the image has a rather broad maximum but decreases sharply at the extremes of the ion-illumination angle setting. Similarly shaped curves are obtained for singly as well as doubly charged ions. These signals from the upper and lower z-axis limiting plates can be utilized for adjustment of one electrode relative to the other such that optimum illumination at the image of the optical system is maintained.

Electromechanical system

Electronic circuitry. An inexpensive and straightforward means of providing an electromechanical balancing system was employed by utilizing appropriate sensing and feedback circuits, and the pen-drive circuits and their servo-motors from electronic recording potentiometers. The electronic block diagram of the system is shown in Fig. 4. The sensing and feedback circuits are conventional. (The complete electronic schematic diagram can be supplied upon request.)

Mechanical system. A two-dimensional, accurately machined rack and pinion device was obtained (military surplus tank or artillery ranger) which provided the means of changing from the rotary movement of the servo-motors to an x-y co-ordinate movement. A three-dimensional schematic diagram of the mechanical system is shown in Fig. 5. A worm and anti-backlash spur-gear combination gives a turns ratio of 340 between the servo-motor and the pinion. One full turn of the pinion produces 2 in. of rack movement. Thus with the lever system employed, (lever arms through the fulcrum are approximately equal) 0·0001 in. of spark electrode movement is obtained for 6° of motor drive. Linear resistors attached to the racks permit presetting of spark electrode positions by providing feedback in a manual-adjust mode.

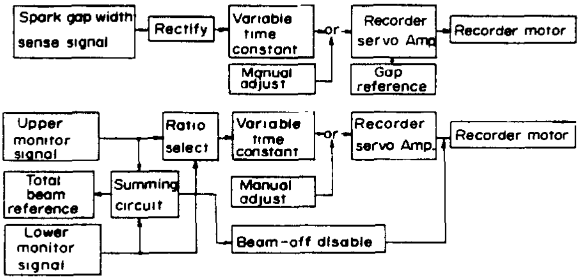

Fig. 4. Block diagram of electronic circuitry for spark-gap and ion-illumination angle control.

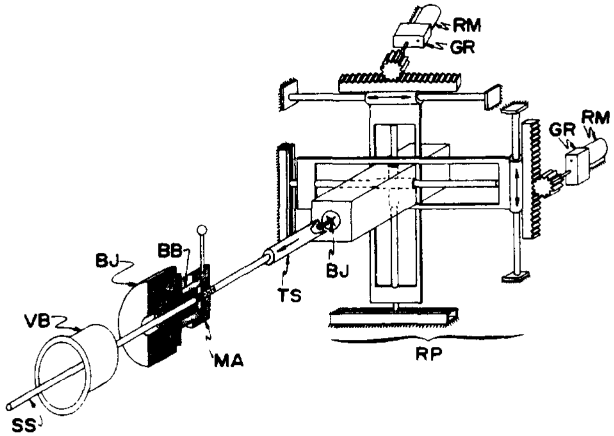

Fig 5. Three-dimensional schematic diagram of mechanical system.
GR = gear reduction. RM = recorder motors. BJ = ball joint. RP = x-z rack and pinion. TS = telescopic slip joint. MA = y-axis manual adjustment. SS = spark electrode holder. VB = vacuum bellows seal. BF = ball-joint fulcrum. BB = ball-bearing.

RESULTS

Figure 6 illustrates the advantage of maintaining a constant ion-illumination angle. Starting at the righthand side of the figure one observes an ion current signal from a spark which is being adjusted automatically only for a constant gap width. The signal is maintained but with a gradual decrease in intensity and a tendency to become more erratic. This is commonly observed when no adjustment is made for non-uniform gap erosion. Eventually the spark could become completely "hidden" from the ion-optics system, causing the ion signal at the image of the instrument to be non-existent.

The automatic illumination angle control was turned on as indicated near the centre of the figure. Immediate movement of the lower spark electrode occurs to bring the spark back to a position where the illumination angle is optimized. During an induction period the ion current begins to increase. After the control has reached the equilibrium or steady-state point as indicated, the ion signal is maintained at the desired level and its fluctuations are less erratic.

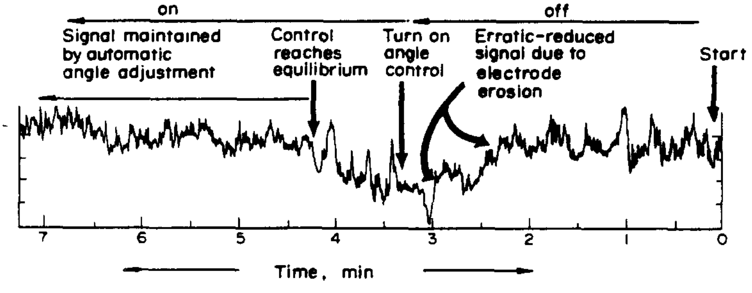

Fig 6 Illustration of improved ion-current stability with automatic control of ion-illumination angle.

Although instrument sensitivity can be maintained at a more constant level as indicated above, a greater concern is the reproducibility of the ratio of the signal at the image of the instrument to the signal at the total beam monitor. Figure 7 is a plot of consecutive image-to-monitor ratio recordings for various ion-illumination angle settings. The experiment should be followed from left to right across the figure. The first ion-illumination angle setting is 0·78 as indicated above the arrow on the left of Fig. 7, but after three readings the setting was changed to 0·51. When this setting was changed the electromechanical system automatically adjusted the spark-electrode geometry to provide a UZ to LZ ion-current signal ratio of 0·51. As this adjustment occurred, sequential measurements of the image to monitor ratio were made. The results of these measurements are shown by the points immediately to the right of the arrow above 0·51. After the automatic control reached equilibrium as evidenced by a steady-state balancing of the x-axis motor, one additional measurement was made. Then the illumination angle was changed to 0·38 and the new image-to-monitor ratios are shown by the points to the right of the arrow. Again, after steady-state balancing of the x-axis motor was noted, one additional measurement was made and then the setting was changed to 0·51. The procedure was repeated with the settings shown above the arrows and the resulting sequential image-to-monitor ratios were plotted to the right of the arrows. The experiment illustrates that variation in the image-to-monitor ion-current ratio will occur if, as the spark-source electrodes erode, the ion-illumination angle is allowed to be altered by irregular electrode erosion. However, automatic control of the angle should permit measurements of the image-to-monitor ratio to be made with good reproducibility.

Table 2 shows results of isotopic abundance measurements with spark-source electrodes of highly purified dysprosium metal. A Faraday cup was used at the image slit and vibrating reed electrometer amplifiers were used at the image and monitor. The equipment and technique for electrical detection with the spark source has been described.[7] In this experiment, currents for doubly-charged ions were measured to permit higher accelerating voltages to be employed. The first column of Table 2 gives the mass of the isotope focused at the image slit. Three readings, shown in the second column, were made for each mass. Each reading consists of an approximately 10-sec measurement of the ratio of the mass-analysed signal to the signal at the total beam monitor. The third and fourth columns contain the average and per cent relative average deviations respectively. The series of seven isotopes was analysed three times with each series being used as a

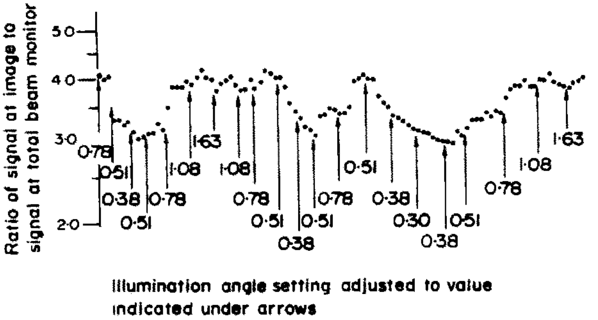

Fig. 7. Effect of illumination angle setting on ratio of signal at image to signal at total beam monitor.

Table 1. Experimental conditions

Instrument:	Model Graf II-2, Nuclide Corporation
Pressure (during sparking):	Analyser chambers ~ 1×10^{-7} torr Ion source chamber ~ 5×10^{-6} torr
Spark-excitation circuit parameters:	Spark voltage ~ 40 kV Circuit frequency ~ 1 MHz Repetition rate = 32 pulses/sec Pulse width = 30 μsec
Spark-electrode geometry:	
Electrode shape:	width = 1 mm height = 3 mm length = 20 mm
Configuration:	overlap = 1 mm spark area = 1 mm^2 gap width ~ 0·2 mm distance from electrodes (SS in Figs. 1, 2) to high-voltage plate (HV in Figs. 1, 2) is ~2 mm.
Electrical detection:	
Individual measurement:	Time duration ~ 10 sec. Monitor charge accumulation = 10^{-9} C
General:	VRE input resistors = 10^9 Ω Image slit width = 0·5 mm Magnetic field ~ 8·5 kG

Table 2. Dysprosium isotopic abundance measurements

Mass	Reading	Average	Relative average deviation, %	Computed isotopic abundance, %
156	1·934 1·988 1·990	1·971	1·2	0·046
158	3·596 3·618 3·491	3·568	1·4	0·084
160	96·96 96·98 98·96	97·63	0·9	2·286
161	789·4 796·4 795·3	793·7	0·4	18·57
162	1076 1079 1107	1087	1·2	25·46
163	1041 1067 1089	1066	1·5	24·96
164	1226 1196 1238	1220	1·3	28·57
156	2·076 2·019 2·058	2·051	1·0	0·048

Table 2—*Continued*

Mass	Reading	Average	Relative average deviation, %	Computed isotopic abundance, %
158	3·612 3·835 3·552	3·666	3·1	0·085
160	99·14 97·89 99·26	98·76	0·6	2·300
161	790·0 811·3 796·6	799·3	1·0	18·61
162	1120 1081 1090	1097	1·4	25·55
163	1078 1067 1085	1077	0·6	25·08
164	1210 1220 1214	1216	0·4	28·32
156	2·084 2·148 2·102	2·111	1·2	0·049
158	3·699 3·632 3·624	3·652	0·9	0·084
160	101·4 103·1 102·6	102·4	0·6	2·360
161	826·7 828·7 790·9	815·4	2·0	18·79
162	1111 1074 1104	1096	1·4	25·26
163	1096 1096 1076	1089	0·8	25·09
164	1211 1234 1249	1231	1·1	28·37

determination of relative abundances. The last column gives the computed abundances for each of the three series.

Table 3 is a summary of the isotopic abundance data.

CONCLUSIONS

Good precision of readings and reproducibility of isotopic abundance data over relatively long periods of time, as illustrated above, indicate that the spark geometry is maintained constant by automatic control of both gap and ion-illumination angle.

Table 3. Summary of dysprosium isotopic abundance measurements

Mass	Measured† abundance	Relative average deviation, %	Range of literature[8] values
156*	0·0477	1·9	0·052– 0·064
158*	0·0843	0·4	0·090– 0·105
160*	2·315	1·3	2·29 – 2·36
161	18·66	0·5	18·73 –19·0
162	25·42	0·4	25·36 –25·53
163	25·04	0·2	24·91 –24·97
164	28·42	0·4	28·11 –28·47

* Uncalibrated range corrections used for masses 156, 158 and 160.

† Average of three determinations in Table 1.

Variations in the data cited include contributions due to changes in degree of ionization, as well as other uncertainties, since the measurements were made with signals for doubly-charged ions and the total beam monitor is affected by 1+, 2+, and 3+ ion signals.

Automatic control of both the spark gap and the ion-illumination angle causes the ratio of the image-signal to monitor-signal to remain constant over longer periods of time than has been previously possible. Thus, instrument sensitivity is maintained at a high and constant level.

Some limitations in utilizing this means of automatic ion-illumination angle control with other spark-source instruments should be noted. The application may not be possible in instruments employing *z*-focusing or the use of additional electrostatic lenses. The control may not be as effective in instruments which possess different ion-optics parameters from those of the one used for this work (*e.g.*, object distance of the electrostatic analyser employed here is 1·189 in). Spark-source electrodes with large cross-sections or very narrow gap-widths may exhibit peculiar ion-illumination effects and thus may not be suitable.

Acknowledgement—The authors wish to acknowledge the co-operation and help of their colleagues, especially David Birlingmair who aided in the initial overall design, Raymond C. Prior who designed and constructed the electronic circuit, and Edward R. Clark who designed much of the details and supervised the construction of the mechanical unit. The contributions of James Jensen, Wayne A. Rhinehart, and Clarence Ness are also gratefully acknowledged.

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Zusammenfassung—Die automatische Nachregelung lediglich der Länge der Funkenstrecke in einem Massenspektrometer mit Funkenquelle gewährleistet nicht, daß die optimalen Bedingungen der Elektrodengeometrie bezüglich des ionenoptischen Systems eingehalten werden. Es wurde eine Vorrichtung entwickelt, die gleichzeitig eine konstante Länge der Funkenstrecke sowie einen besser konstanten Ionenbeleuchtungswinkel in der z-Achse aufrecht erhält. Es handelt sich hier um die erste Entwicklung, die Parameter der Ionenoptik verwendet, um die funkenliefernden Elektroden automatisch einzustellen. Das System hält die Elektroden in einer optimalen Konfiguration, sodaß automatisch eine höhere und konstantere Empfindlichkeit des Instruments eingehalten wird. Zusätzlich zeigt sich eine wesentliche Verbesserung in der Ansprechgenauigkeit des Instruments. Anscheinend können relative Isotopenhäufigkeiten direkt mit der Funkenquellenmethode bestimmt werden, die mit denen vergleichbar sind, die man in einigen Fällen durch Oberflächenionisation oder Elektronenbeschuß erhalten hat. Es werden Ergebnisse mitgeteilt, die diese Behauptung stützen.

Résumé—Le réglage automatique de la largeur de l'éclateur seulement dans un spectromètre de masse à source d'étincelle n'assure pas que les conditions optimales de la géométrie d'électrode sont maintenues par rapport au système optique ionique. On a élaboré un dispositif qui maintient simultanément une largeur constante d'intervalle et aussi un angle axe des z-irradiation d'ion plus constant. Ceci est le premier développement qui utilise les paramètres d'optique ionique pour ajuster les électrodes d'étincelle automatiquement. Le système maintient les électrodes dans une configuration optimale telle qu'une sensibilité d'instrument plus élevée et plus constante est maintenue automatiquement. De plus, on décèle une amélioration importante dans la fidélité de la réponse instrumentale. Il apparaît que des abondances isotopiques relatives qui peuvent être déterminées par la méthode à source d'étincelle sont comparables à celles obtenues dans quelques cas par ionisation de surface ou par bombardment électronique. On donne des résultats qui soutiennent cette conception.

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ACID-BASE EQUILIBRIA IN ETHYLENE GLYCOL—I

DEFINITION OF pH AND DETERMINATION OF pK-VALUES OF ACID-BASE INDICATORS

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Summary—A pH-scale in ethylene glycol is defined, based on potentiometric measurements for a cell without liquid junction:

$$\begin{array}{c|c|c} \text{glass} \\ \text{electrode} \end{array} \Big\| \; 0{\cdot}1\text{M (HCl + KCl)}, \begin{array}{c}\text{ethylene}\\ \text{glycol}\end{array} \Big| \; \text{AgCl; Ag}$$

and a potentiometric-spectrophotometric method for the determination of p*K*-value of acid-base indicators in ethylene glycol on the basis of this pH scale is proposed, in which the pH scale is established and the p*K*-value determined in a single titration at constant ionic strength. The following p*K*-values of indicators are reported: Cresol Red—3·00, Thymol Blue—3·39, Bromophenol Blue—6·49, Bromocresol Green—7·38, Bromocresol Purple— 9·00 and Cresol Red (2nd change)—11·07. A linear relationship was found between the p*K*-values of four sulphonphthalein indicators in ethylene glycol and in water according to the following equation $(pK_{HI}{}^{c})_{EG} = 2{\cdot}3 + 1{\cdot}1\ (pK_{HI}{}^{c})_{W}$. An attempt is made to explain this dependence, based on the idea of solute-solvent interaction of species of the same charge type.

Ethylene glycol (EG) and its mixtures with other solvents find application as media in the determination of many organic compounds, particularly those with basic properties.[1] Nevertheless acid-base equilibria in EG have not been investigated in detail. Data for pH measurements are scarce, although the successful use of the hydrogen and glass electrodes in this solvent has been mentioned.[1-3] There is also a lack of data for acid-base equilibrium constants of protolytes in EG.[2]

In this and subsequent papers a detailed study of acid-base equilibria in EG and its mixtures, based on a well-defined pH-scale, will be described. The p*K*-values of many organic compounds and acid-base indicators will be reported and suitable conditions for quantitative determinations in this solvent will be examined.

The present paper deals with the definition of a pH-scale in EG, and the performance of a potentiometric-spectrophotometric method of determining p*K*-values of acid-base indicators in EG.

Definition of pH-scale in ethylene glycol

The following galvanic cell (I) was used:

$$\begin{array}{c}\text{glass}\\ \text{electrode}\end{array} \Big\| \; 0{\cdot}1M\ \text{(HCl + KCl), EG} \; \Big| \; \text{AgCl; Ag} \qquad \text{(I)}$$

It does not contain a phase boundary, thus avoiding unknown liquid junction potentials, and the measurements refer to a constant ionic strength (0·1*M* KCl) so that variations in activities need not be considered. The scale used is therefore a pc_H-scale, referring to the concentration of hydrogen ions and not to the activity.

The potential of the cell (I) is given by the Nernst equation

$$E = E_{GE}{}^0 - E_{RE}{}^0 + k \log c_H f_H c_{Cl} f_{Cl} \alpha_{KCl} \tag{1}$$

where $E_{GE}{}^0$ and $E_{RE}{}^0$ are the standard potentials of the glass and reference electrodes, $k = 2{\cdot}303\ RT/F = 0{\cdot}05916$ at 25°C; c_H and c_{Cl} are the molar concentrations of hydrogen and chloride ions, and f_H and f_{Cl} their activity coefficients; α_{KCl} represents the degree of dissociation of potassium chloride in EG, assumed as a constant under the conditions in question. At constant chloride-ion concentration equation (1) takes the form

$$E = E^{0'} + 0{\cdot}05916 \log c_H = E^0 - 0{\cdot}05916\ pc_H \tag{2}$$

where $E^{0'} = E_{GE}{}^0 - E_{RE}{}^0 + k \log c_{Cl} f_{Cl} f_H \alpha_{KCl}$, and is a constant for the series of experiments. Equation (2) permits the calculation of hydrogen ion concentration as a function of the measured potential, provided the $E^{0'}$-value is known from a preliminary experiment:

$$pc_H = \frac{E^{0'} - E}{0{\cdot}05916} \tag{3}$$

The determination of $E^{0'}$ for aqueous solutions does not present any difficulty, because the hydrochloric acid is fully dissociated, the hydrogen ion concentration is equal to the total content of the hydrochloric acid, and hence $E^{0'}$ can be calculated from equation (4). The lower dielectric constant of EG ($\varepsilon = 37{\cdot}7$) in relation to water ($\varepsilon = 80{\cdot}4$), as well as the acid–base properties of EG as solvent, would lead one to expect that hydrochloric acid might not dissociate completely in this solvent. A preliminary condition for the definition of a pc_H-scale in EG by the potentiometric method is therefore proof that dissociation is complete as shown by agreement between measured potentials and those predicted by equation (2) when the hydrogen ion concentration (c_H) in equation (2) is replaced by the total concentration of the hydrochloric acid (c_{HCl}), in cell (I):

$$E = E^{0'} + 0{\cdot}05916 \log c_{HCl} \tag{4}$$

As the results from this investigation showed, in the concentration region used, hydrochloric acid does dissociate fully and pc_H can be calculated by means of equation (3) from experimentally determined values of $E^{0'}$.

It should be emphasized that the pc_H-scale thus defined refers only to solutions of hydrochloric acid and potassium chloride at a constant ionic strength of $c_{HCl} + c_{KCl} = 0{\cdot}1M$* at 25 .

Determination of pK*-values of acid–base indicators in ethylene glycol*

The method used in the present investigation does not differ in principle from those widely used for aqueous solutions,[4] but some differences exist, both in the pc_H concept

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* As a matter of fact, the dissociation of potassium chloride in EG is probably not complete, and it cannot be stated categorically that the ionic strength in the investigated solution is $\mu = 0{\cdot}1$. It can be accepted, however, that the ionic strength is constant, owing to the constancy of the degree of dissociation of potassium chloride.

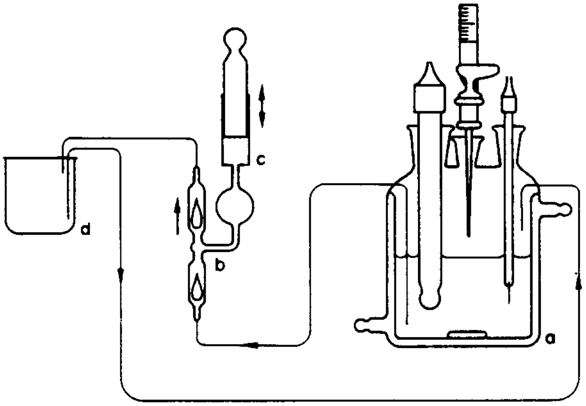

Fig. 1. Schematic representation of apparatus for the potentiometric-spectrophotometric determination of indicator pK-values in EG.

and in the apparatus. The latter allows simultaneous measurement of the e.m.f. of the cell and the absorbance of the solution, and employs a convenient circulating system (Fig. 1), similar to that described by Havel.[5] The pK-values of the acid-base indicators are found from the equations

$$\mathrm{p}K_{\mathrm{HI}}{}^{\mathrm{c}} = \mathrm{p}c_{\mathrm{H}} + \log\frac{c_{\mathrm{HI}}}{c_{\mathrm{I}}} = \mathrm{p}c_{\mathrm{H}} + \log\frac{D_{\mathrm{I}} - D}{D - D_{\mathrm{HI}}} \tag{5}$$

where c_{HI} and c_{I} are the concentrations of the acid and base forms of the indicator, D_{HI} and D_{I} are the absorbances of the solutions containing only the acid and only the base forms of the indicator respectively, and D is the absorbance of the solution corresponding to a particular pc_{H}. The p$K_{\mathrm{HI}}{}^{\mathrm{c}}$-values are found by numerical or graphical solution of equation (5). These constants are referred to constant ionic strength at 0·1M KCl solution (see footnote on p. 2).

EXPERIMENTAL

Reagents

Ethylene glycol. Reagent grade solvent was distilled under reduced pressure (10 torr) over anhydrous sodium sulphate.

Hydrochloric acid in EG. Prepared by saturation with dry hydrogen chloride. A 0·01M solution was obtained by dilution and then standardized after mixing with an equal volume of water.

Potassium chloride and acetate. Reagent grade chemicals were used without purification.

Diphenylguanidine. Recrystallised from benzene.

The indicators Thymol Blue (TB), Bromophenol Blue (BPB), Bromocresol Green (BCG), Bromocresol Purple (BCP) and Cresol Red (CR) were used without purification.

Apparatus

The experimental arrangement is schematically shown in Fig. 1. It consists of a thermostated vessel for titration (*a*), circulating system (*b,c*) connected to a flow-cell (*d*) in the Spekol spectrophotometer (C. Zeiss, Jena) In the vessel (*a*) a Radiometer glass electrode type G202B and a silver-silver chloride electrode of the Brown type[6] were immersed in the solution. The potential of cell (I) was measured on a Radiometer pH-meter type PHM-4 with a precision of ±0·2 mV.

For the determination of the pK-values of the different indicators the following buffers were used: potassium acetate for TB, BPB, and BCG, diphenylguanidine for CR, and a mixture of potassium acetate and diphenylguanidine for BCP. The measurements were started in alkaline medium, *i.e.*, solution containing the base form of the indicator, for which a spectral band with maximum absorption was chosen. The wavelength was not changed during the whole experiment. To this solution appropriate portions of acid were added and both the potential and absorption were measured.

Procedure

In the titration vessel were placed (*a*) 50·00 ml of ethylene glycol which was 0·1*M* in potassium chloride, $10^{-3}M$ in potassium acetate or diphenylguanidine and *ca.* $10^{-5}M$ in the indicator. Portions of an ethylene glycol solution 0·01*M* in hydrogen chloride, 0·09*M* in potassium chloride and of the same indicator concentration as the basic solution (to avoid dilution effects) were added from a burette. When mixing was complete after each addition the potential and the absorbance were measured [the value D in equation (5)]. When the indicator had changed into its acid form, the titration was continued without measurement of the absorbance and the results were used for the calibration of the cell (I). The absorbance of the last point of the titration gave the value of D_{HI} in equation (5), and D_{I} was obtained from a measurement of the same solution made very alkaline by addition of potassium hydroxide in ethylene glycol after completion of the titration, the values being corrected for dilution. In the case of Cresol Red (an indicator with a second acid-base interval in the pH region investigated), the absorbance measurements were continued after the equivalence point. The results obtained were used both for the calibration of the cell and for the determination of the second (lower) constant. The value of $D_{\text{H}_2\text{I}}$ was found from a measurement of the same solution after addition of an excess of acid.

RESULTS

The experimental results from a typical titration with the indicator Cresol Red are shown in Table 1. This indicator shows two colour changes in EG, just as in aqueous solution. The treatment of the primary data (see Table 1a) is performed in two stages as

Table 1. Experimental data and their treatment from one acid-base titration in EG of cresol red

1-a. Primary data

V_{HCl}, *ml*	E, *mV*	D (λ = 579 *nm*)	V_{HCl}, *ml*	E, *mV*	D (λ = 526 *nm*)
0·00	−194·0	0·485	5·00	+ 4·2	0·012
0·30	−185·1	0·441	6·00	+239·0	0·047
0·50	−180·2	0·410	6·50	+261·5	0·104
0·80	−175·3	0·375	7·00	+273·3	0·152
1·00	−170·8	0·353	8·00	+288·2	0·229
1·30	−163·9	0·312	9·00	+297·4	0·288
1·60	−158·2	0·275	10·00	+303·3	0·331
2·00	−147·7	0·220	11·50	+310·4	0·385
2·30	−137·3	0·158	13·00	+315·5	0·425
2·60	−124·9	0·110	15·00	+319·8	0·466
3·00	−106·2	0·055	17·00	+325·0	0·503
4·00	− 50·8	0·000	20·00	+330·1	0·532

1-b. Determination of the equivalence point and the $E^{0'}$ value

V_{HCl}, *ml*	$V_t = 50 + V_{\text{HCl}}$	ψ*	c_{H}, *mmole/V_t*	$-\log c_{\text{H}}$	$\times$ 59·16	$E^{0'}$, *mV*
6·00	56·00	0·613	0·0554	4·256	251 8	490·8
6·50	56·50	1·484	0·1408	3·852	227·9	489·4
7·00	57·00	2·370	0·2246	3·649	215·9	489·2
8·00	58·00	4·305	0·3880	3·411	201·8	490·0
9·00	59·00	6·265	0·5458	3·263	193·0	490·4
10·00	60·00	8·020	0·6984	3·156	186·7	490·0
11·50	61·50	10·830	0·9180	3·037	179·7	490·1
13·00	63·00	13·530	1·127	2·948	174·4	489·9
15·00	65·00	16·500	1·373	2·862	169·3	489·1
17 00	67·00		1·639	2·785	164·8	489·8

* $\psi = (50 + V_{\text{HCl}}) \times 10^{E/59\cdot16}$; mean value $E^{0'} = 489{\cdot}9 \pm 0{\cdot}5$.

1-c. Calculation of pK_{HI}^{c} and $pK_{H_2I}^{c}$ of cresol red

E, mV	pc_H	D (λ = 579 nm)	$D_I - D$	$D - D_{HI}$	$\log \frac{D_I - D}{D - D_{HI}}$	pK_{HI}^{c}
−194·0	11·560	0·485	0·153	0·485	−0·511	11·049
−185·1	11·410	0·441	0·198	0·441	−0·347	11·063
−180·2	11·327	0·410	0·228	0·410	−0·225	11·072
−175·3	11·224	0·375	0·263	0·375	−0·154	11·070
−170·8	11·168	0·353	0·285	0·353	−0·093	11·075
−163·9	11·051	0·312	0·326	0·312	+0·019	11·070
−158·2	10·955	0·275	0·363	0·275	+0·121	11·076
−147·7	10·780	0·220	0·418	0·220	+0·279	11·059
−137·3	10·600	0·158	0·480	0·158	+0·483	11·083
−124·9	10·392	0·110	0·528	0·110	+0·681	11·073

mean value pK_{HI}^{c} = 11·07 ± 0·02

E, mV	pc_H	D' (λ = 526 nm)	$D' - D_I'$	$D_{HI}' - D'$	$\log \frac{D' - D_I'}{D_{HI}' - D'}$	$pK_{H_2I}^{c}$
+261·5	3·861	0·104	0·094	0·691	−0·866	2·955
+273·3	3·661	0·152	0·142	0·643	−0·656	3·005
+288·2	3·409	0·229	0·219	0·566	−0·412	2·997
+297·4	3·253	0·288	0·278	0·507	−0·261	2·992
+303·3	3·154	0·331	0·321	0·474	−0·169	2·985
+310·4	3·033	0·385	0·375	0·420	−0·049	2·984
+315·5	2·947	0·425	0·415	0·370	+0·050	2·997
+319·8	2·875	0·466	0·456	0·329	+0·142	3·017
+325·0	2·787	0·503	0·493	0·292	+0·227	3·014
+330·1	2·701	0·532	0·522	0·273	+0·284	2·985

mean value $pK_{H_2I}^{c}$ = 3·00 ± 0·01

Conditions: 50 ml of EG, $10^{-3}M$ in diphenylguanidine, 0·1M in potassium chloride and $1·45 \times 10^{-5}M$ in CR are titrated with EG solution that is $9·71 \times 10^{-3}M$ in hydrogen chloride, $9 \times 10^{-2}M$ in potassium chloride and $1·45 \times 10^{-5}M$ in CR. $D_I = 0·638$ (579 nm); $D_{HI} = 0·00$ (579 nm); $D_{HI}' = 0·010$ (526 nm); $D'_{H_2I} = 0·795$ (526 nm).

shown in the same table. First the equivalence point of the neutralization of the added bases is found. This is done very accurately by means of a Gran plot[7,8] (see Table 1b). The $E^{0'}$ value is then determined by means of equation (4). The calculated values for $E^{0'}$ are also shown in Table 1b with their mean and standard deviation. Secondly, for every experimental point the pc_H-value is calculated from equation (3) (see Table 1c). The date for pc_H, D_I, and D_{HI} are used for the graphical (Fig. 2) or numerical (Table 1c) solution of equation (5).

By analogous methods and with appropriate indicator concentrations of pK-values of TB BPB, BCG and BCP were determined (see Table 2 and Fig. 2). This set of indicators was selected to cover a large part of the pc_H-scale of EG.

DISCUSSION

The investigations have shown that the pc_H-scale in ethylene glycol can be established by potentiometry with glass and silver–silver chloride electrodes. The glass electrode responds quickly to changes in acidity and gives stable and reproducible potentials as is evident from the values of the calculated $E^{0'}$ values shown in Table 1b, where the standard deviation of the mean is ±0·5 mV or ±0·008 pc_H-units.

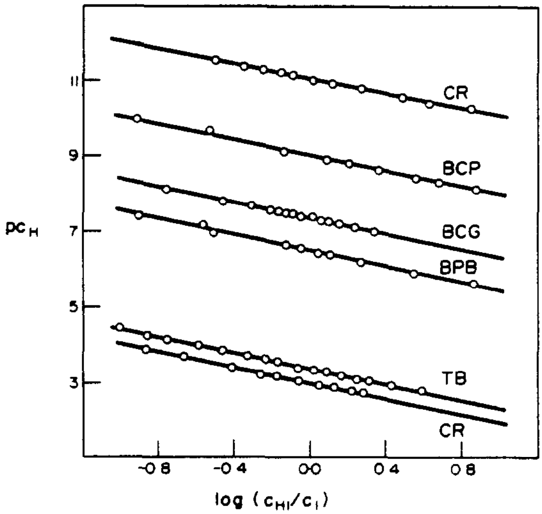

Fig. 2. Plot of pc_H *vs.* $\log(c_{HI}/c_I)$.

This method is experimentally convenient and makes possible both measurement and calibration in each experiment, thus reducing some of the possible errors.

The sulphonphthaleins exhibit a behaviour in EG similar qualitatively to that in water.[10] In aqueous solution these indicators show two colour changes. Not taking the possible quinoid structure into consideration, it is accepted that the yellow form corresponds to a zwitterion or a hybrid ion with the charge expressed as $(I^{\mp})^{-}$. The colour change on going into acidic medium is explained by the formation of the $(I^{\mp})$ zwitterion, and that on going into a alkaline medium by the dissociation of the phenolic group forming the $(I^{\mp})^{2-}$ zwitterion.

The two indicators CR and TB exist as the uncharged species H_2I (probably zwitterions) in acid medium and as HI^- in alkaline medium. The colour change from yellow to red corresponds to the reaction $H^+ + HI^- = H_2I$. The p*K*-values of the indicators CR and TB in ethylene glycol and in water differ by about 1·8 units (see Table 2).

For the other indicators BPB, BCG, BCP and CR the colour change from intensely coloured base form to yellow acid form could be expressed by the equation $H^+ + I^{2-} = HI^-$. For these indicators $\Delta pK_{HI}{}^c$ varies from 2·7 to 3·0 (see Table 2). It is interesting to

Table 2. Constants ($pK_{HI}{}^c$), with their standard deviations, and some spectrophotometric characteristics of sulphonphthaleins in EG

Indicator	Charge on I	λ_{max}	Colour change I	HI	$(pK_{HI}{}^c)_{EG}$	$(pK_{HI}{}^c)_W$*	ΔpK_{HI}
CR	1−	526	yellow	red	3·00 ± 0·01	1·2	1·8
TB	1−	550	yellow	red	3·39 ± 0·01	1·6	1 8
BPB	2−	598	violet	yellow	6·49 ± 0·07	3·85	2·66
BCG	2−	623	blue	yellow	7·38 ± 0·02	4·66	2·72
BCP	2−	597	purple	yellow	9·00 ± 0·03	6·12	2·88
CR	2−	579	red	yellow	11·07 ± 0·02	8·10	2·97

* See ref. (9).

note, however, that the relationship between the pK-values of these indicators in EG and in water is linear and follows the equation

$$(\mathrm{p}K_{\mathrm{HI}}{}^{c})_{\mathrm{EG}} = 2{\cdot}3 + 1{\cdot}1(\mathrm{p}K_{\mathrm{HI}}{}^{c})_{\mathrm{W}} \tag{6}$$

where the slope 1·1 is very near to the ratio of the autoprotolysis constants, $(\mathrm{p}K_s)_{\mathrm{EG}}/(\mathrm{p}K_s)_{\mathrm{W}} = 1{\cdot}12$. The intercept 2·3 can be interpreted as a difference in the combined solvation effects on the proton and the zwitterion in ethylene glycol and water. It can probably be assumed that by using equation (6) the $(\mathrm{p}K_{\mathrm{HI}}{}^{c})_{\mathrm{EG}}$-values of other sulphonphthaleins of the same charge type could be calculated approximately. The dependences found in this investigation affirm once more the specific behaviour of interaction of the medium with charged species from the same group of substances.

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Zusammenfassung—Es wird eine pH-Skala in Äthylenglykol definiert, die auf potentiometrischen Messungen an einer Zelle ohne Überführung begründet ist:

Glaselektrode || 0·1 M (HCl + KCl), Äthylenglykol | AgCl; Ag.

Weiter wird eine pontentiometrisch-spektrophotometrische Methode zur Bestimmung von pK-Werten von Säure-Basen-Indikatoren in Äthylenglykol auf der Basis dieser pH-Skala vorgeschlagen, bei der in einer einzigen Titration bei konstanter Ionenstärke die pH-Skala aufgestellt und der pK-Wert bestimmt wird. Folgende pK-Werte von Indikatoren werden mitgeteilt: Kresolrot 3·00, Thymolblau 3·39, Bromphenolblau 6·49, Bromkresolgrün 7·38, Bromkresolpurpur 9·00 und Kresolrot (2. Umschlag) 11·07. Es wurde eine lineare Beziehung zwischen den pK-Werten von vier Sulfonphthalein-Indikatoren in Äthylenglykol und Wasser entsprechend der Gleichung $(\mathrm{p}K^{c}_{\mathrm{HI}})_{\mathrm{EG}} = 2{\cdot}3 + 1{\cdot}1(\mathrm{p}K^{c}_{\mathrm{HI}})_{\mathrm{W}}$ gefunden. Es wird versucht, diese Beziehung auf Grund der Wechselwirkung zwischen Lösungsmittel und Gelöstem bei Spezies desselben Ladungstyps zu erklären.

Résumé—On définit une échelle de pH dans l'éthylène glycol, basée sur des mesures potentiométriques pour une cellule sans jonction liquide:

$$\left.\begin{array}{c}\text{Electrode}\\ \text{de verre}\end{array}\right|\ (\mathrm{HCl} + \mathrm{KCl})\ 0.1M,\ \begin{array}{c}\text{éthylène}\\ \text{glycol}\end{array}\left|\ \mathrm{AgCl};\ \mathrm{Ag}\right.$$

et on propose une méthode potentiométrique-spectrophotométrique pour la détermination des valeurs de pK d'indicateurs acide-base dans l'éthylène glycol sur la base de cette échelle de pH, dans laquelle l'échelle de pH est établie et la valeur de pK déterminée en un seul titrage à force ionique constante. On rapporte les valeurs de pK d'indicateurs suivantes: Rouge de Crésol — 3,00; Bleu de Thymol — 3,39; Bleu de Bromophénol — 6,49; Vert de Bromocrésol — 7,38; Pourpre de Bromocrésol — 9.00 et Rouge de Crésol (2ème virage) — 11.07. On a trouvé une relation linéaire entre les valeurs de pK de quatre indicateurs sulfonephtaléïnes en éthylène glycol et dans l'eau selon l'équation $(\mathrm{p}K_{\mathrm{HI}}{}^{c})_{\mathrm{EG}} = 2.3 + 1.1\ (\mathrm{p}K_{\mathrm{HI}}{}^{c})_{\mathrm{W}}$ Un essai est fait pour expliquer cette dépendance, basé sur l'idée d'une interaction soluté-solvant d'espèces du même type de charge.

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TRACE ANALYSIS BY MICROWAVE EXCITATION OF SEALED SAMPLES—I

PRELIMINARY INVESTIGATIONS

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Summary—An important limitation to the sensitivity of analytical methods using atomic spectroscopy is the short residence-time of the atoms in the light-path. The possibility has been studied of sealing the samples in a quartz tube where they are forced to emit light by microwave excitation. The detection of amounts below one ng in a volume of 0·5 ml seems possible.

An important limitation in the sensitivity of most applications of analytical atomic spectroscopy is the short residence-time of the atoms in the optical path. In atomic-absorption and atomic-fluorescence spectroscopy attemps have been made to increase this residence-time with, for example, the Massmann furnace and the carbon rod.[1] A further improvement of the sensitivity seems possible if the sample is present in a closed system.

The closed system used by us for analytical emission-spectroscopy is adapted from atomic-fluorescence spectroscopy (AFS). In AFS a high sensitivity can only be obtained when a light-source with a high intensity is used. For this purpose an electrodeless discharge tube (EDT) is generally used. The preparation and performance of these EDT's has been extensively described by West and co-workers[2,3] and by Winefordner and co-workers.[4]

An EDT generally consists of a quartz tube of about 1 ml capacity, containing μg or ng amounts of the desired metal or its halide, and a noble gas at a pressure of a few torr. The EDT is placed in a microwave cavity and after ignition the tube emits the atomic spectrum of the noble gas and the metal.

Table 1. Quantities, evaporated at 600°C and 1 torr in a volume of 1 ml

Species	Amount, μg	Species	Amount, μg
Zn	2	$InCl_3$	6
$ZnCl_2$	3·5	Pb	6×10^{-3}
Cd	3·3	$PbCl_2$	8
$CdCl_2$	5·5	Tl	4×10^{-2}
Hg	6	TlCl	7
$HgCl_2$	8	Ge	2×10^{-6}
In	3×10^{-6}	$GeCl_4$	7

The amount of metal or metal halide evaporated in the EDT depends on temperature, volume and pressure. For a rough calculation, values of 600°, 1 ml and 1 torr may be assumed for these parameters. In Table 1 the amounts evaporated under these conditions are given.

It shows that in many cases the very high intensity is due to only a few μg of the evaporated material. It is evident that the detection of quantities far below one μg must be possible, if the background noise does not interfere. For practical analytical applications the introduction of metal chloride solutions may often be preferable to the introduction of the metals; therefore so far only metal chloride solutions have been tested.

EXPERIMENTAL

Apparatus

The vacuum apparatus used for the preparation of the EDT's (Fig. 1) is a modification of the apparatus used by West and co-workers. The dimensions of the EDT's used were: length of the bulb 25 mm, i.d. 10 mm and wall thickness about 1 mm. Some of the measurements were performed with a Hilger and Watts "Large Quartz Spectrograph" (slit 20 μm) and photographic detection. Other measurements were carried out with the monochromator (slit 25 μm) and the detector of the Techtron AA4 atomic-absorption spectrophotometer with mechanical modulation. The microwave generator used was an EMS Microtron 200 with reflected-power meter (frequency 2450 MHz). Two cavities were used: an EMS 214 L and an EMS 216 L.

Preparation of EDT's

First the EDT is degassed for one min under vacuum by heating with a propane/oxygen burner to remove volatile contamination. After disconnection of the EDT from the vacuum line, 100 μl of metal chloride solution is added with an Eppendorf pipette, the tube is reconnected to vacuum, and the solution is cooled with liquid nitrogen and frozen to dryness. After this, helium is added up to a pressure of 10 torr. The EDT is sealed with the propane/oxygen burner and ready for use. The complete preparation of six EDT's takes about 1 hr.

Preliminary experiments

The investigations were started with tubes containing some μg of zinc and mercury chlorides. The emission spectra of these EDT's were recorded with the Hilger spectrograph. The tube was placed in the EMS 214 L cavity and 75-W power was applied. The spectra showed the atomic lines of zinc and mercury but intense band spectra were present, seriously hampering analytical application Elimination of these spectra was necessary and therefore identification of the emitters was needed.

Comparison with band spectra of EDT's filled with air and chlorine showed that part of the spectra was due to these gases. Practically all of the other band spectra were due to water (OH-bands), C_2 (Swan-bands) and metal monochlorides.[5]

The air bands probably result from small leaks in the vacuum system; the chlorine bands are caused by partial thermal dissociation of the metal chlorides and perhaps also by reactions with the quartz wall. The OH-bands are certainly caused by traces of water The origin of the C_2-bands is not quite clear

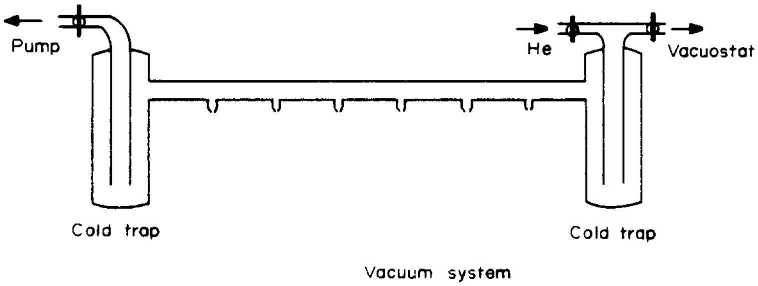

Fig. 1. Vacuum line for preparation of the EDT.

Further investigations

First we investigated whether the band spectra could be suppressed. From vacuum technique it is known that certain metals ("getters") react rapidly at rather high temperature with traces of gases. This might solve our problem but there are some restrictions as to the metals which can be used. A suitable "getter" metal M_e must not react with the metal chloride MCl_x in the tube, *i.e.*, the reaction

$$M_e + MCl_x \xrightarrow{\qquad} M_eCl_y + M$$

should not occur This could be predicted thermodynamically if the exact conditions were known and if free energy data at high temperatures were available. Unfortunately, this is not the case and only a rough estimate based on enthalpy values for standard conditions can therefore be made Some values are listed in Table 2 From these it can be expected that the reaction above will not occur for Pd, Bi, Cu or Ge "getters" with Zn, Cd, Tl, In or Pb metal chlorides and the elements Pd, Bi, Cu or Ge should therefore be suitable as "getters" to suppress the band spectra.

Table 2. Enthalpy of some metal chlorides, in kcal per g atom of chlorine

$PdCl_2$	−23	$CdCl_2$	−48
$CuCl_2$	−30	$HgCl_2$	−28
$BiCl_3$	−30	$PbCl_2$	−43
$GeCl_4$	−28	$InCl_3$	−43
$ZnCl_2$	−50	TlCl	−49

Palladium was tried first, but it did not meet our requirements because of its low reactivity. With copper and bismuth most of the interfering band spectra disappeared. Copper, however, had two disadvantages. It reacts with quartz, with a resultant significant decrease in the transmittance and it also forms copper(I) chloride which emits a strong interfering band spectrum. Bismuth has a low melting point and many metal chlorides are soluble in the molten metal. With germanium the bands due to air, chlorine, C_2 and OH disappeared. Germanium(I) chloride is formed by the reaction with free chlorine gas; it emits a band spectrum with maximal intensity between 280 and 330 nm, which is the main origin of the remaining background.

It was expected that excitation conditions of the EDT would be governed more or less by the bulk of the vapour present. Therefore the presence of a constant amount of matrix in all experiments seemed useful. If germanium is used as a "getter", germanium(IV) chloride seems to be a suitable matrix, but unfortunately it is very volatile (b.p. 86·5°). It was expected that addition of a small amount of another metal chloride ($CuCl_2$, $PdCl_2$) to the germanium would result in the formation of $GeCl_4$. Unfortunately these reactions do not proceed very reproducibly. Therefore we use $ZnCl_2$ as a matrix, but of course zinc could then not be determined. To each EDT 50–100 μg of solid germanium were added just before the addition of the metal chloride solution Zinc chloride was added simultaneously with the metal chloride solution. The quantity added was adjusted to give 1 μg of $ZnCl_2$ in each EDT. EDT's prepared in this way always burn for 30 min or longer.

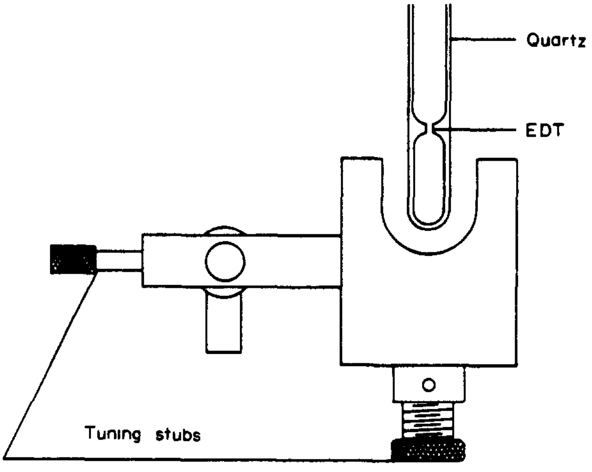

Fig. 2 Arrangement of the EDT in the microwave cavity.

Quantitative measurements

For these measurements we used the Techtron AA4 atomic-absorption spectrophotometer. To compare intensities over a wide range the relative gain of the amplifier was measured for each of the twenty different steps. We used the EMS 216 L cavity with the EDT fixed in it as shown in Fig. 2.

The tuning stubs were adjusted to give minimum reflected power. The net power was 75W. During the measurements it was observed that some germanium sublimed onto the wall of the quartz tube. If this coating was situated in the optical path the signal measured was decreased. This effect may be eliminated by the use of an internal standard in the EDT. Because zinc was present as matrix it was also used as the internal standard (the zinc 328·2 nm line). A second advantage of the use of an internal standard is that it may correct to some extent for variations in the excitation conditions. Because I_M/I_{Zn}, the ratio of the relative intensities of the metal and zinc emission-lines, changed with time, measurements were made at a fixed time after switching on. Background intensity ratios were measured by setting the wavelength just clear of that corresponding to the metal line.

RESULTS

Measurements were performed with six tubes, three of them containing about 5 ng each of Cd, Tl and In, and the other three containing the same amount of Pb and Hg. Some results are given in Table 3.

Table 3. Relative line-intensities and background intensities

Line, *nm*	Time after switch-on, *min*	I_M/I_{Zn}			I_{backgr}/I_{Zn}			Relative gain*
Cd 228·8	10	77	92	74	2	2	2	2·85
Tl 377·6	14	104	151	108	3	3	3	12·3
In 410·2	16	91	128	109	15	12	15	55·5
Pb 405·8	14	100	152	110	32	43	30	202
Hg 253·6	10	156	184	144	3	8	4	4·90

* Gain required to give about half-scale deflection for the signal from the metal investigated.

From the table it is easily calculated that the relative standard deviation is between 20 and 30%, and because the noise in the background is usually not more than 2% (partly due to the amplifier) detection limits below one ng seem possible in many cases. Determination of other elements seems possible, but has not yet been investigated. The maximum volume to be used is about 0·5 ml.

CONCLUSIONS

The experiments show that the determination of extremely low quantities of elements is possible if the sample is sealed in an EDT and excited in a 2450-MHz field. Some precautions are necessary, however, to eliminate the interference of emission bands. The reproducibility at the 5–10 ng level is about 30%.

As the signal to background ratio is between 5 and 50 and the background may be measured with low noise (usually about 2%, which is partly due to the amplifier), analysis at much lower levels seems possible with the present system. A better signal to noise ratio may be obtained by using more suitable matrix elements, a monochromator with higher resolving power and simultaneous integration of signal and background. The experiments are being continued.

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5. R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, p. 330. Wiley, New York, 1965.

Zusammenfassung—Eine eichtige Einschränkung der Empfindlichkeit analytischer Methoden mit Atomspektroskopie ist die kurze Verweilzeit der Atome im Lichtweg. Es wurde die Möglichkeit untersucht, die Proben in einem Quarzrohr einzuschmelzen, wo sie durch Anregung mit Mikrowellen zur Emission von Licht gebracht werden. Der Nachweis von Mangan unter einem Nanogramm in einem Volumen von 0·5 ml erscheint möglich.

Résumé—Une importante limitation à la sensibilité de méthodes analytiques utilisant la spectroscopie atomique est le court temps de séjour des atomes dans la trajectoire de la lumière. On a étudié la possibilité de sceller les échantillons dans un tube en quartz où ils sont forcés d'émettre de la lumière par excitation micro-ondes. La détection de quantités au-dessous de un nanogramme dans un volume de 0,5 ml semble possible.

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THE SIGNAL *vs.* CONCENTRATION RELATIONSHIPS IN FLUORIMETRY

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Summary—Formulae for the fluorescence signal are derived which take into account some factors hitherto neglected. From these formulae conditions are deduced, for which a linear relationship exists between the concentration of the fluorescent components and the intensity of the fluorescence. In some cases of practical interest the fulfilment of these conditions cause too low a sensitivity. For such cases a method of optimization is outlined, by means of which the conditions are found which lead to the least deviation from linearity at the required sensitivity.

In the last few years the importance of fluorimetry as an analytical tool in trace analysis has greatly increased, because the limit of determination in fluorimetry is generally lower than in many other analytical methods. Unfortunately, no sufficiently complete theoretical basis for quantitative fluorimetric determinations has been developed. As a result, unreliable procedures have sometimes been proposed in fluorimetry. Therefore, it seems desirable to make available a somewhat more sophisticated theory of the dependence of the fluorescence intensity upon the composition of the fluorescent solution.

Owing to the rather complex mathematical expressions that result from such a theory, straightforward conclusions cannot always be drawn. For this reason a number of conclusions will be discussed in some detail.

"Perpendicular-type" fluorimeters, which constitute the bulk of the apparatus commercially available, have several disadvantages compared with other types of fluorimeter.[1–6] Therefore, the present investigation is extended to "transmission-type" and "reflection-type" fluorimeters. Schematic representations of the different types of fluorimeter are given in Fig. 1.

DERIVATION OF THE EQUATIONS

To keep the derivations reasonably simple the following assumptions have been made:

(a) the cell is rectangular
(b) the cell walls do not absorb any light
(c) the excitation light is a homogeneous, parallel and monochromatic beam, which enters the cell perpendicular to a cell face
(d) the intensity of the excitation light is not so large as to have a marked influence on the absorption coefficients of the components present in the sample
(e) the part of the fluorescence reaching the detector forms a parallel beam, which leaves the cell perpendicular to a cell face
(f) only a nearly monochromatic part of the fluorescence reaches the detector
(g) the refractive index of the sample is constant.

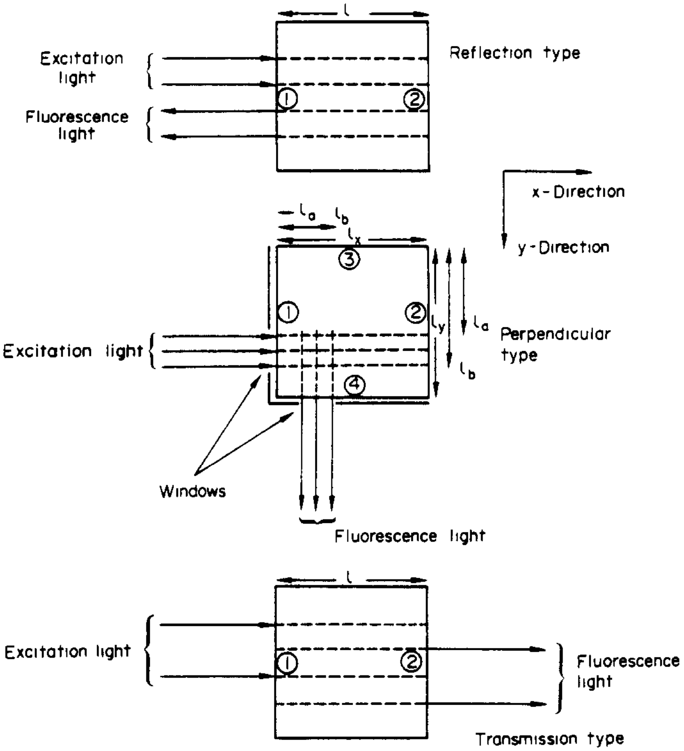

Fig. 1. Schematic representation of the different types of fluorimeter. The numbers in circles refer to the cell-wall numbers as used in the derivations.

Most of these assumptions do not really impair the applicability of the formulae, but some attention must be paid to them. The assumptions about the cell are easily fulfilled. The necessity of assuming rectangular cells arises from the fact that for cylindrical cells the light beams cannot pass perpendicularly through the cell walls. In such cases refraction and reflection effects play a very confusing role in the formulae.

If the excitation light and the measured part of the fluorescence are not monochromatic, the derived formulae have to be integrated over the relevant wavelength ranges.

The presence of substances which quench the fluorescence process is reflected in a change in the quantum efficiency of this process. Therefore, the presence of such substances need not be taken explicitly into account.

Effects of the intensity of the excitation light and of the refractive index of the sample can generally be neglected. A fuller discussion of these, and the previously mentioned effects is given elsewhere.[7]

If the intensity of the excitation light outside the cell is $I_{0,\mathrm{ex}}$, then, according to Beer's law, the intensity at a depth x inside the cell is:

$$I_{x,\mathrm{ex}} = I_{0,\mathrm{ex}} \,.\, \exp[-E_{\mathrm{ex}} \,.\, x] \tag{1}$$

where E_{ex} is the absorbance per unit path length (based on natural logarithms).

The decrease in intensity of the excitation light, caused by the ith absorbing component, in the thin layer between x and $x + \mathrm{d}x$, is:

$$\mathrm{d}I_{x,\mathrm{ex},i} = I_{x,\mathrm{ex}} \,.\, k_{\mathrm{ex},i} \,.\, c_i \,.\, \mathrm{d}x \tag{2}$$

where $k_{ex,i}$ is the absorption coefficient of the ith component at the excitation wavelength λ_{ex}, and c_i is the concentration of the ith component. In the fluorescence process the absorbed excitation light is converted into fluorescence with quantum efficiency $\Phi_{ex,i}$. Not all the emitted fluorescence arrives at the detector: only a fraction α goes in the right direction; only a fraction $\phi_{fl,i}$ has the right wavelength; only a fraction F is not absorbed by the sample solution. Therefore, the intensity of the fluorescence emitted by the ith component, originating in the layer between x and $x + dx$, having wavelength λ_{fl} and arriving at the detector, is given by:

$$dI_{x,fl,i} = \alpha \, . \, \phi_{fl,i} \, . \, \Phi_{ex,i} \, . \, F \, . \, dI_{x,ex,i} \tag{3}$$

It will be clear that F depends on the position of the layer from which the fluorescence originates, as well as on the arrangement for measuring the fluorescence intensity. For the arrangements with which this paper is concerned (see Fig. 1 for configurations and symbols) F is given by:

"reflection-type" arrangement:

$$F^0 = \exp[-E_{fl} \, . \, x] \tag{4}$$

"perpendicular-type" arrangement:

$$\begin{aligned} F^{90} &= \int_{l_a'}^{l_b'} \frac{\exp[-E_{fl} \, . \, (l_y - y)]}{l_b' - l_a'} \, dy \\ &= \frac{\exp[-E_{fl} \, . \, (l_y - l_b')] - \exp[-E_{fl} \, . \, (l_y - l_a')]}{(l_b' - l_a') \, . \, E_{fl}} \end{aligned} \tag{5}$$

"transmission-type" arrangement:

$$F^{180} = \exp[-E_{fl} \, . \, (l - x)] \tag{6}$$

Combining equations (1), (2) and (3) and the relevant equation for F yields, after integration, the desired formula for the fluorescence intensity:

"reflection-type" arrangement:

$$I_{fl}^{\,0} = T \, . \, \frac{1 - \exp[-(E_{ex} + E_{fl}) \, . \, l]}{E_{ex} + E_{fl}} \tag{7}$$

"perpendicular-type" arrangement:

$$I_{fl}^{\,90} = \frac{T}{l_b' - l_a'} \, . \left\{ \frac{\exp[-E_{fl}(l_y - l_b')] - \exp[-E_{fl}(l_y - l_a')]}{E_{fl}} \right\} . \left\{ \frac{\exp[-E_{ex} \, . \, l_a] - \exp[-E_{ex} \, . \, l_b]}{E_{ex}} \right\} \tag{8}$$

"transmission-type" arrangement:

$$I_{fl}^{\,180} = T \, . \, \frac{\exp[-E_{fl} \, . \, l] - \exp[-E_{ex} \, . \, l]}{E_{ex} - E_{fl}} \tag{9}$$

In (7), (8) and (9) the abbreviation T is used. If one fluorescent component is present T is given by

$$T = \alpha \,.\, I_{0,\,\mathrm{ex}} \cdot \Phi_{\mathrm{ex}} \cdot \phi_{\mathrm{fl}} \cdot k_{\mathrm{ex}} \cdot c \tag{10a}$$

if more fluorescent components are present T is:

$$T = \sum_{\mathrm{i}} T_{\mathrm{i}} = \alpha \,.\, I_{0,\,\mathrm{ex}} \cdot \sum_{\mathrm{i}} \Phi_{\mathrm{ex,\,i}} \cdot \phi_{\mathrm{fl,\,i}} \cdot k_{\mathrm{ex,\,i}} \cdot c_{\mathrm{i}} \tag{10b}$$

Correction for the effects of light reflection by the cell walls

The fraction of light that is reflected by a surface between two dielectrics is, at normal incidence, given by:[8]

$$r_{\perp} = \left(\frac{n - n'}{n + n'}\right)^2 \tag{11}$$

where n and n' are the refractive indices of the first and second dielectrics respectively.

A light-beam passing through a cell wall meets two reflecting surfaces. In this case the fraction of light that is reflected, ρ_{r} has to be calculated from a geometrical progression:

$$\rho_{\mathrm{r}} = \frac{r_{\mathrm{a}} + r_{\mathrm{b}} - 2r_{\mathrm{a}} \,.\, r_{\mathrm{b}}}{1 - r_{\mathrm{a}} \,.\, r_{\mathrm{b}}} \tag{12}$$

where r_{a} is the reflectivity of the first surface and r_{b} that of the second surface.

The fraction of light transmitted through the wall is:

$$\rho_{\mathrm{t}} = 1 - \rho_{\mathrm{r}} = \frac{(1 - r_{\mathrm{a}}) \,.\, (1 - r_{\mathrm{b}})}{1 - r_{\mathrm{a}} \,.\, r_{\mathrm{b}}} \tag{13}$$

Of course, the light-reflections by the cell walls influence the intensity of the fluorescence. The way to correct the formulae for this effect is by adding terms for the reflected light intensities to equations (1), (4), (5) and (6). The exact formulation of these equations is found by summing the terms of the geometrical progression:

$$I_{\mathrm{x,\,ex}} = I_{0,\,\mathrm{ex}} \cdot \rho_{\mathrm{t,\,ex,\,1}} \cdot \frac{\exp[-E_{\mathrm{ex}} \,.\, x] + \rho_{\mathrm{r,\,ex,\,2}} \,.\, \exp[-E_{\mathrm{ex}}(2l - x)]}{1 - \rho_{\mathrm{r,\,ex,\,1}} \cdot \rho_{\mathrm{r,\,ex,\,2}} \,.\, \exp[-2E_{\mathrm{ex}} \,.\, l]} \tag{1a}$$

$$F^0 = \rho_{\mathrm{t,\,fl,\,1}} \cdot \frac{\exp[-E_{\mathrm{fl}} \,.\, x] + \rho_{\mathrm{r,\,fl,\,2}} \,.\, \exp[-E_{\mathrm{fl}}(2l - x)]}{1 - \rho_{\mathrm{r,\,fl,\,1}} \cdot \rho_{\mathrm{r,\,fl,\,2}} \,.\, \exp[-2E_{\mathrm{fl}} \,.\, l]} \tag{4a}$$

$$\begin{aligned} F^{90} &= \int_{l_{\mathrm{a}}}^{l_{\mathrm{b}}'} \frac{\rho_{\mathrm{t,\,fl,\,4}}}{l_{\mathrm{b}}' - l_{\mathrm{a}}'} \cdot \frac{\exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} - y)] + \rho_{\mathrm{r,\,fl,\,3}} \,.\, \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} + y)]}{1 - \rho_{\mathrm{r,\,fl,\,3}} \cdot \rho_{\mathrm{r,\,fl,\,4}} \,.\, \exp[-2E_{\mathrm{fl}} \,.\, l_{\mathrm{y}}]} \,\mathrm{d}y \\ &= \frac{1}{l_{\mathrm{b}}' - l_{\mathrm{a}}'} \cdot \frac{\rho_{\mathrm{t,\,fl,\,4}}}{1 - \rho_{\mathrm{r,\,fl,\,3}} \cdot \rho_{\mathrm{r,\,fl,\,4}} \,.\, \exp[-2E_{\mathrm{fl}} \,.\, l_{\mathrm{y}}]} \\ &\quad \frac{\begin{array}{l} \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} - l_{\mathrm{b}}')] - \exp[-E_{\mathrm{fl}} \,.\, (l_{\mathrm{y}} - l_{\mathrm{a}}')] \\ \qquad + \rho_{\mathrm{r,\,fl,\,3}} \,.\, \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} + l_{\mathrm{a}}')] - \rho_{\mathrm{r,\,fl,\,3}} \,.\, \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} + l_{\mathrm{b}}')] \end{array}}{E_{\mathrm{fl}}} \end{aligned} \tag{5a}$$

$$F^{180} = \rho_{\mathrm{t,\,fl,\,2}} \frac{\exp[-E_{\mathrm{fl}}(l - x)] + \rho_{\mathrm{r,\,fl,\,1}} \exp[-E_{\mathrm{fl}}(l + x)]}{1 - \rho_{\mathrm{r,\,fl,\,1}} \cdot \rho_{\mathrm{r,\,fl,\,2}} \,.\, \exp[-2E_{\mathrm{fl}} \,.\, l]} \tag{6a}$$

The subscripts 1, 2, 3 or 4 used with ρ, denote the reflecting cell-faces in the way indicated in Fig. 1. The fluorescence intensity can now be obtained from the corrected equations together with equations (2) and (3). After integration the final formulae for the fluorescence intensity are:

$$I_{\mathrm{fl}}{}^{0} = T \cdot \frac{\rho_{\mathrm{t,\,ex,\,1}}}{1 - \rho_{\mathrm{r,\,ex,\,1}} \cdot \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-2E_{\mathrm{ex}} \cdot l]} \cdot \frac{\rho_{\mathrm{t,\,fl,\,1}}}{1 - \rho_{\mathrm{r,\,fl,\,1}} \cdot \rho_{\mathrm{r,\,fl,\,2}} \cdot \exp[-2E_{\mathrm{fl}} \cdot l]}$$
$$\cdot \left[\frac{1 - (1 - \rho_{\mathrm{r,\,ex,\,2}} \cdot \rho_{\mathrm{r,\,fl,\,2}})\exp[-(E_{\mathrm{ex}} + E_{\mathrm{fl}}) \cdot l] - \rho_{\mathrm{r,\,ex,\,2}} \cdot \rho_{\mathrm{r,\,fl,\,2}} \exp[-2(E_{\mathrm{ex}} + E_{\mathrm{fl}}) \cdot l]}{E_{\mathrm{ex}} + E_{\mathrm{fl}}} \right.$$
$$\left. + \frac{(\rho_{\mathrm{r,\,ex,\,2}} - \rho_{\mathrm{r,\,fl,\,2}}) \cdot \exp[-(E_{\mathrm{ex}} + E_{\mathrm{fl}})l] + \rho_{\mathrm{r,\,fl,\,2}} \cdot \exp[-2E_{\mathrm{fl}} \cdot l] - \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-2E_{\mathrm{ex}} \cdot l]}{E_{\mathrm{ex}} - E_{\mathrm{fl}}} \right] \tag{7a}$$

$$I_{\mathrm{fl}}{}^{90} = \frac{T}{l_{\mathrm{b}}{}' - l_{\mathrm{a}}{}'} \cdot \frac{\rho_{\mathrm{t,\,ex,\,1}}}{1 - \rho_{\mathrm{r,\,ex,\,1}} \cdot \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-2E_{\mathrm{ex}} \cdot l_{\mathrm{x}}]} \cdot \frac{\rho_{\mathrm{t,\,fl,\,4}}}{1 - \rho_{\mathrm{r,\,fl,\,3}} \cdot \rho_{\mathrm{r,\,fl,\,4}} \cdot \exp[-2E_{\mathrm{fl}} \cdot l_{\mathrm{y}}]}$$
$$\frac{\exp[-E_{\mathrm{ex}} \cdot l_{\mathrm{a}}] - \exp[-E_{\mathrm{ex}} \cdot l_{\mathrm{b}}] + \rho_{\mathrm{r,\,ex,\,2}} \exp[-E_{\mathrm{ex}}(2l_{\mathrm{x}} - l_{\mathrm{b}})] - \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-E_{\mathrm{ex}}(2l_{\mathrm{x}} - l_{\mathrm{a}})]}{E_{\mathrm{ex}}}$$
$$\frac{\exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} - l_{\mathrm{b}}{}')] - \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} - l_{\mathrm{a}}{}')] + \rho_{\mathrm{r,\,fl,\,3}} \cdot \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} + l_{\mathrm{a}}{}')] - \rho_{\mathrm{r,\,fl,\,3}} \cdot \exp[-E_{\mathrm{fl}}(l_{\mathrm{y}} + l_{\mathrm{b}}{}')]}{E_{\mathrm{fl}}} \tag{8a}$$

$$I_{\mathrm{fl}}{}^{180} = T \cdot \frac{\rho_{\mathrm{t,\,ex,\,1}}}{1 - \rho_{\mathrm{r,\,ex,\,1}} \cdot \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-2E_{\mathrm{ex}} \cdot l]} \cdot \frac{\rho_{\mathrm{t,\,fl,\,2}}}{1 - \rho_{\mathrm{r,\,fl,\,1}} \cdot \rho_{\mathrm{r,\,fl,\,2}} \cdot \exp[-2E_{\mathrm{fl}} \cdot l]}$$
$$\left[\frac{\exp[-E_{\mathrm{ex}} \cdot l] - \exp[-E_{\mathrm{fl}} \cdot l] + \rho_{\mathrm{r,\,ex,\,2}} \cdot \rho_{\mathrm{r,\,fl,\,1}}(\exp[-(2E_{\mathrm{ex}} + E_{\mathrm{fl}}) \cdot l] - \exp[-(E_{\mathrm{ex}} + 2E_{\mathrm{fl}}) \cdot l])}{E_{\mathrm{fl}} - E_{\mathrm{ex}}} \right.$$
$$\left. + \frac{\rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-E_{\mathrm{ex}} \cdot l] + \rho_{\mathrm{r,\,fl,\,1}} \cdot \exp[-E_{\mathrm{fl}} \cdot l] - \rho_{\mathrm{r,\,ex,\,2}} \cdot \exp[-(2E_{\mathrm{ex}} + E_{\mathrm{fl}}) \cdot l] - \rho_{\mathrm{r,\,fl,\,1}} \exp[-(E_{\mathrm{ex}} + 2E_{\mathrm{fl}}) \cdot l]}{E_{\mathrm{fl}} + E_{\mathrm{ex}}} \right] \tag{9a}$$

DISCUSSION OF THE FORMULAE

It seems useful to start this discussion with some examples of the dependence of the fluorescence intensity on the variables which occur in the formulae. The most convenient way to do so is graphically. For the "reflection-type" and "perpendicular-type" arrangements two different cases will be distinguished, according to whether the cell-walls opposite to the excitation light beam and opposite to the fluorescence beam exhibit only their natural reflection, or are silvered to make them highly reflective (this is, of course, impossible in the "transmission-type" arrangement). All values for ρ_{r} for normal cell-walls are taken to be 0·05, and for silvered cell-walls ρ_{r} is supposed to be 1·00. In Fig. 2 the ratio R of the corrected fluorescence intensity to the uncorrected intensity is given as a function of the absorbance at the excitation wavelength. A, the absorbance per

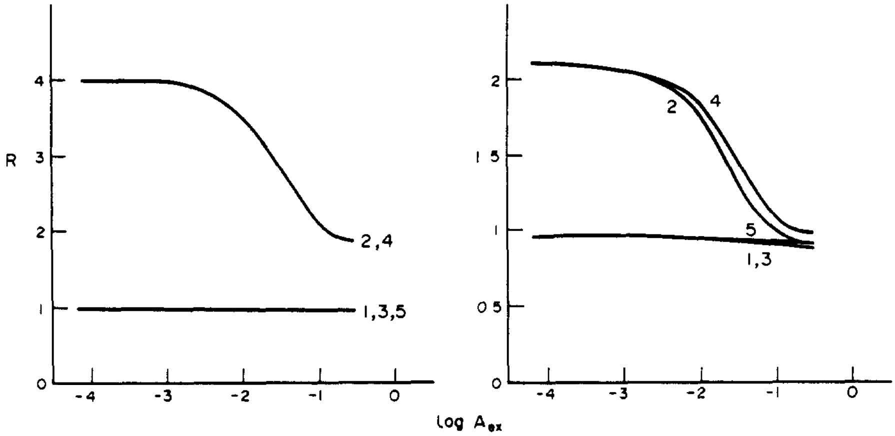

Fig. 2. The dependence of R on the absorbance per mm at the excitation wavelength.
Conditions: $l = l_x = l_y = 10$ mm. $l_a = l_a' = 1$ mm.
$l_b = l_b' = 9$ mm. $\rho_{r,ex,i} = \rho_{r,fl,i}$.
1. "Reflection-type" arrangement, $\rho_{r,1} = \rho_{r,2} = 0{\cdot}05$.
2. "Reflection-type" arrangement, $\rho_{r,1} = 0{\cdot}05$, $\rho_{r,2} = 1$.
3. "Perpendicular-type" arrangement, $\rho_{r,1} = \rho_{r,2} = \rho_{r,3} = \rho_{r,4} = 0{\cdot}05$.
4. "Perpendicular-type" arrangement, $\rho_{r,1} = \rho_{r,4} = 0{\cdot}05$, $\rho_{r,2} = \rho_{r,3} = 1$.
5. "Transmission-type" arrangement, $\rho_{r,1} = \rho_{r,2} = 0{\cdot}05$.
The curves in the left-hand figure are computed with $A_{fl} = 10^{-7}$, those in the right-hand figure are for $A_{fl} = 10^{-1}$.

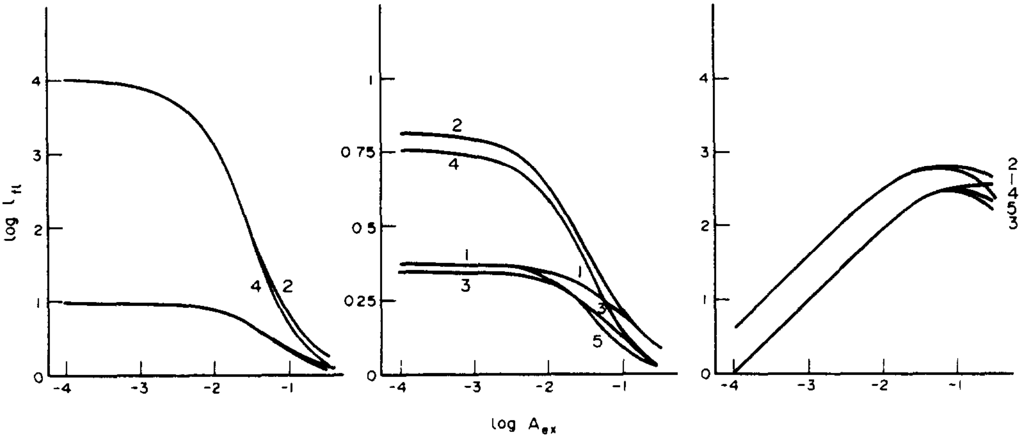

Fig. 3. The dependence of the fluorescence intensity on the absorbance per mm at the excitation wavelength.
Conditions as in Fig. 2.
1. "Reflection-type" arrangement, $\rho_{r,1} = \rho_{r,2} = 0{\cdot}05$.
2. "Reflection-type" arrangement, $\rho_{r,1} = 0{\cdot}05$, $\rho_{r,2} = 1$.
3. "Perpendicular-type" arrangement, $\rho_{r,1} = \rho_{r,2} = \rho_{r,3} = \rho_{r,4} = 0{\cdot}05$
4. "Perpendicular-type" arrangement, $\rho_{r,1} = \rho_{r,4} = 0{\cdot}05$, $\rho_{r,2} = \rho_{r,3} = 1$.
5. "Transmission-type" arrangement, $\rho_{r,1} = \rho_{r,2} = 0{\cdot}05$.
(a) $A_{fl} = 10^{-7}$; $k_{ex} . c = 10^{-7}$
(b) $A_{fl} = 10^{-1}$; $k_{ex} . c = 10^{-7}$.
(c) $A_{ex} = 10A_{fl} = k_{ex}$ c.
For all arrangements the intensity scale is such that $I_{fl} = 1$ for $A_{ex} = 10^{-4}$, $A_{fl} = 10^{-7}$ and $\rho_{r,1} = \rho_{r,2}(= \rho_{r,3} = \rho_{r,4}) = 0{\cdot}05$.

unit path length (based on Briggsian logarithms) is used in the figures and tables instead of E to facilitate comparison with practice. The dependence of R upon the absorbance at the fluorescence wavelength is quite similar to the dependence of R on the absorbance at the excitation wavelength. For this reason no separate graphs are given for the dependence of R on A_{fl}. As appears from Fig. 2 the correction for the effects of light-reflections can be quite large.

The dependence of the fluorescence intensity I_{fl} on the absorbance at the excitation wavelength is again rather similar to the dependence of I_{fl} on the absorbance at the fluorescence wavelength. Therefore, only graphs for I_{fl} as a function of A_{ex} will be given. These graphs are given for the case where the concentration of the fluorescent components is constant and $A_{\mathrm{fl}} = 0$ (Fig. 3*a*; for computational reasons the graph is given for $A_{\mathrm{fl}} = 10^{-7}$, but this does not influence the curve). In Fig. 3b the concentration of the fluorescent components is constant and $A_{\mathrm{fl}} = 0{\cdot}1$. Figure 3c is given for the case where the change in A_{ex} is caused by a change in the concentration of the fluorescent component.

In the "perpendicular-type" arrangement the measured fluorescence intensity depends on six parameters, which describe the position and dimensions of the cell and the windows. For the sake of brevity only some general remarks about these dependences can be made here. It is found that sensitivity and linearity of the fluorescence measurement are optimal if:

(a) l_a and $(l_y - l_b')$ are as small as possible
(b) $(l_b - l_a)$ and $(l_b' - l_a')$ are not too large (not larger than 10 mm in most cases), and
(c) l_x and l_y are only slightly larger than the windows in the cell faces.

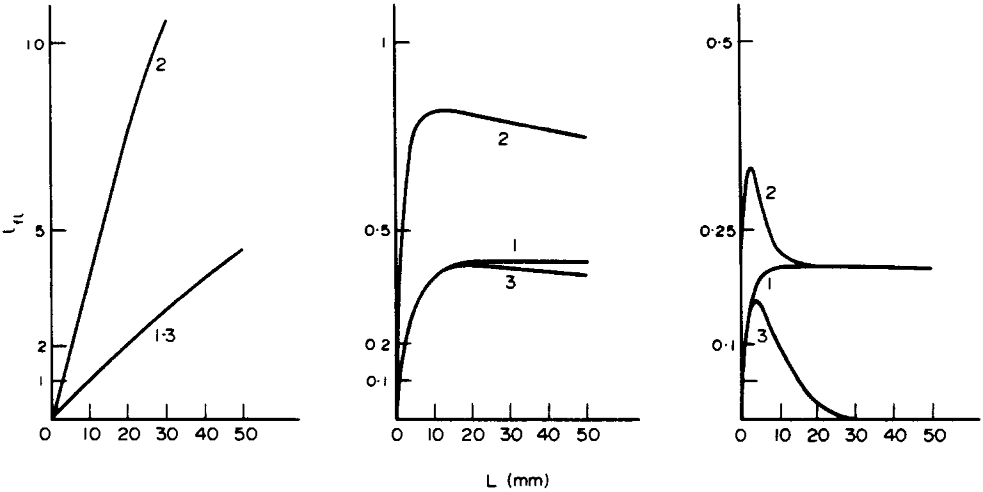

Fig. 4. The dependence of the fluorescence intensity on the cell length. $\rho_{r,\,\mathrm{ex}} = \rho_{r,\,\mathrm{fl}}$.
1. "Reflection-type" arrangement, $\rho_{r,\,1} = \rho_{r,\,2} = 0{\cdot}05$.
2. "Reflection-type" arrangement, $\rho_{r,\,1} = 0{\cdot}05$, $\rho_{r,\,2} = 1$.
3. "Transmission-type" arrangement, $\rho_{r,\,1} = \rho_{r,\,2} = 0{\cdot}05$.
(*a*) $A_{\mathrm{ex}} = A_{\mathrm{fl}} = 10^{-3}$
(*b*) $A_{\mathrm{ex}} = 10^{-3}$, $A_{\mathrm{fl}} = 10^{-1}$.
(*c*) $A_{\mathrm{ex}} = A_{\mathrm{fl}} = 10^{-1}$
The intensity scales are such that $I_{\mathrm{fl}} = 1$ for both arrangements, if $A_{\mathrm{ex}} = 10^{-4}$, $A_{\mathrm{fl}} = 10^{-7}$, $l = 10$ mm and $\rho_{r,\,1} = \rho_{r,\,2} = 0{\cdot}05$.

For the "reflection-type" and "transmission-type" arrangements the dependence of I_{fl} on the cell length is given in Figs. 4a ($A_{ex} = A_{fl} = 10^{-3}$), 4b ($A_{ex} = 10^{-3}$, $A_{fl} = 10^{-1}$) and 4c ($A_{ex} = A_{fl} = 10^{-1}$).

Linearity of the signal vs. *concentration curves*

The formulae for the fluorescence intensity can be written in a general way as:

$$I_{fl} = C \, . \, c_i \, . \, f(E_{ex}, E_{fl}, \rho_{r,ex}, \rho_{r,fl}, l) \tag{14}$$

where C is a proportionality constant. Values for the geometrical parameters l are nearly always fixed for a given apparatus. $\rho_{r,ex}$ and $\rho_{r,fl}$ generally do not change much on variation of the concentrations of the fluorescent substances. Therefore deviations from a linear relationship between I_{fl} and the concentrations c_i originate from changes in E_{ex} and/or E_{fl}. It is now to be considered whether a linear relationship between I_{fl} and c_i is possible. In the simplest case E_{ex} and E_{fl} are equal to the absorbance per mm due to the fluorescent substance. In that case a change in the concentration of the fluorescent substance always results in a change in E_{ex}. Therefore no truly linear relationship between I_{fl} and c can exist in this case.

In a seemingly more complicated case a change in the concentration of a fluorescent component brings about changes in the concentrations of other components. The changes in the absorbance per mm now are:

$$\Delta E = k_i \, . \, \Delta c_i + \sum_j k_j \, . \, \Delta c_j \tag{15}$$

[equation (15) holds both at the wavelength of fluorescence measurement and at the excitation wavelength]. According to the stoichiometry of the reaction, Δc_j is related to Δc_i by:

$$\Delta c_j = -\gamma_j \, . \, \Delta c_i \tag{16}$$

ΔE becomes zero if

$$k_i = \sum_j \gamma_j \, . \, k_j \tag{17}$$

Equation (17) can often be satisfied in practice. Many fluorimetric determinations of metals are based on the formation of a fluorescent complex. Let the metal (M) to ligand (L) ratio in such a complex (ML) be 1 : 1. In the wavelength range suitable for excitation there is nearly always a point where $k_{ML} = k_M + k_L$. Therefore, equation (17) is then satisfied for the excitation wavelength. Equation (17) can also be satisfied for the wavelength of fluorescence measurement, because it is often possible to choose this wavelength so that $k_M = k_L = k_{ML} = 0$. In a future communication an example will be given of a procedure that satisfies equation (17).

Wavelength choice if equation (17) *cannot be fulfilled*

Sometimes the excitation wavelength for which equation (17) is satisfied is such that k_{ex} is very small. Then the sensitivity of the measurement, which is directly proportional to k_{ex}, is very low too. On the other hand the background absorbance either at the excitation wavelength or at the wavelength of fluorescence measurement can be large, which also results in a low sensitivity. In such cases it may be necessary to choose an excitation wavelength or a wavelength for fluorescence measurement at which equation (17) is not fulfilled. Even then deviations from linearity in the I_{fl}–c_i relationship should preferably be as small as possible. To facilitate the choice of wavelength, tables are given which relate the change in absorbance per mm to the change in the fluorescence intensity (for fixed concentrations of the fluorescent components). If the wavelength dependences of the absorbance and the change in absorbance are known, it is possible with the use of the tables to find the wavelength combination where the deviations from linearity are minimal (a useful approximation is that the changes in I_{fl} caused by changes in A_{ex} and A_{fl} are additive for small values of ΔA_{ex} and ΔA_{fl}). However, even if $\Delta A_{ex} = -\Delta A_{fl}$, no strictly linear relationship between I_{fl} and c_i can be obtained. It seems useful to illustrate the use of the tables with an example. Assume a case for which equation (17) is satisfied at an excitation wavelength where owing to a high value of A_{ex}, the sensitivity of the determination is too low. Now, with the use of Fig. 3, select an A_{ex} value for which the sensitivity is high enough. From spectral data calculate ΔA_{ex} at this wavelength. Then use the relevant table for ΔA_{ex} to calculate the deviation from linearity. The % deviation from linearity is found as approximately ΔA_{ex} (calc)/ΔA_{ex} (table). If this deviation is unacceptable, the procedure has to be repeated at the wavelength of fluorescence measurement in such a way that the deviation from linearity due to ΔA_{ex} is as much as possible counteracted by the deviation caused by ΔA_{fl}.

Table 1. The change ΔA_{ex} in A_{ex}, which results in a change of 1% in I_{fl} for fixed concentrations of the fluorescent substances ("Reflection-type" arrangement. $l = 10$ mm; $\rho_{r,ex,1} = \rho_{r,fl,1} = \rho_{r,ex,2} = \rho_{r,fl,2} = 0{\cdot}05$. Tabulated values are $\Delta A_{ex} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·79	0·79	0·80	0·80	0·83	0·94	1·33	3·21
$10^{-3\cdot5}$	0·79	0·79	0·80	0·80	0·84	0·94	1·33	3·21
10^{-3}	0·79	0·80	0·80	0·81	0·84	0·94	1·34	3·21
$10^{-2\cdot5}$	0·80	0·80	0·80	0·81	0·84	0·95	1·35	3·24
10^{-2}	0·81	0·82	0·82	0·83	0·86	0·98	1·39	3·30
$10^{-1\cdot5}$	0·87	0·87	0·88	0·89	0·93	1·06	1·53	3·51
10^{-1}	1·11	1·12	1·12	1·15	1·22	1·43	2·08	4·20
$10^{-0\cdot5}$	1·99	1·99	2·02	2·09	2·31	2·96	4·16	6·40

Table 2. The change ΔA_{ex} in A_{ex}, which results in a change in I_{fl} of 1%. ("Reflection-type" arrangement. $l = 10$ mm. $\rho_{r,1} = 0{\cdot}05$. $\rho_{r,2} = 1$. Tabulated values are $\Delta A_{ex} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·40	0·40	0·40	0·41	0·44	0·55	1·06	3·19
$10^{-3\cdot5}$	0·40	0·40	0·40	0·41	0·44	0·55	1·06	3·19
10^{-3}	0·40	0·40	0·40	0·41	0·44	0·55	1·06	3·19
$10^{-2\cdot5}$	0·40	0·40	0·40	0·41	0·44	0·55	1·06	3·19
10^{-2}	0·40	0·40	0·40	0·41	0·44	0·55	1·06	3·21
$10^{-1\cdot5}$	0·40	0·40	0·40	0·41	0·44	0·57	1·12	3·35
10^{-1}	0·40	0·40	0·40	0·41	0·46	0·63	1·54	4·13
$10^{-0\cdot5}$	0·40	0·40	0·40	0·42	0·49	0·83	3·24	6·40

Table 3. The change ΔA_{ex} in A_{ex}, which results in a change in I_{fl} of 1%. ("Perpendicular-type" arrangement. $l_x = l_y = 10$ mm. $l_a = l_a' = 1$ mm. $l_b = l_b' = 9$ mm. $\rho_{r,1} = \rho_{r,2} = \rho_{r,3} = \rho_{r,4} = 0\cdot05$. Tabulated values are $\Delta A_{ex} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}–$10^{-0\cdot5}$	0·79	0·79	0·80	0·80	0·83	0·90	1·12	1·86

Table 4. The change ΔA_{ex} in A_{ex}, which results in a change in I_{fl} of 1%. ("Perpendicular-type" arrangement. $l_x = l_y = 10$ mm. $l_a = l_a' = 1$ mm. $l_b = l_b' = 9$ mm. $\rho_{r,1} = \rho_{r,4} = 0\cdot05$. $\rho_{r,2} = \rho_{r,3} = 1$. Tabulated values are $\Delta A_{ex} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}–$10^{-0\cdot5}$	0·40	0·40	0·40	0·41	0·44	0·54	0·92	1·85

Table 5. The change ΔA_{ex} in A_{ex}, which results in a change in I_{fl} of 1%. ("Transmission-type" arrangement. $l = 10$ mm. $\rho_{r,1} = \rho_{r,2} = 0\cdot05$. Tabulated values are $\Delta A_{ex} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·79	0·79	0·80	0·80	0·83	0·94	1·33	3·21
$10^{-3\cdot5}$	0·79	0·79	0·80	0·80	0·83	0·94	1·33	3·21
10^{-3}	0·79	0·79	0·79	0·80	0·83	0·94	1·32	3·20
$10^{-2\cdot5}$	0·78	0·78	0·79	0·80	0·83	0·93	1·32	3·18
10^{-2}	0·77	0·77	0·77	0·78	0·81	0·91	1·28	3·12
$10^{-1\cdot5}$	0·72	0·72	0·73	0·73	0·76	0·89	1·16	2·92
10^{-1}	0·61	0·61	0·61	0·62	0·63	0·67	0·86	2·28
$10^{-0\cdot5}$	0·49	0·50	0·50	0·50	0·50	0·50	0·53	0·87

Table 6. The change ΔA_{fl} in A_{fl}, which results in a change in I_{fl} of 1%. "Reflection-type" arrangement. $l = 10$ mm. $\rho_{r,1} = \rho_{r,2} = 0\cdot05$. Tabulated values are $\Delta A_{fl} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·79	0·79	0·79	0·80	0·81	0·87	1·11	1·98
$10^{-3\cdot5}$	0·79	0·79	0·80	0·80	0·82	0·87	1·11	1·99
10^{-3}	0·80	0·80	0·80	0·80	0·82	0·88	1·12	2·02
$10^{-2\cdot5}$	0·80	0·80	0·81	0·81	0·83	0·89	1·14	2·08
10^{-2}	0·84	0·84	8·84	0·84	0·86	0·93	1·21	2·31
$10^{-1\cdot5}$	0·94	0·94	0·94	0·95	0·98	1·06	1·43	2·95
10^{-1}	1·34	1·34	1·34	1·35	1·39	1·54	2·08	4·15
$10^{-0\cdot5}$	3·22	3·22	3·23	3·25	3·31	3·52	4·22	6·40

Table 7. The change ΔA_{fl} in A_{fl}, which results in a change in I_{fl} of 1%. "Reflection-type" arrangement. $l = 10$ mm. $\rho_{r,1} = 0{\cdot}05$. $\rho_{r,2} = 1$ Tabulated values are $\Delta A_{fl} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·40	0·40	0·40	0·40	0·40	0·40	0·40	0·40
$10^{-3\cdot5}$	0·40	0·40	0·40	0·40	0·40	0·40	0·40	0·40
10^{-3}	0·40	0·40	0·40	0·40	0·40	0·40	0·40	0·40
$10^{-2\cdot5}$	0·41	0·41	0·41	0·41	0·41	0·41	0·41	0·42
10^{-2}	0·44	0·44	0·44	0·44	0·44	0·44	0·46	0·49
$10^{-1\cdot5}$	0·55	0·55	0·55	0·55	0·56	0·57	0·63	0·83
10^{-1}	1·06	1·06	1·06	1·06	1·06	1·12	1·55	3·25
$10^{-0\cdot5}$	3·21	3·21	3·21	3·21	3·22	3·36	4·14	6·40

Table 8 The change ΔA_{fl} in A_{fl}, which results in a change in I_{fl} of 1%. "Perpendicular-type" arrangement $l_x = l_y = 10$ mm. $l_a = l_a' = 1$ mm. $l_b = l_b' = 9$ mm. $\rho_{r,1} = \rho_{r,2} = \rho_{r,3} = \rho_{r,4} = 0{\cdot}05$. Tabulated values are $\Delta A_{fl} \times 10^3$)

A_{ex}	A_{fl}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}–$10^{-0\cdot5}$	0·79	0·79	0·80	0·80	0·83	0·90	1·12	1·86

Table 9 The change ΔA_{fl} in A_{fl}, which results in a change in I_{fl} of 1%. ("Perpendicular-type" arrangement. $l_x = l_y = 10$ mm $l_a = l_a' = 1$ mm. $l_b = l_b' = 9$ mm. $\rho_{r,1} = \rho_{r,4} = 0{\cdot}05$. $\rho_{r,2} = \rho_{r,3} = 1$. Tabulated values are $\Delta A_{fl} \times 10^3$)

A_{ex}	A_{fl}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}–$10^{-0\cdot5}$	0·40	0·40	0·40	0·41	0·44	0·54	0·92	1·86

Table 10 The change ΔA_{fl} in A_{fl}, which results in a change in I_{fl} of 1%. ("Transmission-type" arrangement. $l = 10$ mm. $\rho_{r,1} = \rho_{r,2} = 0{\cdot}05$. Tabulated values are $\Delta A_{fl} \times 10^3$)

A_{fl}	A_{ex}							
	10^{-4}	$10^{-3\cdot5}$	10^{-3}	$10^{-2\cdot5}$	10^{-2}	$10^{-1\cdot5}$	10^{-1}	$10^{-0\cdot5}$
10^{-4}	0·79	0·79	0·79	0·78	0·77	0·72	0·61	0·50
$10^{-3\cdot5}$	0·79	0·79	0·79	0·78	0·77	0·72	0·61	0·50
10^{-3}	0·80	0·80	0·79	0·79	0·77	0·73	0·61	0·50
$10^{-2\cdot5}$	0·80	0·80	0·80	0·80	0·78	0·73	0·62	0·50
10^{-2}	0·83	0·83	0·83	0·83	0·81	0·76	0·63	0·50
$10^{-1\cdot5}$	0·94	0·94	0·94	0·93	0·91	0·84	0·68	0·50
10^{-1}	1·33	1·33	1·33	1·32	1·28	1·16	0·86	0·53
$10^{-0\cdot5}$	3·22	3·22	3·21	3·19	3·13	2·93	2·30	0·88

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Zusammenfassung—Es werden Formeln für das Fluoreszenzsignal abgeleitet, die einige bisher vernachlässigte Faktoren in Rechnung stellen. Aus diesen Formeln werden Bedingungen gefolgert, bei denen zwischen der Konzentration der fluoreszierenden Komponenten und der Fluoreszenzintensität eine lineare Beziehung besteht. In einigen Fällen von praktischem Interesse führt die Erfüllung dieser Bedingungen zu einer zu geringen Empfindlichkeit. Für solche Falle wird eine Optimierungsmethode skizziert, durch die diejenigen Bedingungen aufgefunden werden, die bei der verlangten Empfindlichkeit zu der kleinsten Abweichung von der Linearität führen.

Résumé—On établit des formules pour le signal de fluorescence qui prennent en considération quelques facteurs jusque là négligés. De ces formules on déduit les conditions pour lesquelles une relation linéaire existe entre la concentration des composants fluorescents et l'intensité de la fluorescence. Dans quelques cas d'intérêt pratique le respect de ces conditions provoque une sensibilité trop faible. Pour de tels cas, on donne un aperçu d'une méthode d'optimalisation, au moyen de laquelle on trouve les conditions qui mènent à la moindre déviation de la linéarité à la sensibilité requise.

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SHORT COMMUNICATION

NEW SPOT-TEST FOR CYANIDE ION AND CYANOGEN GAS

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A rich literature is available on the determination of the cyanide ion. Bark and Higson[1] have published a review of the methods existing for the detection and determination of small amounts of cyanide. Later many other methods were suggested, and these include titrimetric with visual[2] or instrumental end-point,[3] polarographic,[4] gas-chromatographic[5] and colorimetric[6] finishes.

Similarly, many spot-tests for the cyanide ion have been proposed and these are already described in detail by Feigl.[7] Sabo[8] advocated the use of silver chromate-impregnated paper for the detection of a great variety of anions, including cyanide. The cyanide ion gives rise to a green fluorescence with solutions of quinone monoxime benzenesulphonate ester and *p*-benzoquinone in dimethylsulphoxide.[9] Direct detection of cyanide was possible through its catalytic effect on the condensation of picolinaldehyde.[10] In general, the methods described by Feigl[7] are less sensitive than those developed later.

However, in the present work a new spot-test was developed for cyanide which has two main advantages: (*i*) its sensitivity is superior to most of the existing spot-test methods,[7,8] and (*ii*) it is applicable, with slight modification, to the detection of cyanogen gas. The existing test for cyanogen is that it forms a polycyanide with cyanide ions, which gives a red colour with 8-hydroxyquinoline.[11] However, this detection[11] is reliable only in absence of compounds which split off water when heated; water vapour readily hydrolyses cyanogen gas to hydrogen cyanide and cyanic acid:

$$(CN)_2 + H_2O\ (\text{vapour}) \longrightarrow HCNO + HCN$$

The new test involves the reaction of cyanide ion with ammonium molybdate–copper(II) solution in acetic acid medium, to give a blue colour. Cyanogen gives the same colour but only after its conversion into cyanide in alkaline medium. The reaction is sensitive down to 0·15 μg of cyanide in a 0·1-ml drop (*i.e.*, 1·5 ppm), which is reasonable for detection purposes, without the need of any special equipment. The conditions of reaction and the interference of many other anions and cations are discussed below.

EXPERIMENTAL

Reagents

Unless otherwise specified, all reagents are of analytical grade.

Procedure

Detection of cyanide ion. Put a drop of the test solution (containing not less than 0·15 μg of cyanide ion) on a spot-plate. Add one drop of 0·01% copper sulphate solution followed by 1 or 2 drops of 5% ammonium molybdate solution in concentrated hydrochloric acid. A blue colour is developed immediately.

The lower limit of identification is 0·15 μg of cyanide per 0·1 ml (*i.e.*, 1·5 ppm), and the lower limit of dilution is 1 : 30000.

Detection of cyanogen gas. Pass the test gas either through a test-tube containing a mixture of copper sulphate solution (0·01%) and sodium hydroxide solution (1%) or a filter paper impregnated with the same mixture. Add 2–5 drops of 5% ammonium molybdate solution in concentrated hydrochloric acid. A blue colour is developed immediately if cyanogen was present.

DISCUSSION

Reaction conditions

Cyanide ion reduces copper(II) to copper(I). The latter reduces ammonium molybdate in concentrated hydrochloric acid to give a blue colour which is most probably that of molybdenum blue. When the test is to be used for detection of cyanogen gas, this should first be converted into cyanide ion by allowing it to react with sodium hydroxide:

$$(CN)_2 + NaOH \longrightarrow NaCNO + NaCN$$

The concentrations of both acid and ammonium molybdate as well as the sequence of the addition of the reagents are critical. A 5% solution of ammonium molybdate in concentrated hydrochloric acid was found quite suitable. The order of addition of reagents to the cyanide ion should start with copper(II) followed by the addition of ammonium molybdate–hydrochloric acid solution. When the latter solution was added before the copper(II) solution, no colour was developed, owing to the volatilization of hydrocyanic acid.

Interferences

Cyanate, nitrite, sulphite, phosphate, arsenate, thiocyanate, germanate, silicate, carbonate, chloride, sulphate, nitrate, chlorate, iodate and chromate did not interfere with the test. However, iron (II), tin(II), antimony(III), thiosulphate, and iodide give a blue colour with the copper–molybdate mixture.

Also, as expected, ferrocyanides and tetracyanozincate(II) interfered. Despite the reducing nature of the ferrocyanide ion, it reacted preferentially with copper, forming the brown copper ferrocyanide. In the case of complex zinc cyanide a blue colour was obtained, presumably owing to the relative instability of the complex and the sensitivity of the test.

The presence of tolerable amounts of thiocyanate, silicate, phosphate, arsenate and germanate caused only a slight decrease in the colour intensity and thus the test was still sufficiently sensitive for the detection of the cyanide ion. In general, this test is applicable for the cyanide ion in absence of either reducing or oxidizing substances and of cations with strong complexing properties towards the cyanide ion [*e.g.*, iron(III), cobalt(II), cobalt(III), and nickel(II)].

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Summary—A new, rapid and simple spot test has been developed for detection of both cyanide ion and cyanogen gas. The cyanogen gas must first be converted into cyanide ion by reaction with sodium hydroxide. On addition of a Cu(II) solution the cyanocuprate(I) complex formed reduces the molybdate solution to molybdenum blue.

Zusammenfassung—Eine neue schnelle und einfache Tüpfelprobe zum Nachweis von Cyanidionen und gasförmigem Dicyan wurde entwickelt. Das Dicyan muß zuerst durch Reaktion mit Natriumhydroxid in Cyanid überführt werden. Bei Zugabe einer Kupfer(II)-Lösung reduziert der gebildete Cyanocuprat(I)-Komplex Molybdatlösung zu Molybdänblau.

Résumé—On a élaboré un nouvel essai à la touche, rapide et simple, pour la détection à la fois de l'ion cyanure et du gaz cyanogène. Le gaz cyanogène doit d'abord être converti en ion cyanure par réaction avec la soude. Par addition d'une solution de Cu (II) le complexe cyanocuprate (I) formé réduit la solution de molybdate en bleu de molybdène.

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ANALYTICAL DATA

SPECTROPHOTOMETRIC DETERMINATION OF THE STABILITY CONSTANTS OF $HgCl_3^-$ AND $HgCl_4^{2-}$ IN AQUEOUS ETHANOL

(*Received* 1 *November* 1972. *Accepted* 26 *November* 1972)

Unlike the situation in water,[1] mercuric chloride does not complex with chloride ions in ethanol.[2] Our kinetic studies on the solvolysis of alkyl chlorides, catalysed by mercuric chloride, have also shown that the electrophilic activity of the catalyst is less in aqueous ethanol than in aqueous acetone solvents of the same water content.[3] Solubility measurements (which have only semi-quantitative significance since neither ionic strength nor acidity could be controlled) also support this conclusion.[4] We have now determined the stability constants for $HgCl_3^-$ and $HgCl_4^{2-}$ in 60% aqueous ethanol (v/v) at 25° by ultraviolet-region spectrophotometry under conditions of constant ionic strength (0·5*M*; $LiClO_4$) and acidity (0·01*N*; $HClO_4$). The data were processed by an adaptation of the Legatrop method[5] to Thamer's equation,[6] and the following values obtained: $\beta_1 = 3 \pm 1$ and $\beta_2 = 9 \pm 3$. These values are lower than those for the water system.[1]

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Summary—The stability constants of $HgCl_3^-$ and $HgCl_4^{2-}$ in 60% aqueous ethanol (v/v) were determined by spectroscopy at 25° and constant ionic strength and acidity; β_1 was 3 ± 1 and β_2 9 ± 3.

Zusammenfassung—Die Stabilitätskonstanten von $HgCl_3^-$ und $HgCl_4^{2-}$ in 60 Vol-% wäßrigem Äthanol wurden durch Spektrophotometrie bei 25°, konstanter Ionenstärke und Acidität bestimmt: β_1 betrug 3 ± 1 und β_2 9 ± 3.

Résumé—On a déterminé les constantes de stabilité de $HgCl_3^-$ et $HgCl_4^{2-}$ an éthanol aqueux à 60% (v/v) par spectroscopie à 25° et à force ionique et acidité constantes; β_1 est 3 ± 1 et β_2 9 ± 3.

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OXIDATION WITH PERMANGANATE IN PRESENCE OF FLUORIDE

POTENTIOMETRIC DETERMINATION OF MANGANESE(II)

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Summary—The effects of acidity, fluoride concentration, temperature and concentration of manganese in the reaction between $KMnO_4$ and Mn(II) were studied potentiometrically. The rate of reaction is increased by increasing the fluoride concentration and/or decreasing the acidity of the solution. The formal redox potentials of the MnO_4^-/Mn(III) and the Mn(III)/Mn(II) systems were determined at different pH values. The E° values obtained by extrapolation to pH = 0 were 1·58 and 1·52 V respectively. The amount of Mn(II) determined was varied from 5 to 56 mg. The net reaction can be represented as $MnO_4^- + 10HF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O$

Oxidation of manganous ions with potassium permanganate in presence of fluoride has been investigated before as a method for determination of manganese(II).[1,2] The visual method has proved successful for small amounts of manganese(II) and when copper(II) is used as catalyst, but cannot be used for high concentrations of Mn(II) or in the presence of coloured ions. The potentiometric method does not suffer from this drawback and for this reason the potentiometric titration of manganese(II) with permanganate in fluoride solutions has been studied.

EXPERIMENTAL

Reagents

Twice-distilled water was used in the preparation of all solutions. Analytical-grade reagents were used where possible.

Manganous sulphate solutions, 0·0926 *and* 0·0635*M*. Prepared in 0·1*M* sulphuric acid to prevent hydrolysis, and standardized by the pyrophosphate method.[3,4] Solutions of lower concentrations were prepared by appropriate dilution.

Potassium permanganate solution. Prepared according to the method of Stamm,[5] and standardized with oxalate.[6]

Sodium fluoride solution, 2%(~ 0·48*M*).

Sulphuric acid, 0·5 *and* 5*M*.

Manganese(III) solution, $2·5 \times 10^{-3}M$. Prepared from equivalent amounts of Mn(II) and $KMnO_4$ in presence of fluoride ions under the optimum conditions previously given.[1,7]

Equipment

The potentiometric titration apparatus was similar to that described elsewhere.[8] The cells used for the redox potential measurements were as follows:

(*a*)

$$\begin{array}{c} \text{Hg} \mid \text{Hg}_2\text{Cl}_2 \parallel \text{KCl} \\ \text{(saturated)} \end{array} \left\Vert \begin{array}{l} \text{Mn(III)} \\ \text{MnO}_4^- \\ [\text{NaF}] = m_1, [\text{H}^+] = m_2 \end{array} \right| \text{Pt}$$

(*b*)

$$\begin{array}{c} \text{Hg} \mid \text{Hg}_2\text{Cl}_2 \parallel \text{KCl} \\ \text{(saturated)} \end{array} \left\Vert \begin{array}{l} \text{Mn(III)} \\ \text{Mn(II)} \\ [\text{NaF}] = m_1, [\text{H}^+] = m_2 \end{array} \right| \text{Pt}$$

In this study m_1 was kept constant, while m_2 was varied by adding different amounts of 2·5*M* sulphuric acid. The ratio [OX]/[Red] in both systems was either 1 : 1 or 2 : 1. The potentials were measured 3 hr after immersion of the electrodes, although slight variations were observed within the following 24 hr.

Titration procedure

A volume of manganous solution containing 5–56 mg of manganese(II) was placed in the titration cell and mixed with the required quantities of 0·5*M* sulphuric acid and 2% sodium fluoride solution. The mixture was diluted to 100 ml and then titrated with permanganate at room temperature. The e.m.f. of the titration cell was measured by a direct reading mV meter, with a saturated calomel electrode (SCE) as reference half-cell.

RESULTS AND DISCUSSION

The values of reported potentials in all tables, plots and treatments are referred to the normal hydrogen electrode (NHE).

Effect of acidity

The effect of acidity on the reaction was studied by titrating 10 ml of 0·01*M* manganese(II) mixed with 75 ml of 2% sodium fluoride solution (~0·36*M*) in presence of varying concentrations of sulphuric acid. The curves are shown in Fig. 1, and the corresponding results in Table 1. In absence of additional acid, the titration curve (*A*) shows two breaks close to each other, the second corresponding to the oxidation of Mn(II) to MnO_2 and the other undoubtedly representing formation of manganese(III) but occurring later than at the theoretical value. With 1·0–1·5 ml of 0·5*M* sulphuric acid present the two inflections still occur but deviate largely from the theoretical end-points. With 2·0–8·0 ml of the acid added, only one inflection is observed for Mn(III), and the end-point agrees fairly well with the theoretical. The single inflection shows that manganese(III) is stable to oxidation under the optimum conditions, but not at lower acidities, when some but not all of it is oxidized to MnO_2. Hydrolysis may occur with formation of a precipitate of Mn_2O_3 which is then oxidized only at the surface. At pH 8·5–9·0 the second end-point approaches the theoretical for production of MnO_2. The equilibrium potential is attained more rapidly at lower acidity than at higher, 3–5 min being necessary for stabilization under the optimum conditions.

At lower acidity there may also be partial oxidation of Mn(II) to MnO_2 by atmospheric oxygen.

Effect of sodium fluoride concentration

Figure 2 and Table 2 show the results of titrating 10 ml of 0·01*M* manganese(II) in presence of 8·0 ml of 0·5*M* sulphuric acid and 25–75 ml of 2% sodium fluoride solution. Good results are obtained only in presence of 50–75 ml of fluoride solution.

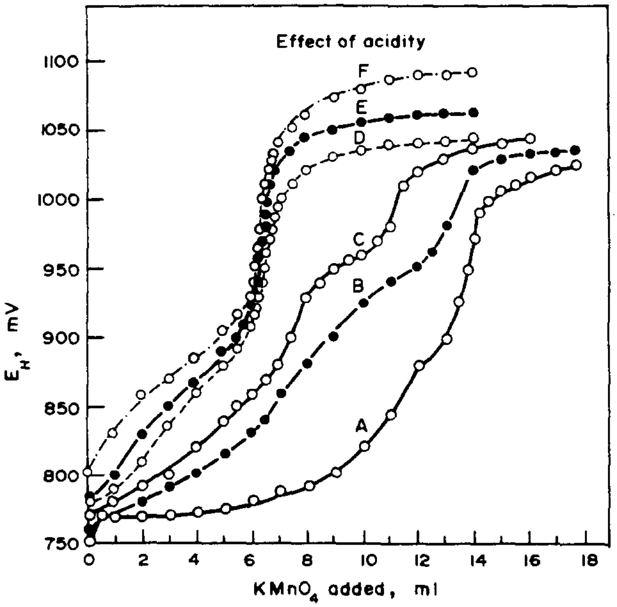

Fig. 1. Titration of 10 ml of 0·01*N* $MnSO_4$ with 0·0192*N* $KMnO_4$ (for $Mn^{7+} \rightarrow Mn^{2+}$) in presence of 75 ml of 2% NaF solution and varying amounts of 0·5*M* H_2SO_4: (*A*) no acid (*B*) 1·0 ml (*C*) 1·5 ml (*D*) 2·0 ml (*E*) 4·0 ml (*F*) 8·0 ml.

Addition of 25 ml of the fluoride solution is more than sufficient for complexation of the Mn(III) and was earlier[9] found to yield good results; the need for more is due to protonation of part of the fluoride by the extra strong acid added.

Effect of manganese concentration

The results in Table 3 show that 5–56 mg of Mn(II) can be titrated successfully under the optimum conditions. At higher concentration of Mn(II) the reaction medium becomes slightly turbid owing to the hydrolysis of Mn(III) to Mn_2O_3.

Table 1. Titration of 10 ml of 0·01*N* $MnSO_4$ with 0·0192*N** $KMnO_4$ in presence of 75 ml of 2% NaF solution and varying amounts of 0·5*M* H_2SO_4, total volume made up to 100 ml with water

0·5*M* H_2SO_4 added, *ml*	Composition of the reaction mixture†	$\frac{[H_2SO_4]}{[NaF]}$ initially added	$\frac{[HF]}{[NaF]}$ present	Theoretical end-point, *ml*		Experimental end-point, *ml*		Error, %		Max. $\Delta E/\Delta V$ *m V*/0·1*ml*	
				a‡	*b*‡	*a*‡	*b*‡	*a*‡	*b*‡	*a*‡	*b*‡
0·0	0·36*M* NaF	—	—	6·49	17·39	11·5	13·9	+77	−20	4	10
1·0	0·01*M* HF + 0·35*M* NaF	1 : 72	1 : 35	6·49	17·39	8·5	13·5	+31	−22	2	4
1·5	0·015*M* HF + 0·345*M* NaF	1 : 48	1 : 23	6·49	17·39	7·75	11·25	+19	−35	6	2
2·0	0·02*M* HF + 0·34*M* NaF	1 : 36	1 : 17	6·49		6·35		−2·2		21	
6·0	0·06*M* HF + 0·30*M* NaF	1 : 12	1 : 5	6·49		$6{\cdot}44_5$		−0·7		19	
7·0	0·07*M* HF + 0·29*M* NaF	1 : 10	1 : 4	6·49		$6{\cdot}47_5$		−0·2		23	
8·0	0·08*M* HF + 0·28*M* NaF	1 : 9	1 : 3·5	6·49		$6{\cdot}47_5$		−0·2		23	

* On the basis of $Mn^{7+} \rightarrow Mn^{2+}$.

† Calculated on basis of added acid and NaF.

‡ (*a*) $Mn^{2+} \rightarrow Mn^{3+}$; (*b*) $Mn^{2+} \rightarrow Mn^{4+}$

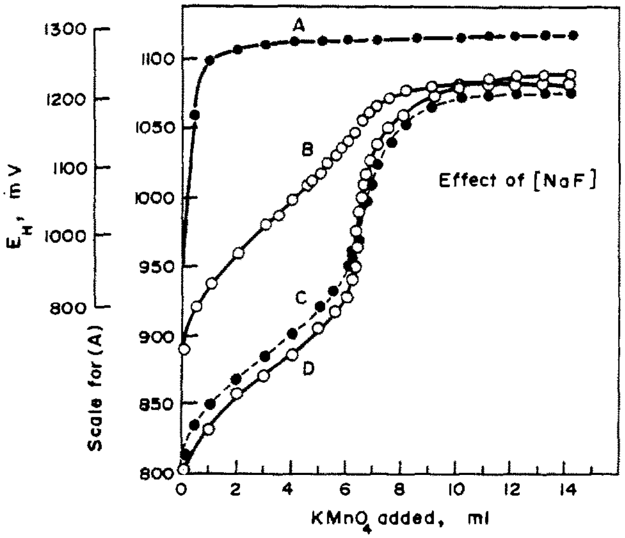

Fig. 2. Titration of 10 ml of 0·01*N* $MnSO_4$ with 0·0154*N* $KMnO_4$ (for $Mn^{7+} \rightarrow Mn^{3+}$) in presence of 8·0 ml of 0·5*M* H_2SO_4 and varying amounts of 2% NaF solution: (*A*) no NaF (*B*) 25 ml (*C*) 50 ml (*D*) 75 ml.

Formal redox potentials of MnO_4^-/Mn(III) *and* Mn(III)/Mn(II) *systems*

The formal redox potentials were determined from potential measurements of the cells mentioned above. Measurements were made over the pH range 0·9–6·0, [Mn(III)] and [NaF] being kept constant and the ratios [Mn(III)]/[Mn(II)] and [MnO_4^-]/[Mn(III)] varied.

The values of $E°$ for the two half-cells were determined from the Nernst equation, neglecting activity coefficients (Tables 4 and 5):

$$E_H = E° + \frac{RT}{nF}\ln\frac{[Ox]^A}{[Red]^B} + \frac{RT}{nF}\ln[H^+]X$$

Table 2. Titration of 10 ml of 0·01*N* $MnSO_4$ with 0·0154*N** $KMnO_4$, with 8·0 ml of 0·5*M* H_2SO_4 in presence of varying amounts of 2% NaF solution (~0·48*M*), and dilution to 100 ml with water

2% NaF added, *ml*	Composition of the reaction mixture	$\frac{[H_2SO_4]}{[NaF]}$ initially added	$\frac{[HF]}{[NaF]}$ present	Theoretical end-point, *ml*	Experimental end-point, *ml*	Error, %	Max. $\Delta E/\Delta V$, *mV*/0·1*ml*
0·0	0·04*M* H_2SO_4	–	–	6·49	(no reaction)		
25	0·08*M* HF + 0·04*M* NaF	1 : 3	2 : 1	6·49	6·40	−1·4	5
50	0·08*M* HF + 0·16*M* NaF	1 : 6	1 : 2	6·49	6·45	−0·6	15
65	0·08*M* HF + 0·23*M* NaF	1 : 8	1 : 3	6·49	6·47	−0·3	21
75	0·08*M* HF + 0·28*M* NaF	1 : 9	1 : 3·5	6·49	$6{\cdot}47_5$	−0·2	23

* On the basis of $Mn^{7+} \rightarrow Mn^{3+}$.

Table 3. Titration of Mn(II) with $KMnO_4$ in presence of 8 ml of 0·5*M* H_2SO_4 and 75 ml of 2% NaF solution, with dilution to 100 ml with water ($[H_2SO_4]/[NaF]$ added = 1 : 9, or $[HF]/[NaF]$ present = 1 : 3·5)

Mn(II), *ml*	Mn(II), *mg*	Theoretical end-point, *ml*	Experimental end-point, *ml*	Error, %	Max. $\Delta E/\Delta V$, *mV*/0·1*ml*
Titration of 0·0926*N* $MnSO_4$ with 0·1043*N* $KMnO_4$*					
4·0	20·35	3·55	$3{\cdot}54_5$	−0·14	62
5·7	29·00	5·06	5·05	−0·20	60
8·0	40·70	7·15	7·14	−0·14	60
11·0	55·96	9·76	9·75	−0·20	58
Titration of 0·0475*N* $MnSO_4$ with 0·052*N* $KMnO_4$*					
4·0	10·44	3·654	3·65	−0·10	40
7·0	18·27	6·394	3·38	−0·14	40
Titration of 0·01*N* $MnSO_4$ with 0·0154*N* $KMnO_4$*					
10	5·49	6·490	$6{\cdot}47_5$	−0·23	23
15	8·24	9·740	$9{\cdot}72_5$	−0·15	24
20†	10·98	12·990	$12{\cdot}97_5$	−0·12	26

* On the basis of $Mn^{7+} \rightarrow Mn^{3+}$.

† Total volume of reaction mixture 103 ml.

where X represents the number of H^+ ions and A and B are the number of molecules of oxidant and reductant in the half-cell reaction. This equation can be written in the following forms for the two half-cell reactions at 25° ($A = B = 1$):

$$_{\text{I}}E_{\text{H}} = {}_{\text{I}}E^{\circ} + \frac{0{\cdot}0591}{4}\log\frac{[MnO_4^-]}{[Mn(III)]} - \frac{0{\cdot}0591}{4}X_{\text{I}}\ \text{pH} \tag{1}$$

$$_{\text{II}}E_{\text{H}} = {}_{\text{II}}E^{\circ} + 0{\cdot}0591\log\frac{[Mn(III)]}{[Mn(II)]} - 0{\cdot}0591\ X_{\text{II}}\ \text{pH} \tag{2}$$

where X_{I} and X_{II} represent the numbers of H^+ ions involved in the $MnO_4^-/Mn(III)$ and Mn(III)/Mn(II) half-cell reactions respectively.

Table 4. Values of $_{\text{I}}E_f$ for the $MnO_4^-/Mn(III)$ system at various pH values and 25°C

	$_{\text{I}}E_{\text{H}}$, *V*		$_{\text{I}}E_f$, *V*		
pH	$[MnO_4^-]/[Mn(III)]$ 1 : 1	2 : 1	$[MnO_4^-]/[Mn(III)]$ 1 : 1	2 : 1	Mean value of $_{\text{I}}E_f$, *V*
0·0	1·575	1·585	1·575	1·581	1·578*
0·9	1·487	1·495	1·487	1·491	1·490
1·2	1·446	1·480	1·446	1·476	1·461
2·2	1·373	1·397	1·373	1·393	1·383
2·9	1·332	1·342	1·332	1·338	1·335
4·7	1·134	1·142	1·134	1·138	1·136
5·5	1·080	1·090	1·080	1·086	1·083
6·0	1·030	1·040	1·030	1·036	1·033

* $_{\text{I}}E^{\circ}$ $MnO_4^-/Mn(III)$.

Table 5. Values of ${}_{\text{II}}E_f$ for the Mn(III)/Mn(II) system at various pH values and 25°C

pH	${}_{\text{II}}E_H$, V		${}_{\text{II}}E_f$, V		
	[Mn(III)/[Mn(II)] 1 : 1	1 : 2	[Mn(III)]/[Mn(II)] 1 : 1	1 : 2	Mean value of ${}_{\text{II}}E_f$, V
0·0	1·513	1·508	1·513	1·526	1·520*
0·9	1·404	1·415	1·404	1·433	1·418
1·2	1·357	1·394	1·357	1·412	1·384
2·2	1·257	1·256	1·257	1·274	1·265
2·9	1·191	1·186	1·191	1·204	1·198
4·7	0·958	0·939	0·958	0·957	0·957
5·5	0·860	0·864	0·860	0·882	0·871
6·0	0·805	0·805	0·805	0·823	0·809

* ${}_{\text{II}}E^\circ$ Mn(III)/Mn(II).

Plots of E_H *vs.* pH are straight lines with slopes of 0·095 and 0·115 for the MnO_4^-/Mn(III) and Mn(III)/Mn(II) systems respectively, which on extrapolation to pH = 0, give E° values 1·58 and 1·52 V respectively. These values do not differ sufficiently for the reaction between MnO_4^- and Mn(II) in 1*N* acid solution to be sufficiently quantitative.

The values of $(E_f)_x$, the formal redox potential, for the two systems at pH = *x* were calculated from the values of the measured potential $(E_H)_x$ at this pH, by using the equations

$$({}_{\text{I}}E_H)_x = ({}_{\text{I}}E_f)_x + \frac{0{\cdot}0591}{4}\log\frac{[MnO_4^-]}{[Mn(III)]}$$

and

$$({}_{\text{II}}E_H)_x = ({}_{\text{II}}E_f)_x + 0{\cdot}0591\log\frac{[Mn(III)]}{[Mn(II)]}$$

The results obtained are given in Tables 4 and 5.

Values of the equilibrium constant, K_f, and the extent of completion of the reaction, α, were calculated by use of the relations:

$$\log K_f = Z[({}_{\text{I}}E_f)_x - ({}_{\text{II}}E_f)_x]/0{\cdot}0591 \quad \text{and}$$

$$\alpha = [Mn(III)]/[Mn(II)] \quad \text{at equivalence point}$$
$$= K_f^{1/(n_1+n_2)}$$

where Z is the number of electrons involved in the overall reaction (4 in this case), and n_1 and n_2 are the oxidation-number changes for both systems. The results, given in Table 6, show that the reaction is essentially quantitative at pH 4–6.

The success of the titration depends on the stability of the manganic fluoride complex during the titration. The stability of the complex depends on the Mn(III) concentration, pH and temperature;[1] the complex hydrolyses at higher values of [Mn(III)], pH and temperature, leading to erroneous results.

Table 6. Values of the equilibrium constant, K_f, and the extent of completion, α, for the reaction of Mn(II) with $KMnO_4$ in fluoride medium, at various pH values

pH	${}_{I}E_f$, V	${}_{II}E_f$, V	${}_{I}E_f - {}_{II}E_f$, V	K_f	α‡
0·0	1·578*	1·520†	0·058§	$8{\cdot}41 \times 10^3$	$0{\cdot}61 \times 10^1$
0·9	1·490	1·418	0·072	$7{\cdot}46 \times 10^4$	$0{\cdot}94 \times 10^1$
1·2	1·461	1·384	0·077	$1{\cdot}63 \times 10^5$	$1{\cdot}10 \times 10^1$
2·2	1·383	1·265	0·118	$9{\cdot}69 \times 10^7$	$3{\cdot}96 \times 10^1$
2·9	1·335	1·198	0·137	$1{\cdot}87 \times 10^9$	$7{\cdot}15 \times 10^1$
4·7	1·136	0·957	0·179	$1{\cdot}30 \times 10^{12}$	$2{\cdot}64 \times 10^2$
5·5	1·083	0·871	0·212	$2{\cdot}23 \times 10^{14}$	$7{\cdot}41 \times 10^2$
6·0	1·033	0·809	0·224	$1{\cdot}45 \times 10^{15}$	$1{\cdot}08 \times 10^3$

* ${}_{I}E^{\circ\prime}$.

† ${}_{II}E^{\circ\prime}$.

§ ${}_{I}E^{\circ\prime} - {}_{II}E$.

‡ α = [Mn(III)]/[Mn(II)] at equivalence point.

Since the slope of the E_H *vs.* pH graph is equal to $0{\cdot}0591X/n$, where X is the number of H^+ ions participating in the reaction then, for the MnO_4^-/Mn(III) system X_I is 6 and for the Mn(III)/Mn(II) system X_{II} is 2. Accordingly, the following equations may be written to represent the reactions.

(*a*) $MnO_4^- + 6H^+ + 2HF_2^- + 4e^- \rightleftharpoons MnF_4^- + 4H_2O$

(*b*) $MnF_4^- + 2H^+ + e^- \rightleftharpoons 2HF_2^- + Mn^{2+}$

$MnO_4^- + 10HF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O$

The overall reaction is favoured by decreasing acidity, confirming the experimental results and indicating that the reaction occurs more rapidly and quantitatively at higher pH (4–5·5) than at lower (pH < 4). The validity of this equation is verified by determining the slope of the E_{cell} *vs.* pH curve for the overall cell reaction. According to equations (1) and (2), when

$$[MnO_4^-]/[Mn(III)] = [Mn(III)]/[Mn(II)] = 1, \quad \text{then}$$

$$E_{cell} = E^\circ + \frac{0{\cdot}059}{4}(4X_{II} - X_I)\,pH$$

$$\text{Since} \quad X_I = 6 \quad \text{and} \quad X_{II} = 2,$$

$$E_{cell} = E^\circ + \frac{0{\cdot}059 \times 2}{4}\,pH = E^\circ + 0{\cdot}0295\,pH$$

The slope found experimentally was 0·0294, in excellent accordance with that expected. In accordance with these facts two protons should be involved in the overall reaction, which is in accordance with our findings.

The procedure is simpler than that given by other authors[2,10] and amounts of Mn(II) as low as 5 mg can be determined with fair accuracy.

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Zusammenfassung—Der Einfluß von Acidität, Fluoridkonzentration, Temperatur und Mangankonzentration auf die Reaktion zwischen $KMnO_4$ und Mn(II) wurde potentiometrisch untersucht. Die Reaktion wird durch Erhöhung der Fluoridkonzentration und/oder Erniedrigung der Acidität der Lösung begünstigt. Die formalen Redoxpotentiale der Systeme MnO_4^-/Mn(III) und Mn(III)/Mn(II) wurden bei verschiedenen pH-Werten bestimmt. Die durch Extrapolation auf pH = 0 erhaltenen $E°$-Werte betragen 1·58 bzw. 1·52 V. Die Mn(II)-Menge wurde von 5 bis 56 mg variiert. Die Nettoreaktion kann man als $MnO_4^- + 10HF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O$ darstellen.

Résumé—On a étudié potentiométriquement les influences de l'acidité, de la concentration en fluorure, de la température et de la concentration du manganèse dans la réaction entre $KMnO_4$ et Mn(II). La vitesse de réaction est augmentée par accroissement de la concentration en fluorure et/ou abaissement de l'acidité de la solution. On a déterminé les potentiels redox formels des systèmes MnO_4^-/Mn(III) et Mn(III)/Mn(II) à différentes valeurs de pH. Les valeurs $E°$ obtenues par extrapolation à pH = 0 sont 1,58 et 1,52 V respectivement. On a fait varier la quantité de Mn(II) dosée de 5 à 56 mg. La réaction globale peut être représentée ainsi: $MnO_4^- + 10\ HF_2^- + 4\ Mn^{2+} \rightleftharpoons 5\ MnF_4^- + 2\ H^+ + 4\ H_2O$.

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SIMULTANEOUS DETERMINATION OF *N*-UNSUBSTITUTED- AND *N*-SUBSTITUTED NITROAZOLES AND CRITERIA FOR THEIR IDENTIFICATION—I

NITROIMIDAZOLES AND NITROPYRAZOLES—POLAROGRAPHIC DETERMINATION

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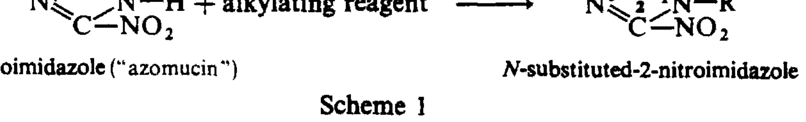
Summary—The *N*-unsubstituted nitroazoles have an imino hydrogen atom in contrast to the *N*-substituted derivatives, and react with hydroxide to give nitroazole anions. The strongly negative shift of $E_{1/2}$ for these anions makes possible simultaneous polarographic determination of any pair of compounds, one of which is an *N*-unsubstituted nitroazole and the other a corresponding *N*-substituted derivative. Simultaneous polarographic determination of three compounds [4(5)- 4- and 5-nitroimidazole] is also possible from alkaline medium, but only when $\Delta E_{1/2}$ between the *N*-substituted isomers is at least 100 mV. Chromatographically, and/or by some other criteria it is possible to distinguish between the *N*-unsubstituted nitroazole and the *N*-substituted derivatives. These compounds appear together in reaction mixtures arising during substitution of the hydrogen atom.

In an earlier publication[1] it was suggested that the polarographic method, using $0{\cdot}1M$ alkali as medium, should be generally applicable to simultaneous determination of some *N*-unsubstituted and the corresponding *N*-substituted heterocyclic compounds, certainly those with properties similar to those of the compounds studied in the paper mentioned (*viz.* nitroazoles). The aim of the present paper was to confirm this assumption, so nitropyrazoles and some other nitroimidazoles have been investigated. The general polarographic and chromatographic behaviour of these groups of compounds is described. On the basis of these investigations it is confirmed that simultaneous polarographic determination of two compounds during the synthetic processes described by schemes 1 and 2, or simultaneous polarographic determination of three compounds in the processes given in scheme 3 is only possible when an alkali is used as a medium.

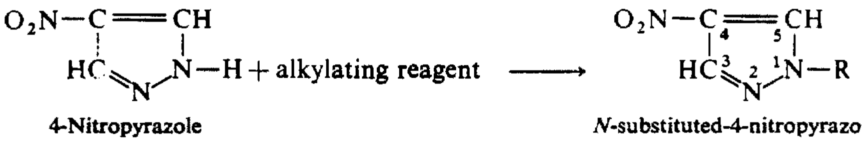
Several methods for thin-layer chromatographic identification,[2–5] and for polarographic determination of nitroimidazoles[6–19] have been reported. However, a simultaneous



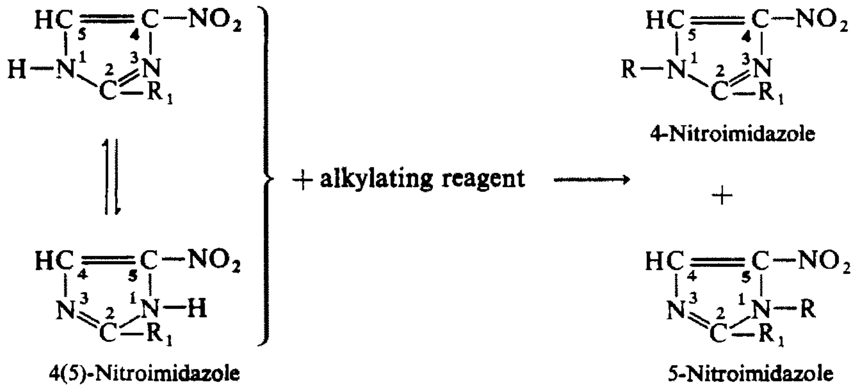
2-Nitroimidazole ("azomucin")

N-substituted-2-nitroimidazole

Scheme 1



Scheme 2



Scheme 3

(R and R_1 = alkyl)

identification and determination of nitroimidazoles, or nitropyrazoles in the reaction mixtures arising during substitution of the imino hydrogen atom has not yet been proposed except in our earlier papers.[1,20]

RESULTS AND DISCUSSION

Chromatographic separations

In Table 1, R_f values are shown for the compounds investigated. For all reaction mixtures we recommend diethylamine as the developer. Tin(II) chloride and *p*-dimethylaminobenzaldehyde mixture[21] was used as detecting reagent. Thin-layer chromatography was done on unactivated 0·25-mm thick layers of silica gel G, in an atmosphere saturated with the developer.

Polarographic investigation

The polarographic behaviour of all compounds was examined in Britton-Robinson buffers over the pH range 1·83–9·30 and in 0·1*M* sodium hydroxide. Most of the compounds investigated give two reduction waves in acidic as well as in neutral media. The first wave corresponds to the 4-electron reduction of the nitro group. The second wave is a 2-electron wave and is caused by reduction of the substituted hydroxylamine formed in the first reduction. In alkaline media some of the compounds investigated give only a 4-electron reduction wave, the second disappearing with increasing pH. However, some of the compounds give a single 6-electron wave in alkaline media.

The number of electrons involved in the reduction process was estimated by comparison of the wave-heights of the compounds investigated with the wave-heights of substances for which the reduction mechanism is known. In addition to this, the diffusion coefficients (*D*) calculated from the uncorrected Ilkovič equation are in accordance with

Table 1. Chromatographic separations

Compound	Reaction mixture	Reaction scheme	R_f values	Colour
2-Nitroimidazole "azomycin"	1	1	0·06	yellow
1-Methyl-2-nitroimidazole			0·60	yellow
4-Nitropyrazole	2	2	0·10	yellow
1-Methyl-4-nitropyrazole			0·59	yellow
4(5)-Nitroimidazole (**A**)	3	3	0·03	red
1-Methyl-5-nitroimidazole (**I**)			0·60	red
1-Methyl-4-nitroimidazole (**II**)			0·20	yellow
A	4	3	0·03	red
1-Ethyl-5-nitroimidazole · HCl (**III**)			0·69	red
1-Ethyl-4-nitroimidazole (**IV**)			0·47	yellow
2-Methyl-4(5)-nitroimidazole (**B**)	5	3	0·08	red
1,2-Dimethyl-5-nitroimidazole "dimetridazole" (**V**)			0·64	red
1,2-Dimethyl-4-nitroimidazole (**VI**)			0·31	yellow
B	6	3	0·08	red
1-(2-Hydroxyethyl)-2-methyl-5-nitroimidazole "metronidazole" (**VII**)			0·70	red
1-(2-Hydroxyethyl)-2-methyl-4-nitroimidazole (**VIII**)			0·32	yellow
B	7	3	0·08	red
1-(Methylcarbamoylmethyl)-2-methyl-5-nitroimidazole (**IX**)			0·41	red
1-(Methylcarbamoylmethyl)-2-methyl-4-nitroimidazole (**X**)			0·18	yellow
B	8	3	0·08	red
1-[(2-Hydroxy-1-methyl)ethyl]-2-methyl-5-nitroimidazole (**XI**)			0·81	red
1-[(2-Hydroxy-1-methyl)ethyl]-2-methyl-4-nitroimidazole (**XII**)			0·56	yellow
2-Isopropyl-4(5)-nitroimidazole (**C**)	9	3	0·25	red
1-Methyl-2-isopropyl-5-nitroimidazole "ipronidazole" (**XIII**)			0·68	red
1-Methyl-2-isopropyl-4-nitroimidazole (**XIV**)			0·59	yellow

the values of *D* for other heterocyclic depolarizers, calculated in the same manner.[22] The solutions examined ($2 \times 10^{4}M$ depolarizer) were prepared by mixing 2 ml of aqueous stock solution of the depolarizer ($10^{-3}M$) with 8 ml of the buffer solution, or 2 ml of the aqueous stock solution with 3 ml of water and 5 ml of 0·2*M* sodium hydroxide. The buffer solutions were twice as concentrated as in the original prescription of Britton–Robinson (*i.e.*, each acid was 0·08*M* and 0·4*M* sodium hydroxide was added). Since many heterocyclic compounds are only slightly soluble in water, it is better to use these more concentrated buffers; the capacity of the buffer would be sufficient even if we had to use—owing to the poor solubility of the depolarizer—larger amounts of the depolarizer stock solution (*e.g.*, 5 ml of aqueous stock solution and 5 ml of the buffer solution).

The direct proportionality between wave-height and the square root of the effective mercury reservoir height as well as the computed temperature coefficients[23] indicate that the first reduction waves are diffusion-controlled over the pH region investigated.

It was found with all the nitroazoles investigated that over the range from 5×10^{-5} to $5 \times 10^{-4}M$ the heights of the first waves are a linear function of the concentration, at any pH value.

The half-wave potentials* for the first wave of the compounds studied, as a function of pH, are shown in Table 2. These values are in accordance with the electron density of the nitro group. Thus 4(5)-nitroimidazoles, which mainly have the 4-nitro form,[24,25] have almost the same $E_{1/2}$ values as the 4-nitroimidazoles (except in 0·1*M* alkali). Their $E_{1/2}$ values are more negative than those of the 5-nitroimidazoles, because the nitro group is located in the vicinity of the electron-donor system (pyridine nitrogen).

Table 2. $E_{1/2}$ as a function of pH

	$E_{1/2}$ V *vs.* S.C.E.									
	pH (Britton–Robinson buffer)									
Compound	1·83	2·23	3·20	4·20	5·03	6·06	7·04	8·22	9·30	0·1*M* NaOH
2-Nitroimidazole	−0·02	−0·03	−0·11	−0·16	−0·23	−0·32	−0·38	−0·50	−0·61	−0·85
1-Methyl-2-nitroimidazole	−0·03	−0·04	−0·13	−0·18	−0·24	−0·34	−0·38	−0·47	−0·51	−0·56
4-Nitropyrazole	−0·24	−0·25	−0·33	−0·40	−0·47	−0·56	−0·63	−0·70	−0·73	−0·92
1-Methyl-4-nitropyrazole	−0·21	−0·22	−0·29	−0·35	−0·42	−0·53	−0·57	−0·65	−0·69	−0·72
4(5)-Nitroimidazoles										
A	−0·21	−0·24	−0·32	−0·40	−0·46	−0·55	−0·60	−0·62	−0·71	−0·95
B	−0·16	−0·19	−0·28	−0·36	−0·42	−0·52	−0·55	−0·61	−0·68	−0·94
C	−0·16	−0·19	−0·29	−0·34	−0·39	−0·53	−0·58	−0·60	−0·66	−0·93
4-Nitroimidazoles										
II	−0·20	−0·23	−0·29	−0·36	−0·43	−0·51	−0·56	−0·63	−0·69	−0·73
IV	−0·19	−0·22	−0·29	−0·36	−0·42	−0·52	−0·56	−0·61	−0·69	−0·72
VI	−0·16	−0·20	−0·29	−0·33	−0·42	−0·52	−0·57	−0·62	−0·69	−0·75
VIII	−0·18	−0·21	−0·29	−0·34	−0·41	−0·50	−0·56	−0·61	−0·68	−0·73
X	−0·17	−0·21	−0·27	−0·34	−0·39	−0·51	−0·56	−0·61	−0·66	−0·71
XII	−0·18	−0·21	−0·29	−0·36	−0·42	−0·53	−0·57	−0·63	−0·70	−0·74
XIV	−0·19	−0·21	−0·29	−0·36	−0·44	−0·53	−0·59	−0·64	−0·70	−0·76
5-Nitroimidazoles										
I	−0·12	−0·13	−0·21	−0·25	−0·33	−0·42	−0·48	−0·54	−0·58	−0·61
III	−0·10	−0·12	−0·18	−0·25	−0·32	−0·42	−0·46	−0·52	−0·57	−0·62
(V)	−0·10	−0·12	−0·18	−0·24	−0·32	−0·40	−0·47	−0·52	−0·57	−0·64
(VII)	−0·10	−0·11	−0·17	−0·25	−0·31	−0·42	−0·47	−0·53	−0·57	−0·62
IX	−0·08	−0·10	−0·18	−0·24	−0·30	−0·41	−0·46	−0·51	−0·60	−0·61
XI	−0·09	−0·11	−0·18	−0·25	−0·30	−0·39	−0·46	−0·50	−0·55	−0·61
(XIII)	−0·07	−0·11	−0·17	−0·25	−0·32	−0·43	−0·47	−0·53	−0·59	−0·64

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* Corrected by comparison with the half-wave potential of thallium in 0·1*M* KCl.

Simultaneous polarographic determination

N-unsubstituted nitroazoles have the ability to form nitroazole anions on treatment with 0·1*M* sodium hydroxide. The difficulty of reducing the nitro group in these anions makes possible the simultaneous polarographic determination of a pair of compounds, one being practically any *N*-unsubstituted nitroazole and the other a corresponding *N*-substituted derivative (*e.g.*, Fig. 1).

Although in reaction mixtures according to scheme 3 three compounds may be expected (the starting compound and two isomers), under the defined experimental conditions of the synthetic process, only two compounds are found to be present; 4(5)-nitroimidazole and 4-nitroimidazole, or 4(5)-nitroimidazole and 5-nitroimidazole. When all three compounds are present in reaction mixtures, the simultaneous polarographic determination is also possible in 0·1*M* sodium hydroxide, but only when $\Delta E_{1/2}$ between isomers is more than 100 mV (Fig. 2).

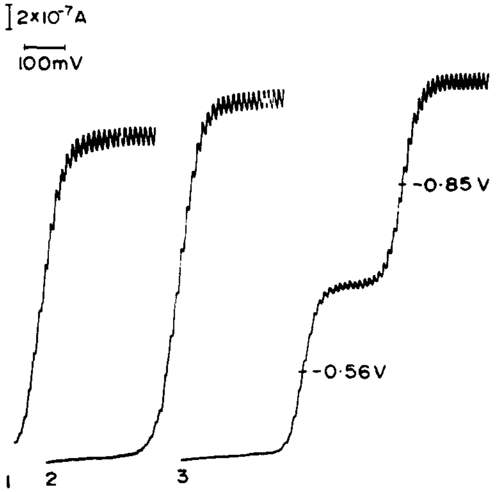

Fig. 1. Equimolar mixtures of 2-nitroimidazole and 1-methyl-2-nitroimidazole polarographed at different pH values. (These compounds appear together in the reaction mixture according to scheme 1.) *1*—pH 2·40; *2*—pH 7·00; *3*—0·1*M* NaOH.

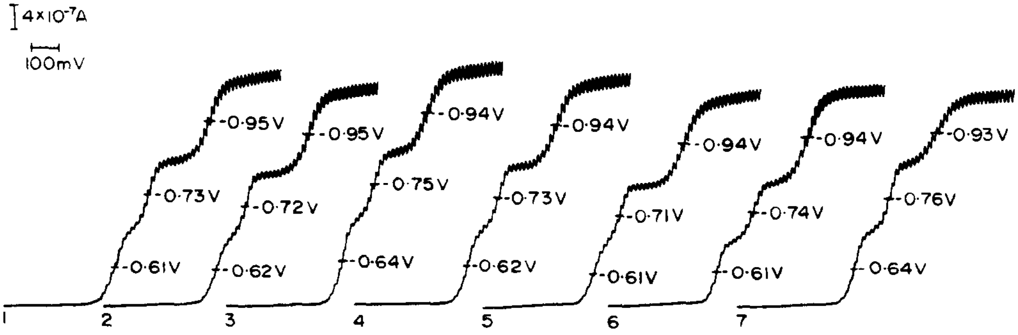

Fig. 2. Curve 1, equimolar mixture of **A**, **I** and **II**. Curve 2, equimolar mixture of **A**, **III** and **IV**. Curve 3, equimolar mixture of **B**, (**V**) and **VI**. Curve 4, equimolar mixture of **B**, (**VII**) and **VIII**. Curve 5, equimolar mixture of **B**, **IX** and **X**. Curve 6, equimolar mixture of **B**, **XI** and **XII**. Curve 7, equilmolar mixture of **C**, (**XIII**) and **XIV**. Supporting electrolyte 0·1*M* NaOH. Concentration of each compound $10^{-4}M$. The curves start at −0·2 V *vs*. S.C.E.

The conditions for the procedure of identification and determination for all synthetic mixtures in the present study were the same as those described earlier,[1] including the use of the method of standard addition. The polarographic method of simultaneous determination of nitroazoles is very useful for monitoring the substitution of the imino hydrogen atom, where it is very important to know when to stop the reaction. For this purpose, the exact amounts of the compounds present need not be known, as their ratio gives satisfactory results. This procedure is very fast—a few drops from a reaction mixture are added to 0·1*M* sodium hydroxide, this solution is then transferred to the polarographic cell, dearated with nitrogen for exactly 5 min, and the polarogram recorded over the range from −0·2 to −1·2 V *vs.* S.C.E. The total wave-heights of all the nitroazole compounds are taken as equivalent to 100%. Although the results are not precise, even in the ratios of amounts of components (the diffusion coefficients of the compounds are different, and the number of electrons consumed in alkaline medium is not the same for all compounds), the information given about the process is adequate.

The criteria for distinction between N*-unsubstituted nitroazoles and their* N*-substituted derivatives*

N-unsubstituted nitroazoles, because of their pseudo-acidic character, have the lowest R_f values in diethylamine, in comparison with the corresponding *N*-substituted derivatives. 5-Nitroimidazoles are stronger bases than 4-nitroimidazoles and hence have the highest R_f values. The 4(5)-nitroimidazoles and 5-nitroimidazoles studied here give a red colour with tin(II) chloride and *p*-dimethylaminobenzaldehyde reagent on silica gel thin layers. The same treatment applied to 4-nitroimidazoles gives a yellow colour.

N-unsubstituted nitroazoles in alkaline media (*i.e.*, 0·1*M* sodium hydroxide) show a strongly negative shift of $E_{1/2}$, compared with the corresponding *N*-substituted derivatives. 4(5)-Nitroimidazoles and 4-nitroimidazoles have almost the same $E_{1/2}$ values over all the pH range (except in 0·1*M* alkali). The $E_{1/2}$ values of 5-nitroimidazoles are more positive.

N-unsubstituted nitroazoles do not decompose on standing in 0·5*M* sodium hydroxide for 24 hr, whereas *N*-substituted ones do. The 4-nitroimidazoles studied show a lower degree of degradation (1–15%) in comparison with the corresponding 5-nitroimidazoles (60–95%) after standing in 0·5*M* sodium hydroxide for 24 hr.

According to the criteria given it is possible to deduce the structure of the nitroazoles directly from the behaviour of the reaction mixtures. Based on these criteria the structures of some new nitroazole compounds[26] have been determined, even though one of them has not yet been isolated from the reaction mixture.

It can be seen that the proposed methods and criteria have wide applicability, not only for the simultaneous identification and determination of nitroazoles, directly in the reaction mixtures, but also for determination of their structures.

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Zusammenfassung—Die nicht *N*-substituierten Nitroazole haben im Gegensatz zu den *N*-substituierten Derivaten ein Iminowasserstoffatom und reagieren mit Hydroxid zu Nitroazol-Anionen. Die stark negative Verschiebung von $E_{1/2}$ dieser Anionen ermöglicht die gleichzeitige polarographische Bestimmung eines beliebigen Paares von Verbindungen, von denen die eine ein nicht *N*-substituiertes Nitroazol und die andere ein entsprechendes *N*-substituiertes Derivat ist. Die gleichzeitige polarographische Bestimmung dreier Verbindungen [4(5)-, 4- und 5-Nitroimidazol] ist in alkalischem Medium ebenfalls möglich, aber nur, wenn $\Delta E_{1/2}$ zwischen den *N*-substituierten Isomeren wenigstens 100 mV beträgt. Man kann zwischen dem nicht *N*-substituierten Nitroazol und den *N*-substituierten Derivaten chromatographisch und/oder nach einigen anderen Merkmalen unterscheiden. Diese Verbindungen treten gemeinsam in Reaktionsgemischen auf, die bei der Substitution des H-Atoms anfallen.

Résumé—Les nitroazoles non substitués à l'azote ont un atome d'hydrogène imino à l'opposé des dérivés N-substitués, et réagissent avec l'hydroxyde pour donner des anions nitroazole. Le déplacement fortement négatif de E 1/2 pour ces anions rend possible le dosage polarographique simultané de n'importe quelle paire de composés, dont l'un est un nitroazole non substitué à l'azote et l'autre le dérivé N-substitué correspondant. Le dosage polarographique simultané de trois composés [4(5)-, 4- et 5-nitroimidazole] est aussi possible dans un milieu alcalin, mais seulement quand $\Delta E1/2$ entre les isomères N-substitués est d'au moins 100 mV. Chromatographiquement, et/ou par quelques autres critères il est possible de distinguer entre le nitroazole non substitué à l'azote et les dérivés N-substitués. Ces composés se présentent ensemble dans les mélanges réactionnels se formant pendant la substitution de l'atome d'hydrogène.

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ANION-EXCHANGE BEHAVIOUR OF VARIOUS METALS ON DEAE-CELLULOSE IN MIXED ACETIC ACID–NITRIC ACID MEDIA

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Summary—A number of nitrato complexes of metals have been found to be adsorbed on DEAE-cellulose from mixed acetic acid–nitric acid media, although none can be adsorbed from aqueous nitric acid solutions. The distribution coefficients of Sc, Mo, La, Sm, W, Re, Bi, Th and U are given as functions of acetic acid and nitric acid concentrations (sometimes in the presence of hydrogen peroxide to prevent hydrolytic precipitation). For 25 other metals column adsorption behaviour is described for a 90% acetic acid–10% 7·6*M* nitric acid mixture. Favourable differences in the distribution coefficients allow useful separations such as Fe–Mo–W and U–Sm–Mo–Bi–Th, to be achieved.

When the weakly basic anion exchanger DEAE-cellulose (abbreviated to DEAE) is used as an adsorbent, only a few metals have been found to be adsorbed from mineral acid media. Thus, Pd(II), Pt(IV)[1] and Hg(II)[2] can be adsorbed on DEAE columns and separated selectively from many other metals in acidic thiocyanate media. Mo(VI), W(VI) and Re(VII) are also adsorbed on DEAE and separated from each other in dilute thiocyanate[3] and chloride[4] media.

Ion-exchange adsorption of metals on DEAE has been found to be improved by the addition of a protic organic solvent to the aqueous mineral acid media such as hydrochloric acid,[5] nitric acid[6] and hydrochloric acid–thiocyanate solutions.[7]

Previously methanol has been used exclusively as the organic protic solvent. In this study we have investigated the adsorption behaviour of metals on DEAE in mixed acetic acid–nitric acid media. Though Th(IV) but none of the metals adsorbed on DEAE from aqueous nitric acid solutions exhibited a pronounced adsorption in methanolic nitric acid, introduction of acetic acid allowed an increasing number of nitrato complexes to be adsorbed. A number of useful analytical separations were accomplished.

EXPERIMENTAL

Reagents

Selectacel DEAE (diethylaminoethylcellulose), 0·84 meq/g, Brown Co., Berlin, N. H., was obtained from Seikagaku Kogyo Co. Ltd., Tokyo. About 10 g of DEAE were slurried with demineralized water, placed in a large column and treated with 200 ml of 1*M* ammonium nitrate acidified to pH 1 with nitric acid. The DEAE converted into the nitrate form was washed with demineralized water by centrifugation until the pH of the supernatant liquid was 2·5. After washing with methanol to remove the adsorbed water, the DEAE was dried at 40° for 1 hr and stored in a desiccator containing saturated potassium bromide solution.

Stock solutions (0·05*M*) of the metal nitrates were prepared so as to be 1*M* in nitric acid. Exceptions were Mo(VI), W(VI) and Re(VII), the 0·05*M* stock solutions of which were made by dissolving their ammonium or sodium salts in demineralized water.

Determination of distribution coefficients

A batch equilibrium method was used to determine the distribution coefficients for Sc(III), Mo(VI), La(III), Sm(III), W(VI), Re(VII), Bi(III), Th(IV) and U(VI). Portions (0·5 g) of DEAE in the nitrate form were weighed and placed in glass-stoppered conical flasks containing 40·0 ml of appropriate acetic acid–nitric acid mixtures of varying composition, which also contained 5 μmole of the metal to be measured. The mixtures were shaken mechanically for 20 hr at 25·0 ± 0·1°. The two phases were separated by filtration and the filtrates were analysed for each metal colorimetrically by the methods given in Table 1. The distribution coefficient was obtained from the formula:

$$K_d = (\text{amount of metal in DEAE phase/g of DEAE})/(\text{amount of metal in solution phase/ml of solution})$$

Table 1. Analytical methods used

Cation	Method
Sc(III)	Titration with EDTA, Xylenol Orange indicator Traces determined colorimetrically with Arsenazo III[12]
Fe(III)	Titration with EDTA, Variamine Blue B
Zn(II), mixed R.E.*	Titration with EDTA, Xylenol Orange
Mo(VI), W(VI)	Colorimetrically with dithiol[13]
La(III)	Colorimetrically with Xylenol Orange[14]
Sm(III)	Colorimetrically with Arsenazo III[15]
Re(VII)	Colorimetrically with thiocyanate[13]
Bi(III)	Colorimetrically with diethyldithiocarbamate[13]
Th(IV)	Colorimetrically with Arsenazo III[16]
U(VI)	Back-titration with Th(IV) in excess of EDTA, Xylenol Orange. Traces determined colorimetrically with Arsenazo III[17]

* Rare earths

Table 2. Separations

Run	Metal	Added, μg	Found, μg	No.*	Eluent†
1	U(VI)	121·4 × 10^3	(123·9 ± 1·5) × 10^3	3	50 ml of *a*
	Th(IV)	11·4	11·5 ± 0·5	3	20 ml of *b*
2	Sc(III)	47·3 × 10^3	(47·3 ± 0·2) × 10^3	3	60 ml of *c*
	Th(IV)	11·4	11·1 ± 0·1	3	20 ml of *b*
3	Mixed R.E.§	109·1 × 10^3	(106·7 ± 0·3) × 10^3	3	60 ml of *a*
	Th(IV)	11·4	11·4 ± 0·1	3	20 ml of *b*
4	U(VI)	102·4 × 10^3	(102·0 ± 0·7) × 10^3	3	120 ml of *d*
	La(III)	104·9	105·2 ± 9·0	3	20 ml of *b*
5	Zn(II)	103·8 × 10^3	(103·6 ± 0·1) × 10^3	3	80 ml of *c*
	Bi(III)	105·4	103·7 ± 1·3	3	20 ml of *b*
6	Mo(VI)	10·0 × 10^3	9·7 × 10^3	1	70 ml of *e*
	W(VI)	9·5	15·3 (Mo 13·2)	1	45 ml of *f*
7	Mo(VI)	1·00 × 10^3	1·05 × 10^3	1	70 ml of *e*
	W(VI)	9·5	7·6 (Mo 28·5)	1	45 ml of *f*
8	Fe(III)	10·1 × 10^3	10·0 × 10^3	1	40 ml of *g*
	Mo(VI)	20·0	20·4	1	45 ml of *e*
	W(VI)	19·0	18·9	1	50 ml of *f*

* No of determinations.

† *a*: Acetic acid–7·6*M* HNO_3 (4 : 1), *b*: 1·1*M* HNO_3, *c*: acetic acid–7·6*M* HNO_3 (9 : 1), *d*: acetic acid–7·6*M* HNO_3 (19 : 1), *e*: acetic acid–0·3*M* HNO_3 (4 : 1) (containing 0·24% H_2O_2), *f*: 0·1*M* NaOH–0·1*M* NaCl, *g*: acetic acid–0·3*M* HNO_3 (19 : 1) (containing 0·24% H_2O_2).

§ A mixture of equal amounts of La(III), Sm(III) and Y(III). For each run the metals were eluted in the order listed.

Column preparation and separation

DEAE (1 g) was slurried with 20 ml of the acetic acid–nitric acid mixture to be used for sample preparation and poured into a conventional ion-exchange column (bore 1·3 cm, length 15 cm). The column was further washed with 30 ml of the same mixture, the bed being 9·0 cm long. For multicomponent separations 1·5 g of DEAE were packed similarly into the column, the bed being 13·5 cm long.

About 5 ml of a sample solution, in the appropriate mixture of acetic acid and nitric acid, were loaded onto the top of the column and allowed to percolate, and then an eluent was applied. The individual procedures are given in Table 2. A flow-rate of 2 ml/min for elution was used throughout. For sample loading a flow-rate of 1 ml/min was used.

RESULTS AND DISCUSSION

Adsorption of metals from acetic acid and nitric acid mixtures

The distribution coefficients of the nine metals on DEAE in acetic acid–nitric acid media are illustrated in Figs. 1 and 2 as a function of acetic acid concentration, where the concentration of nitric acid is kept constant at 7·6*M*. Tungstic acid is precipitated when nitric acid is added to tungstate solution, so we had to determine the distribution coefficients of tungsten(VI) in the presence of hydrogen peroxide. For molybdenum(VI) the coefficients are given both in the presence and absence of hydrogen peroxide. The coefficient increases with increasing concentration of acetic acid for each metal, showing the marked effect of acetic acid on the ion-exchange adsorption of metals on DEAE.

Figure 3 illustrates the effect of nitric acid concentration on the distributon coefficients of Th(IV), Bi(III), Mo(VI), La(III), Re(VII) and U(VI), the concentration of acetic acid being held constant at 90% v/v. The effect of acid concentration is less marked, in accordance with the observation reported by Korkisch and his co-workers,[8,9] for the adsorption of metals on Dowex 1 from acetic acid–nitric acid mixtures. Among the metals tested, the adsorption of U(VI), La(III), Bi(III) and Th(IV) tended to increase with increasing concentration of nitric acid, while oxy-anions exhibited the opposite trend.

The distribution coefficients were also measured for 25 metals other than those

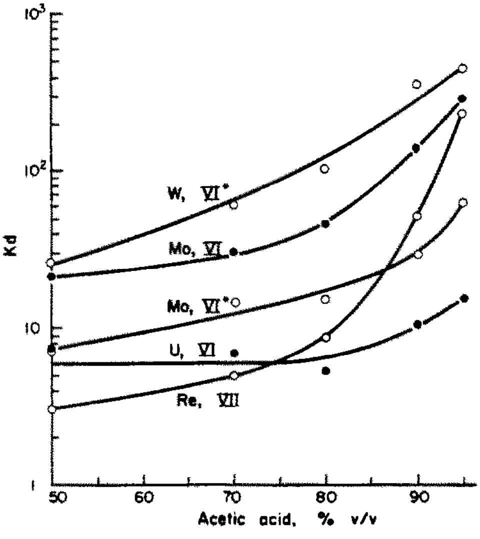

Fig. 1. Distribution coefficients of metals on DEAE in acetic acid–7·6*M* nitric acid media as a function of acetic acid concentration.
* 0·24% H_2O_2 added.

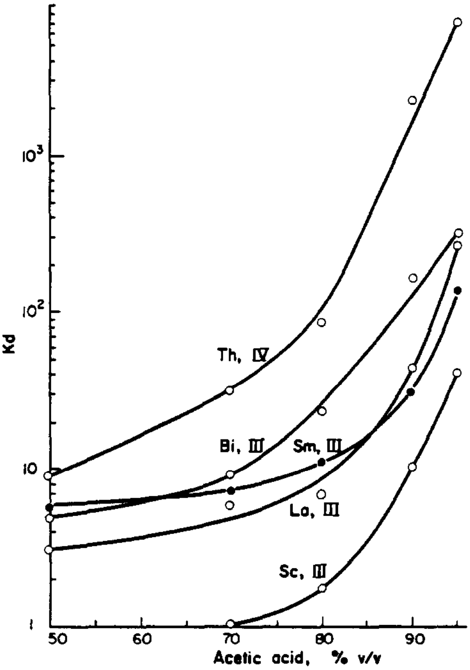

Fig. 2. Distribution coefficients of metals on DEAE in acetic acid–7·6M nitric acid media as a function of acetic acid concentration.

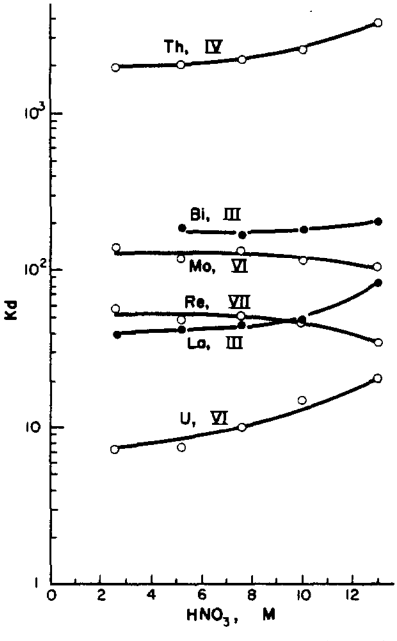

Fig. 3. Distribution coefficients of metals on DEAE in acetic acid–nitric acid (9 : 1) media as a function of nitric acid concentration.

illustrated in Figs. 1 and 2, in a medium of 90% acetic acid–10% 7·6*M* nitric acid by a column method, on a 0·5-g DEAE column. The following metals did not adsorb to any great extent on the column: Be(II), Mg(II), Ca(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), As(V), Y(III), Zr(IV), Ag(I), Cd(II), In(III) and Hg(II). Ge(IV), Ba(II) and Pb(II) were precipitated from the same medium. Pd(II) and Au(III) adsorbed strongly, with coefficients >100 and 105, respectively, in the presence of a minimum amount of chloride. The coefficients for Al(III) and V(V) were 25 and 30, respectively.

To obtain some information on the ease of attainment of ion-exchange equilibrium, U(VI) and Th(IV) were chosen and their distribution coefficients were measured at time intervals, in acetic acid–7·6*M* nitric acid. The volume ratio of acetic to nitric acid was 19 : 1 for U(VI) and 4 : 1 for Th(IV). U(VI) attained equilibrium in 1–2 hr, but Th(IV) took about 6 hr.

The metals showing strong adsorption on DEAE from mixed acetic acid–nitric acid media are very similar to those which adsorb on a strongly basic resin from aqueous nitric acid solution.[10,11] This is the case for Mo(VI), Pd(II), the lighter rare-earth metals, Re(VII), Au(III), Bi(III), Th(IV) and U(VI). Therefore, we see that in the mixed acetic acid–nitric acid media DEAE behaves in a similar way to a strongly basic resin in aqueous nitric acid solutions, the uptake of metals taking place by anion-exchange of their nitrato complexes.

The role of acetic acid is considered to be as follows. The addition of increasing amounts of acetic acid will reduce the concentration of nitrate ions, which compete for the ion-exchange sites with nitrato complexes, and also will reduce the numbers of water molecules around metal ions, thus enabling the nitrato complexes to be formed at a lower concentration of nitric acid. Because of a low concentration of competitive nitrate ions, the nitrato complexes may easily enter the exchange sites without competing with nitrate ions. Accordingly, a lower concentration of nitric acid is sufficient for the anion-exchange in mixed acetic acid–nitric acid media. This is in accord with the slight dependence of the distribution coefficients of metals on nitric acid concentration (Fig. 3).

Korkisch and his co-workers[8,9] have reported the distribution coefficients of many metals on Dowex 1 in acetic acid–nitric acid media. Fewer metals are adsorbable on DEAE than on Dowex 1. Also, there are great differences in adsorbability of metals on DEAE and on Dowex 1. The ratio of the distribution coefficients for metals:

$$\frac{K_d \text{ on Dowex 1 in 90\% acetic acid–10\% } 5M \text{ nitric acid}}{K_d \text{ on DEAE in 90\% acetic acid–10\% } 7{\cdot}6M \text{ nitric acid}}$$

is approximately 10 for UO_2(II), Sc(III) and Sm(III), 20 for Bi(III), 30 for La(III) and 70 for Th(IV). Based on these observations the sequence of adsorption of nitrato complexes according to the ion-exchange system involved is assumed to be: Dowex 1–acetic acid–nitric acid > Dowex 1–nitric acid ~ DEAE–acetic acid–nitric acid > DEAE–methanol–nitric acid > DEAE–nitric acid.

Separations

Even though a large number of metals can be adsorbed on DEAE from mixed acetic acid–nitric acid media, the number of metals which are retained strongly enough on DEAE columns to allow their separation is still low. Th(IV), Bi(III), W(VI), Mo(VI) and Re(VII) may be separated selectively from many other metals. Some quantitative separations were conducted, and the results obtained are given in Table 2. When each

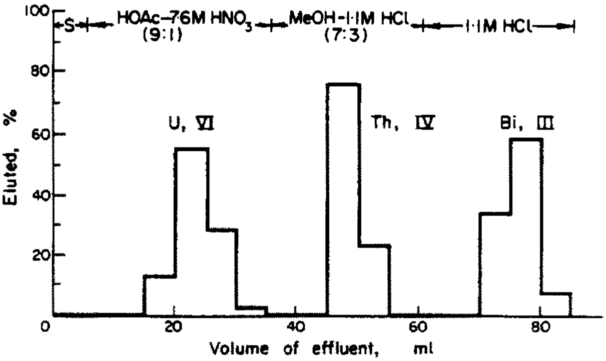

Fig. 4. Chromatographic separation of U(VI), Th(IV) and Bi(III). S: sample solution, acetic acid–7·6*M* HNO_3 (9 : 1).
Added, mg: U 1·24, Th 1·14, Bi 1·05.
Recovered, %: U 98·4, Th 98·3, Bi 101.

separation was repeated more than three times, average and standard deviations are listed for the individual metals. In order to demonstrate the versatility of the present ion-exchange system, most separations were carried out with widely different concentrations (up to 1 : 1000). Under these conditions (runs 6 and 7) traces of Mo(VI) tend to contaminate the W(VI) fraction, but quantitative separation is quite feasible when the two metals are present in comparable amount (run 8).

When W(VI) is involved in separations, the concentration of nitric acid becomes critical. In attempts at separation of Mo(VI) and W(VI) in an acetic acid–7·6*M* nitric acid mixture (4 : 1) containing 0·24% hydrogen peroxide, an appreciable amount of W(VI) passed through the column into the effluent, probably because of the hydrolytic polymerization of tungstic acid. However, this breakthrough of W(VI) was easily avoided by decreasing the concentration of nitric acid to 0·3*M*. Use of increased amounts of the peroxide was not effective in preventing the breakthrough.

Three- and five-component separations are also feasible and are illustrated in Figs. 4 and 5, respectively. The separations were quantitative and no marked tailing was observed.

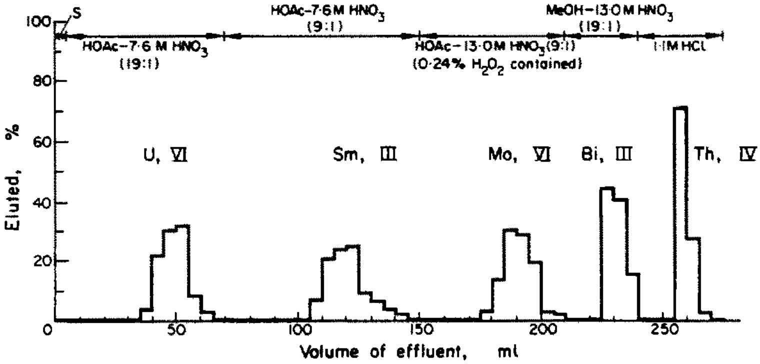

Fig. 5. Chromatographic separation of U(VI), Sm(III), Mo(VI), Bi(III) and Th(IV). S: sample solution, acetic acid–7·6*M* HNO_3 (19 : 1).
Added, μg: U 126, Sm 151, Mo 97·4, Bi 210, Th 114.
Recovered, %: U 107, Sm 101, Mo 98·9, Bi 103, Th 101.

When weakly basic cellulosic ion-exchangers are used in mixed solvents, they do not always exhibit their inherent ion-exchange function, unless a solvent such as methanol or acetic acid is employed. As compared with methanol, addition of which to nitric acid solutions permits only Th(IV) to be taken up on DEAE, acetic acid enhances the formation and stabilization of nitrato complexes to a greater extent, causing many metals to be adsorbed on DEAE. This may be explained by the lower dielectric constant of acetic acid ($\varepsilon = 6{\cdot}2$, 20°) as compared with methanol ($\varepsilon = 32{\cdot}6$, 25°).

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Zusammengassung—Es wurde gefunden, daß eine Anzahl von MetallNitratokomplexen aus gemischten Essigsäure-Salpetersäuremedien an DEAE-Cellulose adsorbiert werden, obwohl aus wäßrigen Salpetersäurelösungen keiner adsorbiert werden kann. Die Verteilungskoeffizienten von Sc, Mo, La, Sm, W, Re, Bi, Th und U werden in Abhängigkeit von den Konzentrationen an Essigsäure und Salpetersäure angegeben (manchmal in Gegenwart von Wasserstoffperoxid, um hydrolytische Fällung zu vermeiden). Für 25 andere Metalle wird das Adsorptionsverhalten an einer Säule in einem Gemisch aus 90% Essigsäure und 10% 7·6 M Salpetersäure beschrieben. Günstige Unterschiede in den Verteilungskoeffizienten erlauben nützliche Trennungen, wie Fe–Mo–W und U–Sm–Mo–Bi–Th.

Résumé—On a trouvé qu'un certain nombre de complexes nitrato de métaux sont adsorbés sur la DEAE-cellulose de milieux mélanges acide acétique–acide nitrique, quoique aucun ne peut être adsorbé de solutions aqueuses d'acide nitrique. On donne les coefficients de partage de Sc, Mo, La, Sm, W, Re, Bi, Th et U en fonction des concentrations en acide acétique et acide nitrique (quelquefois en la présence de peroxyde d'hydrogène pour prévenir la précipitation hydrolytique). Pour 25 autres métaux on décrit le comportement à l'adsorption sur colonne pour un mélange acide acétique 90%-acide nitrique 7,6*M* 10%. Des différences favorables entre les coefficients de partage permettent des séparations utiles telles que Fe–Mo–W et U–Sm–Mo–Bi–Th.

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COMPLEXATION OF POLYVINYL ACETATE WITH IODINE*

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Summary—Polyvinyl acetate and iodine form a characteristic red complex in the presence of potassium iodide. Spectrophotometry of the complex at 510 nm in a methanol–water system at 20° yields linear calibration curves over the range 25–100 mg of polyvinyl acetate per l. of final solution. The limit of detection is 0·1 mg of polyvinyl acetate in 0·5 ml of initial sample. Replacement of acetate groups by inert groups reduces the sensitivity of the method, and other details of the system are discussed.

Iodine–potassium iodide tests for polyvinyl acetate (PVAc) and polyvinyl alcohol are of commercial interest.[1,2] PVAc can be identified after it has been separated chromatographically from polyvinyl alcohol and their graft copolymers, by the development of a deep-red colour when the chromatogram is sprayed with I_2–KI solution.[3] PVAc in vinyl acetate[4] and other media can also be detected in this way after chromatography. Aqueous I_2–KI added to a solution of PVAc in glacial acetic acid and diluted with water yields an intense red-violet colour advocated as a qualitative test which is independent of the presence of some copolymers.[5] Some of the variables affecting colour intensity for this reaction in a methanol–water system have been examined recently by Hayashi and co-workers. Absorbances up to 0·7 at 510 nm were recorded with $\sim 10^{-3}M$ iodine and iodide solutions and up to 700 mg of PVAc per l. of final solution, for which it was mentioned that linear calibration curves may be obtained.[6] Here, we present a quantitative examination of the sensitivity, reproducibility, linearity and general characteristics of the phenomenon. Our conditions are similar to those used previously,[6] but our aim has been to use a maximum concentration of iodine to investigate a wider range of absorbance with well-known commercial polymers of the Western world. Our selection of polymers comprises two pure PVAc resins used in organic-solvent based adhesives, glossy paper coatings, textile stiffening agents, and high-gloss printing inks, and one acrylic vinyl acetate copolymer which finds application in aqueous and alcoholic solution as a component of inks and textile sizes.

EXPERIMENTAL

Materials

Pure PVAc resins were "Gelva" grades V-7 and V-100, of respective approximate molecular weights 5×10^4 and 5×10^5, manufactured in the form of small spheres by the emulsion polymerization of vinyl acetate. The copolymer "Vinavil" grade C4, molecular weight 4×10^4, contains a major proportion of acetate groups and a minor proportion of aliphatic carboxylic acid groups which render it soluble in aqueous sodium carbonate solution. Reagents were of analytical grade.

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* Based in part on a report by F. T. Serra in partial fulfilment of the requirements for the Degree of M.Sc. of the University of London, 1972.

Procedures

Methanolic solutions of the polymers were prepared at concentrations in the range 9–12 g/l. Aliquots of these were diluted accurately and treated with methanolic iodine and aqueous potassium iodine solutions to explore optimum conditions. Spectra of the final solutions were scanned on a Unicam SP 700 spectrophotometer. For the calibration measurements, at least 30 min were allowed[6] for the complex to equilibrate at 20°, then absorbances were measured at 510 nm against a reagent blank on a Hilger–Watts Uvispek spectrophotometer, with 1-cm cells and 0·1-mm slitwidth. The mean of three estimates was taken for each solution. Values of absorbance (A_i) and final polymer concentration (c_i) were determined for optimum conditions, at first with single aliquots, and later with ten replicates of diluted stock polymer solution. For the latter, limits of the true mean values were calculated as $\overline{A}_i \pm ts/\sqrt{10}$, where $\overline{A}_i$ is the mean of 10 results, s is their standard deviation, and t the value of Gosset's t for 99% confidence. Least-squares straight lines were calculated from the A_i and c_i values, and the deviations of individual absorbance values from the lines were calculated from $A_i - c_i \Sigma A_i / \Sigma c_i$ for lines through the point $A_i = 0$, $c_i = 0$, and from $A_i - \{c_i(N\Sigma(A_i c_i) - \Sigma c_i \Sigma A_i) + \Sigma A_i \Sigma c_i^2 - \Sigma c_i \Sigma(c_i A_i)\}/(N\Sigma c_i^2 - (\Sigma c_i)^2)$ for general lines, where N is the number of results. Deviations were also expressed as percentages of the absorbance values on the calculated line.

RESULTS

Table 1 shows the concentrations of iodine and potassium iodide and the order of mixing of reagents adopted in the calibration tests. These concentrations were sufficient to ensure linear calibration curves over the whole range of absorbance available with the Uvispek (0–3), yet just insufficient to cause significant precipitation of polymer provided that due care was exercised. Figure 1 shows spectra of the polymer complexes for these conditions. The maxima occur at 520 and 510 nm for Gelva V-7 and the copolymer, respectively. Concentrations of PVAc in the middle of the range yielded wine-red solutions in which blue and green light is absorbed, mainly by unreacted reagents and the complex respectively. Provided that the methanolic solution was mixed with the aqueous potassium iodide by very gentle swirling, the procedure shown in Table 1 gave a clear solution of complex accompanied merely by a very faint bluish-red film at the surface of the solution. Violent agitation of the final solution produced a deep-red fibrous precipitate of the complex, which reduced the absorbance of the solution, especially in the case of higher concentrations of PVAc. Increase in the concentrations of iodine and potassium iodide by 50% above those listed in Table 1 led to immediate precipitation of deep-red complex mixed with some colourless polymer. A several-fold increase led to a dark, fibrous precipitate of complex even for low concentrations of PVAc. The omission of iodine from the procedure resulted, for example with a 2-g/l. initial solution of PVAc, in a faintly opalescent final solution, owing to precipitated and colloidal PVAc.

Table 2 lists the results of absorbance measurements on single solutions of Gelva V-7 complex prepared according to Table 1. The points deviate less from their general

Table 1. Composition of the colorimetric solution and order of mixing

Component	[Stock solution],		Volume used,	[Final solution],
	g/l.	*M*	*ml*	*M*
1. Methanolic PVAc solution	9·547*	0·01110†	5·00 maximum	0·000213† (183·6 mg/l. maximum*)
2. Methanol			to 5·00	
3. Methanolic I_2 solution	5·117	0·02014	5·00	0·000386
4. Mixture of 1, 2 and 3			1·00	
5. Aqueous KI solution	2·699	0·01626	25·00	0·0156

* For results quoted in Table 3.

† Based on $CH_2CHOCOCH_3$ units.

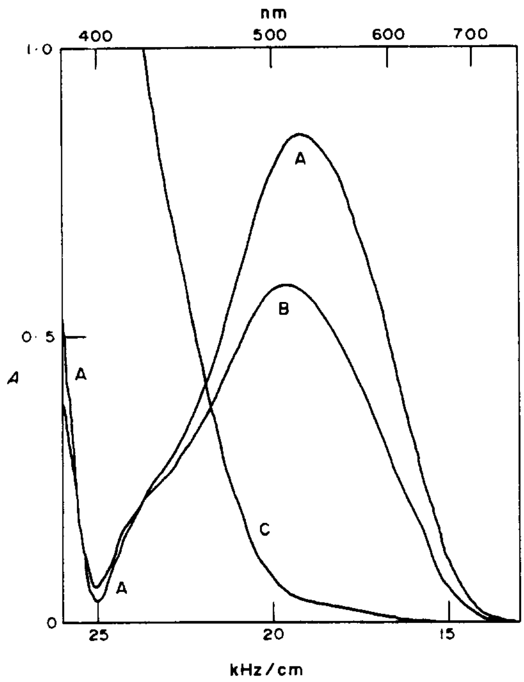

Fig. 1. Spectra of complex formed from (A) 183 mg of Gelva V-7 PVAc and (B) 184 mg of Vinavil C4 copolymer per l. of final solution under the conditions of the analytical method. Spectrum C is the iodine–potassium iodide blank *vs.* a potassium iodide blank.

least-squares straight line than from the least-squares straight line which includes the point $A_i = 0$, $c_i = 0$. In the latter case, the deviations are systematically negative for the lower c_i values. The general line indicates a threshold polymer concentration of 2·7 mg/l. The gradients of the two lines differ by 5%, and the general scatter of results is several per cent. Similar characteristics were observed with Gelva V-100 (not shown) for which the gradient was again ~0·022 l./mg. The sensitivity of the method is not perceptibly

Table 2. Single determinations of absorbance at 510 nm and 20° (A_i) for various concentrations of Gelva V-7 complex, and deviations from the derived least-squares straight lines

[PVAc], c_i, *mg/l.*	Observed A_i	Deviation* for $A = 0{\cdot}02142c$	% Deviation* for $A = 0{\cdot}02142c$	Deviation* for $A = 0{\cdot}0225c - 0{\cdot}0615$	% Deviation* for $A = 0{\cdot}0225c - 0{\cdot}0615$
126·48	2·88	+0·17	+6·3	+0·10	+3·5
110·67	2·42	+0·05	+2·1	−0·01	−0·4
94·86	2·07	+0·04	+2·0	0·00	0·0
79·05	1·695	0·00	+0·1	−0·02	−1·3
63·25	1·323	−0·03	−2·4	−0·04	−2·8
47·43	0·966	−0·05	−4·9	−0·04	−4·0
31·62	0·617	−0·06	−9·0	−0·03	−5·1
15·81	0·279	−0·06	−18	−0·015	−5·0
6·32	0·084	−0·05	−38	+0·003	+3·6

* See Experimental.

Table 3. Single determinations of absorbance at 510 nm and 20° (A_i) for solutions of Copolymer C4 treated with 0·02014*M* iodine and 0·01626*M* potassium iodide, deviations from least-squares straight lines, and reduction in absorbance observed with 0·00403*M* iodine and 0·003252*M* potassium iodide

[Copolymer], c_i, *mg/l.*	Observed A_i	Deviation* for $A = 0{\cdot}0159c$	% Deviation* for $A = 0{\cdot}0159c$	Deviation* for $A = 0{\cdot}0167c - 0{\cdot}0684$	% Deviation* for $A = 0{\cdot}0167c - 0{\cdot}0684$	% Reduction
183·6	3·05	+0·13	+4·5	+0·05	+1·6	> 50
160·7	2·45	−0·10	−3·9	−0·08	−3·1	45
137·7	2·227	+0·039	+1·8	+0·014	+0·6	38
114·8	1·812	−0·012	−0·7	−0·038	−2·1	33
91·8	1·488	+0·029	+2·0	+0·022	+1·5	30
68·9	1·035	−0·060	−5·5	−0·048	−4·4	30
45·9	0·694	−0·035	−4·8	−0·004	−0·6	30
22·9	0·332	−0·032	−8·8	+0·008	−2·4	30
9·18	0·120	−0·026	−18	+0·035	(+41)	
4·59	0·052	−0·023	−31	+0·042	(+520)	

* See Experimental.

affected by a change in molecular weight by a factor of 10 in the range of PVAc polymers most widely employed in industry.

The results of single determinations with Copolymer C4 are listed in Table 3. This copolymer shows similar characteristics to the Gelva polymer, but the gradient of the calibration graph is ~ 0·016 l./mg and a threshold concentration of 4·1 mg/l. is indicated. Table 3 also includes the per cent reduction in absorbance observed when the iodine and potassium iodide concentrations are reduced by a factor of 5. Linearity is retained and absorbance is reduced by 30% for concentrations of copolymer up to 100 mg/l., but for higher concentrations the absorbance levels off to a maximum of ~ 1·5.

The results above show that the dilution of stock solution, preparation of complex solution, and measurement of absorbance generate a random error of up to ~ 5%. Absorbance appears to be particularly low for initial polymer concentrations below about 10 mg/l., owing to a systematic phenomenon. Table 4 shows the results of replicate dilutions and absorbance measurements on solutions of the Gelva V polymers for initial concentrations > 10 mg/l. For the initial polymer concentration range 10–100 mg/l., the

Table 4. Limits of true mean absorbances in the replication experiments, and deviations of means ($\bar{A}_i$) from the least squares line*

[PVAc], c_i, *mg/l.*	$\bar{A}_i$	Limits of true mean $\bar{A}$	% True-mean limits	Deviation for $A = 0{\cdot}02175c$	% Deviation for $A = 0{\cdot}02175c$
Gelva V-7					
126·48	2·76	±0·15	±5·4	+0·01	+0·4
94·86	2·065	0·022	1·1	+0·001	0·0
63·24	1·432	0·007	0·5	+0·056	+4·1
Gelva V-100					
48·30	1·058	0·003	0·3	+0·007	+0·7
24·15	0·473	0·002	0·5	−0·052	−9·9
12·08	0·235	0·002	0·9	−0·028	−10·6

* See Experimental.

mean of 10 replicates can be relied upon to within about 1%. At the lower end of this range the dilution procedure is no doubt critical, and at the top of the range absorbance measurements above 2 become critical. Our measurements on the 126·48-mg/l. solution ($A \sim 2{\cdot}8$) showed singularly poor reproducibility, to which lack of quantitative reproducibility of complex formation may contribute. The best straight line which includes the point $A = 0$, $c = 0$ has a gradient close to 0·022 l./mg and again indicates a threshold effect through the low results for initial polymer concentrations < 25 mg/l. The results for the four highest concentrations in Table 4 yield $A = 0{\cdot}02198c$. The results for the two lowest concentrations make only a minor contribution to the value of the gradient.

DISCUSSION

The absorbance of the pure PVAc complex is given within 2% by the equation $A = 0{\cdot}022c$ for the conditions in Table 1 at 20° and c expressed in mg/l. of final colorimetric solution. Replication was necessary to obtain this reproducibility, and the scaling up of our volumetric procedure is recommended. The range is limited to 25–100 mg of PVAc per l. of final solution by a small threshold effect at lower PVAc concentrations and poor precision at the higher concentrations. The method of standard additions is indicated for the determination of small quantities of PVAc. The threshold effect and the lowest measurable absorbance (~ 0·007) give 3 mg/l. of final solution, or ~ 0·1 mg in 0·5 ml of initial solution, as the limit of detection. As far as the final colorimetric solution is concerned, the sensitivity of the method is comparable to that obtained in the determination of polyvinyl alcohol by the borate–tri-iodide method.[1]

The dispersion of PVAc from methanolic solution into water normally causes the collapse of the extended polymer chains and aggregation of low concentrations of polymer to the colloidal state. High concentrations of PVAc result in precipitation under such conditions, as we observed when iodine was omitted from the procedure in Table 1. In our analytical method, the red complex forms at the limit of its solubility. It is therefore unlikely that the complex is a polyelectrolyte involving charged iodine, because this would almost certainly be water-soluble. Rather, the complex is a polymer aggregate in which neutral iodine is chemisorbed. In the case of very dilute PVAc solutions, a large fraction of the polymer molecules may remain in an extended form preferentially solvated by methanol and give rise to the threshold effect under the conditions of the analytical method.

We have found that greater absorbance per unit concentration of PVAc and a more stable solution with respect to precipitation may be obtained if less water is used to dilute the system, for example, as when the methanolic PVAc–I_2 solution (Table 1) is first diluted with pure water until it contains ~ 35% of methanol, and then almost half of its volume of potassium iodide solution is added as the last step. However, the absorbances of final solutions containing 20–40% of methanol slowly increase with time. This suggests that complex formation is accompanied by slow crystallization or orientation of the polymer chains, which can be rapid in highly aqueous solutions. A similar phenomenon may occur following the disappearance of the absorption-band characteristic of the complex at temperatures > 30°, when the solution is cooled back to 20° and the band returns. The red acetate complex is thermodynamically unstable at 30° and differs in this respect from the blue polyvinyl alcohol–borate–iodine complex which is stable at this temperature.[1,7]

In the presence of sufficient potassium iodide, the proportion of iodine which reacts with PVAc is 7·3% by weight at 20°, whether the PVAc is dispersed *via* methanol in aqueous solution or is merely suspended as a fine solid in contact with the aqueous medium (although the apparent iodine potentials recorded with the two phases differ by ~ 10 mV).[8] This corresponds to one iodine atom for every 20 acetate groups in pure PVAc. Under the conditions of our analytical method, sufficient iodine is present to exceed this requirement by a factor of about 40 in the case of the highest concentration of PVAc used, and this ensures approximate constancy of the contribution made by unreacted reagents to the absorption of the analytical solution. However, the fact that only one acetate group in 20 is involved suggests that iodine is complexed at special sites or that complex formation requires the orientation of several polymer segments.

The sensitivity of the analytical method for Copolymer C4 is reduced by 26% from that for pure PVAc. The proportion of bound iodine must be similarly reduced owing to the lesser number of acetate groups. If a proportionate relationship between concentration of complex and acetate groups is assumed, the analytical method shows about a 74% vinyl acetate contribution in this copolymer. (The threshold concentration for the copolymer is consistently higher than for pure PVAc, but we cannot be sure of the mechanism governing this phenomenon.) The characteristic absorption-band of the red complex is also easily observed for copolymers of vinyl acetate which contain 85–98% of alcohol groups in place of acetate (substantially hydrolysed PVAc).[1] These hydrophilic (co)polymers are very soluble and are in their extended forms in water. We conclude, therefore, that two things are necessary for the formation of the red complex in the I_2–KI system: co-ordination by water, and the orientation of several polymer segments around each iodine unit. The degree of extension of the polymer chain appears in itself to have only a minor influence on the formation of the complex. Further work in this area is clearly desirable.

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Zusammenfassung—Polyvinylacetat und Jod bilden in Gegenwart von Kaliumjodid einen charakteristischen roten Komplex. Die Spektrophotometrie des Komplexes bei 510 nm in einem Methanol-Wasser-System bei 20° gibt im Bereich 25–100 mg Polyvinylacetat pro Liter Meßlösung lineare Eichkurven. Die Nachweisgrenze beträgt 0,1 mg Polyvinylacetat in 0,5 ml anfänglicher Probe. Ersatz der Acetatgruppen durch inerte Gruppen vermindert die Empfindlichkeit der Methode: andere Einzelheiten des Systems werden diskutiert.

Résumé—L'acétate de polyvinyle et l'iode forment un complexe rouge caractéristique en la présence d'iodure de potassium. La spectrophotométrie du complexe à 510 nm dans un système méthanol-eau à 20° fournit des courbes d'étalonnage linéaires dans le domaine 25–100 mg d'acétate de polyvinyle par litre de solution finale. La limite de détection est de 0,1 mg d'acétate de polyvinyle dans 0,5 ml d'échantillon initial. Le remplacement de groupes acétate par des groupes inertes réduit la sensibilité de la méthode, et l'on discute d'autres détails du système.

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A PROPOSED SAMPLING CONSTANT FOR USE IN GEOCHEMICAL ANALYSIS

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Summary—The error in a determination of an element in a rock or mineral sample depends on the analytical error, the weight of sample analysed, and the nature and history of the laboratory sample. The most probable result is not independent of the weight of sample analysed. This is due to the fact that trace constituents often reside in isolated mineral grains. The chance of such mineral grains appearing in any one analysed sample becomes more remote as the sample weight decreases, even when rock or mineral samples are reduced to fine powders. Such subsampling errors can be controlled through the use of sampling constants. These may be estimated by several procedures, including repetitive determination of a constituent and physical measurement of relevant sample characteristics. Sampling constants can be usefully employed during the establishment and certification of reference samples or standards. When subsampling is deficient, analytical results may yield erroneously low values, sometimes with high precision. High precision never implies high accuracy; it may be a symptom of gross error.

Laboratory samples of rocks and minerals frequently yield unrepresentative analytical subsamples.[1–5] Though laboratory subsampling error is sometimes insignificant, it can be much greater than intuition would predict.[6] It becomes more important as the concentration of the element of interest diminishes, and, in analyses for trace elements, probably constitutes one of the largest single sources of experimental error.[7,8]

Most geochemical analyses are now accomplished by rapid instrumental methods which compare signals generated by standards and unknowns. Subsample weights are often dictated by the peculiarities of the method, and may be small, ranging from a gram or less for chemical methods down to a few micrograms or nanograms in spark-source mass spectrometry[5] and electron-probe microanalysis. With the comparison methods, the subsampling characteristics of both standards and unknowns have an effect on the overall experimental error. Quantitative estimation of this effect is desirable.

The relative standard deviation (R, %) of the results for one component, when the laboratory sample has been prepared in a particular way to pass a specific mesh size, varies inversely as the square root of the weight (w) of the analytical subsample,[7,8] and a sampling constant (K_s) can be defined by

$$R = \sqrt{K_s/w} \qquad \text{or} \qquad K_s = R^2 w \tag{1}$$

This relationship presumes that the subsample corresponds to at least a certain minimum number of particles and that the sample is well-mixed, so that a combined result from two subsamples, each of weight w, has the same subsampling variability as a single subsample of weight 2w. This assumption of thorough mixing, sometimes loosely and erroneously referred to as sample homogeneity, is to be understood to apply throughout. It does not require that all the mineral grains be of the same size; it requires only that they be randomly distributed throughout the sample, and randomly taken during removal of the analytical subsample. For our purposes, we shall refer to it as "uniformity." It is a qualitative term, since no mixture of minerals can possibly be either homogeneous or uniform, no matter how finely ground or thoroughly mixed.

The sampling constant, K_s, has the units of mass. It is the subsample weight necessary to ensure a relative subsampling error of 1% (68% confidence) in a single determination. Its square root is numerically equal to the expected coefficient of variation for results obtained on 1-g subsamples in a procedure which is free from analytical error.

It should be noted that grain size and distribution do not enter this relationship. The sampling constant is specific for each constituent of a sample in a given state of subdivision. Further grinding of a sample will usually (not always) lower the sampling constant for each constituent.

Sampling constants will usually be estimated from a series of determinations by the same method under controlled conditions. The observed variability of such a series will include both analytical and subsampling variability, so that the subsampling characteristics cannot be determined from it unless there is an independent estimate of analytical variability, or unless there is good reason to believe that analytical variability is negligible compared to subsampling variability. Generally, if the subsampling error is greater than three times the analytical error, the latter is of no consequence.[9]

Once the subsampling characteristics of a given sample have been determined for any constituent, they should be included in any report of sample composition; in the case of "standard" or "reference" samples, sampling constants should be included in any certification. It would then be possible for an independent investigator, using further subsamples of the same material, to distinguish between the analytical variability of his method of analysis and variability due to his subsampling process. It would also be possible for him to estimate the overall precision attainable by his method, as a function of subsample weight.

Knowing the sampling constant for a constituent of a sample and also the subsample weight, an analyst can readily calculate the contribution of subsampling error to the probable deviation of a single analytical result. In general, this deviation can be translated into error bars of determinable length by using Gaussian statistics. In trace-element analysis, however, and also in the analysis of highly purified materials, the distributions of subsample determinations may be decidedly skew for sufficiently small subsample weights, and probabilities cannot be well measured by using Gaussian statistics. In such cases, better approximations of the probabilities are given by use of Poisson statistics.[10]

The sampling constant principle has been developed previously by Gy,[11,12] Visman,[13] and others in dealing with the collection, reduction, and preparation of samples from large masses of material. While the various statistics that apply in bulk sampling are generally similar to those applying in laboratory subsampling, they cannot be correctly used in the latter operation without modification and shifts of emphasis. In particular, assumptions of symmetrical distribution become less true as sample weight decreases, and at the laboratory subsampling level often lose all validity.

Gy's basic sampling equation has been explained and discussed by Ottley.[14] The validity of Visman's "*General Theory of Sampling*" has been examined by Duncan[15] and by Visman, Duncan and Lerner.[16] Visman proposes the use of two sampling constants, one of which deals with errors arising from the presence of more than one species in the material to be sampled, and the other with errors due to segregation or unmixing. The latter is not relevant to the present discussion, in which it is assumed that unmixing and segregation difficulties may be overcome in good laboratory practice by careful mixing of laboratory samples and the use of appropriate methods for splitting out the analytical subsamples. A test for the "homogeneity" of a mixture has been developed by Schaeffer,[17] who has also written on the problem of sampling mixtures of "multisized" particles.[18]

RESULTS FOR DISCUSSION

Table 1 shows ten sets of K_2O determinations done by a method of high precision,[6] three on samples which are uniform at the 100-mg subsampling level, and seven on non-uniform samples, obtained during a search for suitable calibrating standards. The results show that the laboratory subsampling error may be much greater than is generally recognized. Of the non-uniform samples, the basalt and the granodiorite GSP-1 show variations typical of rock powders of this type; the biotite contains hornblende and other low-potassium impurities; the white mica shows a wide variability in its potassium content under the microprobe, although it appears homogeneous under the microscope; the pyroxene contains feldspar grains which result in discrete differences among the several values; the beryl contains muscovite inclusions which are inseparable even when the sample is ground to pass a 200-mesh sieve.

Table 2 summarizes the results of repetitive determinations of K_2O in various reference samples, together with sampling constants and other information. Potassium determinations are very useful for illustrative purposes because the methods used are intrinsically precise, having been developed over many years by those interested in K–Ar dating.

Table 1. Repetitive determinations of K_2O*

Uniform rocks and minerals			Non-uniform rocks and minerals						
Basalt	Pyroxene	Phlogopite	Basalt	Hornblende	Biotite	White mica	Pyroxene	Beryl	GSP-1
0·667	0·0115	10·17	0·358	0·287	8·97	7·59	0·0157	0·0094	5·52
0·666	0·0115	10·17	0·359	0·277	8·83	8·80	0·0189	0·0093	5·50
0·664	0·0115	10·17	0·363	0·280	8·84	8·90	0·0190	0·0087	5·52
0·665	0·0113	10·16	0·364	0·275	8·90	8·78	0·0113	0·0127	5·49
0·665	0·0115	10·17	0·362	0·288	8·57	8·87	0·0157	0·0138	5·55
0·668	0·0113	10·17	0·363	0·277	8·87	7·90	0·0180	0·0017	5·49
		10·17	0·367	0·284	8·95	7·87		0·0097	5·44
		10·17	0·367	0·282				0·0123	5·48
		10·17	0·358	0·280					5·42
		10·17	0·350	0·289					5·44
		10·17							

* All values reported in % w/w K_2O: each reported value represents a separate analysis: high and low values are underlined: 100-mg subsamples used in every case. Analysts, L. B. Schlocker and C. O. Ingamells. *Procedure.* Mix 0·1000 g of sample and 0·7000 g of K-free $LiBO_2$, transfer to a high-purity graphite crucible, and heat in a muffle at 950° for 15 min. Pour the melt into 100 ml of 4% nitric acid and stir till dissolved (5 min). Read the K/Li ratio with an Instrumentation Laboratories Model 143 flame photometer (after tenfold dilution for samples with >1% K_2O). Use a *uniform* standard and a K-free quartz for calibration and zero setting respectively.

Table 2. Sampling constants for potassium

Sample and description	Method*	No. of detns.	Effective mesh size, μm	K_2O, %	Sampling constant, $\sqrt{K_s}$	References and remarks
Amphibolite-orthoclase	4	40	297–420	0·286	5·0	Engels and Ingamells[6]
Bern Muscovite 4M	4	39		10·40	0·14	This paper
Bern Biotite 4B	4	28		9·47	0·11	This paper
MIT Biotite B-3203	2, 3, 4	13	350	9·05	0·44	Abbey *et al.*,[23] Engels[47]
MIT Biotite B-3203	1, 3	8	125	9·05	0·10	Ground to pass 115 mesh
USGS Muscovite P-207	2	10	300	10·4	0·41	Lanphere and Dalrymple[83,8-
Nancy Biotite Bio-R	4	10	unscreened	8·80	0·11	de la Roche and Govindaraj
Nancy Phlogopite Mica-Mg	4	12		10·18	0·00‡	This paper
Nancy Biotite Mica-Fe	4	16		8·84	0·1	This paper
Biotite LP-6 Bio 40–60 # †	4	100	250–420	10·03	0·07	Engels and Ingamells[44,45]
Nancy Basalt BR	4	9	unscreened	1·38	0·15	Roubault *et al.*[86,87]
Penn State Orthoclase	1, 2, 3, 4	many	297	14·92	0·00‡	Engels and Ingamells[88]
USGS Dunite DTS-1	3	6	unscreened	0·0011	14·	Morgan and Heier[89]
USGS Peridotite PCC-1	3, 4	12	unscreened	0·0011	38·	Flanagan[41]
USGS Basalt BCR-1	4	64	unscreened	1·70	0·57	Goldich *et al.*[40]
USGS Basalt BCR-1	4	6	unscreened	1·70	0·32	Subsamples from same bottle
White Mica, Table 1	4	7	1000	8·4	2·1	Compositional variability
Beryl, Table 1	4	8	74–149	0·01	12·	Muscovite inclusions
USGS Granite G-1	1, 2, 3, 4	12§	177	5·52	0·3	This paper

* Methods of analysis: 1. Lawrence Smith[22] attack, double leach,[20] chloroplatinate separation,[19] conversion into sulph for weighing; minor alkalies determined by flame photometry,[25] and corrections made. 2. Flame photometry.[25] 3. Shapiro a Brannock.[24] 4. $LiBO_2$ fusion, HNO_3 solution, flame photometry using Li from the flux as an internal standard.[6,82]

† LP-6 Bio is a biotite of 99·9% purity[44,45] available from J. C. Engels, 348 Waverly St., Menlo Park, California, USA 94025.

§ The sampling constant reported for G-1 is based on 12 determinations by method 4: results by other methods confirm estimate.

‡ Precision of the method is not good enough to detect any subsampling variability in these samples.

Methods include gravimetric procedures using chloroplatinate,[19] perchlorate,[20] or tetraphenylborate,[21] usually applied after a Lawrence Smith[22] or Berzelius[19] decomposition. Flame emission and absorption methods[23–30] and isotope-dilution mass spectrometry[31] are most often used. Neutron-activation analysis[32–33] and combined neutron-activation and mass spectrometry[34–35] have been applied. X-Ray spectrography is a common method.[36–39]

Because of the effort which has gone into the refinement of all these methods, it is reasonable to assume that they contribute less than usual to the variance of the results. The high precision attainable has been well documented in other work,[6,26] and is supported by data in Table 1.

Repetitive determinations of K_2O in the USGS dunite DTS-1 are shown in Table 3. They demonstrate the effect of subsample weight on analytical results.

Sixty-four determinations of sodium and potassium in the USGS basalt BCR-1, using eight separate bottles of this sample, provided an estimate of sampling constants for K and for Na. Results for potassium are included in Table 2 and for sodium in Table 4. The data are those of Goldich *et al.*[40] During this series of determinations there was evidence of unmixing of the samples, and some of the variance in the results may be due to this. Later work in the USGS Menlo Park laboratories with a single bottle of BCR-1 gives a somewhat lower sampling constant for potassium (Table 2).

Table 3. Repetitive K_2O determinations in dunite DTS-1

% K_2O Subsamples 0·1 g		% K_2O Subsamples 0·5 g
0·0003		0·0015
0·0013		0·0011
0·0030		0·0009
0·0003		0·0009
0·0003		0·00115
0·0003		0·0012
0·0009	(mean)	0·0011

Analyst, L. B. Schlocker.

A large (21-g) sample of the USGS granite G-1 was treated with hydrofluoric, then sulphuric and boric acids; the soluble portion was discarded. The insoluble matter weighed about 5 mg, of which 0·4 mg was chromite in the form of about 100 grains, all of about the same shape and size. These were hand-picked from the residue and their identity confirmed by emission spectroscopy and X-ray diffraction. A simple calculation shows that the chromite accounts for a large part of the chromium content, and that a 100-mg subsample contains, on the average, about half a grain of chromite.

Eight subsamples of the USGS dunite DTS-1 were examined for their chromium content by Goldich *et al.*[40] Sampling constants for chromium are reported in Table 4.

Ferrous iron in the USGS samples AGV-1, BCR-1, and W-1 was determined by the Cooke method[19] on 500-mg subsamples. The method is somewhat difficult to use, as evidenced by the wide variance in inter laboratory results,[41] but can be capable of high precision in skilled hands. Repetitive determinations established its precision as better than ± 0·02% FeO.[42] The method does not always recover all the FeO, some being present in insoluble minerals.[40] The results are reported in Table 4.

The relative standard deviation of 12 determinations of rubidium in 100-mg subsamples of the USGS granite G-1 by the method of Medlin *et al.*,[30] slightly modified, was 10·4%. The relative standard deviation for potassium in the same subsample solutions by the

Table 4. Some estimated sampling constants

Sample	Description	Element	$\sqrt{K_s}$, $g^{1/2}$	References
G-1	USGS Granite	Rb	1·7	This paper
G-1	USGS Granite	K	0·3	This paper
G-1	USGS Granite	Cr	50	This paper
DTS-1	USGS Dunite	Cr	0·38	Goldich *et al.*[40]
AGV-1	USGS Andesite	FeO	0·47	Goldich *et al.*[40]
BCR-1	USGS Basalt	FeO	0·35	Goldich *et al.*[40]
BCR-1	USGS Basalt	Na	0·22	Goldich *et al.*[40]
W-1	USGS Basalt	FeO	0·22	Ingamells and Suhr[42]
LP-6 Bio 40–60 #	Biotite	Na	1	Engels and Ingamells[44,45]
LP-6 Bio 40–60 #	Biotite	Fe	0·07	Engels and Ingamells[44,45]
LP-6 Bio 40–60 #	Biotite	Ca	1·4	Engels and Ingamells[44,45]
LP-6 Bio 40–60 #	Biotite	Al	0·03	Engels and Ingamells[44,45]
LP-6 Bio 40–60 #	Biotite	Si	0·03	Engels and Ingamells[44,45]

method of Engels and Ingamells[6] was 0·3%. Both deviations are corrected for analytical error, measured by repetitive runs on uniform samples. Fabbi found a relative standard deviation of 3·2% in 12 determinations of rubidium in 500-mg pelleted subsamples of G-1 by X-ray fluorescence:[43] relative analytical error, found by repetitive runs on a single pelleted subsample, was about 1%. These results have been used to estimate the subsampling characteristics of G-1 with respect to rubidium and potassium. Results appear in Table 4.

Sampling constants for several constituents of LP-6 Bio 40–60# have been estimated.[44,45] Results for several elements are reported in Table 4, and for potassium in Table 2.

Table 5 shows 12 determinations of potassium in a separated pyroxene. Six determinations on the same mineral after its further purification are shown in Table 1, column 2.

Table 5. Repetitive K_2O determinations on a pyroxene*

K_2O, %w/w	$(x_i - x_{min})$†	$(x_i - x_{min})/2$	$(x_i - x_{min})/3$	$(x_i - x_{min})/4$
0·0113	0·0000			
0·0157	0·0044	0·0022		
0·0157	0·0044	0·0022		
0·0173	0·0060		0·0020	
0·0180	0·0067		0·0022	
0·0185	0·0072		0·0024	
0·0190	0·0077		0·0026	
0·0190	0·0077		0·0026	
0·0203	0·0090			0·0022
0·0203	0·0090			0·0022
0·0203	0·0090			0·0022
0·0207	0·0094			0·0023

* Arranged in order of increasing K_2O. Analyst, L. B. Schlocker. After repurification, the sample yielded values for K_2O ranging from 0·0113 to 0·0115 (Table 1, column 2). The results imply that c is 0·0022–0·0026. Statistical treatment reveals that c is actually half this, and that the subsamples showing 0·0203% K_2O actually carry 8, not 4 grains of high-potassium contaminant.

† $x_i = K_2O$ determined; x_{min} is presumed equal to H.

Twelve determinations of potassium on the amphibolite–orthoclase mixture used by Engels and Ingamells to demonstrate the effects of sample non-uniformity in K–Ar dating[6] are reported in Table 6.

Sampling constants for potassium in the Bern Muscovite 4M, the Bern Biotite 4B, the Nancy Biotite Mica-Fe, and the Nancy Phlogopite Mica-Mg have been determined by repetitive determination. Results are reported in Table 2. The Phlogopite Mica-Mg is probably the purest mineral sample ever prepared in quantity. Even the highly precise method by which most K_2O values reported in this paper were obtained, cannot reveal subsampling non-uniformity in Mica-Mg, and its sampling constant, like that for the Penn State orthoclase Or-1, must be reported as $\leqslant 0·01$ for potassium. Twelve separate determinations of K_2O in Mica-Mg yielded eleven at 10·17% and one at 10·16%. This sample will be of great value to anyone bent on finding the precision of a method for potassium in micas, since all variance in his determinations of K_2O in this sample can be attributed to analytical error.

Table 6. Repetitive K_2O determinations on an amphibolite–orthoclase mix*

Subsample weight, *mg*	K_2O found, %	z_i†
9·10	0·327	1 (1·2)
9·07	0·425	2 (1·8)
8·46	0·143	0 (0·0)
9·35	0·390	2 (1·6)
11·37	0·387	2 (1·9)
10·75	0·317	1 (1·3)
10·14	0·485	2 (2·4)
10·53	0·267	1 (0·9)
12·19	0·297	1 (1·3)
10·04	0·157	0 (0·1)
10·29	0·437	2 (2·1)
10·21	0·287	1 (1·0)

* Engels and Ingamells.[6] An average of 0·286% K_2O was obtained from 40 determinations on 100-mg subsamples, with a standard deviation of 0·045%. The mixture is 99% amphibolite with 0·145% K_2O, and 1% orthoclase with 14·92% K_2O.

† Calculated by using equations (4) and (5); the calculated numbers (in parentheses) have been rounded to whole numbers of grains. The non-integral calculated results may be attributed to non-uniformity of grain size. The probability is 0·98 that at least one of these 12 determinations represents the composition of the amphibolite and that the subsample contains no orthoclase grain.

THE SAMPLING CONSTANT

A sampling constant can usually be well estimated from a series of subsample determinations, provided that the subsample weight is appropriate. If analytical error is small (less than one-third of the subsampling error[9]), and $x_1, x_2, \ldots, x_i, \ldots, x_M$ are the results of M determinations on subsamples of weight w g, K_s is estimated by

$$\hat{K}_s = \hat{R}^2 w = \frac{10^4 w \Sigma (x_i - \bar{x})^2}{(M-1)\bar{x}^2} \tag{2}$$

where $\bar{x}$ is the arithmetic mean of M determinations. The relative standard deviation for the same constituent in a future subsample of weight w_F is then estimated by

$$\hat{R}_F = \sqrt{\hat{K}_s / w_F} \tag{3}$$

The usual reason for computing the estimate $\hat{R}_F$ is that it can be related to probability statements or error bars. Specifically, the probability is about 2/3 that a future subsample will yield a value which differs from the mean value by less than $\hat{R}_F$%, and about 0·95 that the difference from the mean will be less than $2\hat{R}_F$%, always supposing that the analytical error is less than 1/3 the subsampling error. This statement is correct if $\hat{K}_s$ is derived from a sufficiently large number of previous determinations, and there is an approximately Gaussian symmetry of the theoretical distribution of values based on subsample weight w_F. If the estimate $\hat{K}_s$ is based on 10 or more determinations, the statement should not be too far wrong, except under some very important special circumstances mentioned immediately below.

A serious limitation on these statements, one which marks the essential difference between bulk sampling and laboratory subsampling, and which must be considered in analysis for trace elements and when analytical subsamples are small, is the frequent lack of symmetry in the distribution of repetitive analytical results. When a constituent (whether a species of interest or a contaminant) is concentrated in a few mineral grains, the theoretical distribution of single determinations is approximately of Poisson type.[10,46] When the number of such grains averages less than five or six per subsample, this Poisson distribution has a noticeable asymmetry, with low values occurring frequently and high values more seldom. An average of results from too few subsamples will probably be erroneously low. To illustrate this, histograms of results for trace elements in a 200-mesh greywacke[4] are shown in Fig. 1. These may be compared with histograms based on the Poisson distribution, calculated by processes to be described.

In such cases, the observed variability in a series of subsample determinations can be ascribed to a variability in the number, z, of these grains per subsample. If these grains are of approximately equal size, a single analytical result will have the value

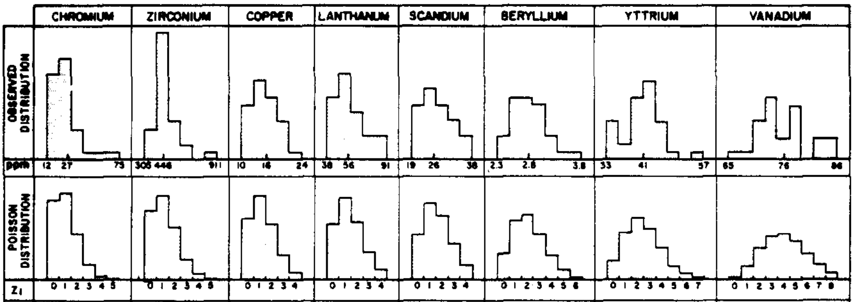
$$x_i = H + cz_i \tag{4}$$

where H is the concentration of the element of interest in the gangue or matrix, and cz_i is the contribution of the z_i "special" grains to the result. The units of c are unusual, namely "absolute whole sample concentration per grain"; i.e. for 6 grains and $(x_i - H) =$ 0·06% absolute, $c = 0{\cdot}01\%$ absolute per grain. There will be a Poisson distribution of z_i among several subsamples of statistical mean z. A good estimate of the contribution of a single such grain to an analytical result is

$$\hat{c} = \frac{s^2}{\bar{x} - H} \tag{5}$$

where s^2 is the variance of the results of M determinations (M large enough).

According to this model, the series average, $\bar{x}$, will be an estimate of $H + cz$, and the series variance, s^2, will be an estimate of c^2z. Further, when z is small and M is sufficiently large, it becomes likely that the smallest determinative value in the series, $x_{\min}$, will have



	CHROMIUM	ZIRCONIUM	COPPER	LANTHANUM	SCANDIUM	BERYLLIUM	YTTRIUM	VANADIUM
$\hat{z}$	1.08	1.22	1.33	1.45	1.67	2.17	2.54	4.22
$\bar{x}$	27.07	446	15.6	56.1	25.9	2.86	41.41	76.0
$x_{\min}$	12.4	305	10.1	38.4	19.0	2.3	32.6	65.0
s	14.13	128	4.74	14.8	5.31	.38	5.53	5.35
$\hat{c}$	13.61	115.9	4.11	12.26	4.12	.258	3.47	2.60
Prob. ($z_i = 0$)	.999+	.999+	.999+	.999	.998	.976	.92	.37

Fig. 1. Histogram of analytical results for trace elements in a greywacke: data from Ondrick and Suhr.[4]

$z_i = 0$, and will provide an estimate of H. In particular, the probability of obtaining a subsample free from "special" grains is

$$P_{(z_i=0)} = 1 - (1 - e^{-\bar{z}})^M \tag{6}$$

For example, if $M = 20$ and $z = 2{\cdot}0$, $x_{\min}$ will estimate H with a probability of about 94%. In such cases, z can itself be estimated by

$$\hat{z} = (\bar{x} - x_{\min})^2/s^2 \tag{7}$$

Obviously this estimate should only be used if it yields a high value for $P_{(z_i=0)}$ when substituted into (6), or if (as is the case with the pyroxene in Table 5) other evidence exists that $x_{\min}$ is a good estimate of H.

To illustrate further, if $x_{\min} = 2{\cdot}05$, $\bar{x} = 2{\cdot}15$, and $s^2 = 0{\cdot}005$, then the implied estimate of z is $\hat{z} = 2{\cdot}0$ by equation (7). As remarked earlier, Gaussian statistics provide an appropriate approximation only when z is greater than about 6; hence, for use of Gaussian statistics in this example, the subsample weight should be increased by a factor of three, or the determinations grouped in threes according to the central limit theorem, before statistical manipulation. The histograms in Fig. 1, showing the calculated and observed distributions of the data of Ondrick and Suhr,[4] illustrate this. The histogram interval is calculated from equation (5), assuming that $x_{\min} = H$. Note that as $P_{(z_i=0)}$ decreases, the pairs of histograms lose their similarity. Spectacular examples of non-Gaussian distributions are given by Jones and Beaven.[10]

In analysis for trace elements, it is always possible that the subsample weight chosen may be small enough for no "special" grains to appear in any of M subsamples, especially when, as often occurs in practice, M is small (duplicate or triplicate samples) and subsamples are small (*e.g.*, 10-mg subsamples in d.c. arc spectroscopy).

An estimate of the probability that $z_i = 0$ for a particular subsample is given (for samples of uniform grain size) by

$$\hat{P}_0 = e^{-dw_F} \tag{8}$$

where d is the number of "special" grains per unit weight of sample. If sufficient subsample determinations are available, and the proportion P_0 of them gives values corresponding to the background (matrix) level, then an estimate of d is given by

$$\hat{d} = \left(\frac{1}{w_F}\right)\ln\left(\frac{1}{P_0}\right) \tag{9}$$

In practice, a subsample weight can be chosen which, in M analytical determinations, will yield results with one of three characteristic distributions.

Distribution 1. An approximately symmetrical (Gaussian) distribution, when the mean z exceeds 5 or 6.

Distribution 2. A skewed, approximately Poisson, distribution, in which the mean z is less than 5 or 6.

Distribution 3. An approximately symmetrical (Gaussian) distribution, when z_i is 0 for all subsamples.

It is often impossible to distinguish between the first and third distributions, especially if all subsamples are of the same size. When analytical error is undefined, it is impossible to be sure that a distribution of the second kind reflects characteristics of the sample. When an analytical method can only use small subsamples (*e.g.*, d.c. arc spectroscopy,

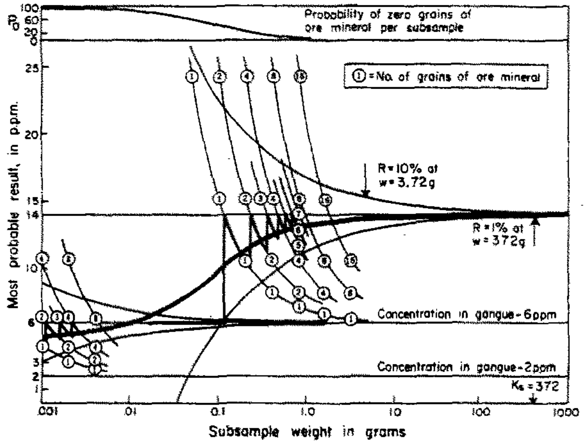


Fig. 2. Subsampling diagram for a hypothetical 200-mesh mixture of three minerals—one of s.g. 4·5 with 50% of an element contributing 8 ppm to the total, one of s.g. 2·7 with 0·2% contributing 4 ppm, and a gangue mineral of s.g. 2·7 with 2 ppm of the element. As subsample weight decreases from 1000 g, relative subsampling error increases to 1% at 372 g, and to 10% at 3·72 g. As the subsample weight continues to decrease, Gaussian statistics no longer yield a reasonable error estimate, the most probable result is determined by the number of grains of ore mineral per subsample, and the plotted relationship becomes discontinuous, following Poisson statistics. At subsample weights less than about 10 mg, any reasonable number of subsamples may not include any grain of ore mineral, and Poisson distribution of the results is due to grains of the mineral with 0·2% of the element of interest. The dark line is drawn to show the general trend of the graph, corresponding to a real situation in which mineral grains are only approximately of uniform size.

spark-source mass spectrometry, electron-probe microanalysis), the possibility that the third distribution applies becomes greater as the concentration of the species of interest diminishes.

Figure 2 is a subsampling diagram for a hypothetical 200-mesh rock powder, in which the species of interest exists in three forms—as a major constituent of a minor mineral, as a minor constituent of a minor mineral, and as a trace constituent of a gangue within which these minerals are randomly distributed. For the purpose of illustration, the overall concentration of the species of interest has been taken as 14 ppm, of which 8 are due to an ore mineral of s.g. 4·5 and containing 50% of the species of interest, 4 are due to a mineral of s.g. 2·7 containing 0·2%, and 2 are evenly distributed in a gangue mineral of s.g. 2·7.

For such a mixture $K_s = 372$ g. If 1-g subsamples are taken, each will contain, on the average, about 8 grains of ore mineral, and repetitive determinations will exhibit a relative standard deviation of $R = \sqrt{K_s/w} = 19\%$. If 100-mg subsamples are taken, the chances are about even that any one of them will contain a grain of ore mineral: results will be highly variable, their distribution will be highly skewed, and unless a very large number of determinations is performed (38 will be necessary to achieve a relative subsampling error of less than 10%), the average will be grossly in error. If a few 10-mg subsamples are taken, the chances are high that no grain of ore mineral will appear in any subsample; variance will be low, the results will appear precise, and their average will be very inaccurate. With still smaller subsamples, the most probable result continues to diminish, until, with techniques like electron-probe microanalysis and spark-source mass spectrometry, only the background concentration of 2 ppm in the gangue mineral will usually be measured.

It may be that reference samples should be certified in terms of each constituent determined at more than one level of subsample weight. There should be a value useful to those whose analytical technique requires small subsamples and who measure the gangue concentration, and another value useful to those who take large subsamples, and who approach (along the major curve of Fig. 2) a measurement of the overall concentration of the element in question. For example, the "gangue" or background concentration of chromium in the USGS granite G-1 is almost certainly about 10 ppm, and this is the value most spectroscopists will find most of the time if they take 10-mg subsamples. The overall concentration of chromium in G-1 is closer to 20 ppm, because at least half of the chromium occurs in isolated chromite grains, which only occasionally appear in the spectroscopist's 10-mg subsamples. On average, only one in twenty 10-mg subsamples of 170 mesh G-1 contains a grain of chromite. The spectroscopist will be tempted to omit the occasional "absurdly" high value of 200 ppm, and may report an average of 10 ppm, claiming high precision except for an occasional "anomalous" result. On the other hand, a chemist using 1-g subsamples in a colorimetric procedure will find his results very variable, since each of his subsamples will contain a randomly variable number of grains of chromite. He will report an average of about 20 ppm, with poor precision. Plainly, prior knowledge of the sampling constant for Cr in G-1 which has been ground to pass a 170-mesh sieve would alert both workers to the inadequacy of G-1 as a standard for chromium determination, and would lead them to avoid controversy concerning their apparently incompatible results.

It must be mentioned that in the 80-mesh G-1 supplied, most of the chromite grains pass a 170-mesh sieve. The sampling characteristics of G-1 for chromium are not greatly improved if it is ground to just pass 170-mesh. Further, the amount of material which is ground must be considered. Whatever weight of sample is made uniform by fine grinding or isoformation retains the error corresponding to that sample weight, and this error cannot be diminished by any subsequent treatment.

Generally, when P_0, as defined in equation (8), is close to 1, it becomes likely that distribution No. 3 will apply, and that all M values will show only the background (gangue) concentration.

The major curve of Fig. 2 corresponds approximately to the relationship

$$Y = K - \frac{(K - H)}{(2z + 1)},$$

where Y is the most probable result and K is the true overall concentration of the species of interest. For samples in which the "special" grains are uniform in size, this relationship is obviously unrealistic; however, for real samples in which an unknown grain-size distribution exists, it may provide a useful means of estimating the probable negative bias due to the use of too small a subsample. In determining Cr in G-1, for example, a 100-mg subsample will yield a most probable value of

$$20 - \frac{(20 - 10)}{(2 \times 0{\cdot}5 + 1)} = 15 \text{ ppm Cr}.$$

It makes no difference whether a single 100-mg subsample or ten 10-mg subsamples be taken; it is the total subsample weight which determines the bias. For example, a spectroscopist taking five 10-mg subsamples and a chemist taking one 50-mg subsample both have exactly the same chance of selecting a "special" grain: the average of 100 determinations on 10-mg subsamples carries the same probable error as a single determination on a 1-g subsample, supposing analytical error to be negligible.

Only occasionally may a sampling constant for one element in a given sample logically be related to that for another. Thus, potassium and rubidium in G-1 do not exhibit similar sampling constants, although these two elements are geochemically related. Concentration of the rubidium in biotite results in a sampling constant that depends on the distribution of biotite grains in the rock powder, whereas the sampling constant for potassium depends as much on the distribution of feldspar grains. On the other hand, the distribution of radiogenic argon may very well be related to potassium distribution, because the former may be expected to occupy the same crystal sites as the potassium which generated it: repetitive determinations of potassium in a mineral sample may be used, in favourable cases, to establish a sampling constant for argon as well as potassium. There are obvious exceptions: for example, a sample containing two generations of biotite, both with the same K_2O content, will probably exhibit a larger sampling constant for argon than for potassium. It may even be possible to utilize this in detecting geochronological inhomogeneity.

Most separated minerals carry no more than one important contaminant. For example, separated hornblendes are most likely to contain biotite as the only important contaminant. It is therefore useful to examine the sampling characteristics of two-component mixtures. Even when more than two species are present, several may often be usefully grouped together and considered as a single species.

For a two-component mixture, the relative standard deviation can be expressed in terms of the physical properties of the analytical subsample:[6]

$$R = \left| \frac{100\sqrt{pq}}{\sqrt{n}} \cdot \frac{B - H}{K} \right| \tag{10}$$

where p is the volume proportion of the species with $H\%$ of the constituent of interest, q is the volume proportion of the species with $B\%$ of the constituent of interest, K is the true overall average concentration of the constituent of interest in %, and n is the effective number of grains in an analytical subsample of weight w.

In dealing with silicate minerals, the simplifying assumption that each has the same density is usually valid. When the minerals in a two-component mixture are of different densities, it is necessary to distinguish between volume proportions p and q, and weight proportions p_w and q_w. The difficulty in doing this has been emphasised by Wilson.[7] The two proportions are related as follows:

$$p = \frac{d_B p_w}{d_B p_w + d_H q_w}; \qquad q = \frac{d_H q_w}{d_B p_w + d_H q_w} \tag{11}$$

where d_B and d_H are the densities of the two mineral species. The total number of grains in a subsample of weight $w = w_B + w_H$ is

$$n = \frac{w_B}{d_B(10^{-4}u)^3} + \frac{w_H}{d_H(10^{-4}u)^3} \tag{12}$$

where u is the effective linear mesh size in μm. Using the identities[6] $p + q = 1$,

$p_w + q_w = 1$, $KR = p_w HR_H - q_w BR_B$, and $K = p_w H + q_w B$, and substituting (10), (11), and (12) in (1) gives

$$K_s = \left(\frac{Bd_B - Hd_H}{K}\right)^2 \cdot \frac{p_w q_w u^3 w}{d_B w_B + d_H w_H} \cdot 10^{-8}\ \text{g} \tag{13}$$

Appropriate approximations can be made in (13), depending on the problem at hand. If a sampling constant for a trace element present as a major constituent of a minor mineral is sought, H and w_B are close to zero, and

$$K_s \sim (B/K)^2 \cdot p_w q_w u^3 d_B \cdot 10^{-8}\ \text{g} \tag{14}$$

In some cases, *e.g.*, that of Cr in G-1, it is possible to estimate each of the factors in (13) or (14) and to calculate a sampling constant. If the average Cr content of G-1 is 20 ppm, half of which resides in chromite grains, and the mesh size is 177 μm (80-mesh), K_s is calculated to be 2200, with $\sqrt{K_s} \sim 47$. A similar value is obtained from the count of chromite grains in G-1, reported above. Since an average 1 g of G-1 contains about 5 grains of chromite, the standard deviation of the number of grains expected in a 1 g subsample is $\sqrt{5}$, and the relative deviation is $100\sqrt{5}/5 = 44\%$, which gives $\sqrt{K_s} = 44$. Calculations of this sort cannot be very exact, but they can quickly provide estimates which are useful for avoiding gross error.

Sometimes microprobe or microchemical data may be useful in estimating sampling constants. For example, individual grains of the MIT biotite B-3203 show 9·38% K_2O,[47] whereas bulk analyses show 9·04%. If the impurities responsible for the difference are all low in potassium, equation (10) may be used to estimate R for a 1-g subsample, and hence a sampling constant from equation (1). Using the identities $p + q = 1$ and $pH + qB = K$, and putting $n = 20{,}000$, $B = 9{\cdot}38\%$, $H = 0\%$, and $K = 9{\cdot}05\%$ gives $R = \sqrt{K_s} = 0{\cdot}55$. This corresponds to an estimate of $\sqrt{K_s} = 0{\cdot}44$ obtained by repetitive determination (Table 2). Grinding the biotite B-3203 to pass a 115-mesh sieve increases n by a factor of about 16, and reduces R for a 1-g subsample, and hence $\sqrt{K_s}$, by a factor of 4. Confirmation of this is given by a value of 0·10 for $\sqrt{K_s}$, obtained through repetitive determination on 0·5-g subsamples of 115-mesh material (Table 2).

In laboratory practice, sampling constants will usually be estimated by doing sufficient determinations, using one or more judiciously selected subsample weights and an analytical method of high precision; but sometimes it may be adequate and convenient to estimate, by optical examination, the distribution of relevant grains of ore minerals. If, for example, each of several 100-mg subsamples of a 100-mesh carbonatite examined under the microscope shows a low and variable number of grains of heavy minerals such as ilmenite, columbite, or magnetite, there is not much point in proceeding with spectrographic analyses for niobium, titanium, or iron unless a procedure can be devised to overcome the essential non-uniformity of the sample.

When analyses of grossly non-uniform materials (*e.g.*, chondritic meteorites) are reported, qualitative observations on the non-uniformity and its adverse effect on precision are not very helpful; a full description of sampling and subsampling procedures, and a statement concerning the subsampling characteristics of the final laboratory sample, would seem to be essential. Such a description is much simplified by use of a sampling constant for each element. Without such a description, the data may have little meaning.

SUBSAMPLING PROCEDURES

The laboratory sample of a rock or mineral is usually supposed to represent a much larger mass of material. The extent to which it is representative may influence the subsampling. Errors introduced in sample collection and reduction may be so large[11,48] that any subsampling error is negligible if the composition of the parent mass is sought. However, if the same rock or mineral powder is to be used as a reference sample, its source is of little significance but its subsampling characteristics are of prime importance. With separated minerals, almost all the sampling error may arise during laboratory subsampling if this is not done with great care, because it is the composition of the pure mineral which is sought.

Fine grinding of the laboratory sample is the most effective way of improving its subsampling characteristics, but this is often contra-indicated because of the possibility of alteration or contamination. Argon, hydrogen, carbon, sulphur, oxygen, mercury and many other elemental constituents may be affected, and erroneous results obtained if grinding is overdone. It is frequently necessary to accept the subsampling error concomitant with the use of coarse sample powders, and this error should be estimated and reported to permit rational evaluation of the results. When fine grinding of the sample is permissible, there is the question of how much to grind, and to what mesh size.

With separated minerals, fine grinding may be intended to break up mineral aggregates before further purification. For this purpose, the portion of the laboratory sample taken is irrelevant, unless the analysis of the purified material is to be used to correct that of the impure material. Purification of separated minerals may actually increase the subsampling error, but the result, though less precise, comes closer to the composition of the pure mineral. Such considerations are of prime importance in geochronology.[49]

Very often, a laboratory sample is subsampled in two steps: a portion is ground to finer mesh size, and this is subsampled for analysis. If the error introduced in the first step is high, no amount of care during the second will correct matters. The results refer only to the portion actually analysed, and if that is not representative of the whole, will give only an estimate of the composition of the whole. Estimation of a sampling constant for each relevant constituent at each stage of the sample reduction process, by one or more of the methods suggested above, will give control of the process. For example, grinding 1 g of granite G-1 to a fine powder cannot reduce the subsampling error for rubidium to less than 1·7% (Table 4), or that for chromium to less than 50%, because these errors are introduced at the time the 1-g subsample is taken.

In some cases, a large subsampling error may be of great value in determining the purity of a contaminated mineral, and fine grinding, although it improves reproducibility, may destroy important information. An example is given in Table 5. Examination of these results for potassium in a pyroxene shows qualitatively that the subsampling variance is probably due to the presence of isolated grains of a high-potassium contaminant, which are randomly selected during subsampling. The table is arranged to show that, qualitatively, the highest value may derive from 4 grains of high-potassium contaminant in the subsample. By use of the principles outlined above, the qualitative observation is shown to be probably incorrect. The data yield the following information: the mean of the 12 determinations is $\overline{x} = 0{\cdot}0180\%$, the estimated standard deviation is $s = 0{\cdot}00272\%$, the matrix content of K_2O is $H = 0{\cdot}0113\%$, the contribution of a single grain of contaminant to an analytical result is $c = s^2/(\overline{x} - H) = 0{\cdot}0011\%$ K_2O, and there are in the average subsample $z = (\overline{x} - H)^2/s^2 = 6{\cdot}1$ grains of contaminant. The grain size of the contaminant cannot be greater than will pass the sieve used to prepare the sample—in this case 177 μm, and this implies that the K_2O content of the contaminant is at least $B = nc = 6\%$, where n is the minimum total number of grains in a subsample, about 6000 from equation (12). Since about six grains of contaminant are present in the average subsample, the purity of the separated mineral is at least 99·9%. Evidently this high degree of purity was inadequate for the purpose.

The pyroxene came from the Dufek massif in Antarctica, and was one of a series of minerals dated by the K–Ar technique in research on pyroxene from various geological environments. The sample was analysed repetitively for potassium because its purity was critical to interpretation of the data. The first analyses showed sampling non-uniformity and hence impurity. The values of Table 5 showed, by the processes outlined above, that the impurity was a high-potassium mineral making up not more than one grain in 1000 of the sample. Such impurity is not likely to be detected in any other way. Further purification yielded a sample which gave the footnote values in Table 5. The collected impurities were examined under the microscope, and potassium feldspar grains were found, despite a failure to find any potassium feldspar during routine examination of the whole rock in powder and thin-section form.[50]

The need for such intensive investigation of a single sample, and for the purity tests outlined, arose because this pyroxene showed an apparent age about 40% lower than that of coexisting plagioclase. A sample of known purity was necessary for interpretation of results. An isochron plot[51] using the corrected results showed that the pyroxene and plagioclase ages were indeed concordant, and that the young apparent age of the pyroxene could be attributed to the use of a false air–argon correction and to subsampling uncertainties caused by the 0·1% of impurity in the original sample.

Selection of a subsample weight for the analysis of the Dufek pyroxene was somewhat fortuitous. The experiment nevertheless directs attention to the possibility of deliberately selecting subsample weights to yield maximum information from repetitive determinations. For best results of this kind, the relative standard deviation of a series of determinations should lie between about 10 and 40%. A similar idea has been expressed by Koch and Link,[52] who recognize that the coefficient of variation is an excellent guide to the number of observations required for sampling an ore body or other geological specimen of unknown variability. At lower relative standard deviations, analytical error is likely to obscure the pattern of the results; at higher standard deviations, Gaussian statistics lose their validity, and a very large number of determinations may be necessary before a true picture can emerge (Fig. 2). To achieve an optimum subsampling error for revealing sample non-uniformity, a subsample weight $K^2K_s z/(K - H)^2 \times 10^{-4}$ g, with $z = 2$ or 3, should be taken. In the example of Fig. 2, subsamples of about 0·2 g will yield the most information. Since, in this example, there are about 8 "special" grains in a 1-g subsample, from equation (8) the probability of a 0·2-g subsample having $z_i = 0$ is $P_0 = e^{-1 \cdot 6} = 0 \cdot 2$, and one in five determinations on 0·2-g subsamples will give as the result the background of 6 ppm. If eight 0·2-g subsamples are taken, equation (6) shows there is a 70% chance that at least one of them will have $z_i = 0$. If the background concentration, H, can be found in this way, it can be used in conjunction with the standard deviation of a series of determinations to estimate z_i:

$$\hat{z}_i = \frac{(x_i - H)(\bar{x} - H)}{s^2} \tag{15}$$

This principle, applied to the pyroxene results in Table 5. shows that the subsamples with 0·0157% K_2O probably contain 4 grains of contaminant, and that those with 0·0203% K_2O probably contain 8.

When z is 6·1 grains, the probability of selecting a subsample with $z_i = 0$ is about 0·002; for $z_i = 4$, about 0·13; for $z_i = 8$, about 0·11. Therefore, selection of a pyroxene subsample with $z_i = 0$ was rather unlikely with only 12 subsamples: ordinarily, such luck cannot be expected. The sample should be repurified (as was done in this case) or smaller subsample weights should be taken to permit a good estimation of the background concentration H.

The use of appropriately small subsample weights to discover the background composition is illustrated in Table 6. The sample is an amphibolite–orthoclase mixture used by Engels and Ingamells[6] to demonstrate the effects of sample non-uniformity in K–Ar dating. None of 40 determinations on 100-mg subsamples showed the base composition of 0·145% K_2O. This is as expected, because the average number of grains of orthoclase in a 100-mg subsample is about 10. With 10-mg subsamples the average number of grains of orthoclase per subsample is close to 1, and two out of twelve such subsamples approximate the base composition. In natural samples, where mineral grains are seldom all exactly the same size, the statistical procedure can obviously not yield an integral value for each z_i. The parenthetical values in Table 6 are those calculated from equations (4) and (5).

USE OF SAMPLING CONSTANTS

For calibration of analytical methods based on comparisons with standards, results may be plotted graphically or computed. Usually a linear relationship between instrumental read-out and elemental composition is assumed, or the read-out may be modified to yield linearity; logarithmic or semi-logarithmic plots may be appropriate, and matrix corrections may have to be applied, as in X-ray fluorescence analysis.[38,39,53] It is sometimes difficult to be sure that a linear relationship exists.[54,55] Standards with poor subsampling characteristics or erroneous certificate values may further obscure the issue.

Unfortunately for those who would use available standard samples to calibrate or evaluate analytical methods for silicate minerals and rocks, there is still some doubt concerning the exact composition of some of them.[41,56–59] As an extreme example, published values for Al_2O_3 in the USGS dunite DTS-1 vary from 0·16 to 1·48%, and for Fe_2O_3 from 0·33 to 4·55%. The averages of all results for these constituents of this sample are almost sure to be in error.[40,57,60] It is probable that much of the error in reported results for Al_2O_3 and Fe_2O_3 is analytical error, and that subsampling error, in these cases, is not of much consequence by comparison, in contrast to the case of Cr in G-1, where subsampling error probably contributes a large share of the variance. These two contrasting sources of error in the certificate values for standard rock samples have been discussed by Vistelius[58,59] and Chayes,[61,62] and it is very important for the user of reference samples to distinguish between them. This can conveniently be done through progressively improving estimates of sample constants. Figure 3 represents a hypothetical standardization or calibration process, with deviations from linearity exaggerated for illustrative purposes. Without consideration of sampling constants, and if there is high confidence in the analytical procedure and in the certificate values for, say, samples 1 and 5, an analyst might be persuaded to draw a calibration curve A. If all results are regarded as equally valid, a linear regression line (not shown) might be drawn.

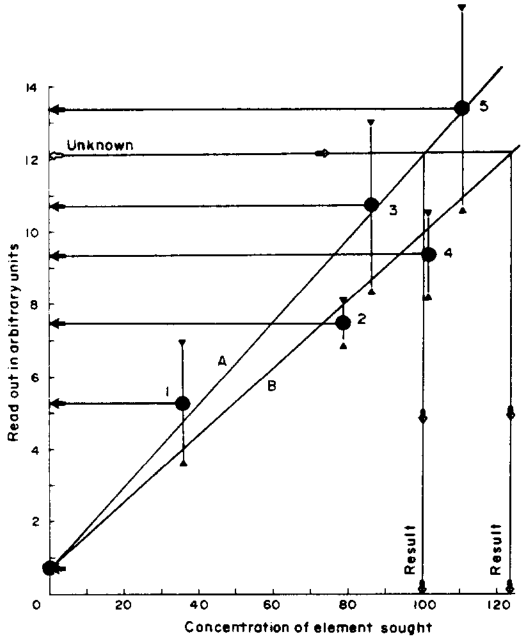


Fig. 3. Calibration of an analytical method, taking into account the subsampling characteristics of the calibration standards.

If subsampling difficulties are recognized and sampling constants are available, they can be used, in conjunction with subsample weights, to calculate the length of error bars from equation (1). It may develop that the best calibration curve (*B*) differs from the alternatives. Note that the preferred line passes through each of the error bars; in practice, this would require that these bars should cover at least plus or minus three standard deviations. Note also that samples with poor subsampling characteristics may give a reasonably good calibration curve if enough of them are used, provided their subsampling characteristics are specifically defined through the use of error bars. Error bars may, of course, be constructed to include both subsampling and analytical error.

When necessary, error bars may be shortened by using more than one subsample of each standard, or (which amounts to the same thing if analytical error is small) increasing the subsample weight.

Careful extension of these principles may reveal the extent of analytical error, and also enable one to ascertain whether it originates in the certificate value or in the analytical method. For example, if the analyst using curve *A* (Fig. 3) were to utilize these principles, he could quickly decide that the "anomalous" results for samples 2 and 4 were not due to analytical error, nor necessarily to an erroneous certificate value, but were due to the bad subsampling characteristics of samples 1, 3 and 5.

These principles may be used to locate errors, but usually an independent analytical method must be used to define them. Some of the difficulties encountered in the resolution of systematic and random analytical errors have been outlined by Ingamells *et al.*[63] Wilson[64,65] has written on the performance characteristics of analytical methods.

The subsampling characteristics of unknowns must, of course, be established before firm confidence limits for the results of an analytical process can be decided. There is not much point in establishing an accurate calibration if the unknowns are not sampled and subsampled properly. The subsampling characteristics of unknowns will often be evaluated by the method of repetitive determination, *e.g.*, the pyroxene in Table 5. Multiple determinations with small subsamples are usually most effective; however, selection of subsample weights for the purpose may be difficult. Table 3 shows how a short series of repetitive determinations may be affected by choice of subsample weight. Figure 1 shows that a similar situation may exist for many trace constituents. Table 1 shows that the difficulty may not be limited to traces, but may also exist in the determination of minor and even major constituents, and even with "pure" separated minerals, the analysis of which is commonly presumed to be free from subsampling error. The principles of selecting subsample weights for the contrasting purposes of measuring subsampling characteristics and discovering the overall composition of a mass of material are outlined by Visman[13] and in the probability considerations discussed above.

It is important to note that the error bars which correctly describe subsampling characteristics and uncertainties in the use of reference samples may not be symmetrical. With small subsample weights and in analyses for trace elements, appropriate error bars will often be unsymmetrical.

In mineral analysis, estimation of sample purity may be critical for the drawing of valid conclusions. In K–Ar dating, the sample purity may be the major factor in the elucidation of discordant ages,[49] and a quick method for its estimation is highly desirable. In many mineral samples, analytical non-uniformity is due to free substitution of one element for another (*e.g.*, the white mica in Table 1, and the standard biotite LP-6 Bio[44,45]); in others, it is due to the presence of included or contaminating grains of foreign minerals (*e.g.*, the beryl in Table 1, and the standard muscovite P-207). A knowledge of the extent and nature of the non-uniformity is necessary if erroneous conclusions from analytical data are to be avoided. Purity estimates can often be made through proper interpretation of the variance of repetitive determinations of critical elements. Other methods of estimating sample purity have been suggested and demonstrated by Engels.[47]

In publishing their results on potential reference samples, analysts have seldom reported complete information on preliminary treatment of the laboratory sample or on their effective subsample weights. Consequently it is difficult, if not impossible, to distinguish analytical from subsampling error. Generally, the averaging of results from several laboratories using different analytical methods and different subsample weights is not sound procedure;[60] however, if each investigator making replicate determinations would report all results (including any which may seem anomalous!), along with a full description of sample pretreatment and a careful estimate of the effective subsample weight, it might be possible to devise an acceptable objective process for comparing and combining interlaboratory results. The most important part of such a process would be the *exclusion* of erroneous values, and the *inclusion* of "anomalous" values which reflect real subsampling aberrations. The use of sampling constants might facilitate this process by providing a simple means for defining subsampling error and separating it from analytical error. For example, a chemist who uses 1-g subsamples and obtains a value of 10 ppm for chromium in G-1 is probably in error: a spectrographer reporting the same value on the basis of 10-mg subsamples is not in error.

DISCUSSION

If the sampling-constant principle is accepted, there will not be much difficulty in establishing a routine separation of analytical error from subsampling error.

Youden,[55,60,66,67] Sandell,[68] Wilson[64,65] and many others have provided useful advice on the estimation of analytical accuracy. Mandel[69] has written on "repeatability and reproducibility". Lashof[70] and Youden[71] have summarized the problems of collaborative testing, and an ASTM committee continues to work in this field. Maurice and Buijs[72] have discussed the detection of interferences in chemical analysis. Taylor and Kolbe,[73] Abbey,[57] Vistelius,[58] and Chayes[61,62] have discussed geochemical standards and attempted an evaluation of published data and its astonishingly large error content. Griffiths,[74,75] Cameron,[76] Howarth and Lowenstein,[77] and many others have assessed the precision and accuracy of geochemical data. Becker,[48] in a series of papers, has dealt with the problems of sample reduction in the mineral industries. Duncan[78] has written on bulk sampling—problems and lines of attack. The pioneer work of Gy[11,12] deals in depth with the practical aspects of the same subject. Numerous papers and texts attack the problems of bulk sampling.[5,8,74,79] The references given are only a small sample of a voluminous literature, yet scant attention has been given to laboratory subsampling problems and the very large effect they may have in geochemical investigations: in particular, sufficient attention has not been given to the principles outlined above, or to the fact that when subsampling is poor, analytical results for critical elements may not only be imprecise, but may be erroneous; nor has it been generally recognized that high precision does not indicate high accuracy—it may be a symptom of gross error. The generally accepted assumptions of Gaussian distribution, as expressed, for example, by Danielsson *et al.*,[80] are commonly used to guide the processes of analysis and the evaluation of data, with only occasional consideration of their validity. An extreme example of the need to consider non-Gaussian distributions is given by Phillips,[46] and a more general discussion of the same subject is due to Jones and Beaven.[10]

Anomalous results are sometimes the subject of interesting papers. For example, Reynolds[81] discusses isotope-abundance anomalies in the solar system. In geochronology, numerous puzzling anomalies remain unpublished. One wonders how many of these will eventually be explained in terms of subsampling statistics.

The implications of these considerations are wide. Their importance to geochemical prospecting and the search for economically useful mineralization should be obvious.

The suggestion has often been made, for example by Flanagan,[41] that geochemists should standardize their analytical procedures during the collaborative study of silicate samples intended for establishment as standards. This would certainly make the task of evaluating the results much easier, and interlaboratory precision would doubtless be improved. There is a danger, however, that systematic errors would remain undiscovered, and that subsampling problems and the sampling characteristics of the intended standards would remain forever obscure. For example, a reference material which gives consistent results for an element at the 1-g subsampling level when a standardized "umpire" method is used, might be worthless as a spectrographic standard in a procedure which uses a few mg of sample.

In any case, the skills, techniques, and equipment available in different laboratories are so varied that standardization of methods is probably impossible. It would be much more useful to insist that all analyses of potential standards be made by primary methods when bulk composition is sought, that the more precise of the instrumental methods (*e.g.*, the flame photometric method for potassium demonstrated in this paper) be used during establishment of subsampling characteristics. and that subsample weights and subsampling procedures always be dutifully reported, together with *all* results. By primary methods are meant those which do not depend on previously analysed standards—usually classical methods. Secondary methods are those which depend on analysed standards for calibration or control; most instrumental methods fall in this category; some are very rapid and precise, but they can never exceed in accuracy the primary classical methods on which they depend for calibration. They should therefore never be used in the establishment of certificate values for reference samples: such usage results in the transfer of analytical error from one standard to another and the accumulation of analytical inaccuracy. Perhaps the concept of the sampling constant may help bring wider attention to this fundamental, often ignored, fact of geochemical analysis, and lead to the distribution of geochemical standards which are truly reliable.

CONCLUSIONS

Possibly the most important conclusion to be drawn from this work is that, when subsampling error is appreciable, a subsample weight and a full description of subsampling procedures should be reported as part of an analysis, in order for the latter to be meaningful. This is especially true in trace element work and in geochemical exploration for rare and economically valuable minerals, when subsampling aberrations are likely to be large.

Standard samples, used to calibrate or evaluate routine methods of analysis, require not only a certification of their overall composition to be useful, but also, for relevant constituents, an estimate of the subsampling precision expected for any subsample weight. Such information may most easily be conveyed through the use of sampling constants.

For major constituents of silicate rocks and minerals, it is improbable (but by no means impossible) that subsampling error often contributes appreciably to overall error, except when subsamples are very small. For minor constituents, it may be serious, especially when high accuracy is mandatory (as in geochronology). For traces, it appears that subsampling error may contribute more to observed variance than analytical error, or (perhaps more important!) that an observed low variance in the results may be a symptom of gross error.

Control of subsampling errors may be facilitated through the use of sampling constants, routinely used by analytical geochemists.

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Zusammenfassung—Der Fehler bei der Bestimmung eines Elements in einer Gesteins- oder Mineralprobe hängt ab vom Analysenfehler, vom Gewicht der analysierten Probe und von Natur und Vorgeschichte der Laboratoriumsprobe. Das wahrscheinlichste Ergebnis ist nicht unabhängig vom Gewicht der analysierten Probe. Das beruht auf der Tatsache, daß Spurenbestandteile oft in isolierten Mineralkörnern konzentriert sind. Die Wahrscheinlichkeit, daß solche Mineralkörner in irgend einer analysierten Probe auftreten, wird mit sinkendem Probengewicht geringer, selbst wenn Gesteins- oder Mineralproben zu feinen Pulvern zerkleinert werden. Solche Probenahmefehler können durch Verwendung von Probenahmekonstanten kontrolliert werden. Diese können auf verschiedene Weise festgestellt werden, etwa durch wiederholte Bestimmung eines Bestandteils und physikalische Messung wesentlicher Eigenschaften der Probe. Während der Erstellung und Bescheinigung von Bezugsproben oder Standards kann man mit Vorteil Probenahmekonstanten benutzen. Bei mangelhafter Probenahme kann man zu niedrige analytische Ergebnisse erhalten, manchmal mit hoher Genauigkeit. Hohe Genauigkeit bedeutet niemals hohe Richtigkeit; sie kann ein Symptom für einen groben Fehler sein.

Résumé—L'erreur dans le dosage d'un élément dans un échantillon de roche ou de minerai dépend de l'erreur analytique, du poids de la prise d'essai analysée, et de la nature et de l'histoire de l'échantillon de laboratoire. Le résultat le plus probable n'est pas indépendant du poids de la prise d'essai analysée. Ceci est dû au fait que des constituants à l'état de traces se situent souvent dans des grains de minerai isolés. La chance qu'ont de tels grains de mineral d'apparaître dans un échantillon analysé devient plus éloignée quand le poids de la prise d'essai décroît, même si les échantillons de roche ou de minerai sont réduits en poudre fine. De telles erreurs de fractionnement peuvent être contrôlées par l'emploi de constantes d'échantillonnage. Celles-ci peuvent être estimées par plusieurs techniques, comprenant le dosage répété d'un constituant et la mesure physique de caractéristiques d'échantillon correspondantes. Les constantes d'échantillonnage peuvent être utilement employées durant l'établissement et la certification d'échantillons ou de standards de référence. Quand le fractionnement est défectueux, les résultats analytiques peuvent donner des valeurs faibles par erreur, quelquefois avec une précision élevée. La précision élevée n'implique jamais une haute exactitude; elle peut être un indice d'erreur flagrante.

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USE OF NON-SELECTIVE REAGENTS IN DIRECT THERMOMETRY

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Summary—A method has been developed for the simultaneous determination of sulphide and thiosulphate with non-selective reagents on the basis of the difference in their heats of reaction. Iodine solution was used as one reagent and bromine water as the other. An error diagram has been calculated and the theoretical errors compared with those obtained in practice.

Individual components in multi-component systems are determined by using the direct thermometric method and selective reagents, measuring separately the change in temperature caused by the heat of reaction between the reagent and the component to be determined.[1] Besides precise experimental conditions, masking of interfering components and use of correction factors become necessary.

We describe here a thermometric method in which we do not utilize selectivity of reaction; on the contrary, we use reagents which react with all the components and for differentation we use the different heats of reaction.

A similar idea was used by Hansen and Lewis,[2] in their simultaneous determination of two weak acids having similar pK values but different ΔH values. Similarly Sajó[3] has worked out a method for the determination of the composition of brass. He determined the copper and zinc in a single sample with potassium cyanide reagent.

The new type of determination is based on use of as many reagents which will react with all the components of the sample solution, as there are components present. If the heat of reaction of each component with each reagent is known (ΔH) and the total heats of reaction (Q) are measured in direct-injection determinations, we can calculate the concentrations of n components, x, y, z, ..., from n equations of the type

$$x\Delta H_{x(n)} + y\Delta H_{y(n)} + \cdots = Q_{(n)} \tag{1}$$

The linear system of equations thus obtained can be solved if the determinant of the system of equations is not zero.

In the case of two components, for example, the solution is

$$x = \frac{D_1}{D}; \qquad y = \frac{D_2}{D} \tag{2}$$

where the determinants D_i are given by

$$D = \begin{vmatrix} \Delta H_{x(1)} & \Delta H_{y(1)} \\ \Delta H_{x(2)} & \Delta H_{y(2)} \end{vmatrix}; \qquad D_1 = \begin{vmatrix} Q_{(1)} & \Delta H_{y(1)} \\ Q_{(2)} & \Delta H_{y(2)} \end{vmatrix}$$
$$D_2 = \begin{vmatrix} \Delta H_{x(1)} & Q_{(1)} \\ \Delta H_{x(2)} & Q_{(2)} \end{vmatrix} \tag{3}$$

We will demonstrate the direct thermometric use of non-selective reagents by the simultaneous determination of thiosulphate and sulphide ions. With iodine in neutral medium we have

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \qquad \Delta H_{S_2O_3^{2-}(1)}$$
$$S^{2-} + I_2 \longrightarrow S + 2I^- \qquad \Delta H_{S^{2-}(1)}$$

and with bromine:

$$S_2O_3^{2-} + 4Br_2 + 5H_2O \longrightarrow 2SO_4^{2-} + 8Br^- + 10H^+ \qquad \Delta H_{S_2O_3^{2-}(2)}$$
$$S^{2-} + 4Br_2 + 4H_2O \longrightarrow SO_4^{2-} + 8Br^- + 8H^+ \qquad \Delta H_{S^{2-}(2)}$$

In the bromine reaction, the solution will become strongly acidic; the pH of a 10^{-2} to $10^{-3}M$ titrand solution will decrease from an initial value of about 8–2 at the end of the reaction. In addition to the heat of oxidation, we measure the heat of solvation of the Br^- and H^+ formed.

The reactions are instantaneous, so apart from taking the usual precautions for direct thermometric determinations, the effect of the surroundings need not be taken into account.

The main problem is to decide which are the principal sources of error. Consider a two-component system. The variance of x and y, if these are calculated from equation (2), is given by

$$\left(\frac{S_x}{x}\right)^2 = \left(\frac{S_{D_1}}{D_1}\right)^2 + \left(\frac{S_D}{D}\right)^2 = \frac{1}{D^2}\left(\frac{S_{D_1}{}^2}{x^2} + S_D{}^2\right) \tag{4}$$

and

$$\left(\frac{S_y}{y}\right)^2 = \left(\frac{S_{D_2}}{D_2}\right)^2 + \left(\frac{S_D}{D}\right)^2 = \frac{1}{D^2}\left(\frac{S_{D_2}{}^2}{y^2} + S_D{}^2\right) \tag{5}$$

where S_y, S_x are the standard deviations of the calculated results and S_{D_1}, S_{D_2}, S_D are the standard deviations of the determinants.

According to experimental results, the standard deviation of the quantity of heat (Q) evolved in the direct thermometric method is independent of Q and is a constant (S_Q) characteristic of the apparatus at a given sensitivity. As a first approach, we can suppose that the heats of reaction $\Delta H_{x(i)}$ and $\Delta H_{y(i)}$ can be more accurately measured than $Q_{(i)}$.

It follows that the standard deviations of the determinants are in the order

$$S_D < S_{D_1}, S_{D_2} \tag{6}$$

Neglecting $S_D{}^2$ in equations (4) and (5) on the basis of equation (6), we obtain

$$\left(\frac{S_x}{x}\right)^2 = \frac{S_{D_1}{}^2}{D^2x^2}; \qquad \left(\frac{S_y}{y}\right)^2 = \frac{S_{D_2}{}^2}{D^2y^2} \tag{7}$$

From equation (3) we have

$$S_{D_1}{}^2 = [\Delta H_{y(2)}]^2 S_Q{}^2 + [\Delta H_{y(1)}]^2 S_Q{}^2 = S_Q{}^2 \Sigma \Delta H_y{}^2$$

and

$$S_{D_2}{}^2 = [\Delta H_{x(1)}]^2 S_Q{}^2 + [\Delta H_{x(2)}]^2 S_Q{}^2 = S_Q{}^2 \Sigma \Delta H_x{}^2 \tag{8}$$

Finally the relative standard deviation of the determination may be obtained from equations (7) and (8):

$$\frac{S_x}{x} = \frac{S_Q}{x} \frac{\sqrt{\Sigma \Delta H_y{}^2}}{D} \tag{9}$$

$$\frac{S_y}{y} = \frac{S_Q}{y} \frac{\sqrt{\Sigma \Delta H_x{}^2}}{D} \tag{10}$$

It can be seen from the expressions above, that the uncertainty in the determination of the individual components increases with increasing heat of reaction of the other component and decreases with the increasing values of the determinant D. It is interesting to see that the deviations are independent of the quantity of the other component, that is of the x/y ratio. This can be concluded from the starting postulate that the value of S_Q is independent of the absolute value of Q.

On the basis of equations (9) and (10) the error function, which depends only on the value of S_Q, can be represented diagramatically.

EXPERIMENTAL

Apparatus

Directhermom (MOM, Hungary).

Reagents

Sodium thiosulphate and sodium sulphide solutions, both 0·01M and standardized in the usual way.[4]

Iodine-potassium iodide solution, about 1M, with heat of dilution partly compensated by addition of methanol.

Saturated bromine water.

Calibration curves

Sodium thiosulphate stock solution (10, 20, 30, 40, 50 ml) was made up to 200 ml with distilled water, transferred to the Directhermom plastic cell and placed in the instrument. The iodine reagent was placed in the dipping pipette of about 2 ml capacity. After waiting for the usual 3 min, the deflection of the galvanometer (in scale divisions) was noted. After correction for the heat of dilution, this value was plotted against the number of mmoles of thiosulphate taken. The experiment was repeated three times. A similar procedure was used for the sodium sulphide solution.

For the bromine reactions, 10, 15, 20, 25, and 30 ml of sodium thiosulphate or sulphide stock solution were diluted to 200 ml and the saturated bromine water added from a pipette of about 10 ml capacity.

Least-squares analysis gave the following slopes for the plots (ΔH values).

$Na_2S_2O_3 + I_2$ $\Delta H_{x(1)} = 31{\cdot}4$ graduations/mmole
$Na_2S_2O_3 + Br_2$ $\Delta H_{x(2)} = 2790$ graduations/mmole
$Na_2S + I_2$ $\Delta H_{y(1)} = 586$ graduations/mmole
$Na_2S + Br_2$ $\Delta H_{y(2)} = 2530$ graduations/mmole

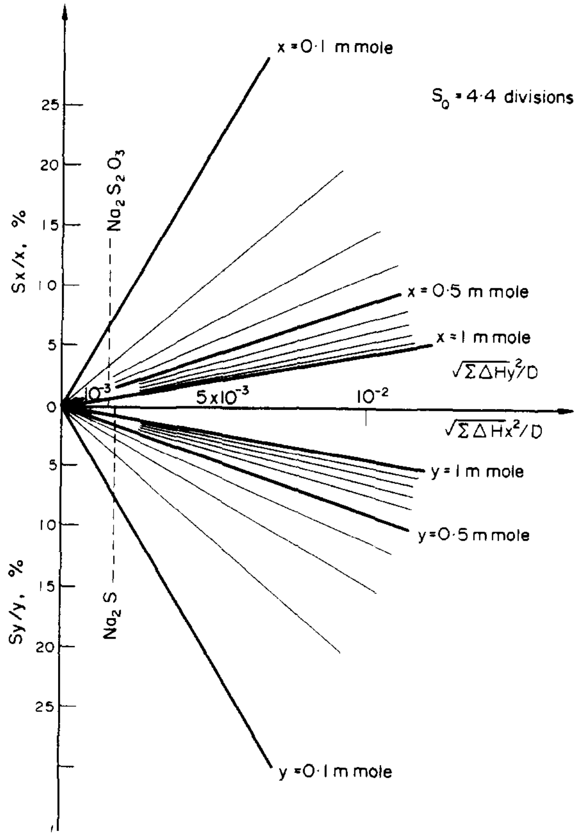

Fig. 1. Relative error diagram.

The standard deviation of the total heat of reaction (60 replicates) is $S_Q = 4\cdot4$ graduations. The determinant D is $D = -1557 \times 10^6$ graduations^2/mmole^2. By substitution of the experimental values in equation (2) we obtain formulae for calculation of x and y:

$$x(\mathrm{Na_2S_2O_3}),\ \text{mmole} = \frac{586Q_{(2)} - 2530Q_{(1)}}{1557 \times 10^6} \qquad (11)$$

$$y(\mathrm{Na_2S}),\ \text{mmole} = \frac{31\cdot4Q_{(2)} - 2790Q_{(1)}}{1557 \times 10^6} \qquad (12)$$

Estimation of error

The general error diagram corresponding to the equations (9) and (10) is given in Fig. 1. For the given determination:

$$\Sigma\Delta H_x{}^2 = 7\cdot785 \times 10^6 \text{ graduations}^2/\text{mmole}^2$$

$$\Sigma\Delta H_y{}^2 = 6\cdot744 \times 10^6 \text{ graduations}^2/\text{mmole}^2$$

From this

$$\frac{\sqrt{\Sigma\Delta H_y{}^2}}{D} = 1\cdot67 \times 10^{-3} \text{ and } \frac{\sqrt{\Sigma\Delta H_x{}^2}}{D} = 1\cdot79 \times 10^{-3}$$

Table 1

Taken, *mmole*		$Q_{(1)}$	$Q_{(2)}$	$x(Na_2S_2O_3)$	Error, %		$y(Na_2S)$	Error, %	
$Na_2S_2O_3$	Na_2S	(with iodine)	(with bromine)	*mmole*	estimated	found	*mmole*	estimated	found
0·09	0·01	19	311·1	0·086	8	−4	0·012	79	+16
0·08	0·02	26	301·8	0·071	9	−11	0·041	39	+102
0·05	0·05	32·7	290·8	0·056	15	+13	0·053	10	+5
0·02	0·08	53	277·5	0·018	37	−8	0·089	10	+12
0·01	0·09	61	271·8	0·003	74	−68	0·104	9	+15
0·27	0·03	35·3	893·5	0·279	3	+3	0·045	26	+46
0·24	0·06	38·3	820·8	0·247	3	+3	0·052	13	−13
0·15	0·15	107·3	830·8	0·138	5	−8	0·176	6	+17
0·06	0·24	137·3	740·5	0·056	12	−7	0·231	3	−4
0·03	0·27	138·7	690·8	0·035	25	+16	0·235	3	−13

The x and y values were calculated by equations (11) and (12) and the errors by equations (13) and (14). The Q values are in scale graduations.

We can estimate the uncertainty of the simultaneous determination of $S_2O_3^{2-}$ and S^{2-} from the error diagram. The relative deviations, which can be read along the broken lines drawn on the diagram, can also be expressed by the equations:

$$\frac{S_{S_2O_3^{2-}}}{\text{mmole}[S_2O_3^{2-}]} = 100\,\frac{4\cdot4}{\text{mmole}[S_2O_3^{2-}]} \times 1\cdot67 \times 10^{-3} = \frac{0\cdot74}{\text{mmole}[S_2O_3^{2-}]}\,\% \qquad (13)$$

$$\frac{S_{S^{2-}}}{\text{mmole}[S^{2-}]} = 100 \times \frac{4\cdot4}{\text{mmole}[S^{2-}]} \times 1\cdot79 \times 10^{-3} = \frac{0\cdot79}{\text{mmole}[S^{2-}]}\,\% \qquad (14)$$

Simultaneous determination of sodium thiosulphate and sulphide

We prepared various mixtures of the two stock solutions with totals of 0·1 and 0·3 mmole in the 200 ml of test solution and made three measurements on each mixture reacted with the total iodine and bromine. Table 1 shows the results.

On the basis of equations (13) and (14), the expected relative standard deviation for 1 mmole of sodium thiosulphate or sulphide is 0·7–0·8%, for 0·1 mmole 7–8% and for 0·01 mmole 70–80%.

It is clear from the table that the error is larger than expected for four of the results for the 0·1-mmole samples and for five of those for the 0·3-mmole ones, sometimes very considerably larger. If we consider the fact that the lower limit for the classical volumetric determination of sulphide and thiosulphate concentrations is about $10^{-2}M$, and that the concentration of the solutions determined here is between 5×10^{-4} and $1{\cdot}5 \times 10^{-3}$ M then the results are encouraging.

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Zusammenfassung—Ein Verfahren zur gleichzeitigen Bestimmung von Sulfid und Thiosulfat mit nichtselektiven Reagentien wurde entwickelt, das auf deren unterschiedlichen Reaktions-wärmen beruht. Als ein Reagens wurde Jodlösung verwendet, Bromwasser als das andere. Es wurde ein Fehlerdiagramm berechnet und die theoretischen Fehler mit den in der Praxis gefundenen verglichen.

Résumé—On a élaboré une méthode pour le dosage simultané de sulfure et de thiosulfate avec des réactifs non sélectifs sur la base de la différence entre leurs chaleurs de réaction. On a utilisé une solution d'iode comme l'un des réactifs et l'eau de brome comme l'autre. On a calculé un diagramme d'erreur et comparé les erreurs théoriques avec celles obtenues en pratique.

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RELATIVE SENSITIVITY COEFFICIENTS FOR RARE EARTHS IN SPARK-SOURCE MASS SPECTROMETRY

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Summary—Relative sensitivity coefficients have been computed for rare earth elements according to empirical models which have been proposed in the literature. Explanations concerning differences between the computed and observed values are based upon possible instrumental discrimination effects which negate some processes occurring in the ion source. Computations relating elemental physical constants to observed results in a semi-random manner are shown which support this contention.

Experimentally determined relative sensitivity coefficients of trace rare earth impurities in rare earth matrices by spark-source mass spectrography have been reported.[1] Several empirical models have been proposed in the literature for relating sensitivity coefficients to fundamental chemical and/or physical properties of the elements.[2-7] The purpose of this report is to compare sensitivities computed from the models with experimental rare earth data; to propose instrumental effects which may cause the models to fail; and to show by comparison of experimental data with physical constants in a semi-random manner how the observed rare earth sensitivity coefficients support the proposed instrumental effects.

This study was motivated and performed with the notion that the rare earths might provide a significant test for the reported models since the experimental sensitivity coefficients, listed in Table 1, were generally found to be independent of matrix effects and of the method of sample preparation and also since rare earths possess uniquely interrelated physical and chemical properties which are well known.

COMPUTED RELATIVE SENSITIVITY COEFFICIENTS

The commonly accepted form[8] for expressing a relative sensitivity coefficient (S_R) is

$$S_R = \frac{\text{mass spectrometrically observed (relative) value}}{\text{true (relative) value}}$$

where the observed value is based upon an ion current which has been corrected for *known* instrumental effects. This corrected value is then placed on a relative basis by comparison with another element which has a known concentration and has been assigned an arbitrary S_R value (*e.g.*, commonly the S_R for iron $\equiv 1{\cdot}00$ although any other element may be selected).

Table 1. Average relative sensitivity coefficients for each matrix and element

Matrix	Y_2O_3			Tm_2O_3			Er_2O_3		Sc_2O_3		Ho_2O_3		Overall average†	Average deviation, %
Element	I*	II*	III*	I	II	III	I	II	II	III	II	III		
Y	—	—	—	—	·83	—	1·20	1·38	1·06	—	—	—	1·12	15
La	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	—	—
Ce	—	0·68	—	—	0·71	—	—	0·66	0·81	—	0·69	—	0·71	5·6
Pr	1·36	1·31	—	(1·00)§	1·42	—	1·29	1·41	1·42	—	1·32	—	1·32 (1·36)	6·6 (3·5)
Nd	1·40	1·43	1·43	(0·84)	1·37	1·26	1·36	1·08	1·25	1·10	1·34	1·31	1·26 (1·30)	10 (7·3)
Sm	1·78	1·99	—	1·73	1·94	—	1·48	1·65	1·63	—	2·18	—	1·80	10
Eu	2·16	2·05	2·20	—	2·88	2·24	1·74	2·30	1·81	1·92	2·38	2·66	2·21	12
Gd	1·05	1·18	—	0·82	1·31	—	1·14	0·97	1·49	—	1·43	—	1·17	15
Tb	—	1·09	—	—	1·17	—	—	0·92	0·98	—	1·17	—	1·07	8·7
Dy	1·36	1·70	1·30	1·30	1·12	0·83	0·93	1·00	1·19	1·06	(1·81)	—	1·24 (1·18)	19 (16)
Ho	1·11	1·34	—	(0·82)	(0·97)	—	(0·46)	(0·66)	1·33	—	—	—	0·96 (1·26)	28 (7·9)
Er	1·20	1·43	—	(0·91)	(0·84)	—	—	—	1·09	—	—	—	1·09 (1·24)	16 (10)
Tm	1·36	1·48	—	—	—	—	(0·43)	(0·93)	1·47	—	(2·13)	—	1·30 (1·44)	32 (3·6)
Yb	2·13	2·58	—	(3·00)	(2·95)	—	(1·12)	—	1·78	—	—	—	2·26 (2·16)	26 (13)
Lu	—	1·05	—	—	0·87	—	—	0·65	0·75	—	1·15	—	0·89	18

* Type of method used for standard preparation: I—dry blending, II—oxalate co-precipitation, III—nitrate calcining.

† Values in parenthesis obtained by recalculation after deleting values enclosed in parenthesis in the body of the table.

§ Values deleted because they fall outside Student's test at 95% confidence level.

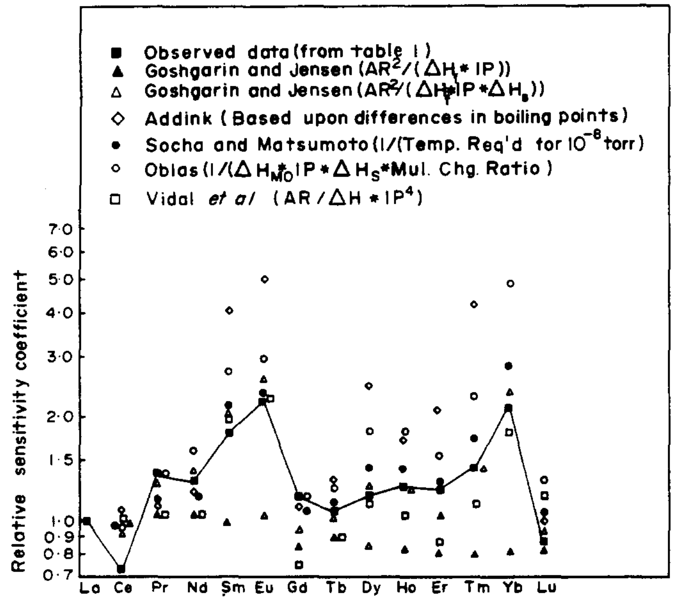

Fig. 1. Plot of computed S_R values according to formulae proposed in the literature. Symbols: AR = atomic radius. ΔH_f = heat of formation of sesquioxide, Re_2O_3. IP = first ionization potential. ΔH_s = heat of sublimation. ΔH_{MO} = heat of formation of the gaseous monoxide.

Accurate values for the physical constants for the rare earths are available and the relationships between these constants have been discussed.[9–13] Except for small mass-dependences, very little change occurs across the entire rare earth series in the heat of formation of the sesquioxide (Re_2O_3—form C), the first ionization potential, and the atomic volume of the tervalent ion. In contrast however, the vapour pressure at a given temperature may differ by approximately eight orders of magnitude.

Relative sensitivity coefficients for rare earths were computed according to empirical models already proposed in the literature.[2–6] The description of these models may be obtained from the references as well as a recent summary and discussion of these and other theoretical proposals for relating observed elemental sensitivities to fundamental properties of the elements.[8] The results of the computations are shown in Fig. 1 with all data normalized to La ≡ 1·00, along with the overall average values from Table 1.

Roaldst[7] worked with rare earths in geological samples and proposed a model for determining S_R values. He found the observed S_R values to be monotonic functions of mass and ionization potential. However his data were not corrected for the photoplate emulsion mass-effect and his conclusions regarding mass and ionization potential dependence are obscured by many mass effects. For this reason no calculation with the rare earths was attempted and no comparison is made here on Fig. 1.

CORRELATION OF COMPUTED AND OBSERVED VALUES

There are several results for which all the models are in disagreement with observed data. None of the models predict the following.

1. The low observed sensitivity for Ce.
2. Pr with a higher sensitivity than Nd.

3. Gd with a higher sensitivity than Tb.
4. Ho with a higher sensitivity than Dy.

The two models giving the best correspondence to the experimental data are those of Goshgarin and Jensen[2] (~AR^2/HF*IP*HS; open triangles of Fig. 1) and of Socha and Masumoto[4] (~1/temp. required for vapour pressure of 10^{-8} mmHg; solid circles of Fig. 1). The Goshgarin and Jensen model, which is based upon the energetics in a Born–Haber cycle, requires the inclusion of a metal vaporization step (*i.e.*, ΔH_s, used for open triangles but not solid triangles of Fig. 1) in order to obtain reasonable agreement with the observed data. The model proposed by Socha and Masumoto is an empirical relationship based upon the different temperatures required to produce the same vapour pressure. Actually, unless diffusion is a predominant process in spark-source electrodes, homogeneously distributed elements should be exposed to the same temperature even though the time scale and the gradient of this temperature might vary greatly. Since vapour pressure is a thermodynamic function proportional to the heat of sublimation, the Goshgarin and Jensen model should be considered to be the more fundamental one. One aspect of this model, the defined inverse relationship of S_R to the first ionization potential, is not widely agreed upon in the literature[8] and this relationship can be examined more closely by using rare earth data.

INSTRUMENTAL DISCRIMINATION EFFECTS

Ionization potential

A plot of S_R *vs.* the first ionization potential for the rare earths is shown in Fig. 2. Considerable scatter is evident although a tendency exists for a positive slope rather than the inverse relationship assumed in certain models. A direct relationship may appear illogical on first considerations. However, several instrumental discriminatory effects may predominate over the first considerations. Two of these effects are described below.

The reason for the dependence of elemental sensitivity upon spark location[14] has not been established and ionization potential (IP) could be a factor in this dependence. Acceleration of singly charged elemental ions of high IP may be favoured owing to more predominant ion formation in different regions of the spark gap. Conversely stated, elements with low IP could effectively be discriminated against owing to predominant ion formation in regions very close to electrode surfaces, *e.g.*, in the cathode drop

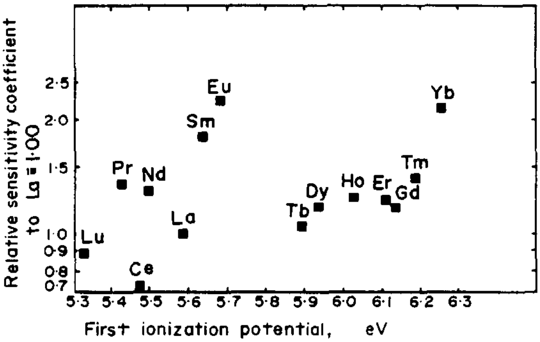

Fig. 2. Plot of S_R *vs.* first ionization potential.

region. Acceleration of these ions along the ion optics axis of the instrument may be less effective because of very narrow gap widths or electrode self-shielding effects, both being common operating characteristics of spark-source mass spectrometers.

A second instrumental discriminatory effect related to IP can occur at the energy-defining slit if ion energy is a function of ionization potential. Mechanisms of ion formation such as those given above would provide this function and lead to two different types of discrimination. One would occur at the defining slit itself and would result in discrimination against certain energies by limiting transmission to a specific ion-energy range. The other type is more complicated and is due to the relationship between line profile and an exact description of the energy and angular divergent parameters of the ion beam.[15]

Mass

Line profiles are mass-dependent (*i.e.*, aberrations are functions of ion-path radii in the magnetic field). Since the energy and angular divergent properties of an ion beam would be very difficult to reproduce, variable mass-dependences of elemental sensitivities may be expected. A means of minimizing or eliminating this variation in line profile has been described by Franzen and Schuy.[16] However, very few instruments have been altered to incorporate this improvement.

Other mass-discrimination effects such as those at the ion detector or in the ion-accelerating region may be relatively constant. However since ion path-length is mass-dependent, a variable dependence of S_R upon ion path-length (mass) may be defined as an alteration in the Z-axis (instrument optical axis parallel to the magnetic field lines) ion-illumination angle.[17]

Space charge broadening

Highly variable sensitivity coefficients for elements with masses adjacent or near to the matrix-mass ion beams have been observed in our own laboratory. (Note data in Table 1.) Generally the observed S_R is uncommonly low by factors of up to 4 for elements immediately adjacent to the matrix. An empirical relationship for estimating the magnitude of this effect, based upon the experimental data, is

$$\text{reduction factor} = [(\text{MS} - \text{MM})/(\text{MS} - \text{MM} + 1)]^2$$

where MS is the mass of the isotope used for the elemental determination and MM is the mass of the isotope of the matrix element adjacent to MS.

Volatility-energy spread

Energy spread and intensity of multiply charged lines have been shown to be dependent upon elemental volatility.[18] Discrimination due to this effect would depend upon the magnitude and the setting of the energy window of the instrument. The procedure used to obtain the experimental results in Table 1 was to maximize the ion current at the centre of the energy window (500 eV wide in this case). For a pure matrix this procedure effectively discriminates against elements with energy spreads (or volatilities) different from those of the matrix. Methods for estimating the degree to which this occurs have not been described and would be very difficult to determine since these particular effects are produced during the unstable and non-reproducible initial stages of spark-gap breakdown. An empirical means for estimating this effect will be desirable for computations described later and is

$$VF = 1/(1 + |(\log VP_i - \log VP_{\mathrm{matrix}})|)$$

where VF is the estimated reduction due to the discrimination noted above, VP_i is the vapour pressure of the impurity element at the particular temperature where the matrix element possesses a vapour pressure, (VP_{matrix}) of 10^{-2} mmHg.

TEST OF MODELS AND OF DISCRIMINATION EFFECTS

A model which encompasses all of the instrumental discrimination factors above would be very difficult to establish. However a different approach may be used to pose a test for the arguments given above as well as for the Goshgarin–Jensen model. This approach consists of a semi-random comparison of the observed results for each of the five matrices and of the overall average data in Table 1 with the rare earth elemental physical constants. Such comparisons were made by relating the observed results to the constants by use of the same form of mathematical expression, *viz.*, multiplication of constants raised to some power, as used in models proposed in the literature.[8] The mathematical expression includes the constants of the Goshgarin–Jensen model as well as the instrumental discrimination factors described above. The general equation is

$$S_R = (MS)^m(HS)^s(IP)^i(AR)^r(HF)^f(VF)^d[(MS - MM)/(MS - MM + 1)]^2$$

where HS is the heat of sublimation, IP is the first ionization potential, AR is the radius of the tervalent rare earth in the oxide, HF is the heat of formation of the C-form rare earth oxide Re_2O_3, and MS, MM, and VF are as defined earlier. The symbols *m*, *s*, *i*, *r*, *f*, and *d* are the exponents of the properties referred to above. For comparison with the overall average data in Table 1 the matrix-dependent factors, VF, MS, and MM were not included in the equation.

The following semi-random procedure was used for comparison of observed data with values computed according to the mathematical expression above. Initially all of the exponents were set equal to zero. The exponent *s* was then incremented, the equation was evaluated for S_R for each rare earth, the S_R values were normalized to La ≡ 1·00 and the average differences between the computed and observed S_R values for the rare earth elements were determined. Incrementation of the exponent by 0·1 unit was permitted in either a positive or a negative direction until best agreement, *i.e.*, minimum average difference between computed and observed S_R values, was obtained. With the exponent *s* retaining its optimized value, the exponent *m* was then optimized in the same manner. This optimization of exponents was continued in the order: *s*, *m*, *s*, *m*, *i*, *s*, *m*, *i*, *r*, *s*, *m*, *i*, *r*, *f*, *s*, *m*, *i*, *r*, *f*, *d*, *s*, *m*, *i*, *r*, *etc.* with each exponent retaining its re-optimized value while the next exponent was being optimized. The exponent *s* was chosen for optimization first since a definite relationship between the heat of sublimation and the observed results was obvious from the Goshgarin–Jensen model. However, no obvious relationships were observed with the other constants. Thus the remaining order of *m*, *i*, *r*, *f*, and *d* was chosen arbitrarily. Re-optimization of the exponents (*e.g.*, *s* re-optimized after the first *m* optimization) was performed for readjustment before continuing to a new exponent. No upper or lower limits were placed on the ultimate values of the exponents. Incrementation was by 0·1 unit except for *d* which was by 0·05 unit.

The final values for the exponents found by the computer programme which was written to perform these tasks are given in Table 2. Figure 3 is a plot (dashed line) of the

Table 2. Exponents of parameters for computer generated model

Matrix Exponent	Y_2O_3	Sc_2O_3	Tm_2O_3	Er_2O_3	Ho_2O_3	Overall	Average
s	−0·8	−0·7	−1·1	−1·1	−1·2	−0·9	−1
m	+0·2	−0·7	+1·4	+0·5	−0·3	−1·9	−0·1
i	+0·3	+1·6	+0·7	+2·1	+4·8	+2·7	+2·0
r	+0·9	+3·6	+3·7	+5·1	+1·9	+2·2	+2·9
f	+0·4	+0·3	−2·1	+0·2	+1·5	—	0
d	0	0	−0·15	0	+0·25	—	0

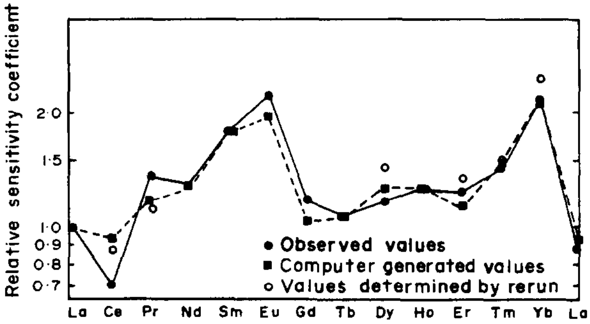

Fig. 3. Plot of observed and computed values for the S_R values of the rare earths.

computer-generated S_R values for the overall average data (column 7 of Table 2) and a plot (solid line) of the experimentally determined S_R values for the overall average data (column 14 of Table 1).

OBSERVATIONS AND CONCLUSIONS

The mathematical procedure above is not an attempt to generate a theoretical model. It is rather an attempt to test arguments for proposed instrumental effects by a semi-random comparison of observed results with physical constants in order to make practical and empirical observations of possible non-random relationships existing between the parameters. The results shown in Table 2 are indeed not random and do indicate relationships which have logical and physical bases as presented earlier. For example the exponent s for the heat of sublimation, HS, deviates very little from the average result of −1 given in column 8 of Table 2. This is in good agreement with the values assumed for this parameter in previously mentioned models. The exponent m of isotopic mass, MS, varies between the values of −1·9 for the overall data and +1·4 for the Tm data. This variation is difficult to assess, owing to the dependence of many physical constants upon mass, as noted earlier. However the variation itself substantiates the arguments posed earlier concerning variable mass discrimination. The positive exponent i for the ionization potential, IP, is in disagreement with values assumed for this parameter in some proposed models. However this direct dependence should not be considered as having no physical basis. This effect was ascribed by previous arguments to possible instrumental discriminations. The radii of the tervalent rare earth ions, AR, change very slightly, across the entire rare earth series of elements. It would be very easy for errors in the observed results to cause the exponent r of this parameter to vary widely without any correlation with physical reality. However, this is not the case. The value of r has an average of approximately $+3$ which is in reasonable agreement with assumptions of some of the models proposed in the literature.[8] The exponent f for the heat of formation, HF, varies considerably and is positive for all matrices except thulium. Possibly the mathematical procedure breaks down in this case. The inability of the mathematical procedure to predict a low enough S_R for Ce may possibly be attributed to an uncertainty concerning which heat of formation should be used, since cerium also forms CeO_2 which has a higher heat of formation than the Ce_2O_3 form-C type oxide. The energy-discrimination effect, VF, was found to be negligible for yttrium, scandium, and erbium. The negative value for d for the thulium matrix and its positive value for the holmium matrix indicate that vapour pressure differences may be significant in these particular cases.

Figure 3 shows the same disagreements between computed and observed S_R values (*i.e.*, low S_{Ce}; $S_{Nd} > S_{Pr}$; $S_{Tb} > S_{Gd}$; $S_{Dy} > S_{Ho}$) as were noted earlier with the S_R values computed from theoretical models. This suggested possible systematic errors in the observed results. Some more recent experimental values for S_R than those given in Table 1 have been obtained for Ce, Pr, Nd, Dy, Ho, Er, Tm, and Yb in three different matrices, Lu_2O_3, Y_2O_3, and Yb_2O_3. In these matrices, S_R values for Pr and Ce were determined relative to $Nd \equiv 1{\cdot}24$ and S_R values for Dy, Er, Tm, and Yb were determined relative to $Ho \equiv 1{\cdot}27$ to permit easier testing of discrepancies with adjacent elements. The experimental procedure used for determining these new S_R values was identical to that used for Method III[1] of Table 1. The experimental results are indicated by the open circles in Fig. 3. The new values for Pr and Ce agree better with the computed values. Also the new value for Dy is greater than that for Ho, in agreement with calculated values. The new values for Tm, Er, and Yb reflect either experimental errors or minor matrix effects.

More rigidly defined experimental work will be needed before better theoretical models can be proposed which will permit accurate *a priori* computation of relative sensitivities for even selected groups of elements. However, with improvements in instrumental reproducibility (*via* automatic control over sparking conditions, increased versatility in ion-detection methods, better characterized solid electrodes, *etc.*) and with the advantages of computer-based techniques, these theoretical models are becoming useful. Instrumental discrimination effects will require more important consideration in future models designed to relate spark-source mass spectra to actual elemental concentration levels in the spark-source samples. It is essential that models continue to be improved upon and tested against observed results so that the complex mechanisms operative in spark-source mass spectrometers may become clearer.

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Zusammenfassung—Für seltene Erden wurden nach in der Literatur vorgeschlagenen empirischen Modellen relative Empfindlichkeitskoeffizienten berechnet. Die Erklärung von Unterschieden zwischen berechneten und beobachteten Werten beruht auf möglichen Diskriminationseffekten im Gerät, die einige in der Ionenquelle ablaufende Prozesse unwirksam machen. Es werden Berechnungen gezeigt, die physikalische Konstanten der Elemente mit den beobachteten Ergebnissen in halb zufälliger Weise verknüpfen; diese stützen die oben aufgestellte Behauptung.

Résumé—On a calculé les coefficients de sensibilité relatifs pour les éléments des terres rares selon des modèles empiriques qui ont été proposés dans la littérature. Les explications concernant des différences entre les valeurs calculées et observées sont basées sur des effets de discrimination instrumentale possibles qui annulent quelques processus se produisant dans la source d'ions. On présente des calculs reliant des constantes physiques élémentaires aux résultats observés de manière semi-désordonnée qui soutiennent cette conception.

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SHORT COMMUNICATION

SYNTHESIS AND ION-EXCHANGE PROPERTIES OF CERIC TUNGSTATE

(*Received* 3 *October* 1972. *Accepted* 14 *December* 1972)

In continuation of our work on the synthesis of some new inorganic ion-exchangers,[1-3] we found ceric tungstate to have useful ion-exchange properties. The present communication summarizes our findings on the preparation, properties and ion-exchange behaviour of ceric tungstate.

EXPERIMENTAL

Reagents

Ceric ammonium nitrate and sodium tungstate (analytical reagent grade) were used without further purification. ^{51}Cr, ^{58}Co, ^{59}Fe, ^{65}Zn, ^{86}Rb, ^{115m}Cd, ^{134}Cs, ^{203}Hg and ^{204}Tl radioisotopes (BARC, Bombay) were used for the determination of distribution ratios. All other reagents used were of analytical grade.

Apparatus

All pH measurements were made with a Cambridge pH meter. A Unicam SP 500 was used for spectrophotometric work. For ^{51}Cr, ^{58}Co, ^{59}Fe, ^{65}Zn, ^{134}Cs and ^{203}Hg γ-counting was done on a scintillation counter. β-counting was done with a G.M. counter in the case of ^{86}Rb, ^{115m}Cd and ^{204}Tl.

Preparation of ceric tungstate

All samples of ceric tungstate were prepared by mixing ceric ammonium nitrate and sodium tungstate at room temperature (35 ± 3°), the total volume being kept to 200 ml. Details of precipitation are summarized in Table 1. The precipitate was filtered off, washed and dried at room temperature. It was sieved to 100–200 mesh for column operation. The ion-exchanger was then converted into its H$^+$ form.

Table 1. Methods of preparation, composition and ion-exchange capacity of ceric tungstate

Sample No.	Concentration of reagents, *M*		pH	Ce^{4+}/WO$_4^{2-}$	Hydrogen-ion liberation capacity, *meq/g*	Hydrogen-ion absorption capacity, *meq/g*
	Ce^{4+}	WO$_4^{2-}$				
1A	0·250	0·250	1	0·51	0·40	0·38
2A	0·050	0·050	1	0·51	0·42	0·38
3A	0·025	0·025	1	0·53	0·42	0·37
4B	0·050	0·050	1	0·52	0·56	0·48
5A	0·050	0·10	1	0·51	0·54	0·47
6A	0·10	0·050	1	0·57	0·40	0·36
7A	0·050	0·050	0	0·50	0·73	0·66
8B	0·050	0·10	0	0·49	0·89	0·81

A—WO$_4^{2-}$ added to Ce^{4+}.
B—Ce^{4+} added to WO$_4^{2-}$.

Composition of ceric tungstate

Known amounts of ceric tungstate samples were dissolved in hot concentrated hydrochloric acid. Cerium[4] and tungsten[5] were determined spectrophotometrically, and the Ce(IV) and W(VI) ratios are reported in Table 1. Control experiments and blanks were run to test the accuracy of the method of determining cerium : tungsten ratios.

Properties

All samples when dried at room temperature are yellow. The samples were in the form of a gel and could be sieved to the desired mesh size. The samples show a negligible tendency to leach. Mineral acids (6*M*) have no effect in the cold but dissolve the exchanger on heating. Alkalis (up to 2*M*) have no effect in the cold, and the ion-exchanger is stable in water, alcohol, benzene, acetic acid, 1·0*M* oxalic acid and in solutions of alkali and alkaline earth metal chlorides.

Determination of the exchange capacity

The ion-exchange capacity is found to depend upon the concentration (Fig. 1b) and the volume of the eluent (Fig. 1a) for column operation. To find the time of complete equilibration, the amount of H^+ liberated by 1*M* sodium chloride solution at different intervals of time was determined (Fig. 1c). The ion-exchange capacity of different samples was measured by the standard method,[6] and the hydrogen-ion liberation capacity for different samples is tabulated in column 6 of Table 1. Column 7 contains the value of the hydrogen-ion absorption capacity of different samples in the Na^+ form. The reproducibility of the method was checked by determining the capacity of different samples from the same batch, and there is a standard deviation of ±0·019 meq/g. The standard deviation for batch samples was ±0·036 meq/g.

The exchange capacity for Na^+ varies little (~10%) with initial pH. The ion-exchange capacity for ions of different size and charge follows the order $Li^+ < Ca^{2+} < Na^+ \leq K^+ \leq NH_4^+ < Ba^{2+}$. Ceric tungstate exchanger dried at up to 100° does not lose its exchange capacity, but when dried at 200° loses half its exchange capacity and almost all if dried at 400°. There is no appreciable loss in the hydrogen-ion liberation capacity in the course of up to 4 regeneration cycles. Since sample 8B has the highest exchange capacity, most studies were carried out on this sample only.

Distribution studies

Distribution coefficients for 22 metal ions were determined by batch operation, using radiometric, complexometric titration, and spectrophotometric methods. About 200 mg of the exchanger were loaded with 20 ml of 0·005*M* metal ion solution. The initial pH of the metal ion solution was adjusted to between 2 and 3 with perchloric acid. The results are reported in Table 2.

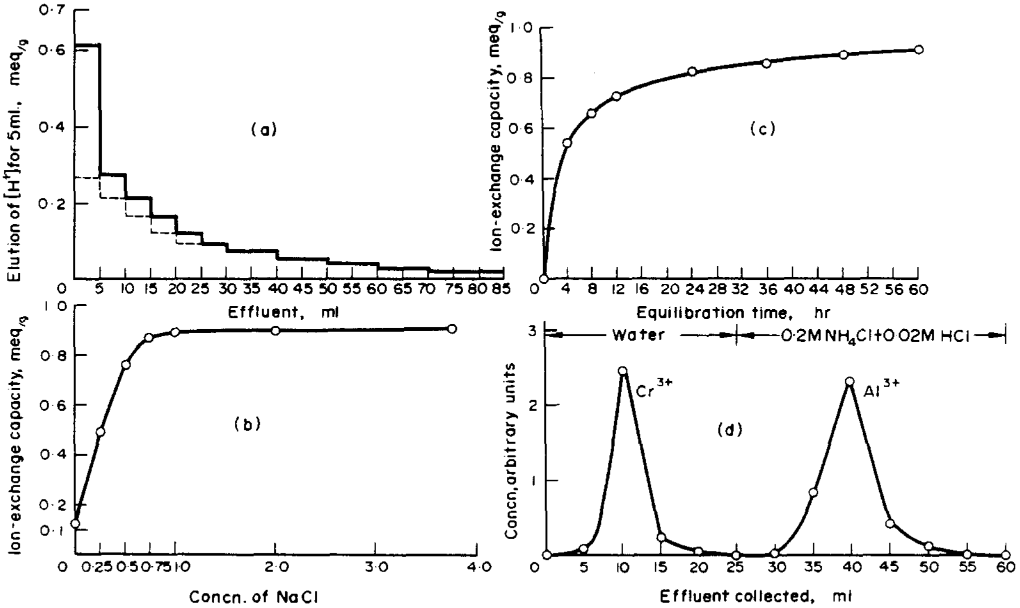

Fig. 1. (a) Elution of hydrogen ion. Continuous line—eluent 1·0*M* NaCl. Dotted line—eluent 0·1*M* NaCl.

(b) Ion-exchange capacity of ceric tungstate (8B) as a function of concentration of Na^+.

(c) Effect of time of equilibration on exchange capacity of ceric tungstate (8B).

(d) Separation on ceric tungstate column (9·0 cm × 0·19 cm^2) flow-rate ~0·15 ml/min.

Table 2. Distribution coefficients for some cations on ceric tungstate (8B)

Cation	K_d, *ml/g*	Cation	K_d, *ml/g*
Rb(I)	68·3	Cd(II)	2·2
Ag(I)	138·3	Ba(II)	1·0
Cs(I)	96·3	Hg(II)	603·0
Tl(I)	617·2	Pb(II)	2·9
Mg(II)	2·8	Al(III)	63·6
Ca(II)	3·1	Cr(III)	4·3
Mn(II)	1·4	Fe(III)	3·6
Co(II)	216·0	Tl(III)	147·8
Ni(II)	6·0	Zr(IV)	1·3
Cu(II)	38·4	Th(IV)	17·1
Zn(II)	5·4	UO_2^{2+}	1·1

Separations of Hg^{2+} from Cd^{2+}, Zn^{2+} and Pb^{2+} (Fig. 2) and Co^{2+} from Mn^{2+} and Fe^{3+} were carried out on a column (5·0 cm × 0·19 cm^2) containing 50–100 mesh ceric tungstate. The column was loaded with 20% of the breakthrough capacity for each metal ion and the elution was started after 20 min at a flow rate of ~0·15 ml/min. Separation of Al^{3+} from Cr^{3+} and Fe^{3+} was carried out on a column 9·0 cm × 0·19 cm^2 (Fig. 1d). Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, or Mn^{2+} were eluted with water (pH 2–3); Hg^{2+} and Co^{2+}, which were retained on the column, were eluted with 0·4*M* ammonium chloride + 0·05*M* hydrochloric acid. Likewise Fe^{3+} and Cr^{3+} were eluted with water (pH 2–3), and Al^{3+} with 0·2*M* ammonium chloride + 0·02*M* hydrochloric acid.

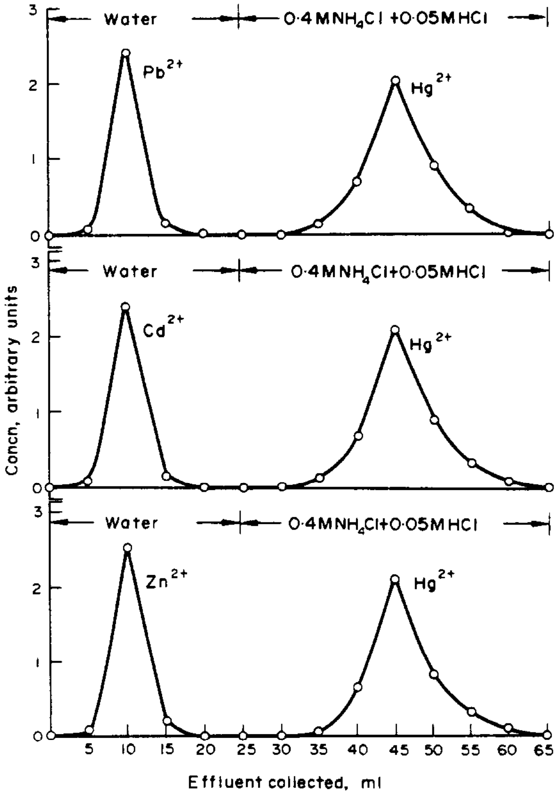

Fig. 2. Separation on ceric tungstate column (5·0 cm × 0·19 cm^2), flow-rate ~0·15 ml/min.

RESULTS AND DISCUSSION

The ion-exchange capacity of the samples is influenced by the ratio of the concentrations of solutions mixed, their order of mixing, and the final pH of the resulting solution. The samples precipitated at pH 0 have higher exchange capacity than those precipitated at pH ~ 1. Also the samples prepared by mixing Ce^{4+} and WO_4^{2-} in 1 : 2 ratio have better exchange capacity than the samples precipitated in 2 : 1 ratio. As noted earlier,[1-3] the order of mixing also affects the exchange capacity. The samples (B) prepared by adding Ce^{4+} to WO_4^{2-} have a higher capacity than those (A) prepared by mixing the reagents in the reverse order. However, all these factors which influence the exchange capacity seem to have a negligible effect on the ceric : tungsten ratio. The titration curve shows only one inflection, suggesting that ceric tungstate behaves as a monofunctional acid.

As regards the effect of neutral salt solution concentration and the time of equilibration on the capacity determined by batch operation, a constant capacity for Na^+ was obtained at $1M$ neutral salt concentration after a 48 hr equilibration. Elution curves reveal that at least 80 ml of $1M$ eluent is required for complete elution, although most of the hydrogen ions are released in the first 20 ml.

The effect of pH on exchange capacity is practically negligible. Ceric tungstate in the acid form gives a buffer system[1] of pH 2–3 and its exchange capacity remains practically unchanged at temperatures up to 100°. This suggests its possible use for buffering aqueous systems at higher temperatures. The exchanger has moderate regeneration properties, and may be used without breakdown of the particle or deterioration in ion-exchange properties.

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Summary—Ceric tungstate has been prepared under varying conditions of precipitation. Its properties and ion-exchange behaviour have been studied. Separations of Hg^{2+} from Zn^{2+}, Cd^{2+} and Pb^{2+}; Co^{2+} from Mn^{2+} and Fe^{3+}; and Al^{3+} from Cr^{3+} and Fe^{3+} have been carried out on ceric tungstate columns.

Zusammenfassung—Cerwolframat wurde unter verschiedenen Fällungsbedingungen hergestellt und seine Eigenschaften und sein Ionenaustauschverhalten untersucht. An Cerwolframatsäulen wurden Trennungen von Hg^{2+} und Zn^{2+}, Cd^{2+} und Pb^{2+}, Co^{2+} von Mn^{2+} und Fe^{2+} sowie Al^{3+} von Cr^{3+} und Fe^{3+} ausgeführt.

Résumé—On a préparé le tungstate cérique dans conditions variables de précipitation. On a étudié ses propriétés et son comportement d'échange d'ions. On a réalisé des séparations de Hg^{2+} de Zn^{2+}, Cd^{2+} et Pb^{2+}, Co^{2+} de Mn^{2+} et Fe^{3+} et Al^{3+} de Cr^{3+} et Fe^{3+} sur des colonnes de tungstate cérique.

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LOCATING THE MORE ACIDIC HYDROXYL GROUP ON DIHYDROXY COMPOUNDS

o,o'-DIHYDROXYAZO-DYE METAL-ION INDICATORS

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Summary—In *o,o'*-dihydroxyazo-dye metal-ion indicators, one hydroxyl group is 10^4 times more acidic than the other. The location of the more acidic group has been a mystery. By methylation of the acidic group, reduction of the monomethylated compound, isolation and characterization of the split methoxyamine and hydroxyamine, the location of the acidic group has been established. Indicators examined include Calmagite, Eriochrome Black T, Eriochrome Blue Black R and 4-(2-pyridylazo)resorcinol (PAR).

Compounds having two or more ionizable hydroxyl groups often show a marked difference in the degree of ionization of these groups. It would be interesting to determine which of the groups on the compound ionizes first. The means to do this are available. Braun, Anton and Weissbach[1] have shown that dimethyl sulphate will methylate ionized hydroxyl groups 10^4 times faster than unionized groups. So if the more acidic hydroxyl group is neutralized while the less acidic is not, methylation should occur exclusively on the oxygen atom of the ionized group. Since methyl ethers are quite stable and often easy to isolate, location of the methyl group on the monomethyl product should be straightforward.

o,o'-Dihydroxyazo-dyes used as metal-ion indicators are good candidates for this method. The acid dissociation constants are known. They show a K_1/K_2 ratio of over 10^4 so the ionization processes are independent. The compounds are also pH indicators and are of a distinctive blue colour in the half-neutralized state. The hydroxyl groups are on different rings, the rings being connected by the azo linkage. The azo linkage on reduction yields two separated amines which can then be isolated to see which one is a methyl ether. Isolation of the other amine to be sure that it is not a methyl ether is definitive. Acetylation of the products, as a routine measure, would yield convenient, stable, crystalline derivatives easy to identify.

Several *o,o'*-dihydroxyazo-dye metal-ion indicators were investigated. Dye I was 1-(2-hydroxy-1-benzeneazo)-2-naphthol, used by Diehl and Ellingboe[2] to help demonstrate that the necessary and sufficient structure needed for a calcium or magnesium azo-dye metal-ion indicator was two hydroxyl groups, one on each ring adjacent to the azo group. Dye II was Calmagite, the indicator developed by Lindstrom and Diehl[3] specifically as a stable indicator for the EDTA titration of calcium plus magnesium and

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investigated later by Lindstrom and Isaac.[4] Dye III was Eriochrome Black T or Mordant Black 11, C. I. 14645[5] the commercially important dye for wool, introduced by Schwarzenbach and Biedermann[6] as the first indicator for the direct titration of calcium plus magnesium with EDTA. Unfortunately stock solutions of this dye do not keep well, which necessitates the repeated preparation of indicator solutions. This dye was later investigated in detail as an indicator by Diehl and Lindstrom.[7] Dye IV was Eriochrome Blue Black R or Mordant Black 17, C. I. 15705[5] a dye also studied by Schwarzenbach and Biedermann[6] and later suggested by Hildebrand and Reilley[8] as an indicator for the EDTA titration of calcium alone, at high pH, and designated Calcon. Dye V was 4-(2-pyridylazo)resorcinol (PAR), suggested by Wehber[9] as an indicator for the EDTA titration of some transition metal ions. This compound is not an *o,o'*-dihydroxyazo-dye but it does contain two hydroxyl groups of widely different strength.[10]

Table 1 lists the dyes investigated along with the negative logarithms of their acid dissociation constants. As has been the custom, these dissociation constants refer only to the hydroxyl groups, even for the sulphonated dyes.

The more acidic hydroxy group is indicated by an arrow in the structural formulae given.

EXPERIMENTAL

Apparatus

Infrared spectrophotometer. Perkin–Elmer Model 137

Ultraviolet Model visible spectrophotometer. Perkin–Elmer 4000A

pH meter. Leeds Northrup model 7405, standardized with reference buffers[11] (phthalate, pH 4·01 at 25°; borax, pH 9·18 at 25°).

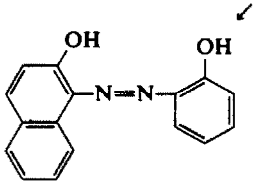
Capillary melting point apparatus. Thomas Hoover 'Uni-melt' apparatus.

The carbon, hydrogen, and nitrogen analyses were done by a commercial laboratory. The hydroxyl determinations were carried out by the procedure described by Siggia.[12]

Reagents

All inorganic chemicals used were reagent grade. All organic chemicals were recrystallized or redistilled as needed. All water used was distilled and demineralized with an ion-exchange column charged with Bio-Rex 501-X8 mixed-bed resin (Bio-Rad laboratories).

1-(2-Hydroxy-1-benzeneazo)-2-naphthol, Dye I



Dye I was prepared by diazotizing 2-aminophenol and coupling to 2-naphthol in basic solution. 2-Aminophenol, 65·5 g, was dissolved in 1000 ml of water with just enough hydrochloric acid to effect solution and the solution was cooled to 5°. Then 41·4 g of sodium nitrite in aqueous solution were added. 2-Naphthol, 95 g, was mixed with 2500 ml of 50% sodium hydroxide to yield a milky suspension which was also cooled to below 5°. The diazonium solution was added to the naphthol with constant stirring while the temperature was kept below 7° by the addition of ice. The mixture was allowed to stand for a day to come to room temperature. The crystals of the sodium salt were filtered off and washed several times with hydrochloric acid (1 + 1) to yield the acid form which was recrystallized from methanol; yield: 53·7%; m.p. 191–193°; required[13] 193°.

For methylation 1·33 g of I were dissolved in 500 ml of dioxan. The pH of the solution was adjusted to approximately 10, with 1*M* sodium hydroxide. The blue solution was cooled to about 0° in an ice-bath, filtered to remove any undissolved material, and placed in the fume-cupboard in an ice-bath. Dimethyl sulphate, 0·46 ml, was added over a period of 1 hr with constant stirring. The solution was then heated on a steam-bath for 1 hr. The methylated dye was isolated by pouring the solution into 1·5 l. of water. The dye was filtered off and washed with water several times. The methylated dye was air-dried and recrystallized from methanol. Yield: 79%. Analysis gave: C, 73·1%; H, 4·8%; N, 10·3%; OH, 6·2%. Calculated for $C_{17}H_{14}N_2O_2$: C, 73·37%; H, 5·07%; N, 10·07%; OH, 6·11%: m.p. 179·5–183°; required[14] 180°.

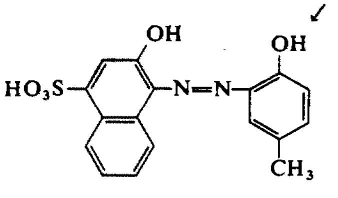
The next step was to reduce the methylated I and separate and identify the hydroxyamine and methoxyamine which would be formed. Reduction was carried out with sodium dithionite ($Na_2S_2O_4 \cdot 2H_2O$) in basic solution. Methylated dye, 0·23 g, was dissolved in 200 ml of absolute ethanol. Fifty ml of 50% sodium hydroxide were added and the solution heated to boiling. Sodium dithionite was added gradually until the solution lost its colour. The solution was steam-distilled for about 30 min. The distillate will be referred to as I-A; the residue remaining in the flask as I-B.

I-A was extracted into ether. The ether was evaporated, leaving an oily material. This oil was acetylated by the method of Noelting, Grandmougin and Freimann,[15] slightly modified. The oil was dissolved in 25 ml of ethyl acetate; 5 ml of acetic anhydride and 2 ml of pyridine were added, and the solution refluxed for 2 hr. The solution was then evaporated to dryness with a rotary evaporator. The residue was extracted with and recrystallized from hot water. Yield: 65% of long white needles: m.p. 88°. Required for 2-acetamidophenol methyl ether[16] 87–88°. 2-Acetamidophenol methyl ether was prepared by the acetylation of 2-anisidine, by the method described previously. The product was recrystallized from hot water. Yield: 92·7%: m.p. 88°. The infrared spectra of the 2-acetamidophenol from the two sources were identical.

The residue I-B was neutralized with dilute hydrochloric acid. Immediately, white flakes precipitated which were filtered off and air-dried. This product was then acetylated as described above. The solution was evaporated to dryness, and the residue was extracted with and recrystallized from hot ethanol. The white crystals separated slowly. Yield: 67%: m.p. 204–206°. Required for 1-acetamido-2-acetoxynaphthalene[17] 206°. 1-Acetamido-2-acetoxynaphthalene was prepared by a similar acetylation of 1-amino-2-naphthol. The product was recrystallized from ethanol. Yield: 91%: m.p. 204–206°. The infrared spectra of the 1-acetamido-2-acetoxynaphthalene from the two sources were identical.

The methylation of 1-(2-hydroxy-1-benzeneazo)-2-naphthol occurred only on the benzene ring so pK_1 is a measure of the acidity of the phenolic hydroxyl group. The resultant compound was C. I. Solvent Red 1, C. I. 12150,[5] which is prepared by coupling diazotized 2-anisidine with 2-naphthol.

Calmagite or 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid, Dye II



Calmagite was prepared by the method of Lindstrom and Isaac.[4] For methylation, 4 g of II were dissolved in 500 ml of dioxan, the pH was adjusted to 10 with 1*M* sodium hydroxide, the blue solution cooled to 0–5°, and filtered to remove any undissolved material. Slowly, with stirring, 4·55 ml of dimethyl sulphate were added over a period of 1 hr. The solution was then heated on a steam-bath for 1 hr. The methylated dye was isolated by the addition of hydrochloric acid (1 + 1). If acid is added to the solution rather than solution to the acid, swelling is decreased, and filtration is easier. This solution was cooled and filtered. The methylated dye was washed by decantation several times with hydrochloric acid (1 + 1), filtered off and air-dried. Yield: 94%. Analysis gave: C, 57·9%; H, 4·3%; N, 7·4%; OH, 4·6%. Calculated for $C_{18}H_{16}N_2O_5S$: C, 58·06%; H, 4·33%; N, 7·52%; OH, 4·57%.

Methylated II was reduced with stannous chloride and hydrochloric acid as suggested by the work of Ruggli, Zimmerman and Knapp.[18] Methylated II, 0·70 g, was added to 25 ml of boiling water followed by 0·70 g of stannous chloride dihydrate dissolved in 8 ml of concentrated hydrochloric acid. The mixture was refluxed for 2 hr. At the end of this time, there was a precipitate present. The solution was cooled and filtered. Yield: 87%. The compound decomposed without melting. The infrared spectrum was the same as the infrared spectrum of Eastman Kodak 1-amino-2-naphthol-4-sulphonic acid, a compound only slightly water-soluble.

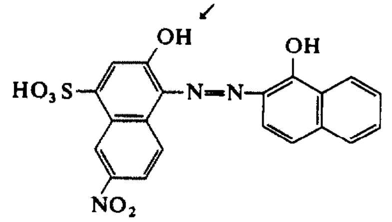
The filtrate was made alkaline and steam-distilled. A white product solidified in the distillate and was filtered off. This product was acetylated by the method described previously and was recrystallized from ethanol. Yield: 86%, m.p. 110°. Required for 2-acetamido-*p*-cresyl methyl ether,[19] 110°.

The first step in the preparation of 2-acetamido-*p*-cresol methyl ether was the nitration of *p*-cresol, by the method of Schultz.[20] *p*-Cresol (20 g) was dissolved in 40 g of benzene. Over a 2-hr period, 11·7 ml of concentrated nitric acid mixed with an equal amount of water were added with constant stirring at 25°. The reaction mixture was allowed to stand in a separatory-funnel until the phases separated. The upper phase was neutralized with sodium bicarbonate solution and then steam-distilled. The benzene distilled first and was extracted several times with 1*M* sodium hydroxide. The extracts were returned to the distillation flask after neutralization with phosphoric acid. The 2-nitro-4-methylphenol was the only material volatile under these conditions. Yield: 75%; m.p. 35°; required[22] 36·5°.

The 2-nitro-4-methylphenol was methylated by the method of Robinson.[22] 2-Nitro-4-methyl phenol, 15 g, was added to 500 ml of xylene. Excess of potassium carbonate, 21 g, was added with 10 ml of dimethyl sulphate. The reaction mixture was refluxed until the red potassium salt of the nitro-compound was replaced by colourless potassium sulphate and potassium methyl sulphate. The xylene was removed by steam-distillation at 92–98°. The nitro-compound followed this. The distillate was extracted several times with ether. The ether was evaporated, leaving a yellow oil which was dissolved in 350 ml of water. To this solution were added 20·0 g of stannous chloride dihydrate dissolved in 115 ml of concentrated hydrochloric acid. This solution was refluxed for 2 hr, made alkaline and steam-distilled. The amine solidified in the distillate and was filtered off. After drying, the amine was acetylated in the usual manner. The product was recrystallized from ethanol. Yield: 46·8%, m.p. 110°. The infrared spectra of the 2-acetamido-*p*-cresyl methyl ether from this synthesis and from the methylated Calmagite were identical.

The methylation of Calmagite occurred only on the benzene ring so pK_1 is a measure of the acidity of the phenolic hydroxyl group.

Eriochrome Black T or 1-(1-hydroxy-2-naphthylazo)-2-naphthol-6-nitro-4-sulphonic acid, Dye III



Dye III was Eastman Kodak Eriochrome Black T and was purified by the method of Diehl and Lindstrom.[7] It was recrystallized from dimethylformamide from which it was isolated as the crystalline dimethylamine salt.

For methylation 2 g of III were dissolved in 500 ml of dioxan. The solution was filtered to remove any undissolved material. The solution was then adjusted to approximately pH 10 with 1*M* sodium hydroxide. The blue solution was kept cooled, and 0·75 ml of dimethyl sulphate was added to the solution over a period of 1 hr, with constant stirring. This was followed by heating on a steam-bath for 1 hr. The dye was isolated by adding excess hydrochloric acid (1 + 1). The precipitate was filtered off and washed several times with the same concentration of acid and was allowed to dry in air. Yield: 75%. Analysis gave: C, 55·4%; H, 3·6%; N, 9·6%; OH, 3·8%. Calculated for $C_{21}H_{15}N_3O_7S$: C, 55·63%; H, 3·34%; N, 9·27%; OH, 3·75%.

Methylated III was reduced by dissolving 1 g of it in 50 ml of boiling water and adding a hot solution of 6·5 g of stannous chloride dihydrate in 15 ml of concentrated hydrochloric acid. The solution was refluxed for 2 hr. Then 50 ml of water were added and refluxing was continued for 30 min. Then, 15 ml of concentrated hydrochloric acid and decolourizing carbon were added. Refluxing was continued for 30 min and the decolourizing carbon was filtered off while the solution was still hot. After cooling, a white precipitate formed and was collected. The yield was 0·45 g (75·8%) of a material which will be referred to as III-A. The melting point of this material could not be determined. The absence of a melting point, the infrared spectra and limited water-solubility led to the belief that III-A might be 1,6-diamino-2-naphthol methyl ether-4-sulphonic acid in the zwitterion form.

To prepare this compound, 1-diazo-2-naphthol-4-sulphonic acid was nitrated as described for the synthesis of dye No. 241 in *Farbstofftabellen.*[14] The 1-diazo-2-naphthol-6-nitro-4-sulphonic acid was recrystallized from ethanol; yield: 66%.

The diazo compound was then coupled with *p*-cresol. Vacuum distilled *p*-cresol, 3·6 g, was dissolved in a solution of 23 g of potassium hydroxide in 35 ml of water. Then a mixture of 10 g of the diazo component in water was added slowly and the mixture slowly heated to 60°. This temperature was maintained until coupling was complete. The solution was cooled and the dye was precipitated by addition of hydrochloric acid (1 + 1). The dye was then recrystallized by dissolving it in 500 ml of ethanol, adding 50 ml of hydrochloric acid (1 + 20), and slowly evaporating the ethanol on a warm steam-bath. The solution was cooled, and the precipitate was filtered off and air-dried. Yield: 38%.

This dye (5 g) was dissolved in 500 ml of dioxan, and excess of 50% sodium hydroxide solution was added, so both hydroxyl groups would be ionized. Dimethyl sulphate (10 ml) was added to the solution at 0–5° with constant stirring, over a period of 1 hr. The solution was then heated on a steam-bath for 1 hr. The methylated dye was then precipitated by the addition of excess of hydrochloric acid (1 + 1). The dimethylated dye was filtered off, then washed several times with hydrochloric acid (1 + 1). Yield: 65·3%.

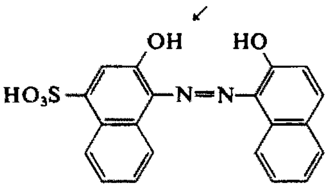
This dimethylated dye, 3·5 g, was added to 200 ml of boiling water. A hot solution of 26·0 g of stannous chloride dihydrate in 45 ml of concentrated hydrochloric acid was added. The solution was refluxed for 2 hr. Hot water (200 ml) was added, and the solution refluxed for 30 min. Decolourizing carbon and 45 ml of concentrated hydrochloric acid were added, and the solution was refluxed for another 30 min, filtered, and cooled. A white precipitate formed upon cooling and was filtered off. Yield: 70%. The infrared spectrum of this 1,6-diamino-2-naphthyl methyl ether-4-sulphonic acid was identical with that of **III-A**.

The filtrate from the separation of **III-A** after the reduction of methylated Eriochrome Black T was treated with hydrogen sulphide to precipitate the tin. The tin sulphide was then filtered off and the filtrate was reduced in volume to about 10 ml. A rose precipitate formed, was filtered off, and acetylated as previously described. The product (referred to as **III-B**) was recrystallized from ligroin. Yield: 70·9%; m.p. 116–117°; required for 2-acetamido-1-acetoxynaphthalene[23] 116°, 117·5°.

2-Amino-1-naphthol was prepared by the method of Grandmougin and Michel.[24] 2-Nitroso-1-naphthol (2 g) was suspended in 250 ml of concentrated hydrochloric acid and cooled to 0°. Stannous chloride dihydrate, 6·90 g, was added. The solution was kept cool until a white precipitate appeared, which was dissolved by the addition of water. Tin was precipitated from the solution by treatment with hydrogen sulphide. After filtration, the solution was reduced in volume until a white precipitate was obtained which was was acetylated as previously described and recrystallized from ligroin. Yield: 52·75%, m.p. 116°. The infrared spectra of 2-acetamido-1-acetoxy-naphthalene from this synthesis and from the reduced, methylated Eriochrome Black T were identical.

The methylation of Eriochrome Black T occurred only on the naphthalene ring, which was sulphonated, so pK_1 is a measure of the acidity of the hydroxyl group on that ring.

Eriochrome Blue Black R or 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid, Dye IV



Dye **IV** had been prepared earlier by the diazotization of 1-amino-2-naphthol-4-sulphonic acid with sodium nitrite in acid solution, followed by coupling to 2-naphthol in concentrated alkaline solution. It had been converted into the acid form, filtered off, air-dried and extracted with solvents to remove any excess of 2-naphthol. It was purified further by dissolving 20 g of product in ethanol, and adding 50 ml of hydrochloric acid (1 + 20). The ethanol was slowly evaporated on a warm steam-bath to precipitate the dye. Yield: 75%.

For methylation 3·94 g of the dye were dissolved in 500 ml of dioxan. The pH was adjusted to approximately 10 with 1*M* sodium hydroxide. The blue solution was cooled to 0–5° and filtered to remove any undissolved material. Dimethyl sulphate, 3·85 ml, was added over a period of 1 hr with constant stirring. The solution was then heated on a steam-bath for 1 hr. The dye was filtered off and washed several times with hydrochloric acid (1 + 1) and dried. Yield: 78·5%. Analysis gave: C, 61·8%; H, 3·7%; N, 6·6%, OH, 4·1%. Calculated for $C_{21}H_{16}N_2O_5S$: C, 61·76%; H, 3·95%; N, 6·86%, OH, 4·16%.

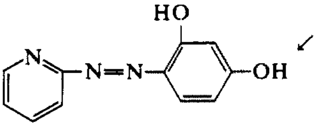
Methylated **IV** was reduced by adding 0·94 g to 25 ml of boiling water and then adding 8 ml of hydrochloric acid containing 1·25 g of stannous chloride dihydrate and refluxing for 2 hr to yield a precipitate. The solution was cooled and the precipitate filtered off. The precipitate was expected to be the sulphonated portion of methylated **IV**, and will be referred to as **IV-A**. The melting point of this compound could not be determined.

1-Amino-2-naphthol methyl ether-4-sulphonic acid was prepared for comparison with **IV-A**. Dye **II**, 2 g, was dissolved in 500 ml of dioxan. Sodium hydroxide, 1*M*, was added until both hydroxyl groups were ionized. The solution was cooled to 0–5° and filtered. Over a period of 1 hr, with constant stirring, 4·55 ml of dimethyl sulphate were added. The solution was heated on a steam-bath for 1 hr. The dye was isolated by adding excess of hydrochloric acid (1 + 1), filtering off and washing several times with hydrochloric acid (1 + 1). After air-drying, the yield was 67·2%. Dimethylated Calmagite was dissolved in 50 ml of boiling water and stannous chloride dihydrate, 2·50 g, in 16 ml of concentrated hydrochloric acid was added. Refluxing for 2 hr yielded a precipitate, which was filtered off after cooling. Yield: 89%. The infrared spectra of 1-amino-2-naphthol methyl ether-4-sulphonic acid prepared as above and of **IV-A** from the reduction of methylated Eriochrome Blue Black R were identical.

The solution remaining from the filtration of **IV-A** was treated with hydrogen sulphide to remove the tin. The filtered solution was then neutralized. A white precipitate appeared which was filtered off, air-dried and acetylated by the method described previously. The product was recrystallized from ethanol. Yield: 82·5%: m.p. 204–206°. Required for 1-acetamido-2-acetoxynaphthalene[17] 206°. This portion will be referred to as **IV-B**. The infrared spectra of **IV-B** and 1-acetamido-2-acetoxynaphthalene, which had been prepared for the study of **I**, were identical.

The methylation of Eriochrome Blue Black R occurred only on the naphthalene ring, which was sulphonated, so pK_1 is a measure of the acidity of the hydroxyl group on that ring.

4-(2-Pyridylazo)resorcinol, (PAR), Dye V



The PAR used was prepared by the method of Pollard, Hanson and Geary.[25] A solution of sodium ethoxide was prepared by dissolving 2·4 g of metallic sodium in 37 ml of absolute ethanol. 2-Aminopyridine, 10 g, was dissolved in the minimum possible quantity of absolute ethanol, and 12 g of isoamyl nitrite were added. The solutions were mixed, and refluxed gently for 2 hr. The diazotate formed a brown solid. The coupling reaction was carried out directly. Resorcinol, 16 g, was dissolved in the minimum possible quantity of water and added to the diazotate solution. The mixed solutions were allowed to cool in the refrigerator for 40 hr. If there was any difficulty in precipitating the dye, ether was added to force precipitation. The disodium salt of the dye was filtered off and washed thoroughly with ether. A saturated solution of the dye in water was made. Hydrochloric acid, 0·5*M*, was added with stirring to precipitate the acid form of V. This material was air-dried and recrystallized from methanol. Yield: 10%.

V, 2 g, was mixed with a solution of 10 g of potassium hydroxide in 25 ml of water. The solution was cooled to 0–5°, and filtered. Dimethyl sulphate, 0·5 ml, was added, and the solution was shaken for 30 min. Dimethyl sulphate, 0·5 ml, was again added and the solution shaken for 30 min. This was repeated three more times. A total of 2·5 ml of dimethyl sulphate was used. Ethanol, 25 ml, was added to make the solution about 50% v/v ethanol. Ether was added to the solution to precipitate the methylated dye. The methylated dye was recrystallized from methanol. Yield: 71·8%; m.p. 170° d. Analysis gave: C, 63·0%; H, 4·6%; N, 18·3%; OH, 7·5%. Calculated for $C_{12}H_{11}N_3O_2$: C, 62·87%; H, 4·84%; N, 18·33%; OH, 7·42%.

For the reduction, 1 g of methylated V was dissolved in 10 ml of ethanol. This solution was warmed with a solution of 2·4 g of stannous chloride dihydrate in 20 ml of concentrated hydrochloric acid. A dark reddish-brown precipitate appeared immediately: the tin double salt of 2-aminopyridine. The solution was filtered. The filtrate was treated with hydrogen sulphide to remove tin sulphide. The filtrate was evaporated to dryness, and the residue was extracted with and recrystallized from dilute hydrochloric acid. This product was acetylated in 50% acetic acid with acetic anhydride by refluxing for 2 hr. The resulting solution was evaporated to dryness and the residue taken up in hot water. The solution was treated with bone-black and filtered. The acetyl derivative separated upon standing. Yield: 74·1%, m.p. 163–164°; 4-acetamidoresorcinol-1-methyl ether,[26] 166°. This material will be referred to as V-A.

The first step in the preparation of 4-acetamidoresorcinol-1-methyl ether was the methylation of resorcinol by the method of Perkin, Rây and Robinson.[27] Resorcinol (55 g) was dissolved in 50 ml of absolute ethanol, along with 60 ml of dimethyl sulphate. Potassium hydroxide (20 g dissolved in 50 ml of water) was added to the solution at 25°. The solution was shaken frequently for 1 hr and cooled under running water. Potassium hydroxide (20 g dissolved in 50 ml of water) was added to the solution. The solution was then heated on the steam-bath for 45 min. The solution was cooled, acidified, and extracted with benzene. The extracts were washed with 10% sodium hydroxide solution until no more material was removed. The washings were then acidified and again extracted. The benzene extracts were then distilled. The monomethyl ether of resorcinol distilled at 239–241°; literature value[27] 240–242°. Yield: 32·3%.

Nitrosation of the monomethyl ether of resorcinol was carried out by the method of Henrick and Rhodius.[28] Resorcinol monomethyl ether (20 g) was dissolved in 50 ml of absolute ethanol. Glacial acetic acid (32 g) was added. Sodium nitrite (17 g) was dissolved in 32 ml of water. Both solutions were cooled to below 5°. After all the sodium nitrite had been added dropwise, the solution was stirred for 30 min. The temperature was maintained below 5° at all times. The solution was then strongly acidified, cooled, and the precipitate filtered off. The product was dried over calcium oxide in a vacuum desiccator. After the crystalline mass was dry, it was completely dissolved in cold benzene. From this solution, about half the benzene was distilled. The more insoluble material precipitated in large, dark-green crystals upon cooling. This was the labile form of 4-nitrosoresorcinol-1-methyl ether. At 140°, the labile form is converted into the stable form. Yield: 32·3%.

This material (3 g) was introduced stepwise into a solution of stannous chloride in concentrated hydrochloric acid. During the addition, the reaction product began to separate out. After all had been added, the mixture was warmed on a steam-bath for a very short time, and cooled. The crystals which precipitated were the tin double salt. These crystals were dissolved in 1*M* hydrochloric acid, and the solution was treated with hydrogen sulphide to remove the tin. The tin sulphide was filtered off, and the filtrate was evaporated to dryness. The residue was extracted with and recrystallized from dilute hydrochloric acid and air-dried. Acetylation was then carried out in 50% acetic acid with acetic anhydride. The solution was refluxed for 2 hr, then evaporated to dryness, and the residue was extracted with hot water. This solution was treated with bone-black and filtered; crystals separated upon standing. Yield: 23% of 4-acetamido-resorcinol-1-methyl ether, m.p. 163–164°. The infrared spectra of this compound and V-A were identical. Therefore, the hydroxyl group *para* to the azo linkage is the more acidic.

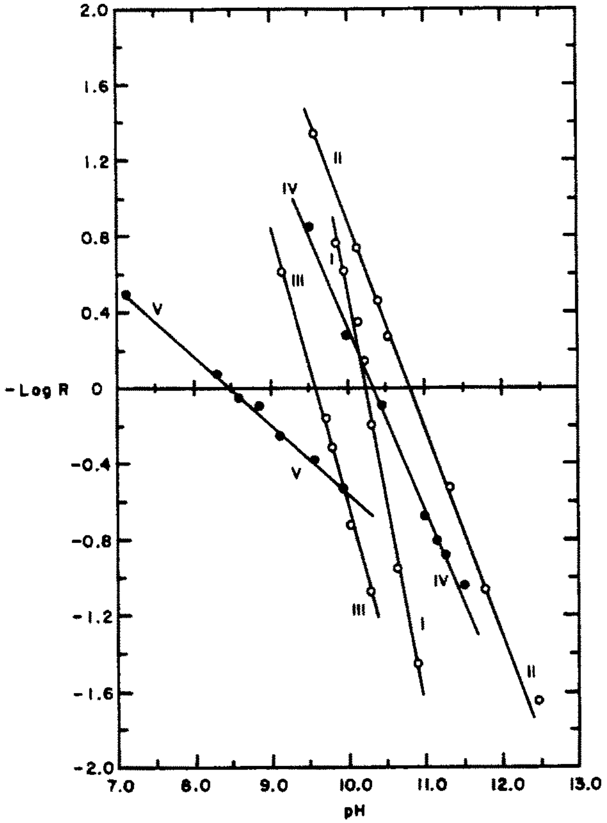


Fig. 1. Plots for the determination of acid dissociation constants of the monomethylated dyes. Dyes are designated with their corresponding Roman numeral.

Determination of acid dissociation constants

Stock solutions of each of the monomethylated dyes were made up, each containing 0·1 mole of potassium chloride: I, 0·0489 g/250 ml, 95% ethanol; II, 0·0447 g/250 ml, water; III, 0·0881 g/250 ml, water; IV, 0·0459 g/250 ml, water; V, 0·0233 g/250 ml, water. So that all absorption and pH measurements could be made at constant ionic strength, $\mu = 0{\cdot}10$, a procedure described by Bates[11] was used in preparing buffers for each pH range. A stock solution A was made up, that was 0·05*M* in monobasic weak acid or monobasic weak base, and 0·05*M* in potassium chloride. The pH was then varied by adding various amounts of stock solution B, which was 0·2*M* in hydrochloric acid or sodium hydroxide, and 0·1*M* in potassium chloride. For pH values from 6 to 7·5, potassium dihydrogen phosphate and hydrochloric acid were used; from 7·5 to 9, tris-(hydroxymethyl)-aminomethane and hydrochloric acid; from 9 to 10·5, sodium borate decahydrate and sodium hydroxide; from 10·5 to 12, disodium monohydrogen phosphate and sodium hydroxide.

Ten ml of the stock solution of methylated dye were transferred by pipette into a 100-ml volumetric flask. The appropriate stock solution A (50 ml) was added, and the pH was varied by adding different volumes of stock solution B. The solution was then made up to volume with 0·1*M* potassium chloride. The absorption spectra of the solutions were run and the pH measured with a previously standardized pH-meter. Figure 1 shows the plot of pH *vs.* $-\log R$ where R is $(A - A_{\min})/(A_{\max} - A)$. The acid dissociation constants found are listed in Table 2. A represents the absorbance of the monomethylated dye solution at the stated pH, $A_{\max}$ the highest absorbance and $A_{\min}$ the lowest absorbance, all measurements being made at the wavelength of maximum spectral change with pH.

RESULTS AND DISCUSSION

The proposed method of investigation of *o,o*′-dihydroxyazo-dye indicators has yielded the desired information. The five dyes studied were methylated on one hydroxyl group with dimethyl sulphate, and reduced to methoxyamines and hydroxyamines. These amines

Table 1. Hydroxyl group acidity, dihydroxyazo-dyes

Dye	pK_1	pK_2	Reference
I	7·7	12·4	2
II	8·14	12·35	3
III	6·91	11·50	6, 7
IV	7·36	13·5	6, 8
V	5·48	12·31	10

were then separated and characterized by comparison of the infrared spectra with those of known compounds. It was found that *o*-hydroxybenzeneazo-2-naphthol and Calmagite were methylated on the phenolic hydroxyl group. Eriochrome Blue-Black R and Eriochrome Black T were methylated on the sulphonated portion of the dye, and PAR was methylated on the hydroxyl group which is *para* to the azo group.

Methylations were carried out in basic solution with dimethyl sulphate both in dioxan and water. Dioxan was chosen as the best reaction medium because the dyes were much more soluble in it than in water. Also, dioxan had no hydroxyl group to compete in the reaction. When dioxan was used as the solvent, some methylated material remained in solution upon the addition of hydrochloric acid (1 + 1). However, the yield was still greater than if the same volume of water were used. The basic azo-dye solutions were completely opaque. Before methylation, the solutions were filtered to remove any undissolved dye.

Some of the metal-ion indicator dyes investigated were sulphonated and the ionized sulphonic acid groups would be expected to yield methyl esters while the hydroxyl groups are being converted into methyl ethers. Sulphonic acid esters are very reactive and will rapidly react with water in a manner similar to dimethyl sulphate.

Two methods of reduction were used: by sodium dithionite in basic solution and by stannous chloride in acid solution. Reduction by sodium dithionite was quick and easy, but the reaction products had to be stable to air oxidation in basic solution so that the two amines could be separated. In the case of methylated I, air-oxidation was slow enough for separation to be carried out. In the cases of dyes II–V, one of the reduction products was so quickly oxidized in basic solution that the separation was impossible. The reduction of these dyes in acid media with stannous chloride was quite successful. In addition, the aminonaphthol sulphonic acids proved to be insoluble in the acid media, which made separation quite easy. It was found that acetylation yielded very stable products.

Table 2 lists the negative logarithms of the acid dissociation constants of the monomethylated azo dye indicators. It will be noted that the pK_a values of the methylated dyes

Table 2. Hydroxyl group acidity, monomethylated dihydroxyazo-dyes

Dye	pK_a	$\frac{1}{2}(pK_1 + pK_2)$*
I	10·25	10·05
II	10·80	10·25
III	9·56	9·20
IV	10·33	10·43
V	8·45	8·90

* From Table 1.

are quite close to the average of the pK_1 and pK_2 values of the parent dyes, so methylation of one hydroxyl group and determination of the acidity of the remaining hydroxyl group would not give correct information about pK_2 for the parent dye. Nor would proton magnetic resonance be expected to be useful. The differences in the slopes in Fig. 1 are caused by the difference in the molar absorptivities of the dyes.

This method of experimental determination of the exact sequence of ionization has been found to be easy and flexible and should be applicable to many similar problems.

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Zusammenfassung—In *o,o'*-Dihydroxyazofarbstoffen, die als Metallionenindikatoren verwendet werden, ist eine Hydroxylgruppe 10^4-mal saurer als die andere. Wo die saurere Gruppe liegt, war bisher ungeklärt. Durch Methylierung der sauren Gruppe, Reduktion der Monomethylverbindung, Isolierung und Charakterisierung der bei der Spaltung entstandenen Methoxyamine und Hydroxyamine wurde die Lage der sauren Gruppe festgestellt. Unter den überprüften Indikatoren waren Calmagit, Eriochromschwarz T, Eriochromblauschwarz R und 4-(2-Pyridylazo)-resorcin (PAR).

Résumé—Dans les indicateurs d'ions métalliques colorants *o,o'*-dihydroxyazo, un groupe hydroxyle est 10^4 fois plus acide que l'autre. La localisation du groupe le plus acide était un mystère. Par méthylation du groupe acide, réduction du composé monométhylé, isolement et caractérisation de la méthoxyamine et de l'hydroxyamine de coupure, on a établi la localisation du groupe acide. Les indicateurs examinés comprennent: Calmagite, Noir Eriochrome T, Bleu Noir Eriochrome R et 4-(2-pyridylazo) résorcinol (PAR).

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APPLICATION OF VARIOUS ELECTRODES IN POTENTIOMETRIC TITRATION OF CALCIUM

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Summary—In complexometric titrations various indicator electrodes may be employed for monitoring the course of titration and for detection of the end-point. Several of them, including the silver, mercury, bivalent cation membrane, calcium membrane and manganese dioxide electrodes were investigated and compared in their usefulness. As titrant, EDTA was mostly used, but results with similar chelating titrants were also obtained. The practical utility of the electrodes in titrations depends on their selectivity, magnitude of the end-point break and precision in determination of the end-point. For the electrodes studied, in some instances there is good correlation between the theoretical and experimental titration curves, but it is not always possible to predict the electrode response in the low activity range. In other cases poor correlation does not mean that reasonably good analytical results may not be obtained.

A revolution in methods of calcium determination began over 20 years ago when ethylenediaminetetra-acetic acid was introduced as a titrant for metal ions. Since that time many visual indicators have successfully been used, and attempts have been made to use electrometric end-point detection, which should be less subject to personal error, and remove the necessity of finding a suitable indicator. Examples of application of amperometry, potentiometry and even chronopotentiometry may be found in the literature. This study is devoted to comparative investigation of various potentiometric methods of calcium titration.

In potentiometry the crucial factor is the existence of a suitable indicator electrode. For many years no direct-indication calcium electrode was available, so the first procedures were based on indirect indicator-ion systems. Of this group the mercury,[1–4] silver[5–9] and manganese oxide electrodes[10] were reinvestigated in our laboratory. The advent of ion-selective electrodes has resulted in the construction of liquid ion-exchanger electrodes for calcium and for bivalent ions. Each offers some advantages, but has its drawbacks. As reported earlier[11] the potential of these electrodes is measured indirectly on the basis of the exchange reaction

$$\mathrm{W} + \mathrm{CaY} \rightleftharpoons \mathrm{Ca} + \mathrm{WY},$$

where W represents the indicator ion. This reaction directly influences the electrode according to the general equation

$$E = E_{\mathrm{W}}{}^{0} + \frac{RT}{nF}\ln\frac{C_{\mathrm{W}}\,.\,K'_{\mathrm{CaY}}}{\alpha_{\mathrm{W}}\left(K'_{\mathrm{WY}}\,.\,\dfrac{[\mathrm{CaY}']}{[\mathrm{Ca}']} + K'_{\mathrm{CaY}}\right)},$$

derived by using the concept of conditional constants K' and side-reaction coefficients α.

It enables us to predict the shape of the titration curve, the end-point position and the smallest concentration of metal which can still be titrated.

Silver electrode

Because the calcium complex with EDTA is more stable than that of silver the titration curve is evidently asymmetrical. The smallest conditional stability constant in this system is that for the silver complex, and under the best conditions (borax buffer, pH 9–10) its value is $10^{7 \cdot 0}$. The product of this constant and the calcium concentration defines the total potential change in the titration. About 100 mV change between titration fraction $f = 0{\cdot}5$ and $f = 2{\cdot}0$ corresponds to $10^{-5}M$ calcium solution and excellent agreement has been found between theory and practice.[11]

Mercury electrode

Because many metal complexes are less stable than that of mercury the titration curve is symmetrical. This is not the case for calcium, however, because in the pH range 9–10, the conditional mercury stability constant is about $10^{8 \cdot 0}$, whereas that of calcium is nearly $10^{10 \cdot 0}$. When the total potential change is calculated by means of the equation:

$$\Delta E_{0 \cdot 5/2} = \frac{RT}{nF} \ln(C_{\mathrm{Ca}} \,.\, K'),$$

where K' is the smallest conditional constant in the system, the limiting concentration is found to be close to $10^{-5}M$. Further, in this case the agreement between theory and practice is not so good, because at potentials close to $-0{\cdot}05$ V *vs.* S.C.E. the presence of oxygen decreases the potential change, especially for larger titrand concentrations.

Manganese dioxide electrode

This electrode has been prepared by covering platinum with manganese dioxide.[12] Its potential is dependent on the manganese(II) concentration in solution. It should be defined by an equation similar to that given previously, differing only by the presence of a pH-dependent term and the minus sign of the last term.

$$E = E^{0}_{\mathrm{MnO_2/Mn^{2+}}} - \frac{2RT}{F} \,.\, \mathrm{pH} - \frac{RT}{2F} \ln \frac{C_{\mathrm{Mn}} \,.\, K'_{\mathrm{CaY}}}{\alpha_{\mathrm{Mn}}\left(K'_{\mathrm{MnY}} \dfrac{[\mathrm{CaY'}]}{[\mathrm{Ca'}]} + K'_{\mathrm{CaY}}\right)}.$$

The potential change during a calcium titration should depend on the calcium stability constant, which over the whole pH range is lower than that of the manganese complex. However, for this electrode the experimental potential changes are smaller than the predicted ones. This behaviour can be attributed to several factors: oxidation of the Mn(II) complex in solution, heterogeneous reaction between MnO_2 and the Mn(II) complex, and to some extent to slow kinetics. The latter factor is probably responsible for the poor indication at very low calcium concentrations, but at slightly higher ones the electrode seems useful.

Calcium and bivalent ion electrodes

Some electrodes which are very useful in many practical applications[13–17] have drawbacks which limit their use in titrations, the most important being insufficient selectivity and the lower limit of response.[18] The end-point error in complexometric titrations has been discussed by Schultz[19] and by Carr.[20]

The detailed mathematical treatment given by Schultz[19] has led to the exact expression describing the electrode potential:

$$E = E' + \frac{RT}{nF}\ln\left| M + \sum_{i} \frac{K_i C_i^{n/z_i}}{(1 + rf)^{n/z_i}} + \sum_{j} K_j C_j^{n/z_j}\left(\frac{rf}{1 + rf}\right)^{n/z_j} \right|,$$

where

$$M = \frac{\beta + \sqrt{\beta^2 + \dfrac{4C}{(1 + rf)K}}}{2} \quad \text{and} \quad \beta = \frac{(1 - f)C}{(1 + rf)} - \frac{1}{K},$$

and C = concentration of titrand

C_i, C_j = concentrations of interfering ions in the sample and titrand respectively

K = stability constant of the complex

K_i, K_j = selectivity coefficients of ions i and j, respectively

r = dilution factor equal to titrand to titrant concentration ratio

f = fraction titrated

n, z_i, z_j = charges of determined and interfering ions, respectively

From this equation the systematic titration error has been calculated for titration of calcium in the presence of interfering sodium ions in the sample and in the titrand.

Assuming as an approximation that the conditional stability constant of the complex is much larger than the reciprocal of the calcium concentration: $K'_{\mathrm{CaY}} > 1/C_{\mathrm{Ca}}$ the total potential change for $f = 2$ may be evaluated according to the equation:

$$\Delta E_{0,2} = \frac{RT}{nF}\ln\frac{(C_{\mathrm{Ca}} + C_{\mathrm{Na}}{}^2 \,.\, K_{\mathrm{Na}})(1 + 2r)^2}{K_{\mathrm{Na}}(C_{\mathrm{Na}}{}^2 + 4C_{\mathrm{Na(t)}}^2 \,.\, r^2)},$$

where C_{Na} and $C_{\mathrm{Na(t)}}$ represent the sodium concentration in the sample and in the titrand, respectively, and K_{Na} is the selectivity coefficient.

The most questionable value in this expression is the selectivity coefficient, which for the same electrode may depend on the method of determination and concentration level for which it is calculated. For example, the Orion 92-20 calcium electrode may have a selectivity coefficient for sodium ions ranging from 10^{-4},[21] to 10^{-2},[22] or even 0·45.[23] The manufacturer's value is given as 0·003, whereas for the Orion 92-32 bivalent ion electrode it is 0·015. If the potential change $\Delta E_{0,2}$ has been calculated from the maker's values the correlation between it and the experimental results is rather poor (Fig. 1). Changing those values to approximately 0·01 for the calcium electrode and 0·39 for the bivalent ion electrode gives a great improvement. The same effect is seen in Fig. 2 where titration curves for the selectivity coefficient values indicated have been calculated theoretically. The experimental curve is still above the calculated one, suggesting the coefficient should have a value in the vicinity of 0·01.

Another interesting result is shown in Figs. 3 and 4. The various amounts of sodium in the sample (bivalent ion electrode) and the titrant (calcium electrode) exert a significant effect on the titration curves. The experimental values are in sufficient agreement with the calculated ones, though the differences are sometimes as large as 10 mV. This is to some extent attributable to insufficiently reproducible measurements, this uncertainty

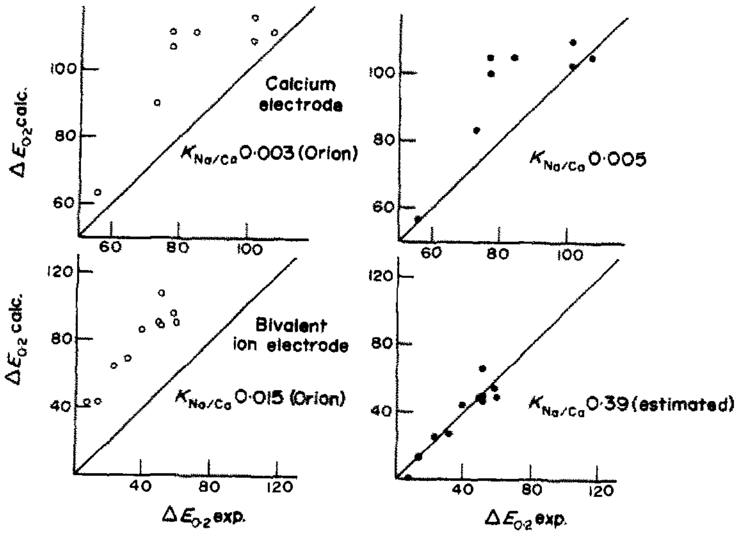

Fig. 1. Comparison of calculated and experimental values of $\Delta E_{0\cdot2}$ for complexometric titrations of calcium using calcium and bivalent ion indicator electrodes.

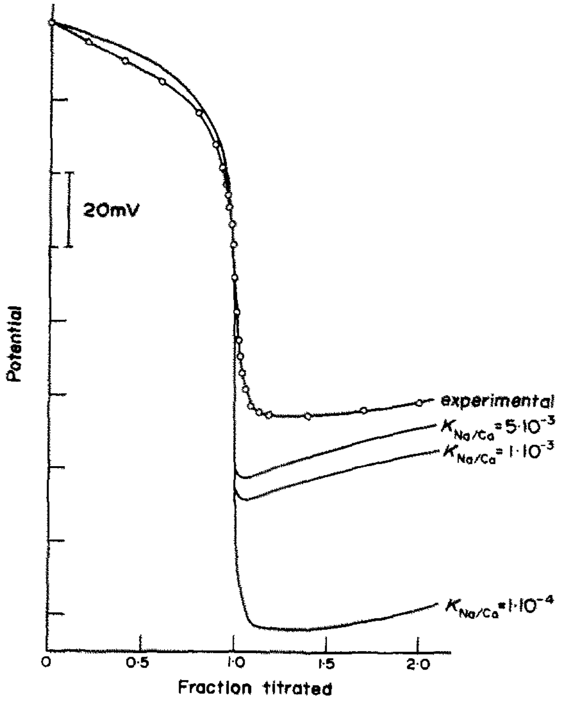

Fig. 2. Calculated for various selectivity coefficients and experimental complexometric titration curves of calcium with calcium indicator electrode.

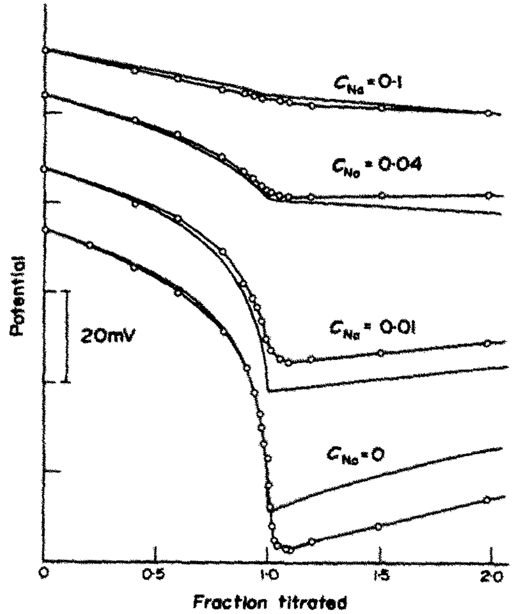

Fig. 3. Effect of various contents of sodium in the sample on the titration curves of calcium with bivalent ion indicator electrode calculated curves for K_{Na} = 0·39 (solid lines), experimental curves at pK 9·5 (lines with points).

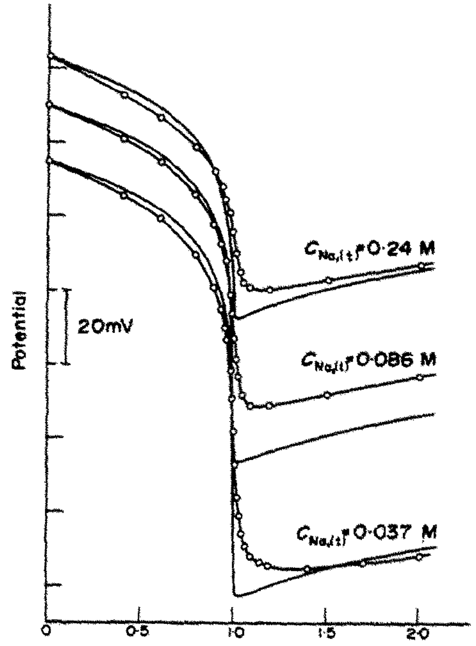

Fig. 4. Effect of various contents of sodium in the titrant on the titration curves of calcium with calcium indicator electrode. Calculated curves for K_{Na} = 0·005 (solid lines) experimental curves (lines with points).

being greater for small calcium concentrations. A very important factor which has not been taken into account is the limit of electrode response. The manufacturer's value for the Ca electrode is $5 \times 10^{-6}M$. Our experiments show a value of $\sim 10^{-5}M$ and the corresponding potential value is approx. −0·11 V. On inspecting all the titration curves we see that in any case the titration curve goes below this value, being determined by the properties of the membrane.

The important conclusion from these experiments and calculations is that a significant discrepancy exists between the theoretical and observed titration curves for calcium and that the calculated curve depends markedly on the selectivity coefficient used.

The equations which describe the potential of the electrode may be used for calculation of the theoretical error. This is understood as the difference between the f-values for which the second derivatives of the theoretical and observed curves have zero value. The results given in Tables 1–4 show that such errors are always much smaller than the real ones. The main factors responsible for this are the accuracy of the Gran method used for end-point determination (an account of distorted symmetry of the titration curve) precision of the potential reading (±0·2 mV) and probably other factors that are not yet fully understood.

All these parameters seriously interfere in the determination of very small concentrations of calcium, *e.g.*, of the order of $10^{-5}M$. Even when the electrode detection limit is

Table 1. Calculated and experimental titration errors for various conditional stabilities of the EDTA complex of calcium

		Titration error, %	
Electrode	log K'_{CaEDTA}	Calculated	Experimental
Ca^{2+}	9·8	−0·04	−0·1
	8·4	−0·08	−0·5
Me^{2+}	9·8	−0·22	−0·8
	8·4	−0·62	−1·4

Table 2. Calculated and experimental titration errors at various initial sample concentrations of calcium and various dilution factors

			Titration error, %	
Electrode	Concentration of calcium M	Dilution factor	Calculated	Experimental
	0·001	0·1	−0·03	0
Ca^{2+}	0·002	0·2	−0·04	−0·1
	0·004	0·4	−0·05	−0·6
	0·001	0·1	−0·20	−1·2
Me^{2+}	0·002	0·2	−0·22	−0·8
	0·004	0·4	−0·24	−1·1

Table 3. Calculated and experimental titration errors at various concentrations of sodium ions in sample

Electrode	C_{Na}, *M*	Titration error, %	
		Calculated	Experimental
Ca^{2+}	0	−0·04	−0·1
	0·001	−0·04	−0·8
	0·01	−0·05	−0·8
	0·1	−0·15	−0·5
Me^{2+}	0	−0·22	−1·4
	0·001	−0·22	−2·2
	0·01	−0·24	−1·9
	0·04	−0·39	−2·9
	0·1	−0·63	(~ −6)

Table 4. Calculated and experimental titration errors at various concentrations of sodium ions in titrant

Electrode	$C_{Na(t)}$, *M*	Titration error, %	
		Calculated	Experimental
Ca^{2+}	0·037	−0·04	−0·1
	0·086	−0·08	−0·2
	0·24	−0·17	+0·7
Me^{2+}	0·037	−0·22	−0·8
	0·086	−0·41	−2·9
	0·24	(+83)	—

sufficiently low the inevitable sodium content (and probably that of other common cations) suppresses the potential change in such a manner that estimation of a sufficiently precise and accurate end-point is impossible.

Final conclusions

On the basis of experiment and theoretical considerations it can be concluded that the end-point in titration of calcium with EDTA may be detected by means of several electrodes. For comparison, titration curves of $10^{-3}M$ solutions under the best conditions are given in Fig. 5. None of the procedures is free from interferences and drawbacks but all can be used when the titrand concentration is not very low. To illustrate this, the results of calcium determinations, with different electrodes, are presented in Table 5, for 0·1-mmole amounts of metal.

Comparison of the analytical characteristics of the electrodes shows without any doubt that the silver electrode gives the best end-point in pure solutions at the lowest concentrations (even below $10^{-5}M$). Its main drawback is the interference of accompanying

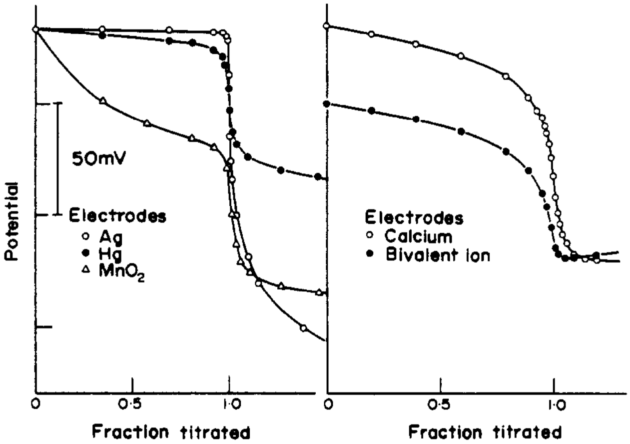

Fig. 5. Titration curves of 0·1 millimole of calcium with various indicator electrodes.

substances. Only in some instances can other ions be masked[9] (*e.g.*, with sulphosalicylate, triethanolamine) and excess of ions precipitating or complexing silver may also interfere.

The mercury electrode seems to be less subject to such interferences, because more masking agents may be used, but the potential change is seriously reduced by the presence of oxygen. This effect is difficult to predict, but the decrease is smaller at lower concentrations, so with some care $10^{-5}M$ calcium may be titrated. Deaeration of solutions is advantageous, but more troublesome in practice.

The main objections to the manganese dioxide electrode are the slow reaction rate and the still unknown reactions of the Mn(II) complex, especially after the end-point.

The ion-exchange electrodes present quite a different problems. The factors which play a decisive role in determining the potential change during titration are the selectivity of the electrode and the response limit.

The first of these factors is the most important for bivalent ion electrode, the second for calcium electrodes. The selectivity of the electrode permits in general the use of various masking agents, but the danger exists of introducing along with them other interfering ions, especially sodium ions. When the limit of detection with the electrode is as high as for the calcium electrode ($5 \times 10^{-6}M$[16]) it is not possible to titrate concentrations below $10^{-4}M$. In this respect the copper membrane electrode, which was not investigated in this study, probably presents many advantages.[24,25]

This study was mainly devoted to the electrode effect in titration with EDTA, which is not the most convenient titrant. The advantages of other complexing substances are

Table 5. Comparison of results of calcium determination by complexometric titration with various indicator electrodes

Electrode	Ag	Hg	MnO$_2$	Ca^{2+}	Me^{2+}
Amount of Ca^{2+} found, *mmole*	0·0955 0·0956	0·0957 0·0954	0·0957 0·0955 0·0953 0·0954	0·0554 0·0953 0·0950 0·0955	0·0942 0·0947 0·0945 0·0944

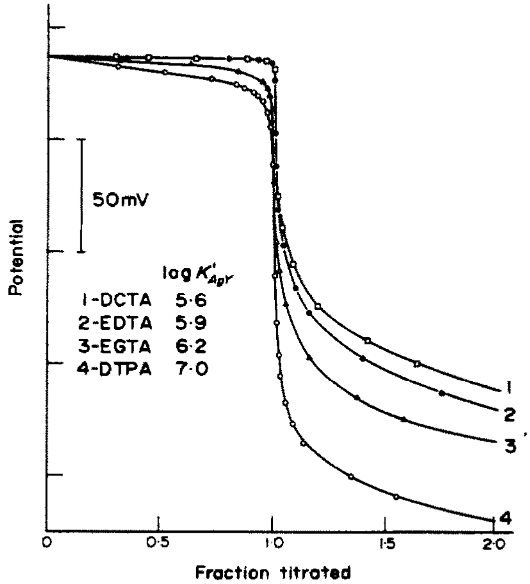

Fig. 6. Titration curves of calcium with various complexones using the silver indicator electrode: pH = 9·2; half-saturated borax buffer, $C_{Ag} = 10^{-6}$ M.

shown in Fig. 6, which shows DTPA as the best, the potential jump being nearly 50% greater than for EDTA. Nevertheless this effect of increased stability cannot be fully exploited with membrane electrodes.

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Zusammenfassung—Bei komplexometrischen Titrationen kann man zur Überwachung des Titrationsverlaufs und zur Bestimmung des Endpunktes verschiedene Indikatorelektroden verwenden. Mehrere davon, darunter die Silber- und Quecksilberelektrode, Membranelektroden mit zweiwertigen Kationen und Calcium und die Mangandioxidelektrode wurden untersucht und in ihrer Nützlichkeit verglichen. Als Titrant wurde meistens EDTA verwendet, aber es wurden auch Meßergebnisse mit ähnlichen chelatbildenden Titranten erhalten. Der praktische Nutzen der Elektroden bei Titrationen hängt ab von ihrer Selektivität, der Höhe des Sprungs am Endpunkt und der Genauigkeit bei der Endpunktsbestimmung. Bei den untersuchten Elektroden entsprechen sich in einigen Fällen die theoretischen und die experimentellen Titrationskurven gut, aber nicht immer ist es möglich, das Ansprechen der Elektrode im niedrigen Aktivitätsbereich vorherzusagen. In anderen Fällen bedeutet eine schlechte Entsprechung nicht, daß keine ausreichend guten analytischen Ergebnisse erhalten werden könnten.

Résumé—Dans les titrages complexométriques on peut utiliser diverses électrodes indicatrices pour contrôler la marche du titrage et pour déceler le point final. Plusieurs d'entre elles, comprenant les électrodes à argent, à mercure, à membrane de cation bivalent, à membrane de calcium et à bioxyde de manganèse ont été étudiées et comparées dans leur utilité. En tant qu'agent de titrage, on a principalement utilisé l'EDTA, mais on a aussi obtenu des résultats avec des agents de titrage chélatants similaires. L'utilité pratique des électrodes dans les titrages dépend de leur sélectivité, de la grandeur de la brisure du point final et de la précision dans la détermination du point final. Pour les électrodes étudiées, il a dans quelques cas une bonne corrélation entre les courbes de titrage théoriques et expérimentales, mais il n'est pas toujours possible de prédire la réponse d'électrode dans le domains de faible activité. Dans d'autres cas, une médiocre corrélation ne signifie pas que des résultats analytiques sensiblement bons ne peuvent être obtenus.

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COMPARATIVE STUDY OF TITANIUM(IV)-BASED EXCHANGERS IN AQUEOUS AND MIXED SOLVENT SYSTEMS

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Summary—The antimonate, arsenate, tungstate, molybdate and selenite of titanium have been synthesized. Their composition and chemical and thermal stability have been determined. Effects of pH and temperature on ion-exchange capacity have been studied. Titanium antimonate was found to be the most stable. The utility of these ion-exchangers for analytical separations was examined by determining the distribution coefficients for 26 metal ions in some aqueous, non-aqueous and mixed solvent systems. Quantitative separations of Hg–Cd, Pb–Cu and Pb–Zn have been achieved on titanium tungstate columns, and La–Ba mixtures have been separated on a titanium arsenate column.

Since the classical work of Amphlett,[1] numerous synthetic inorganic ion-exchangers have been synthesized and their properties studied. However, the methods of preparation of the same ion-exchanger by different workers are not always the same. It has been shown that selectivity of an inorganic ion-exchanger depends not only upon its composition but also upon the pH at which the precipitation is performed. It is important that the various ion-exchangers should be synthesized again under the same conditions and their properties studied. Szirtes[2] made an interesting study of the phosphates of titanium, zirconium and chromium and compared their ion-exchange properties. A comparative study of the chromium(III) salts has been made in our laboratory.[3] We have therefore decided to investigate the various insoluble compounds of titanium.[4–8] We have chosen to compare those samples of the particular exchanger which are reported to be the most stable.

Another limitation in the earlier studies on inorganic ion-exchangers was the selection of eluents. Almost all were aqueous solutions of simple salts. The possibilities of enhancing and reversing selectivities of ion-exchangers by addition or exclusive use of organic solvents is receiving increased attention. The nature of the solvent affects the solubility, dissociation and solvation of the solutes and the behaviour of the ion-exchanger. Many separations have been improved by addition of organic solvents.[9,10] We have therefore extended the investigation of the analytical properties of these ion-exchangers to mixed solvent systems and to less common aqueous systems.

EXPERIMENTAL

Reagents

Titanium(IV) chloride (15% w/v solution), antimony pentachloride (density 2·3 g/ml), sodium tungstate, sodium arsenate and sodium selenite were used. Reagents used were analytical-reagent grade whenever possible. In the determination of K_d values either chlorides or nitrates of the cations were used with the exception of vanadyl sulphate.

Table 1. Conditions for the synthesis of some titanium-based exchangers

Exchanger	Concentration of Ti(IV), *M*	Concentration of anionic, species *M*	Mixing ratio Ti : A*	pH
Titanium tungstate	0·30	0·30	1 : 1	1
Titanium antimonate	0·10	0·10	1 : 1	2
Titanium arsenate	0·05	0·05	1 : 1	2
Titanium selenite	0·05	0·05	1 : 2	2
Titanium molybdate	0·025	0·025	2 : 1	2

* A = anionic species

Preparation of the samples

Five samples were prepared by mixing the solution of titanium(IV) chloride with the sodium tungstate, sodium arsenate, sodium selenite, sodium molybdate or antimony pentachloride solutions; the conditions are given in Table 1. In the case of titanium antimonate the pH was adjusted with ammonia. The precipitates were allowed to stand for 24 hr at room temperature and then washed with distilled water by decantation, filtered off and dried at 40°. Only the titanium tungstate was dried at 80°. The dry product broke down into small particles when immersed in water. It was converted into the hydrogen form by treatment with 2*M* nitric acid and finally washed with demineralized water. All the samples were again dried at 40° except titanium tungstate which was dried at 80°.

The chemical composition of these ion-exchange materials was determined as described in earlier papers.[4-7]

Chemical stability

A 0·5-g portion of the exchanger was shaken in a flask with 50 ml of the solution concerned, in a temperature-controlled shaker for 6 hr until equilibrium was reached. The undissolved portion of the exchanger was removed by filtration. Titanium, antimony, tungsten, arsenic, selenium and molybdenum were determined in the filtrate spectrophotometrically by the hydrogen peroxide,[11] Rhodamine B,[12] ammonium thiocyanate,[13] molybdenum blue,[14] diaminobenzidene[15] and ammonium thiocyanate[16] methods respectively (Fig. 1).

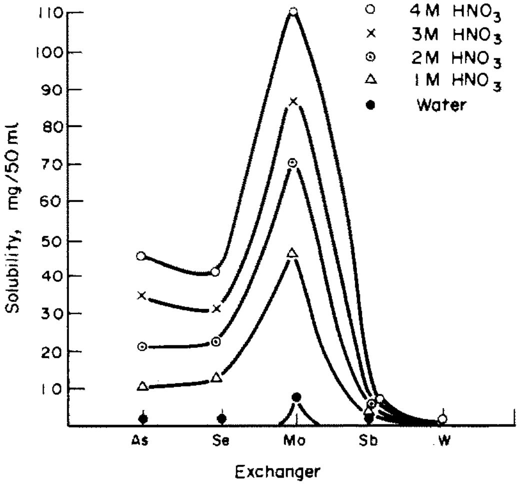

Fig. 1. Solubility of Ti(IV)-based exchangers.

Table 2. Ion-exchange capacities and composition of same titanium-based exchangers

Exchanger	Ion-exchange capacity *meq/g*	Reported capacity *meq/g*	Composition	Reported composition
Titanium tungstate	0·58	0·82	1 : 1·1	1 : 1·1
Titanium arsenate	0·99	0·93	1 : 1·8	1 : 2
Titanium antimonate	0·77	0·71	1 : 1·4	1 : 1·4
Titanium selenite	0·58	0·78	1 : 1·2	1 : 1·35
Titanium molybdate	1·08	1·05	—	—

RESULTS

Ion-exchange properties

The ion-exchange capacity, determined by the standard method,[17] is given in Table 2. It was also determined at different pH values by the batch method. The results are plotted in Fig. 2. All the samples were heated at different specified temperatures for 2 hr and the ion-exchange capacity was determined in each case. The results are shown in Fig. 3.

Distribution studies

Distribution coefficients of 26 metal ions in water, nitric acid of different concentrations, 0·1*M* ammonium nitrate, 0·1*M* formic acid, and some acetone–nitric acid mixtures were determined. For this purpose 0·5 g of the exchanger was shaken with 50 ml of the

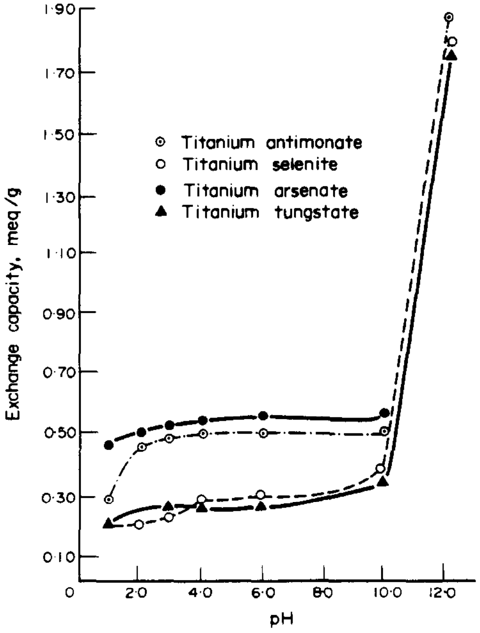

Fig. 2. Ion-exchange capacity as a function of pH.

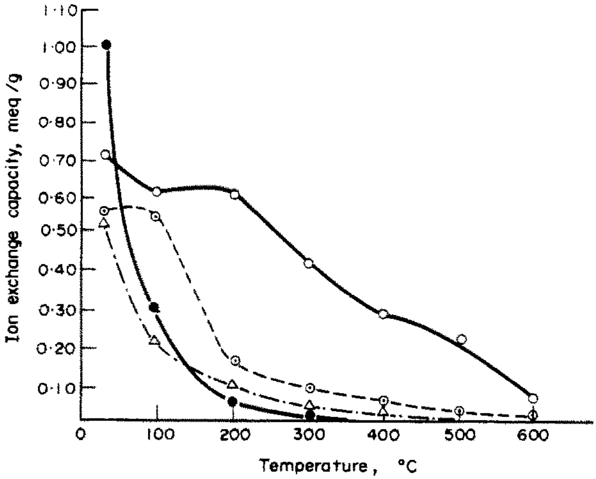

Fig. 3. Ion-exchange capacity as a function of temperature.

—●— Titanium arsenate
—○— Titanium antimonate
—⊙— Titanium tungstate
—▲— Titanium selenite

Table 3. Distribution coefficients (values given are $K_d \times 10^{-2}$) of metal ions on titanium antimonate in acetone and acetone–nitric acid systems

Cation \ Solvent system	Acetone	Acetone + 0·1*M* HNO_3 (9 : 1)	Acetone + 0·1*M* HNO_3 (1 : 1)	Acetone + 0·1*M* HNO_3 (1 : 9)	Acetone + 4*M* HNO_3 (1 : 1)
Mg(II)	0·79	1·0	1·6	N.A.	N.A.
Al(III)	40	10	79	3·2	32
Ca(II)	4·0	6·3	79	0·08	N.A.
V(V)	40	3·6	10	5·0	20
Mn(II)	4·0	3·2	2·5	1·6	N.A.
Fe(III)	0·8	3·2	4·0	2·0	1·3
Co(II)	25	2·5	6·3	1·3	1·6
Ni(II)	6·3	0·40	3·2	1·3	0·40
Cu(II)	10	2·0	6·3	1·3	0·50
Zn(II)	2·5	1·0	6·3	0·25	N.A.
Ga(III)	7·9	5·0	5·0	3·2	0·50
Sr(II)	40	1·0	2·5	N.A.	N.A.
Y(III)	32	C.A.	1·6	10	N.A.
Zr(IV)	13	C.A.	6·3	10	3·2
Cd(II)	40	1·3	3·2	1·0	N.A.
In(III)	3·2	3·2	6·3	2·5	0·25
Ba(II)	C.A.	1·6	10	0·30	N.A.
La(III)	C.A.	32	40	16	N.A.
Ce(IV)	C.A.	13	20	63	N.A.
Pr(III)	C.A.	C.A.	40	C.A.	20
Nd(III)	C.A.	C.A.	50	C.A.	20
Sm(III)	C.A.	C.A.	20	C.A.	20
Hf(IV)	4.0	C.A.	79	C.A.	2·5
Hg(II)	6·3	0·63	2·5	1·6	1·0
Pb(II)	40	13	10	6·3	1·0
Th(IV)	40	C.A.	25	C.A.	3·2

C.A. = Complete adsorption.
N.A. = Negligible adsorption.

solution for 6 hr. The amount of cation in solution was estimated by EDTA titration and the K_d values were calculated from the expression

$$K_d = \frac{I - F}{F} \times \frac{50}{0{\cdot}5},$$

where I is the volume of EDTA consumed by the original solution and F is the volume of EDTA consumed after equilibrium.

Solutions of each cation were prepared in demineralized water for the determination of K_d values in all the systems studied. The loading of the cation was less than 3% of the ion-exchange capacity of the ion-exchanger. The results are given in Tables 3–7.

Separations

Separations of Cd(II) from Hg(II), Ba(II) from La(III), Zn(II) from Pb(II) and Cu(II) from Pb(II) have been achieved on the basis of the K_d values. The elution curves for the separations achieved are given in Figs. 4 and 5.

Table 4. Distribution coefficients ($K_d \times 10^{-2}$) of metal ions on titanium antimonate

Solvent system / Cation	Water	0·01*M* HNO_3	0·1*M* HNO_3	0·1*M* NH_4NO_3	0·1*M* HCOOH
Mg(II)	10	0·10	N.A.	N.A.	5·0
Al(III)	40	10	N.A.	0·13	C.A.
Ca(II)	1·3	0·32	0·10	0·63	C.A.
V(V)	31	0·32	N.A.	1·6	C.A.
Mn(II)	40	N.A.	N.A.	0·50	16
Fe(III)	20	1·0	N.A.	1·6	5·0
Co(II)	16	0·10	N.A.	1·3	C.A.
Ni(II)	40	0·10	N.A.	1·0	C.A.
Cu(II)	13	0·40	N.A.	0·8	63
Zn(II)	2·5	0·03	N.A.	2·5	C.A.
Ga(III)	0·32	1·0	0·3	4·0	C.A.
Sr(II)	40	0·03	0·13	2·5	C.A.
Y(III)	C.A.	1·0	0·40	2·5	C.A.
Zr(IV)	C.A.	C.A.	C.A.	C.A.	C.A.
Cd(II)	32	1·0	0·10	2·5	C.A.
In(III)	10	1·3	N.A.	8·0	3·2
Ba(II)	13	0·40	1·0	5·0	C.A.
La(III)	C.A.	16	16	6·3	10
Ce(IV)	C.A.	13	1·3	C.A.	C.A.
Pr(III)	C.A.	6·3	1·3	16	C.A.
Nd(III)	C.A.	1·3	16	16	C.A.
Sm(III)	C.A.	13	1·3	16	100
Hf(IV)	C.A.	C.A.	C.A.	C.A.	C.A.
Hg(II)	10	63	0·80	16	C.A.
Pb(II)	10	40	1·0	20	C.A.
Th(IV)	C.A.	C.A.	C.A.	C.A.	C.A.

C.A. = Complete adsorption.
N.A. = Negligible adsorption.

Table 5. Distribution coefficients ($K_d \times 10^{-2}$) of metal ions on titanium arsenate

Solvent system / Cation	Water	0·01M HNO_3	0·1M HNO_3	0·1M NH_4NO_3	0·1M HCOOH	Acetone + 0·1M HNO_3 (9 : 1)
Mg(II)	0·15	N.A.	N.A.	0·02	N.A.	N.A.
Al(III)	0·32	0·32	N.A.	0·02	0·63	1·0
Ca(II)	0·39	N.A.	N.A.	0·02	N.A.	N.A.
V(II)	0·63	N.A.	N.A.	0·12	N.A.	40
Mn(II)	0·32	N.A.	N.A.	0·05	N.A.	0·39
Fe(III)	100	N.A.	N.A.	0·25	7·9	2·5
Co(II)	0·70	N.A.	N.A.	0·03	0·10	0·39
Ni(II)	10	N.A.	N.A.	0·03	0·10	0·06
Cu(II)	0·25	N.A.	N.A.	0·03	N.A.	0·39
Zn(II)	1·0	N.A.	N.A.	0·03	3·0	N.A.
Ga(III)	6·3	N.A.	N.A.	0·03	2·5	0·08
Sr(II)	1·3	N.A.	N.A.	0·03	N.A.	0·03
Y(III)	7·9	N.A.	N.A.	0·10	1·3	1·3
Zr(IV)	6·3	0·32	N.A.	2·0	10	N.A.
Cd(II)	6·3	N.A.	N.A.	0·10	3·2	N.A.
In(III)	2·5	N.A.	N.A.	0·15	N.A.	N.A.
Ba(II)	1·6	N.A.	N.A.	0·03	0·32	1·6
La(III)	100	0·20	N.A.	0·63	3·2	N.A.
Ce(IV)	100	0·32	N.A.	4·0	13	10
Pr(III)	3·2	N.A.	N.A.	0·03	2·0	1·3
Nd(III)	6·3	0·20	N.A.	1·6	6·3	1·3
Sm(III)	100	7·9	N.A.	3·0	0·60	0·39
Hf(IV)	7·9	0·63	0·50	C.A.	5·0	1·3
Hg(II)	5·0	1·6	N.A.	7·9	10	3·2
Pb(II)	63	1·6	N.A.	100	20	63
Th(IV)	10	5·0	N.A.	7·9	32	1·3

C.A. = Complete adsorption.
N.A. = Negligible adsorption.

DISCUSSION

A comparison of the chemical stability of the various ion-exchangers is given in Fig. 1. It is apparent that titanium molybdate is the least stable and titanium tungstate is the most stable. It is clear from Fig. 2 that titanium arsenate has the highest ion-exchange capacity and therefore if we are interested in exchangers of high capacity we should choose the arsenates.

Most inorganic ion-exchangers usually exhibit high thermal stability and it is worthwhile to compare their performance after treatment at high temperatures. It follows from Fig. 3 that titanium antimonate has the highest thermal stability. Even after heating to 500° it shows sufficient exchange capacity and therefore can still be used as an ion-exchanger. Other materials exhibit only a negligible exchange capacity after heating to this temperature.

It can be inferred from Fig. 2 that in almost all cases pH does not affect ion-exchange capacity significantly if it is below pH 10. However a sharp increase in exchange capacity is observed as the pH is raised above 10. This is probably due to the hydrolysis of the exchange materials at higher pH values. The ion-exchangers based on titanium behave like weakly acidic cation-exchangers, which differs from the findings of

Table 6. Distribution coefficients ($K_d \times 10^{-2}$) of metal ions on titanium tungstate

Cations \ Solvent system	Water	0·01M $\mathrm{HNO_3}$	0·1M $\mathrm{HNO_3}$	0·1M $\mathrm{NH_4NO_3}$	0·1M HCOOH	Acetone + 0·1M $\mathrm{HNO_3}$ (9 : 1)
Mg(II)	1·6	N.A.	N.A.	0·16	N.A.	N.A.
Al(III)	0·32	0·10	N.A.	0·16	63	N.A.
Ca(II)	1·6	0·04	N.A.	0·16	N.A.	N.A.
V(V)	0·25	N.A.	N.A.	0·50	N.A.	0·39
Mn(II)	5·0	0·25	N.A.	0·16	N.A.	N.A.
Fe(III)	N.A.	N.A.	N.A.	0·16	2·0	6·3
Co(II)	1·0	7·9	N.A.	0·16	0·16	0·10
Ni(II)	10	N.A.	N.A.	0·16	0·16	7·9
Cu(II)	1·3	N.A.	N.A.	0·16	0·16	0·12
Zn(II)	5·0	0·25	N.A.	0·16	0·20	N.A.
Ga(III)	0·63	N.A.	N.A.	0·16	3·2	0·50
Sr(II)	13	0·12	N.A.	0·16	0·16	0·50
Y(III)	0·63	N.A.	N.A.	0·10	0·63	1·0
Zr(IV)	10	1·3	N.A.	0·16	0·40	7·9
Cd(II)	7·9	3·2	N.A.	0·16	N.A.	N.A.
In(III)	N.A.	N.A.	N.A.	0·79	N.A.	N.A.
Ba(II)	7·9	N.A.	N.A.	0·16	N.A.	0·31
La(III)	0·25	N.A.	N.A.	0·63	0·20	16·0
Ce(III)	0·05	N.A.	N.A.	0·16	0·25	N.A.
Pr(III)	0·10	N.A.	N.A.	0·16	0·10	N.A.
Nd(III)	0·25	N.A.	N.A.	0·25	4·0	0·31
Sm(III)	6·3	N.A.	N.A.	0·16	0·12	0·1
Hf(IV)	5·0	0·32	N.A.	6·3	7·9	3·2
Hg(II)	32	0·10	N.A.	79	2·0	3·2
Pb(II)	25	0·10	N.A.	16	6·3	4·0
Th(IV)	0·12	0·25	N.A.	1·0	0·32	0·15

N.A. = Negligible adsorption.

Szirtes and co-workers.[2] Phosphates of zirconium, titanium and chromium show a moderately strong-acid behaviour.

A comparison of the K_d values of metal ions on these exchangers in demineralized water shows some outstanding features. Thus the antimonate has the highest ion uptake of the four exchange materials studied. This may be due to the fact that amorphous antimony oxide has the largest number of free exchange sites available for the metal ions to be adsorbed. Therefore the antimonates can be of use only at low pH values, where the ion uptake can be distinguished between various ions. The tungstate, arsenate and selenite on the other hand show high selectivities even in neutral medium. In the case of the tungstate the K_d values vary from $3{\cdot}3 \times 10^3$ for Hg(II) to zero for In(III) and Fe(III). This is a characteristic feature of titanium tungstate because all the other exchangers have a very high affinity for Fe(III). In the case of the arsenate the highest K_d value is for Pb(II) which shows high K_d values on almost all the exchangers. The lanthanides have the lowest K_d values on titanium tungstate, their highest K_d values being for titanium antimonate as expected.

The study of the effect of hydrogen ion concentration on the K_d values reveals that when the hydrogen ion concentration is raised from $10^{-7}M$ to $10^{-2}M$ most of the metal

Table 7. Distribution coefficients ($K_d \times 10^{-2}$) of metal ions on titanium selenite

Cation \ Solvent system	Water	0·01*M* HNO_3	0·1*M* HNO_3	0·1*M* NH_4NO_3	0·1*M* HCOOH	Acetone + 0·1*M* HNO_3 (9 : 1)
Mg(II)	0·63	N.A.	N.A.	0·02	N.A.	N.A.
Al(III)	1·0	0·10	N.A.	0·02	N.A.	0·10
Ca(II)	0·50	0·10	N.A.	0·02	N.A.	10
V(V)	0·50	N.A.	N.A.	7·9	1·0	1·0
Mn(II)	1·0	N.A.	N.A.	0·02	N.A.	0·19
Fe(III)	1·0	N.A.	N.A.	0·10	3.2	6·3
Co(II)	0·31	N.A.	N.A.	0·02	N.A.	N.A.
Ni(II)	1·0	N.A.	N.A.	0·02	N.A.	0·25
Cu(II)	10	0·10	N.A.	0·12	N.A.	1·0
Zn(II)	1·0	N.A.	N.A.	0·02	0·31	N.A.
Ga(III)	3·2	N.A.	N.A.	1·0	1·0	2·5
Sr(II)	6·3	10	N.A.	0·02	N.A.	0·04
Y(III)	1·0	0·10	0·10	0·12	1·0	1·6
Zr(IV)	6·3	0·12	N.A.	0·03	1·0	10
Cd(II)	2·5	N.A.	N.A.	1·0	0·12	0·79
In(III)	1·0	0·03	N.A.	0·15	3·2	1·6
Ba(II)	4·0	N.A.	N.A.	1·0	0·19	2·5
La(III)	7·9	N.A.	N.A.	0·08	0·31	0·39
Ce(IV)	7·9	N.A.	0·15	0·25	3·2	0·06
Pr(III)	7·9	N.A.	0·19	0·10	1·0	0·12
Nd(III)	10	N.A.	N.A.	0·08	0·25	0·19
Sm(III)	7·9	N.A.	N.A.	0·25	0·25	0·12
Hf(IV)	C.A.	0·50	0·19	0·03	1·0	C.A.
Hg(II)	0·12	0·12	N.A.	3·2	10	3·2
Pb(II)	10	0·79	1·0	7·9	1·6	10
Th(IV)	C.A.	0·06	N.A.	10	7·9	1·0

C.A. = Complete adsorption.
N.A. = Negligible adsorption.

ions show negligible adsorption on all the exchangers except titanium antimonate, which behaves peculiarly. At this hydrogen ion concentration most of the metal ions show very high uptake on titanium antimonate. Therefore the behaviour of metal ions at high concentrations of acid has also been studied in the case of titanium antimonate. At pH 2, Al(III), Zr(IV), Hf(IV), Th(IV), La(III), Ce(IV) and Sm(III) have K_d values of more than 10^3. This behaviour makes the titanium antimonate a promising cation-exchanger for some interesting separations. Thus Al(III) can be separated from Ga(III), In(III), Zn(II), Mg(II), Fe(III), Co(II), Ni(II) and Mn(II).

Two important separations which may be achieved on titanium tungstate in 0·01*M* nitric acid are Cd(II) from numerous metal ions, including Zn(II) and Zr(IV) from numerous metal ions, including Hf(IV).

Zr(IV) can also be separated from Hf(IV) on titanium tungstate in 0·1*M* ammonium nitrate.

A comparison of the K_d values on titanium antimonate in acetone and acetone–nitric acid media is very interesting. If we replace pure acetone by a solution which is 50% in acetone and 0·05*M* in nitric acid then there is very little difference between the K_d values in the two systems for almost all the metal ions, except Ba, La, Ce, Pr, Nd and Sm, which have exceptionally high values. On the other hand if the nitric acid

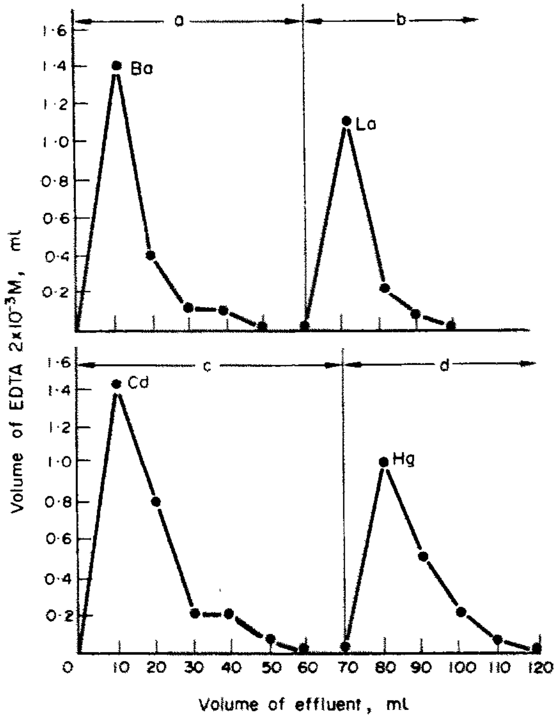

Fig. 4. Separation of Ba(II) from La(III) on titanium arsenate and Cd(II) from Hg(II) on titanium tungstate columns. *a*, Acetone + 0·1*M* HNO_3 (9 : 1); *b*, 2*M* HNO_3 ; *c*, 0·1*M* NH_4NO_3 ; *d*, 1*M* HNO_3.

concentration is increased from 0·05*M* to 2*M* then a significant difference is observed which shows a possibility of a number of important separations. The 26 metal ions may be conveniently divided into two groups.

(1) Those which have almost zero K_d values, *i.e.*, Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Mn(II), Y(III), Ce(IV) and La(III).

(2) The rest, which have very high K_d values.

Thus it is obvious from this classification that one of the ions in the first group can be separated from any one or a group of ions in the second group, *e.g.*, Hg(II) from Cd(II), Zr(II), Ba(II), Sr(II), Mg(II) and Mn(II); Ce(IV) or La(III) from Zr(IV), Hf(IV), Th(IV), Pr(III), Nd(III) and Sm(III).

A comparison of the acetone +0·1*M* nitric acid systems (1 : 9 and 9 : 1 ratios) shows that there is not much difference in the K_d values for most ions except Mg(II), Ca(II), Ce(IV) Sr(II) and Ba(II). However, the selectivity sequence is altered for the group Mg(II), Ca(II), Sr(II) and Ba(II). Thus in water we have Sr > Ba > Mg > Ca and in the acetone–nitric acid systems (1 : 9) and (9 : 1) the sequences are Ba > Ca > Sr = Mg and Ca > Ba > Sr = Mg respectively.

Various factors such as swelling, formation of complexes, nature of the chemical bond and solvent distribution may be responsible for this behaviour of the ion-exchanger. It is also apparent from Table 3 that on changing the composition of the aqueous acetone

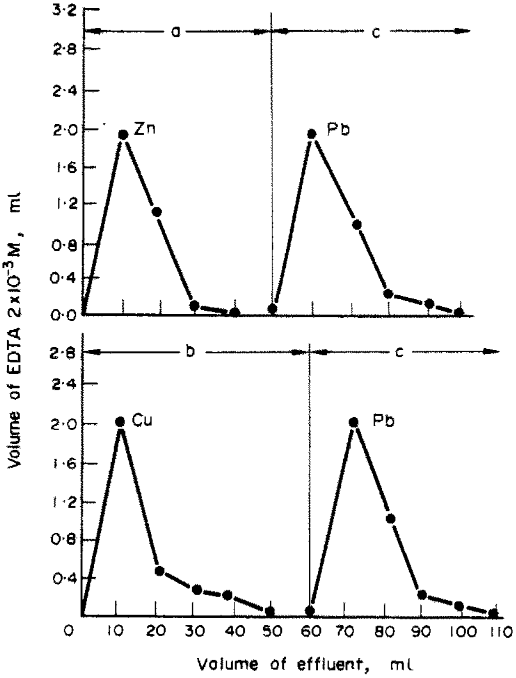

Fig. 5. Separation of Zn(II) from Pb(II) and Cu(II) from Pb(II) on titanium tungstate columns. *a*, Acetone + 0·1*M* HNO_3; *b*, 0·1*M* formic acid; *c*, 0·1*M* HNO_3.

media the preference of the ion-exchanger for various cations changes, hence enhancing the selectivity. It is also interesting to note (Tables 8 and 9) that the separation factor is generally higher in the mixed solvent media (aqueous and non-aqueous) than in purely aqueous or non-aqueous media. As with organic ion-exchangers, the pores of inorganic ion-exchangers may play a significant role in exchanging ions. That is to say they can accumulate water in their pores, and this is accompanied by electrolytic sorption. Thus by change of the solvent system a new separation may become possible.

Table 8. Separation factors (α) for Pb–Cu and Pb–Zn in various solvent systems

Solvent	Titanium arsenate		Titanium tungstate		Titanium selenite		Titanium antimonate	
	α_{Cu}^{Pb}	α_{Zn}^{Pb}	α_{Cu}^{Pb}	α_{Zn}^{Pb}	α_{Cu}^{Pb}	α_{Zn}^{Pb}	α_{Cu}^{Pb}	α_{Zn}^{Pb}
Water	83	31	16	4	> 1	13	> 1	20
0·01*M* HNO_3	20	316	1	1	8	8	79	316
0·1*M* HNO_3	> 1	> 1	> 1	> 1	10	10	10	10
0·1*M* HNO_3 + acetone (1 : 9)	251	84	40	30	100	10	4	12
0·1*M* HNO_3 + acetone (9 : 1)	—	—	—	—	—	—	5	21
0·1*M* HNO_3 + acetone (1 : 1)	—	—	—	—	—	—	> 1	> 1
4*M* HNO_3 + acetone (1 : 1)	—	—	—	—	—	—	33	10
Acetone	—	—	—	—	—	—	158	6
0·1*M* Formic acid	126	42	63	> 2	16	5	2	1
0·1*M* NH_4NO_3	63	63	100	100	100	100	> 1	4

Table 9. Separation factors (α) for Hg–Cd and La–Ba in various solvent systems

Solvent	Titanium arsenate		Titanium tungstate		Titanium selenite		Titanium antimonate	
	α^{Hg}_{Cd}	α^{La}_{Ba}	α^{Hg}_{Cd}	α^{La}_{Ba}	α^{Hg}_{Cd}	α^{La}_{Ba}	α^{Hg}_{Cd}	α^{La}_{Ba}
Water	32	16	32	66	4	8	3	71
0·01*M* HNO_3	60	< 1	32	1	1	2	63	25
0·1*M* HNO_3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
0·1*M* HNO_3 + acetone (1 : 9)	19	16	19	52	2	8	> 1	32
0·1*M* HNO_3 + acetone (9 : 1)	—	—	—	—	—	—	4	52
0·1*M* HNO_3 + acetone (1 : 1)	—	—	—	—	—	—	> 1	8
4*M* HNO_3 + acetone (1 : 1)	—	—	—	—	—	—	10	1
Acetone	—	—	—	—	—	—	5	1
0·1*M* Formic acid	> 1	21	1000	6	4	6	1	1
0·1*M* NH_4NO_3	32	6	32	3	62	> 1	3	> 1

The following conclusions can be drawn if we compare the distribution coefficients of metal ions on titanium antimonate in water and pure acetone.

1. There is almost no change in the K_d values for Zn(II), Sr(II), Cd(II), La(III), Ce(IV), Pr(III), Nd(III), Sm(III), Pb(II), V(V) and Al(III) in the two systems.
2. K_d values are higher in acetone than in water for Ga(III), Ba(II) and Ca(II), Co(II).
3. K_d values are higher in water for Mn(II), Fe(III), Ni(II), Cu(II), Y(III), Zr(IV), Hf(IV), Th(IV), In(III), Hg(II) and Mg(II).

The decrease in K_d values for a large number of metal ions in acetone media may be attributed to the fact that the mobilities of the counter ions in the exchanger are usually not as great as in aqueous systems because of the decreased dissociation.[18] Also

Table 10. Possible separation on titanium-based exchangers

Exchanger	Solvent system		
	0·1*M* HNO_3	0·1*M* NH_4NO_3	0·1*M* HCOOH
Titanium antimonate	Mg–Ba; Zn-Hg; Ga–Al,In; Pb–Cu,Fe,Mn,Co,Ni,V,Zn,Mg	Mg–Zn,Sr,Cd,Pb, Al,In,Ga,V, rare earths	—
Titanium arsenate	—	Zn–Hg,La,Zr,Ce,Hf; Al–Hg; Pb–Ga; Pb–Mn,Mg,Ca,Ba	Ca–La,Ba,Hg; Mg–Al; In–Ga; V–Pb; Mn–Pb; Cu–Fe; Hg–V,Mn
Titanium Selenite	Hf–La,Zr,Th,Nd, Sm; Pr–Nd,Sm,La; Fe–Cu,Co,Ni,In; Al–Hg	Ba–Ca,Mg,Sr; Zn–Cd,Hg; Pb–Ni,Co,Mn; Al–Ga; V–Ni,Co	Ba–Mg–Ca,Sr; Al–In,Ga Fe–In
Titanium tungstate	—	V–Mn; Hg–Cd,Al, Cu,Ga,Fe,Co,Ni; Pb–Cd,Al,Ga,Fe, Cu,Co,Ni	Zn–Mg,Ba,Sr; Ca–Cd; Fe–Cu,Co,Ni,Mn,In; In–Ga,Al

the swelling is insignificant and the particle diffusion is relatively slow. The higher ion uptake for Ga(III), Ba(II), Co(II) and Ca(II) in acetone may be due to ion-pair formation with anions in acetone.

Ammonium nitrate solution (0·1*M*) is especially useful because in this solvent system large differences in K_d values are observed for similar ions. Thus, Sm, Nd and Pr can be separated on titanium arsenate columns. The difficult separation of Zr(IV) and Hf(IV) can be achieved on titanium tungstate columns. A number of possibilities exist for difficult analytical separations, which are summarized in Table 10.

On the basis of the separation factors (Tables 8 and 9) four new quantitative separations have been achieved, with titanium tungstate and titanium arsenate columns. Figures 4 and 5 illustrate the elution curves.

Acknowledgement—The authors are grateful to Prof. W. Rahman for providing research facilities.

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Zusammenfassung—Antimonat, Arsenat, Wolframat, Molybdat und Selenit von Titan wurden hergestellt. Ihre Zusammensetzung und ihre chemische und thermische Stabilität wurden ermittelt sowie der Einfluß von pH und Temperatur auf die Austauschkapazität untersucht. Es stellte sich heraus, daß Titanantimonat thermisch am stabilisten war. Der Nutzen dieser Ionenaustauscher für analytische Trennungen wurde durch Bestimmung der Verteilungskoeffizienten für 26 Metallionen in einigen wäßrigen, nichtwäßrigen und gemischten Lösungsmittelsystemen überprüft. Quantitative Trennungen von Hg–Cd, Pb–Cu und Pb–Zn wurden auf Titanwolframatsäulen erzielt; La-Ba-Gemische wurden auf einer Titanarsenatsäule getrennt.

Résumé—On a synthétisé les antimoniate, arséniate, tungstate, molybdate et sélénite de titane. On a déterminé leur composition et leur stabilité chimique et thermique. On a étudié les influences du pH et de la température sur la capacité d'échange d'ions. On a trouvé que l'antimoniate de titane est le plus stable thermiquement. On a examiné l'utilité de ces échangeurs d'ions pour des séparations analytiques en déterminant les coefficients de partage pour 26 ions métalliques dans quelques systèmes aqueux, non aqueux et mélanges de solvants. On a réalisé des séparations quantitatives de Hg–Cd, Pb–Cu et Pb–Zn sur des colonnes de tungstate de titane, et on a séparé des mélanges La–Ba sur une colonne d'arséniate de titane.

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OXIDATIVE COULOMETRIC TRACE DETERMINATION OF SULPHUR IN HYDROCARBONS

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Summary—A new combustion system for the oxidative coulometric determination of sulphur in liquid hydrocarbons is described. The conditions were selected so that the recovery as SO_2 was close to 100%. The relative standard deviation was <1% for sulphur in the range 2–1000 mg/l., with thiophene in cyclohexane as a test substance. Thermodynamic data on the equilibrium between SO_2, O_2 and SO_3 were used to select the operating conditions. To increase the recovery of SO_2 the combustion gas mixture was diluted with an inert gas to lower the partial pressure of oxygen. A temperature of 1000° in the equilibrium zone resulted in a recovery of 99%. The SO_2 was titrated with coulometrically generated iodine, the concentration of which was controlled by a Pt-redox electrode. The response of this electrode has been examined. A rather high concentration of I^- was used to suppress iodine losses during the analysis. The time of analysis was 2–5 min, and sample sizes were 3–7 μl. An LKB 16300 Coulometric Analyzer governed the titration procedure.

Petroleum and related compounds often contain substances like hydrogen sulphide, thiols, organic sulphides and thiophenes. Even small amounts of such compounds will give the product undesirable properties; an unpleasant odour, corrosiveness or catalyst poisoning. As a consequence, trace analysis for sulphur is of great importance in the field of product control and in desulphurization processes.

A review of the most important methods for determining sulphur will be found in a recent volume in three parts by Karchmer.[1] One of the most general methods is the oxy-hydrogen Wickbold burner method with a colorimetric or turbidimetric titration of the sulphate formed. With careful work a reproducibility of $(1{\cdot}5 + 0{\cdot}20S)$ ppm can be achieved,[2] where S is the sulphur content in ppm. The time of analysis will increase to about 2 hr for the low-ppm range as 50 g of sample must be burnt.

Fensom *et al.*[3] modified Granatelli's Raney nickel method in which sulphur is reduced to hydrogen sulphide which is absorbed in alkali and titrated. They determined total sulphur in light petroleum distillate in the range 0·1–0·4 ppm w/v with a precision of ±9%.

In a recent American Petroleum Institute report,[5] the correlation programme carried out showed that the microcoulometric procedure, first proposed by Coulson and Cavanagh,[6] had better precision and higher speed than some of the earlier methods, but that its usefulness was at present restricted to the lighter fuel oils. Dixon[7] modified the method to determine sulphur in lubricating oil fractions and heavy fuel oils. In this method sulphur is oxidized to a mixture of sulphur dioxide and trioxide in a quartz tube at 700–900°. The sulphur dioxide formed is titrated with iodine which is generated coulometrically. The practical limit of this method is 0·1 ppm of sulphur. Wallace and Kohlenberger[8] compared the oxidative and reductive methods for the microcoulometric determination of sulphur in hydrocarbons. They stated that the oxidative method is simpler to use and has lower interference from nitrogen. However, it suffers from interference by chlorine and heavy metals and a non-stoichiometric conversion of sulphur into sulphur dioxide. The recovery for a standard of thiophene in kerosene was 84% and the precision ±0·3 ppm in the range 3–12 ppm of sulphur.

Several other authors[9–12] have used the oxidative coulometric procedure and obtained recoveries varying between 65 and 95% sulphur dioxide, depending on temperature and combustion atmosphere used. The relative standard deviation for their methods is 2% or more.

This paper describes a new oven construction in which the combustion conditions were selected to give a recovery of close to 100% sulphur dioxide after oxidation of the sulphur in a quartz tube. In earlier microcoulometric methods the main drawback was the varying recovery, and the present method gives much better reproducibility.

HIGH TEMPERATURE EQUILIBRIA

Sulphur dioxide may be oxidized to sulphur trioxide according to the reaction

$$SO_2 + 1/2\, O_2 \rightleftharpoons SO_3. \tag{1}$$

The thermodynamic equilibrium constant is given by

$$K_p = \frac{p_{SO_3}}{p_{SO_2} \cdot p_{O_2}^{1/2}}, \tag{2}$$

which can be written

$$\frac{p_{SO_2}}{p_{SO_2} + p_{SO_3}} = \frac{1}{1 + K_p\, p_{O_2}^{1/2}} \tag{2a}$$

$$\Delta G^\circ = -RT \ln K_p, \tag{3}$$

ΔG° is a function of temperature and for the temperature interval used in combustion analysis is given by[13]

$$\Delta G^\circ = -22600 + 21{\cdot}36T \text{ (cal/mol)}. \tag{4}$$

The theoretical recovery of sulphur dioxide in percent is given by equation (2*a*) if it is multiplied by 100. A higher recovery should thus be obtained at a lower partial oxygen pressure. As K_p decreases with increasing temperature, a higher temperature will give a higher recovery. Figure 1 shows the recovery as a function of temperature and oxygen pressure. From this point of view complete conversion of sulphur into sulphur dioxide, at equilibrium and at a certain temperature, should be possible in a combustion, provided that the oxygen pressure in the final gas mixture is sufficiently low. In practice, however, there must be a rather high partial oxygen pressure to obtain complete combustion. Under these conditions only a fraction of the sulphur is present in the form of the dioxide, *i.e.*, the recovery becomes less than 100%. If this fraction could be kept constant, a lower

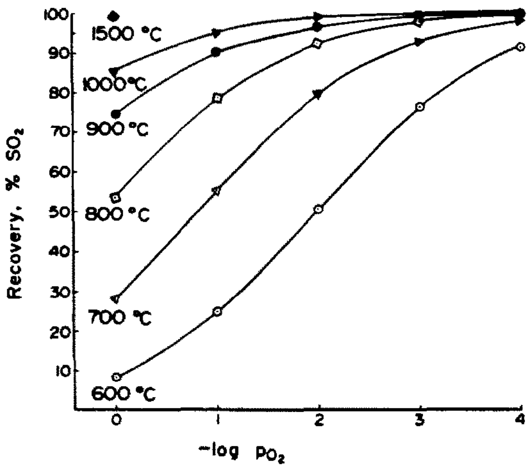

Fig. 1. Theoretical recovery of SO_2 in equilibrium with O_2 and SO_3 as a function of temperature (°C) and oxygen pressure (atm).

recovery could easily be compensated for in the calculation of the result. High-temperature combustion of inorganic and some organic compounds can be arranged so that the recovery remains essentially constant, *e.g.*, combustion at 1315° with $P_{O_2} = 1$ atm gives a recovery of 97%.[1] The combustion of organic compounds may be more complicated, owing to reactions other than those considered above. If an oil contains less than 0·06% sulphur, high-temperature combustion may give erroneous results. Various low-temperature combustion methods have therefore been developed. When the temperature is lowered the reaction rate becomes important. The equilibrium, equation (4), is reached slowly up to about 800°, so the fraction of sulphur dioxide may be higher than that calculated according to equation (2*a*) because sulphur dioxide is the main product of combustion and equilibrium is never reached. Many substances, *e.g.*, heavy metals, platinum, quartz, are known to catalyse the reaction, resulting in a closer approach to equilibrium. The recovery then becomes lower and is subject to large variations. Many of the difficulties reported in the papers referred to in the introduction were caused by variations in recovery. At 900° or more the reaction rate is so high that equilibrium is normally reached in a combustion tube.

EXPERIMENTAL

Combustion trains

Six electrically heated ovens were arranged as shown in Fig. 2. Ovens 1–5 were provided with thermoelements coupled to electronic regulators. The temperatures of the ovens could be set on dials. The thermostats kept the temperature constant within 10°. The combustion tube was made from quartz. The inlet section was fitted into the tube *via* a B14 ground joint. The outlet tube was also provided with a ground joint. The fast nitrogen flow N_2(II) was purified as shown in the figure but the nitrogen could be used without purification in the slow flow N_2(I). The gases were taken from high-pressure cylinders *via* reduction valves, needle valves and rotameters. The oxygen flow was rather critical and a constant-flow controller. Brooks Instrument model 8744 A, was therefore used to regulate this gas flow.

The ovens attained their operating temperatures about 10 min after the instrument had been switched on. The gas flow was adjusted and iodine was generated in the titration cell to obtain a slight excess. After this the instrument was ready for operation.

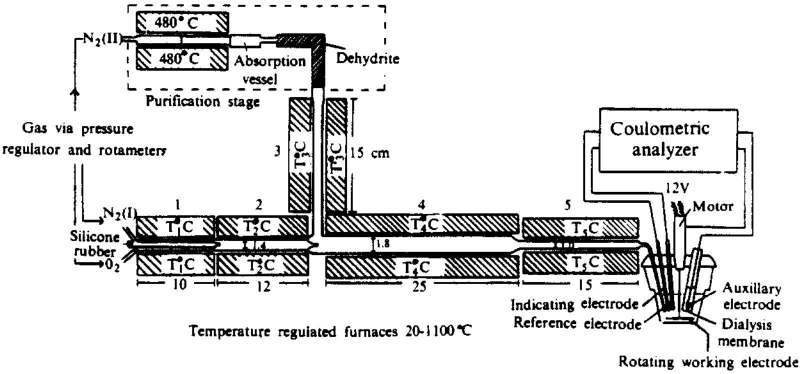

Fig. 2. Experimental arrangement.

Sample introduction

Samples were introduced *via* a silicone-rubber septum with Hamilton 701 N 10-μl or 75 N 5-μl syringes. The procedure was similar to that described by Marsh.[11] The sample was drawn into the syringe to a mark which was noted. The tip was wiped and the liquid was drawn back further until the air meniscus was at 1 μl. The syringe tip was inserted into the pyrolysis chamber so that the sample in the tip was removed. The syringe was removed until the titration of the traces on the tip was completed. The syringe was then inserted again and normally a 3–7 μl sample was injected at a uniform rate which was less than 0·2 μl/sec. The syringe was withdrawn and the meniscus was again set to the 1 μl mark. The difference in plunger reading was taken as the volume of the sample.

The relative standard deviation of a normal volume measurement with these syringes was found to be 0·5–0·8%, depending on sample size. The standard deviation of the procedure described above was probably higher but it could not be differentiated from the standard deviation of the sulphur determination. The withdrawal of the meniscus into the barrel was necessary because there was a large fluctuation in the amount of solvent evaporated from inside the tip.

Titration procedure

The absorption medium was 30 ml of an aqueous solution containing 0·40% potassium iodide, 0·055% sodium azide and 0·68% acetic acid, taken in a Metrohm titration vessel EA 880-20. Iodine was generated electrolytically at a rotating platinum electrode. A platinum spiral was used as auxiliary electrode and was separated from the sample solution by a dialysis membrane. The anode reaction is

$$2I^- \longrightarrow I_2 + 2e^-, \tag{5}$$

which is followed by

$$I_2 + I^- = I_3^- \qquad (K = 710\ \text{l./mole}). \tag{6}$$

The excess of iodine was determined potentiometrically with a platinum-foil indicator electrode *vs.* a Radiometer K 601 Hg/Hg_2SO_4 reference electrode. The electrode responds according to

$$E = E' + \frac{RT}{2F}\ln\frac{[I_2]}{[I^-]^2} = E' + \frac{RT}{2F}\ln\frac{[I_3^-]}{K\cdot[I^-]^3}. \tag{7}$$

The electrodes were connected to an LKB-16300 Coulometric Analyzer which compares the redox potential of the indicating electrode with a preset value. This preset value corresponds to the desired iodine concentration in the absorption medium. If the actual iodine excess is too low, an error signal will be produced in the analyser, which causes a current to be passed through the generating electrode system so that more iodine will be produced. This will continue until the redox potential reaches the desired value.

When sulphur dioxide enters the cell the following reaction will occur

$$SO_2 + 2H_2O + I_3^- \longrightarrow SO_4^{2-} + 3I^- + 4H^+. \tag{8}$$

When $[I_3^-]$ decreases, generation of more iodine starts automatically so that sulphur dioxide is titrated continuously as it enters the cell.

The amount of electricity required to titrate the absorbed sulphur dioxide was determined by electronic integration in the analyser. The integrator could be read to 2×10^{-11} equivalents, corresponding to 1×10^{-11} mole of SO_2.

RESULTS AND DISCUSSION

The reaction system is shown in Fig. 2. A sample is introduced through a septum into a pyrolysis chamber flushed with a slow nitrogen flow, N_2(I). This flow was usually 25 ml/min and the temperature of oven 1 was normally 400°. The vaporized and pyrolysed products enter the combustion zone through this jet. An oxygen stream (normally 9 ml/min) is passed into the combustion zone coaxially with the pyrolysis chamber. The combustion zone is normally kept at 700° by oven 2 but when a sample enters through the pyrolysis chamber a visible flame can sometimes be seen when the solvent burns, which indicates that the actual combustion temperature may be higher. The combustion products which contain the sulphur as a mixture of the dioxide and trioxide enter the equilibrium chamber through a nozzle. A fast stream of nitrogen (normally 190 ml/min), preheated to 1000° in oven 3, meets and dilutes the combustion products. The equilibrium zone is normally kept at the same temperature as the preheating zone, 1000°. In this zone the oxygen/nitrogen ratio decreases relative to that during the combustion. The temperature is so high that the sulphur oxides reach thermodynamic equilibrium. The flow-rates mentioned above will give a partial oxygen pressure of 0·04 kg/cm^2. During combustion of a sample some oxygen will be consumed, resulting in a still lower partial pressure of oxygen. The results indicate that the actual oxygen pressure during the determination is about 0·01 kg/cm^2, which according to Fig. 1 corresponds to 98·5% recovery. Still higher temperature for extended periods would result in a decreased life of the quartz tube. The diameter of the quartz tube decreases so that a high linear gas velocity is obtained when the gas enters the outlet zone which normally is kept at 500°. This temperature is so low that the reaction rate is negligible and the equilibrium attained at the preceding stage is not reversed. It is known from high-temperature equilibrium studies that equilibrium conditions can be frozen if the temperature is decreased rapidly.

A short bent tube transfers the gas to the titration vessel. After 10 min the tube has been sufficiently heated by the gas to prevent condensation. This tube can be disconnected for cleaning, which may be necessary if combustion becomes incomplete. The tip of the outlet tube is drawn out so that small gas bubbles are dispersed into the medium 2–3 cm below the liquid surface. The rotating platinum gauze anode disperses the bubbles further into the solution and the absorption of sulphur dioxide is quantitative up to a total gas flow of 250 ml/min. The sulphur dioxide is then titrated as described later.

A number of parameters have been varied one at a time and the result will be discussed below. A solution of thiophene in cyclohexane, containing about 200 ppm of sulphur, was used as a test substance. The points in Figs. 3, 4 and 5 are each mean values of about 10 determinations.

Figure 3 shows the recovery as a function of the temperature in the preheating and the equilibrium zones in ovens 3 and 4, for two different values of the oxygen partial pressure. At 900° there is a drop in recovery because the reaction rate becomes so high that equilibrium is reached. The points at 900 and 1000° correspond to the conditions shown in Fig. 1. At 1000° the recovery has increased somewhat because the equilibrium constant decreases with temperature. At 800° or below, equilibrium is not attained and the recovery is higher than that corresponding to the equilibrium shown in Fig. 1. The recovery will however depend on the combustion conditions and eventual presence of catalysts will decrease it. It was found that the standard deviations were higher than those of the determinations at 900° and 1000°. The recovery at 800° or below was also

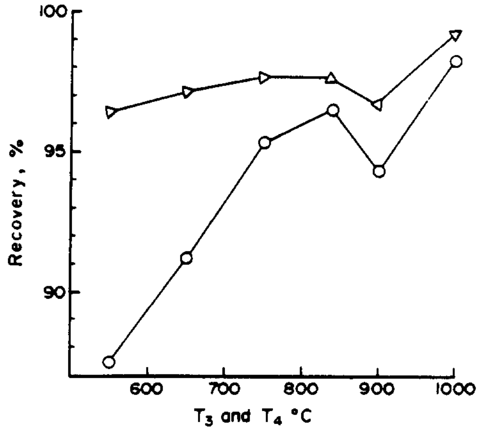

Fig. 3. Recovery of sulphur as a function of temperature in zones 3 and 4. $N_2(I) = 25$ ml/min, $N_2(II) = 190$ ml/min, $T_1 = 400°$, $T_2 = 700°$, $T_5 = 500°$. ○ $O_2 = 50$ ml/min; △ $O_2 = 9$ ml/min.

dependent on the way the sample was introduced, which further demonstrates the increased uncertainty of a method not operating at equilibrium conditions.

The effect of variations in the flow-rate of nitrogen, $N_2(II)$, was next investigated with all ovens at normal operating temperatures. Two different oxygen flows were used and the results are shown in Fig. 4. Decreasing the nitrogen flow results in a higher partial oxygen pressure and as expected from Fig. 1 the recovery decreases, especially at the higher oxygen flow. When the flow-rate is increased above 200 ml/min there is a slight decrease in recovery again, mainly because of less than 100% absorption in the titration vessel. There will also be a slight decrease in recovery at high flow-rates, owing to the way iodine losses arise.

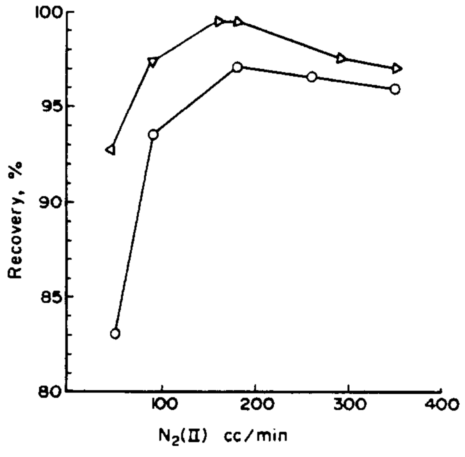

Fig. 4. Recovery of sulphur as a function of the flow-rate of diluting gas, $N_2(II)$. $N_2(I) = 25$ ml/min, $T_1 = 400°$, $T_2 = 700°$, $T_3 = T_4 = 1000°$, $T_5 = 500°$. △ $O_2 = 9$ ml/min; ○ $O_2 = 50$ ml/min.

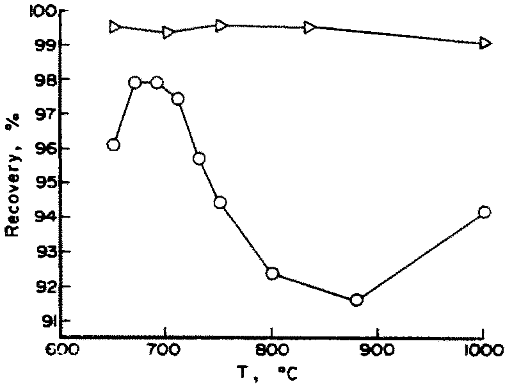

Fig. 5. Recovery of sulphur as a function of combustion temperature T_2. $T_1 = 400°$, $T_3 = T_4 = 1000°$, $T_5 = 500°$, N_2(I) = 25 ml/min, N_2(II) = 190 ml/min. △ O_2 = 9 ml/min; ○ O_2 = 40 ml/min.

Figure 5 shows the effect of temperature variations in the combustion zone, at two different oxygen flows. There is a decrease in recovery at higher temperatures and partial oxygen pressure, which probably involves the formation of a side-product containing sulphur. Further work to identify this side-reaction is in progress. A similar decrease in recovery with increasing combustion temperature was observed earlier.[8] Figure 5, as well as Figs. 3 and 4, shows the importance of low oxygen pressure but there must be sufficient oxygen to facilitate complete combustion. If the combustion is incomplete there is a formation of products which consume iodine and give high results. By introducing the sample at a slow rate it is possible to obtain complete combustion even at a comparatively low oxygen flow.

In selecting an end-point potential for the titration of sulphur dioxide with iodine, several aspects must be considered. It is advantageous to titrate to an end-point corresponding to an excess of iodine. If a large excess of iodine were selected there would be a need for a higher relative precision in the determination of the redox potential and in addition there would also be higher iodine losses if gases were blown through the cell. Figure 6 shows another aspect which is important in selecting the end-point potential. A number of nmole of iodine were generated rapidly and the potential of the redox electrodes was read after 15 sec, 2 min and 3 min. The figure shows that the electrode response is slow in the presence of small excesses of iodine, but that at higher excesses it becomes so rapid that the curves merge at around −145 mV. In normal operation a potential of −140 mV *vs.* Hg/Hg_2SO_4 reference electrode was used. The slope of the titration curve is only slightly influenced by the concentration of I^-.

Equation (6) shows that as the $[I^-]$ is increased the concentration of the volatile I_2 decreases and more I_3^- is formed. In order to decrease the amount of iodine lost through evaporation a high concentration of I^- should be selected. The selected iodide concentration was 24m*M* which is about ten times that normally used in earlier microcoulometric determinations of sulphur. With 24m*M* I^- 5·5% of the total iodine is present as I_2 and the rest as the non-volatile I_3^-. If 2·4m*M* I^- had been selected 37% of the iodine would have been present as I_2 and 63% as I_3^-. The lower iodide concentration would thus have given a blank value about seven times higher at a given gas flow. Moreover, as the iodine concentration varies during a titration the blank correction would have

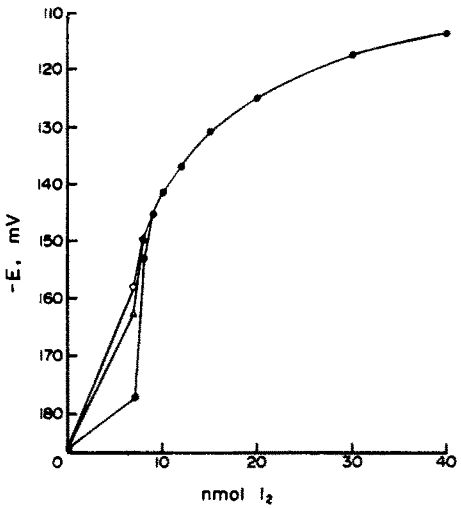

Fig. 6. Pt-indicating electrode response at various iodine concentrations in 30 ml of 0·40% KI, 0·055% NaN_3 and 0·68% CH_3COOH solution.
● Potential read after 15 sec; △ potential read after 2 min; □ potential read after 3 min.

been more difficult. The Coulometric Analyzer has a variable gain control which makes it easy to compensate for the lower slope of the titration curve obtained under the selected conditions. If an instrument with a lower sensitivity had been used this aspect would have had to be taken into account in determining the optimum conditions.

The blank value is composed of iodine losses as discussed above and of impurities from the gases. By insertion of a combustion oven in the line carrying the fast nitrogen stream the sulphur blank value could be reduced from 1×10^{-9} mole/min to $0{\cdot}2 \times 10^{-9}$ mole/min. This value will vary somewhat with time and from one gas cylinder to another. Over a period of 5 min the blank value was found to be stable within $\pm 0{\cdot}01 \times 10^{-9}$ mole/min. Purification of the other two gas streams would probably have decreased the blank value further. The purification train consisted of copper(II) oxide and silver gauze at 480° followed by an absorption vessel containing 0·4*M* sulphuric acid/4m*M* hydrogen peroxide. The gas was dried with "Dehydrite" and entered the preheating zone *via* a glass filter disc.

Determination of sulphur

Figure 7 shows the time-dependence obtained when a series of determinations was made. The samples were thiophene in cyclohexane. A recorder was connected to the coulometric analyser in order to display the titration. The result was always read from the integrator on the analyser, which had greater resolution and accuracy than the recorder plot. The time of a titration was of course longer when the sample introduction was slow, as in the present case where a large amount of hydrocarbons was consumed. Determinations of sulphur in water samples were also performed and then the injection could be made instantaneously, resulting in a short, high peak. The time of integration was noted in each case so that the blank value could be subtracted.

Table 1 shows the results of a number of determinations. The relative standard deviations found are equal to those expected from the sample.

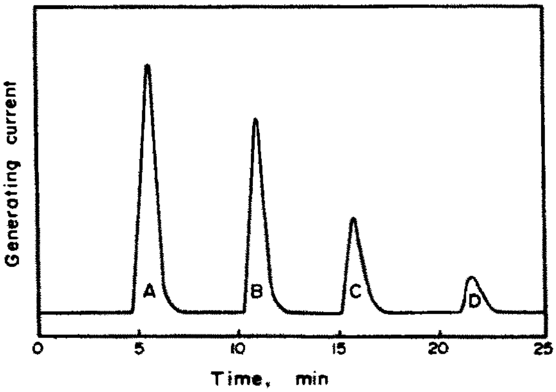

Fig. 7. Time-dependence in the determination of four different amounts of thiophene in cyclohexane.
A, $5{\cdot}00 \times 10^{-9}$ mole S; *B*, $4{\cdot}00 \times 10^{-9}$ mole S; *C*, $2{\cdot}80 \times 10^{-9}$ mole S; *D*, $0{\cdot}84 \times 10^{-9}$ mole S.

Table 1. Determination of sulphur in a test solution of thiophene in cyclohexane (3–7 μl sample)

S added, *mg/l.*	S found, (mean value) *mg/l.*	*nmole/μl*	No. of detns.	Rel. std. devn %	Recovery mean value %
0*	$0{\cdot}1_9$	0·006	3	—	—
$1{\cdot}9_2$	$1{\cdot}9_1$	0·060	3	0·4	99
16·6	16·5	0·516	3	1·1	99·3
245	242	7·55	5	0·7	99·1
747	737	23·0	3	0·5	98·7

* Cyclohexane alone.

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Zusammenfassung—Ein neues Verbrennungssystem zur oxidativen coulometrischen Bestimmung von Schwefel in flüssigen Kohlenwasserstoffen wird beschrieben. Die Bedingungen wurden so ausgewählt, daß die SO_2-Ausbeute nahe an 100% lag. Die relative Standardabweichung für Schwefel lag bei 2–1000 mg/l unter 1%, mit Thiophen in Cyclohexan als Testsubstanz. Zur Wahl der Arbeitsbedingungen wurden die thermodynamischen Daten des Gleichgewichts zwischen SO_2, O_2 und SO_3 herangezogen. Um die Ausbeute an SO_2 zu erhöhen, wurde das Verbrennungsgasgemisch mit einem Inertgas verdünnt, um den Sauerstoffpartialdruck zu erniedrigen. Eine Temperatur von 1000° in der Gleichgewichtszone ergab eine Ausbeute von 99%. Das SO_2 wurde mit coulometrisch erzeugtem Jod titriert; dessen Konzentration wurde mit einer Pt-Redoxelektrode kontrolliert. Das Ansprechverhalten dieser Elektrode wurde überprüft. Es wurde eine ziemlich hohe J^--Konzentration verwendet, um Jodverluste während der Analyse zu unterdrücken. Die Analysenzeit betrug 2–5 min, die Probengrößen 3–7 μl. Ein coulometrisches Analysengerät LKB 16300 regulierte die Titration.

Résumé—On décrit un nouveau système de combustion pour le dosage coulométrique par oxydation du soufre dans des hydrocarbures liquides. On a sélectionné les conditions de manière à ce que la récupération à l'état de SO_2 soit proche de 100%. L'écart type relatif est $<1\%$ pour le soufre dans le domaine 2–100 mg/l, avec le thiophène en cyclohexane comme substance d'essai. On a utilisé des données thermodynamiques sur léquilibre entre SO_2, O_2 et SO_3 pour sélectionner les conditions opératoires. Pour accroître la récupération de SO_2, le mélange de gaz de combustion à été dilué avec un gaz inerte pour abaisser la pression partielle de l'oxygène. Une température de 1000° dans la zone d'équilibre a pour résultat une récupération de 99%. Le SO_2 a été titré par de l'iode engendré coulométriquement, dont la concentration a été contrôlée par une électrode redox-Pt. On a examiné la réponse de cette électrode. On a utilisé une concentration en I^- plutôt élevée pour supprimer les pertes d'iode pendant l'analyse. Le temps d'analyse a été de 2–5 mn, et les dimensions d'échantillon étaient de 3–7 μl. Un Analyseur Coulométrique LKB 16300 réglait la technique de titrage.

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SUPPRESSION OF INTERFERENCE IN THE AAS DETERMINATION OF CHROMIUM BY USE OF AMMONIUM BIFLUORIDE

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Summary—Addition of 1% of ammonium bifluoride successfully suppresses interference by diverse ions in the atomic-absorption determination of chromium(VI). If the sample solutions also contain chromium(III) addition of 1% of ammonium bifluoride and 0·2% of sodium sulphate is recommended for the suppression.

Traces of chromium in rocks and minerals are usually determined spectrophotometrically[1] after conversion of chromium(III) into chromium(VI). More recently the technique of atomic-absorption spectrophotometry (AAS) has made chromium analyses easier and more rapid. However, chromium assay in rocks and minerals by AAS is rendered difficult by the fact that diverse ions interfere in the determination and several reagents have been used with varying degrees of success to suppress such interferences. Ammonium chloride[2,3] was found to reduce the depressant effect of iron on the chromium absorbance, and pyrosulphate[4,5] and persulphate[6] were found to suppress interference from aluminium, iron and titanium. Lanthanum chloride[7] was effective in eliminating interference from aluminium and phosphate. Strontium chloride[8] was found to suppress interference from a number of elements. Sodium sulphate (1%) was used by Hurlbut and Chriswell[9] for suppressing interference in the AAS determination of chromium(VI) by 1000 ppm of Ba, Ti, Mo, Mn, W, Fe, Ni, Co, Cu, Ag, Cd, Hg, Al, and Ce but it failed to remove the interference caused by Ca, Mg, Sb, Sn, sulphuric, phosphoric and perchloric acids and sodium hydroxide. It was also observed that 1% sodium sulphate was not quite effective in suppressing interferences by Ca, Mg, As, Pb, Zn, Sn, Ni, Mo and Cd with chromium(III) absorbance. Not all earlier workers have made an interference study for both oxidation states of chromium though both may be present in the resultant solutions when samples are decomposed with oxidizing acid mixtures. The behaviour of interfering ions differs with the oxidation state of chromium in the sample solutions, as stated by Suzuki and Takeuchi[10] who observed that Mn and Ni depress the absorption of chromium(III) but not that of chromium(VI). It is thus clear from the literature that no single suppressing agent so far proposed can be satisfactorily used to eliminate interference for both chromium(III) and (VI). Therefore attempts were made to find such a suppressing agent. Several reagents which would either precipitate or complex the interfering ions have been tried. They include ammonium hydroxide, diammonium hydrogen phosphate, sodium carbonate, ammonium carbonate and ammonium bifluoride. Among these ammonium bifluoride was found to be highly effective for suppressing the interference of diverse ions with Cr(VI) whereas a mixture of 1% ammonium bifluoride and 0·2% sodium sulphate was found suitable when both oxidation states are present.

EXPERIMENTAL

Reagents

Standard Cr(VI) solution, 1000 ppm. Prepared from potassium dichromate and demineralized water, and diluted to give 100 and 10 ppm standards.

Standard Cr(III) solution, 100 ppm. Prepared by reducing 10 ml of 1000-ppm chromium(VI) solution with a few drops of 30% hydrogen peroxide in 0·5*M* hydrochloric acid. The solution was diluted to 100 ml with 0·5*M* hydrochloric acid. Hydrogen peroxide does not have any deleterious effect.

Ammonium bifluoride solution (10%).

Sodium sulphate solution (2%).

Analytical grade reagents and demineralized water were used.

Apparatus

A model AA 100 Techtron Atomic Absorption Spectrophotometer with HSL hollow-cathode lamp was used. The most sensitive Cr absorption line (wavelength 357·9 nm) was used for measuring the absorbance values. The working conditions were as follows.

Lamp current 10 mA
Acetylene pressure 10 psig, flowmeter reading 6–6·5 (flow-rate 1·7 l./min)
Air pressure 15 psig (flow-rate 4 l./min)
Fuel-rich flame
Slitwidth 0·10 mm
A standard 10-cm stainless-steel AB51 burner with a 0·5-mm wide slot was used.

Calibration

After adjustment of the height and angle of the burner to give maximum absorbance for the highest standard, absorbance values were measured for 0, 0·5, 1·0, 2·0, 3·0, 5·0, 7·0 and 10·0 ppm chromium(VI) solutions containing 10 ml of 10% ammonium bifluoride solution in a total volume of 100 ml, and a calibration curve was drawn. When sodium sulphate was also found necessary in the analysis of samples a separate calibration curve was drawn with standards containing 0·2% sodium sulphate in addition to ammonium bifluoride.

Procedure

Different methods of treatment have been found necessary for different types of samples.

Silicates. Weigh a 0·2–0·5 g sample into a polythene beaker and treat it with 1 ml of conc. nitric acid and 10 ml of 40% hydrofluoric acid. Digest the mixture on a water-bath and evaporate it to dryness. Repeat the process to ensure complete decomposition of the sample. Dissolve the residue in 10 ml of *aqua regia* and transfer completely to a 250-ml Pyrex beaker. Evaporate the solution nearly to dryness, then dissolve the residue in a minimal volume of 0·5–1·0*M* hydrochloric acid, add 2–4 ml of ammonium bifluoride solution and 2 ml of sodium sulphate solution and dilute to 20 ml in a standard flask. Mix, allow to settle and measure the absorbance.

Refractory materials. Weigh a 0·1–0·2 g sample into a nickel crucible, mix it with 0·5–1 g of sodium peroxide, and fuse at dull red heat till the sample is completely decomposed. Cool the mass, extract it with hot water and make up to 100 ml. Take a suitable aliquot, add ammonium bifluoride solution, dilute to 20 ml and aspirate into the flame.

Sulphide minerals, steels and alloys. Weigh a 0·1–0·5 g sample into a dry 25-ml graduated cylinder (of a type which can be stoppered) and digest it on a hot plate with 5 ml of *aqua regia* until the solution is evaporated nearly to dryness. Extract the mass with 0·5–1*M* hydrochloric acid, add 2–4 ml of ammonium bifluoride solution and 2 ml of sodium sulphate solution, and make up to 20 ml with demineralized water. Measure the absorbance.

RESULTS AND DISCUSSION

Effect of air–acetylene ratio and lamp current

The air–acetylene ratio has considerable influence on the chromium absorbance. It can be seen from Table 1 that maximum absorbance was attained with acetylene at a delivery pressure of 10 psig and a flow-rate of 1·7 l./min and air at a pressure of 15 psig. From a series of experiments conducted separately, it was found that the lamp current has no significant effect.

Table 1. Effect of air–acetylene ratio on chromium absorbance in presence and absence of foreign ions
Air pressure 15 psig, acetylene delivery pressure 10 psig, 10 ppm Cr(VI), 2500 ppm foreign ion

	Absorbance						
Foreign ion added	Acetylene flowmeter setting	4·5	5	5·5	6·0	6·5	7·0
—		0	0·03	0·145	0·29	0·32	0·25
Al			0·03	0·10	0·20	0·20	0·20
Ca			0·025	0·13	0·28	0·27	0·24
Mg			0·03	0·11	0·24	0·22	0·13
Ni			0·03	0·10	0·165	0·22	0·20
Mo(VI)			0·025	0·10	0·26	0·25	0·17
Fe(III)			0·025	0·10	0·12	0·11	0·10

Though there is no doubt that in the hotter fuel-lean air–acetylene flames interference effects are almost negligible, the sensitivity is too low to permit determination of traces of chromium (0–50 ppm) in rocks, minerals and soils. It is clear that there is a tenfold increase in sensitivity between the fuel-lean and fuel-rich flames corresponding to acetylene flowmeter readings of 5 and 6·5 respectively. It is because this is accompanied by an increase in interference that a suppressing agent is needed.

Effect of ammonium bifluoride

Ammonium bifluoride not only suppresses the interference from foreign ions but also enhances the absorption by chromium [either (VI) or (III)]. It can be seen from Table 2 that the presence of 0·5–3% (w/v) of ammonium bifluoride enhances the absorbance by 30% while at concentrations higher than 5% of bifluoride the absorbance value falls to that obtained without addition of bifluoride. It is necessary that an optimum concentration of bifluoride be maintained in sample and standard solutions.

Table 2. Effect of ammonium bifluoride on absorbance of chromium (10 ppm)

Ammonium bifluoride, %(w/v)	0	0·5	1·0	2·0	3·0	5·0	7·0
Absorbance	0·30	0·425	0·425	0·425	0·425	0·37	0·35

Effect of acids and interference from diverse ions

As most of the chromium samples require decomposition by acids or fusion with sodium peroxide it was necessary to study the effect of these reagents on the chromium absorbance (Table 3). While hydrochloric and nitric acids have no effect on both Cr(III) and Cr(VI) absorbance, sulphuric, perchloric and phosphoric acids of 0·5–1*M* concentration act as depressants. Ammonium bifluoride eliminates the interference of sulphuric acid but not that of perchloric acids. Addition of calcium or potassium in addition to bifluoride and sodium sulphate is recommended where digestion procedures involve the use of phosphoric and perchloric acids respectively. The usual procedures recommended for attack of chromium-bearing samples involve the use of *aqua regia*, hydrofluoric plus nitric acid, or fusion with sodium peroxide, depending on the nature of the sample.

Table 3. Effect of acids and bases on chromium absorbance

Acid or base	Cr(VI) recovered, *ppm* No masking agent	Cr(VI) recovered, *ppm* 1% NH_4HF_2 added	Cr(III), recovered, *ppm* No masking agent	Cr(III), recovered, *ppm* 1% NH_4HF_2 added
1*M* HCl	9·9	9·8	10·0	9·8
1*M* HNO_3	10·0	10·0	10·0	10·2
0·5*M* H_2SO_4	8·2	9·7	9·0	9·8
1*M* $HClO_4$	8·5	8·5; 9·6*	9·9	10·1
1*M* H_3PO_4	4·0	4·0; 9·6†	4·0	4·0; 9·6†
1*M* NH_3	9·2	9·8	§	§
1*M* NaOH	9·8	9·8	§	§

* 10000 ppm K and 0·2% Na_2SO_4 also added.
† 10000 ppm Ca and 0·2% Na_2SO_4 also added.
§ Cr(III) precipitates.

A study of the interference of diverse ions (Table 4) revealed that a large number of cations, *viz.* Fe(III), Al, Ca, Mg, Co(II), Ni, Mn(II), Mo(VI), W(VI), Hg(II), As(III), Ba and Cd interfere either by enhancing or depressing the absorbance of Cr(VI) or Cr(III). Addition of ammonium bifluoride successfully eliminated interference by most of these ions except Ni and K. The presence of 500–1000 ppm Al in addition to ammonium bifluoride, and use of 0·5–1*M* hydrochloric acid medium, completely eliminates the interference by Ni. Ammonium bifluoride, though effective in suppressing interference by diverse ions in Cr(VI) determination, fails to do so in the case of Cr(III) when K, Cu(II), Co(II), Ni and W(VI) are present [Table 4]. As procedures involving acid digestion produce a mixture of Cr(III) and Cr(VI) in sample solutions, addition of 0·2% of sodium sulphate as well as ammonium bifluoride is recommended for suppression of interference. While almost complete recovery of Cr(VI) could be achieved by using ammonium bifluoride alone as the suppressing agent [10 ppm of Cr(VI) in combination with a foreign ion mixture containing 5000 ppm of each ion] the recovery was low with Cr(III) even if the concentration of individual ions in the mixture was only 1000 ppm. A comparative study was made of the effect of ammonium bifluoride with

Table 5. Recovery for Cr(VI) from mixtures containing 1000 and 5000 ppm each of Fe, Mn, Al, Ca, Mg, Co and Ni, in the presence and absence of masking agents

Masking agent	Recovery, % 1000-*ppm* mixture Cr 1 *ppm*	Cr 5 *ppm*	Cr 10 *ppm*	5000-*ppm* mixture Cr 1 *ppm*	Cr 5 *ppm*	Cr 10 *ppm*
None	65	50	50	50	35	35
1% NH_4HF_2*	100	100	99	100	99	98
1% Na_2SO_4	90	80	80	75	45	40
1% NH_4Cl	100	88	82	75	50	50
1% $K_2S_2O_7$	100	100	99	75	50	45

* 2% NH_4HF_2 was used for the 5000-ppm foreign ion mixture.

Table 4. Recovery for 10 ppm Cr(VI) or Cr(III) from mixtures containing 1000 ppm of foreign ion in the presence and absence of masking agents

Foreign ion added	Cr(VI), *ppm*			Cr(III)* *ppm*			
	In the absence of masking agent	In the presence of 1% NH_4HF_2	In the presence of 1% NH_4HF_2 + 0.2% Na_2SO_4	In the absence of masking agent	In the presence of 1% Na_2SO_4 (Hurlbut and Chriswell method[8])	In the presence of 1% NH_4HF_2	In the presence of 1% NH_4HF_2 +0·2% Na_2SO_4
Al	9.0	9.8*	9.8	8.5	9.6	6.3	9.8
Ca	9.0	10.0	9.8	12.8	9.0	10.2	10.0
Mg	8.4	9.7*	9.8	7.0	3.2	9.5	9.8
Ba	6.5	9.8*	10.0	10.0	10.0	10.3	10.2
Cu(II)	9.0	9.8	10.2	13.0	9.8	9.0	9.7
Pb	9.0	10.0*	10.0	10.0	9.0	10.0	9.7
Zn	9.8	10.0	9.9	9.0	9.2	10.2	9.7
Fe(III)	2.8	10.3*	10.2	2.5	10.4	10.0	10.2
Ni	3.0	7.7; 9.8†	10.0	5.0	8.8	4.5	9.7
Co(II)	3.0	10.0	10.2	4.5	9.6	6.5	9.7
Mn(II)	7.2	9.7	10.0	12.0	9.8	9.8	9.7
Sb(III)	10.8	10.0	10.2	10.6	10.0	10.0	9.9
As(III)	10.8	10.0	9.7	11.0	9.0	10.0	10.0
Bi(III)	10.7	10.0	10.2	11.5	10.0	10.0	9.9
Sn(IV)	9.0	9.8	9.6	10.7	9.0	10.0	9.8
Hg(II)	9.3	9.8	10.1	10.0	9.8	10.0	9.8
Mo(VI)	9.1	10.2	10.1	8.0	8.8	9.8	9.6
W(VI)	9.2	9.8	10.2	13.0	9.8	8.0	10.2
Cd	11.0	10.3	10.0	15.0	11.0	10.8	10.2
Ag	6.5	9.8	10.0	10.0	10.0	9.5	10.1
Ce(IV)	10.9	10.0	10.0	11.5	10.2	10.0	10.0
K	10.0	9.0	10.2	10.0	10.0	9.0	10.0

* Solution 0.5*M* in HCl.

† 1000 ppm Al added and solution made 0.5*M* in HCl in addition to 1% NH_4HF_2.

Table 6. Analysis of standard samples

Sample	Cr found, *ppm*	Certificate value,* *ppm*	Mean, *ppm*	Mean deviation, *ppm*	Standard deviation, *ppm*†	Relative standard deviation, %
Granodiorite GSP-1	15, 13, 14, 15	13	14·2	0·8	1	7
Basalt BCR-1	15, 15, 17, 16	16	15·7	0·8	1	6
Andesite AGV-1	12, 13, 13, 14	13	13·0	0·5	1	8
Diabase W-1	125, 120, 120, 124	124	122	3	2·5	2
Peridotite PCC-1	3165, 3125, 3062, 3000	2970	3078	47	83	2·7
Dunite DTS-1	4000, 4150, 4040, 4020	4200	4086	58	75	1·8
Diorite DR-N	30, 31, 33, 34	40	32	1·5	2	6
Basalt BR	350, 350, 360, 340	340	352	6	10	2·9
Serpentine UB-N	2500, 2587, 2512, 2500	2500	2524	31	44	1·8
Sulphide mineral SU-1	310, 310, 318, 310	340	312	3	4	1·3

* References for certificate values:

AGV-1, BCR-1, GSP-1, G-2, PCC-1 and DTS-1: F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.

G-1 and W-1: M. Fleischer, *ibid.*, 1969, **33**, 65.

SU-1: N. M. Sine, W. O. Taylor, G. R. Webber and C. L. Lewis, *ibid.*, 1969, **33**, 121.

UB-N and DR-N: H. de la Roche and K. Govindaraju, *Geochimie Appl.*, 1969, 29.

† Calculated from the range R by $s = 0{\cdot}48R$.

that of various suppressing agents recommended by earlier workers. The results in Table 5 reveal that while none of the earlier reported suppressing agents could eliminate interference by 5000 ppm of foreign ions, bifluoride could do so easily. This is probably because bifluoride not only complexes some of the metal ions [Fe(III), Sn(IV)] but also precipitates such ions as Ca, Mg, Ba, Pb, thereby reducing the total ion content of the sample solution. A number of international rock standards have been analysed for Cr by this method and the results given in Table 6 are in close agreement with the literature values. Good agreement was also obtained for a number of standard steels and alloys with certificate values.

Acknowledgement—We wish to express our sincere thanks to the United States Geological Survey, British Chemical Society, Canadian Association for Applied Spectroscopy and Centre de Recherches Petrographique et Geochimiques (France) for kindly making available to us their standards used in this investigation.

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Zusammenfassung—Die Zugabe von 1% Ammoniumhydrogenfluorid unterdrückt mit Erfolg die Störung durch verschiedenartige Ionen bei der Atomabsorptionsbestimmung von Chrom(VI). Wenn die Probenlösungen auch Chrom(III) enthalten, wird zur Unterdrückung die Zugabe von 1% Ammoniumhydrogenfluorid und 0·2% Natriumsulfat empfohlen.

Résumé—L'addition de 1% de bifluorure d'ammonium supprime avec succès l'interférence de divers ions dans le dosage par absorption atomique du chrome (VI). Si les solutions d'échantillons contiennent aussi du chrome (III), l'addition de 1% bifluorure d'ammonium et 0, 2% de sulfate de sodium est recommandée pour la suppression.

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o-(2-HYDROXY-5-DODECYLPHENYLAZO)-BENZOESÄURE UND -ARSONSÄURE ALS CHELATBILDNER FLÜSSIGER IONENAUSTAUSCHER

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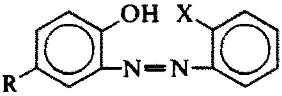
Zusammenfassung—Die Synthesen der Chelatbildner *o*-(2-Hydroxy-5-dodecylphenylazo)-benzoesäure und -arsonsäure werden beschrieben. Diese werden, in Benzin bzw. Chloroform gelöst, als flüssige Ionenaustauscher zur Trennung (Be(II)/Al(III) bzw. Zr(IV)/Hf(IV) erprobt. Beide flüssigen Ionenaustauscher sind auch zur Abtrennung von Fe(III)-Spuren aus Salzlösungen geeignet.

In einigen vorhergehenden Veröffentlichungen[1-7] wird über *o,o'*-disubstituierte Azofarbstoffe berichtet, bei denen einerseits der Alkylrest R, andererseits die Gruppe X variiert werden kann:



R = —CH_3, X = —COOH ergibt ein selektives Reagenz auf Be(II), das für die Extraktion,[1] Polarographie[2] und Photometrie[3] heranzuziehen ist. Ist R ein polymeres Gerüst, liegt ein fester Chelataustauscher vor. Mit X = —COOH dient er u.a. zur Abtrennung von Erdalkaliionen aus konzentrierten Alkalisalzlösungen,[4] von Fe(III)-Spuren aus konzentrierten Salzlösungen[5] und zur Trennung Be(II)/Al(III).[6] Der feste Austauscher mit X = —AsO_3H_2 bindet Zr(IV) wesentlich stärker als Hf(IV).[7]

Ziel der vorliegenden Arbeit ist es, als R einen langen aliphatischen Rest (—$C_{12}H_{25}$) einzuführen. Die Produkte, gelöst in einem mit Wasser nicht mischbaren organischen Lösungsmittel stellen flüssige Ionenaustauscher dar.

EXPERIMENTELLER TEIL

Chemikalien

p-Dodecylphenol *ca.* 95–98% (BASF); Anthranilsäure purum, 98% (Fluka); Petroleumbenzin (Naphthabenzin) Kp = 100–140° (Merck); *o*-Arsanilsäure F = 152°C (Schuchardt).

Salze in *p.a.* Qualität, $Al(NO_3)_3 \cdot 9H_2O$ rein, $BeSO_4 \cdot 4H_2O$ reinst (Merck); Hafnium 99,9% (Fluka); $ZrO(NO_3)_2$, Verunreinigungen Hf < 200 ppm, andere Metalle 15 ppm (HEK-GmbH). Darstellung von $ZrOCl_2 \cdot 8H_2O$ und $HfOCl_2 \cdot 8H_2O$ nach Hönigschmidt *et al.*[8]

Leitisotope (Buchler): ^{7}Be als Chlorid in 0,1*M* HCl (trägerfrei); ^{59}Fe als Chlorid in 0,1*M* HCl (20 mCi/mg); $^{175+181}$Hf als Chlorid in 2*M* HCl (8 mCi/mg); ^{95}Zr als Oxalatokomplex in oxalsaurer Lösung (trägerfrei). Die Überführung des ^{95}Zr in das Sulfat geschieht durch mehrmaliges Abrauchen mit konz. H_2SO_4.

Geräte

pH-*Messung.* Schott- Einstabmeßkette mit angeschlossenem Röhrenvoltmeter der Fa. Knick.

Polarographische Al(III)-Bestimmung.[9] Gleichstrompolarograph, Typ Polariter PO 3 der Fa. Radiometer, Kopenhagen in Verbindung mit einer Quecksilbertropfelektrode und einer gesättigten Kalomel-Vergleichselektrode.

Radiochemische Analysen. Bohrlochszintillationszähler mit Meßplatz der Fa. Berthold (^{7}Be, ^{59}Fe und $^{175+181}$Hf). Lithium gedrifteter Germaniumdetektor, Typ Ge PC 10, der Gesellschaft für Festkörperphysik mbH, in Verbindung mit einem Ortec-Verstärker, Modell 410 und dem 400-Kanal Impulshöhenanalysator der Fa. Laben, Mailand (^{95}Zr).

Synthesen

o-(2-Hydroxy-5-dodecylphenylazo)benzoesäure.[10]

o-(2-Hydroxy-5-dodecylphenylazo)arsonsäure 0,1 Mol Arsanilsäure in 50 ml Äthanol unter Erwärmen gelöst und mit 30 ml 37%iger HCl versetzt. Man kühlt in einer Eis-Kochsalz-Mischung auf 0° ab; dabei verdünnt man mit wenig Wasser so, daß die Mischung gut rührbar bleibt. Nun tropft man eine konzentrierte wäßrige Lösung von 0,105 Mol $NaNO_2$ langsam zu. Am Ende der Nitritzugabe erhält man eine klare braune Lösung. Nach 10 Minuten wird der Überschuß an HNO_2 mit Amidosulfonsäure entfernt.

Die Lösung von 0,075 Mol *p*-Dodecylphenol in 300 ml Äthanol kühlt man auf 0° ab, fügt auf einmal die diazotierte Arsanilsäure hinzu und versetzt unter Rühren mit einer $Ca(OH)_2$-Aufschlämmung [50 g $Ca(OH)_2$ in 100 ml H_2O]. $Ca(OH)_2$ wirkt als Base und zugleich als Aktivator für die Azokupplung.[11] Man rührt noch etwa 3 Stunden und läßt über Nacht stehen. Nach Zugabe von etwa 100 ml H_2O wird das Calciumsalz der *o*-(2-Hydroxy-5-dodecylphenylazo)arsonsäure abgesaugt, in 200 ml Äthanol suspendiert und nochmals wie oben beschrieben mit diazotierter Arsanilsäure gekuppelt.

Das abgesaugte, mit Wasser gewaschene Produkt kocht man nun in einem Becherglas mit HCl (1 : 1) bis sich eine dunkelrote, plastische Masse auf der Oberfläche abscheidet. Die wäßrige Lösung wird verworfen, die Behandlung des Niederschlages mit HCl wiederholt. Die entstandene freie Säure extrahiert man mit Benzol. Nach gründlichem Waschen der Benzolphase bis zur Chloridfreiheit wird das Lösungmittel abgedampft und die erhaltene zähe Masse im Vakuumtrockenschrank von Lösungsmittelresten bei 90° befreit.

Aus den elementaranalytisch erhaltenen N- bzw. As-Werten und den Äquivalenzpunkten bei der pH-Titration ergibt sich für *o*-(2-Hydroxy-5-dodecylphenylazo)benzoesäure ein 90%iger, für *o*-(2-Hydroxy-5-dodecylphenylazo)arsonsäure ein 68%iger Ablauf der Kupplungsreaktion. Die Einwaagen der Chelatbildner zur Herstellung der flüssigen Ionenaustauscher werden dementsprechend korrigiert.

ERGEBNISSE

Untersuchungen der Eigenschaften

Die beiden flüssigen Austauscher FAT (= austauschaktive Substanz im organischen Lösungsmittel) haben folgende Zusammensetzung:

FAT I: 0,025 Mol *o*-(2-Hydroxy-5-dodecylphenylazo)benzoesäure bzw. deren NH_4^+-Salz in 1000 ml Benzin gelöst.

FAT II: 0,0125 Mol *o*-(2-Hydroxy-5-dodecylphenylazo)arsonsäure in 1000 ml $CHCl_3$ gelöst.

Gleichgewichtsuntersuchungen. Die in Glas- bzw. Polyäthylenflaschen befindliche wäßrige Salzlösung wird mit dem aus einer Bürette dosierten flüssigen Austauscher durch einen Magnetrührer bei Zimmertemperatur innig vermischt. Nach Einstellung des Gleichgewichtes werden die Konzentrationen des betrachteten Kations in der wäßrigen und organischen Phase bestimmt. Eine etwaige Verteilung der Chelatbildner in der wäßrigen Phase läßt sich durch spektrophotometrische Untersuchungen verfolgen.

Phasentrennung. Bei Kontakt der flüssigen Austauscher in der H^+-Form mit Wasser und Säuren geht die Phasentrennung schnell vor sich. Die Chelatbildner verbleiben in der organischen Phase. Bei Säurekonzentrationen $> 3M$ bilden sich die protonisierten Formen aus. In FAT I flockt der Chelatbildner aus, FAT II färbt sich tiefrot. Im alkalischen Gebiet kann der Übergang der Alkalisalze der Chelatbildner von der organischen in die wäßrige Phase durch genügend hohe Alkalielektrolytkonzentration oder Anwesenheit komplexbildender Kationen unterbunden werden. Unter diesen Bedingungen ist bei Verwendung von Benzin bzw. $CHCl_3$ als Lösungsmittel eine etwaige Emulsionsbildung am geringsten. Bei Kontakt mit alkalischen Medien entstehen in FAT II Trübungen, d.h. die Alkalisalze der *o*-(2-Hydroxy-5-docecylphenylazo)arsonsäure fallen im organischen Lösungsmittel aus.

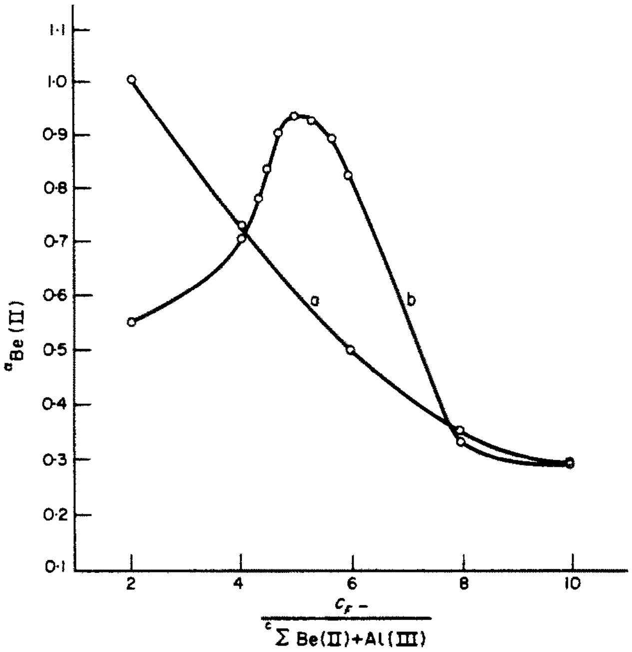


Abb. 1. FAT I—Extraktionskoeffizienten von Be(II) ohne und in Gegenwart von Al(III) bei Anwesenheit von Fluorid. (*a*) Be(II); (*b*) Be(II) in Gegenwart von Al(III). 1,25 · 10^{-3} Mol Be; 2,5 · 10^{-3} Mol Al. Vor der F^--Zugabe wird mit NaOH der Hydroxokomplex dargestellt. pH-wert: 4,5 (HNO_3).

Bedingungen für Abb. 1 und 2:

Organische Phase: 50 ml FAT I in NH_4^+-Form (= 1,25 × 10^{-3} Mol) mit Benzin auf 100 ml verdünnt.

Wäßrige Phase: 100 ml Salzlösung der angegebenen Zusammensetzung

Kontaktzeiten: 45 Minuten.

Anwendung von FAT I

FAT I kann zur Trennung von Be(II) und Al(III) und zur Abtrennung von Fe(III)-Spuren aus *p.a.* Salzlösungen herangezogen werden.

Be(II)/Al(III) Trennung. Mit der Bildung der Be(II)-und Al(III)-Komplexe ab pH 2,5 tritt eine deutliche Farbänderung des FAT von rot nach orange auf. Die Gleichgewichtseinstellung ist bei Zimmertemperatur nach etwa 30 Minuten beendet. Bei 40° verkürzt sich die Zeit auf etwa 4 Minuten.

Die Extraktionskoeffizienten von Be(II) und Al(III) sind bei Gegenwart komplexbildender Anionen so unterschiedlich, daß bei einmaliger Gleichgewichtseinstellung eine Anreicherung bzw. Trennung erfolgt.

Als Komplexbildner werden F^-, $C_2O_4^{2-}$, AeDTE und Tartrat eingesetzt. Bestimmt wird der Verlauf der Extraktionskoeffizienten von Be(II) in Abhängigkeit von der Anionenkonzentration mit und ohne Anwesenheit von Al(III). In Abb. 1 und 2 sind die Extraktionskoeffizienten von Be(II) gegen den Quotienten aus Anionenkonzentration und Konzentration der Summe der Metallionen aufgetragen.

Da einerseits F^- und $C_2O_4^{2-}$, andererseits AeDTE und Tartrat analoge Kurven hervorrufen, ist im folgenden nur der Einfluß von F^- (Abb. 1) und AeDTE (Abb. 2) näher beschrieben.

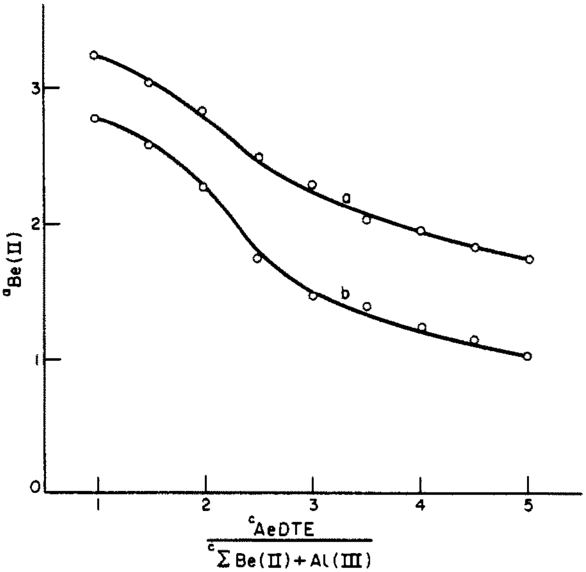


Abb. 2. FAT I—Extraktionskoeffizienten von Be(II) ohne und in Gegenwart von Al(III) bei Anwesenheit von AeDTE (*a*) Be(II); (*b*) Be(II) in Gegenwart von Al(III).
1,25 × 10^{-3} Mol Be; 2,5 × 10^{-3} Mol Al; 4,00 × 10^{-2} Mol CH_3COONH_4 und 1,00 × 10^{-2} Mol KNO_3. Kochzeit zur vollständigen Ausbildung der AeDTE-Komplexe, 2 Minuten. pH-Wert: 4,5 (HNO_3).

Bei F^- werden im Maximum der Kurve *b* (Abb. 1) 48% des Be(II) und 0,73% des eingesetzten Al(III) vom flüssigen Austauscher aufgenommen. Unter den Bedingungen des maximalen $\alpha_{Be(II)}$-Wertes wird das Be(II) von einem 5-fachen Austauscher-Überschuß [bezogen auf Be(II)] quantitativ extrahiert. Es ist mit 1,25% des eingesetzten Al(III) verunreinigt. Mit $C_2O_4^{2-}$ als komplexbildendem Anion in der wäßrigen Phase genügt zur quantitativen Be(II)-Extraktion der 2-fache Austauscher-Überschuß. Dabei werden 3,3% des Al(III) mitaufgenommen.

Durch die Gegenwart von AeDTE werden die Extraktionskoeffizienten von Be(II) wenig beeinflußt. Die Aufnahme von Al(III) wird jedoch verhindert. So ist bei einem der Kationenkonzentrationen entsprechenden 4-fachen AeDTE-Überschuß neben 56% des Be(II) kein Al(III) im flüssigen Austauscher nachzuweisen.

Bei Anwendung von Tartrat liegen die Verhältnisse ähnlich. Bei einem 4-fachen Tartrat-Überschuß werden 35% des Be(II) und kein Al(III) mehr extrahiert.

Fe(III)-Spuren aus p.a. *Salzlösungen.* Bereits ab pH 0,7 bildet die *o*-(2-Hydroxy-5-dodecylphenylazo) benzoesäure mit Fe(III) Komplexe. Die Gleichgewichtseinstellung dauert bei Zimmertemperatur etwa 30 Minuten, bei 40° 10 Minuten.

In einem Einstufenprozeß von 10 Minuten Dauer wird mit einer *ca.* 0,05%igen Lösung des Chelatbildners in Benzin der Fe(III)-Gehalt von 0,1*M* Salzlösungen stark vermindert. In Abb. 3 ist der prozentuale Anteil der vom Hersteller genannten Fe(III)-Verunreinigung nach gewissen Kontaktzeiten mit FAT I aufgetragen.

Auffallend ist die schlechte Fe(III)-Spurenabtrennung aus einer 0,1*M* NaCl-Lösung, die auf die Bildung anionischer Fe(III)-Chlorokomplexe zurückzuführen sein dürfte. Die Abnahme des Fe(III)-Gehaltes des $NaClO_4$ um *ca.* 99% stellt einen Beweis hierfür dar.

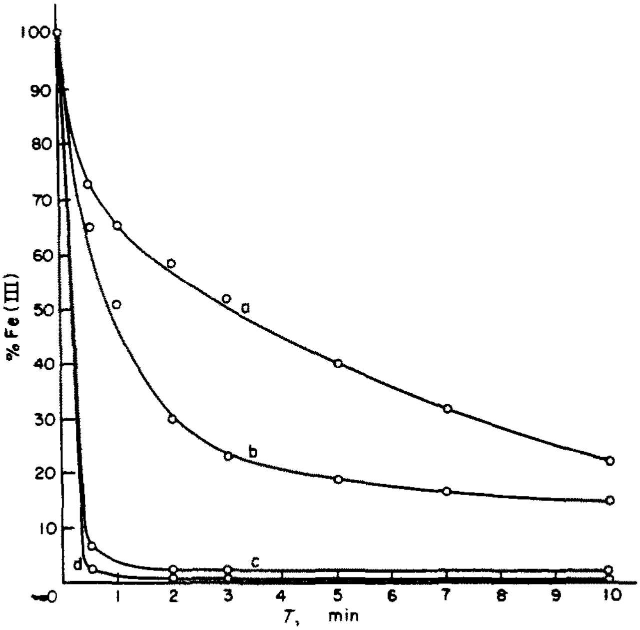


Abb. 3. FAT I—Abtrennung von Fe(III)-Spuren aus 0,1*M* Salzlösungen (*a*) NaCl *p.a.* (0,0002% Fe); (*b*) $Al(NO_3)_3 \cdot 9H_2O$ rein (0,01% Fe); (*c*) $NaClO_4 \cdot H_2O$ *p.a.* (0,0005% Fe); (*d*) CH_3COONH_4 *p.a.* (0.0005% Fe) Organische Phase: 2,5 ml FAT I in NH_4^+-Form; (= $6,25 \times 10^{-5}$ Mol) auf 50 ml verdünnt Wäßrige Phase: Jeweils 50 ml 0,1*M* Lösung des genannten Salzes.

Anwendung von FAT II

FAT II bildet mit Zr(IV) und Hf(IV) noch aus 6*M* HCl Komplexe. Die Gleichgewichtseinstellung bei Raumtemperatur dauert 40 Minuten. Abb. 4 gibt die Extraktionskoeffizienten in Abhängigkeit von der HCl-Konzentration wieder.

Zr(IV) wird bevorzugt vor Hf(IV) von FAT II aufgenommen. Aus 0,09*M* HCl erreicht der Trennfaktor einen Wert von 7. Die Abnahme der Zr(IV)-Extraktionskoeffizienten bei HCl-Konzentrationen <0,09*M* ist auf eine bereits beginnende Hydrolyse des Zr(IV) zurückzuführen.

Auch FAT II bildet mit Fe(III) bereits im sauren Medium Komplexe, wobei eine Farbänderung nach braungrün auftritt. Die Gleichgewichtseinstellung nimmt etwa 30 Minuten in Anspruch. Abb. 5 zeigt die Abtrennung von Fe(III)-Spuren aus 0,1*M* Salzlösungen.

FAT II zeigt sich in der Befreiung der 0,1*M* $Al(NO_3)_3 \cdot 9H_2O$-Lösung von Fe(III) dem FAT I etwas überlegen. Während bei FAT I noch 15% der Fe(III)-Ausgangskonzentration in der Salzlösung verbleiben, sind es bei Anwendung von FAT II noch 1,8%.

DISKUSSION

Gegenüber den Synthesen der entsprechenden festen Austauscher sind die der Chelatbildner für FAT I und FAT II recht einfach. Sie besitzen unter den gegebenen Bedingungen gute Löslichkeit in der organischen und geringe Löslichkeit in der wäßrigen

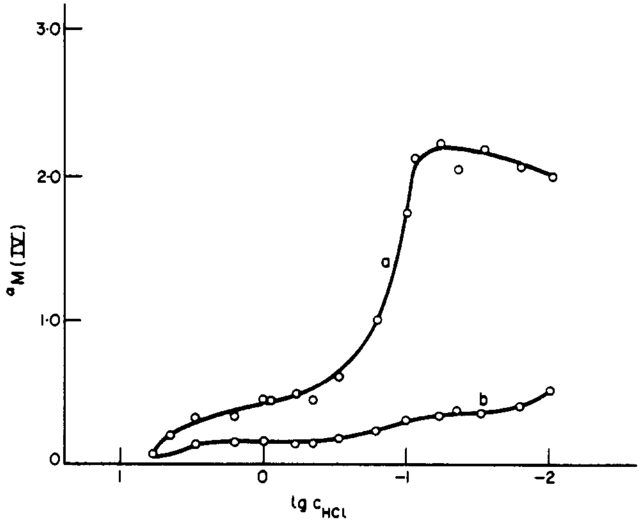


Abb. 4. FAT II—Extraktionskoeffizienten in Abhängigkeit von der HCl-Konzentration; (*a*) Zr(IV); (*b*) Hf(IV).
Organische Phase: 1 ml FAT II in der H^+-Form (= 1,25 . 10^{-5} Mol) auf 25 ml verdünnt.
Wäßrige Phase: 1,25 × 10^{-5} Mol $HfOCl_2 \cdot 8H_2O$ bzw. 1,25 × 10^{-5} Mol $ZrOCl_2 \cdot 8H_2O$; 1,00 . 10^{-3} Mol KNO_3; Lösungsvolumen: 25 ml *xM* HCl, *x* = 0,01 bis 6.
Kontaktzeit: 60 Minuten

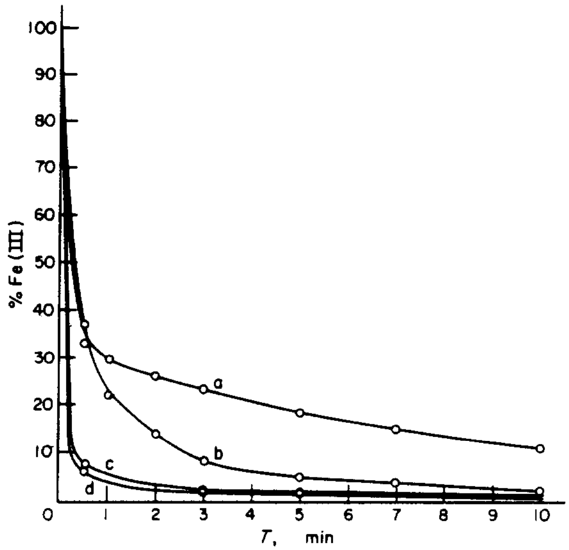


Abb. 5. FAT II—Abtrennung von Fe(III)-Spuren aus 0,1*M* Salzlösungen (*a*) NaCl *p.a.* (0,0002% Fe); (*b*) $Al(NO_3)_3 \cdot 9H_2O$ rein (0,01% Fe); (*c*) $NaClO_4 \cdot H_2O$ *p.a.* (0,0005% Fe); (*d*) CH_3COONH_4 *p.a.* (0,0005% Fe).
Organische Phase: 5 ml FAT II in H^+-Form (= 6,25 × 10^{-5} Mol) auf 50 ml verdünnt.
Wäßrige Phase: 50 ml 0,1*M* Lösung des genannten Salzes.

Phase. Der Dodecylrest reicht also zur Hydrophobierung der chelatbildenden Gruppen aus. Die Gleichgewichte stellen sich im Gegensatz zu festen Austauschern schon im Minutenbereich ein.

Die Extraktionskoeffizienten von Be(II) und Al(III) an FAT I können durch komplexbildende Anionen so unterschiedlich werden, daß eine Anreicherung bzw. Trennung im Satzbetrieb möglich ist. Ursache ist die höhere Stabilität der entsprechenden Al(III)-Komplexe in der wäßrigen Phase. Das erhaltene Maximum bei der Be(II)-Extraktion in Gegenwart von Al(III) und F^- (Kurve *b* in Abb. 1) spricht für die Bildung eines $[AlF_6]^{3-}$-Komplexes. Das bei einer gleichartigen Trennung mit einem flüssigen Anionenaustauscher auftretende Maximum ist jedoch auf die Bildung von AlF_3 zurückzuführen.[12]

Eine Zr(IV)/Hf(IV)-Trennung mit FAT II ist bei einem Trennfaktor von 7 durch multiplikative Verteilung möglich. Die Abtrennung von Fe(III)-Spuren gelingt mit beiden flüssigen Austauschern. Besonders vorteilhaft gegenüber einem analogen festen Austauscher[5] ist die schnelle Gleichgewichtseinstellung. Weiter ist die Anwendung von FAT I flüssigen Austauschern. Besonders vorteilhaft gegenüber einem analogen festen Austauscher[5] ist die schnelle Gleichgewichtseinstellung. Weiter ist die Anwendung von FAT I Aufziehen von *o*-(2-Hydroxy-5-dodecylphenylazo)benzoesäure und -arsonsäure auf hydrophobiertes Kieselgel, worüber in einer weiteren Veröffentlichung berichtet wird.

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Summary—The syntheses of two new chelating agents *o*-(2-hydroxy-5-dodecylphenylazo)-benzoic acid and the corresponding arsonic acid, are described. Solutions of these in benzine or in chloroform have been used as liquid ion-exchangers for the separation of Be and Al, and of Zr and Hf. Both have proved useful for the separation of traces of Fe(III) from solutions of salts.

Résumé—On décrit les synthèses de deux nouveaux agents chélatants, l'acide *o*-(2-hydroxy 5-dodécylphénylazo)benzoïque et l'acide arsonique correspondant. Les solutions de ceux-ci dans le benzène ou le chloroforme ont été utilisées comme échangeurs d'ions liquides pour la séparation de Be et Al, et de Zr et Hf. Tous deux se sont montrés utiles pour la séparation de traces de Fe (III) de solutions de sels.

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DETERMINATION OF IMPURITIES IN HIGH-PURITY GOLD, WITH A GAS-STABILIZED LOW-TEMPERATURE ARC

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Summary—A gas-stabilized arc with aerosol supply has been used for emission spectrometric determination of Al, B, Be, Co, Cr, Fe, Ga, In, Mg, Mn, Ni, Pd, Rh and Zn, as impurities in high-purity gold. Two analytical procedures were compared: (*a*) direct aspiration of dissolved samples containing 2% of gold and 0·25*M* KCl as buffer, and (*b*) separation of impurities by ether extraction of gold from 1*M* HCl followed by impurity determination with a stabilized arc. Limits of detection, precision and recovery of the extraction procedure are given.

Radioactive gold has been widely applied in medicine for diagnosis and therapy of various cancerous diseases. In achievement of better nuclear balance in ^{198}Au isotope production, the gold target purity is of great importance.

Until recently, most analyses of impurities in gold were performed by emission spectroscopy or atomic absorption. However, both of these methods have inherent disadvantages. Spectrographic analysis has poor precision and standard preparation is often rather complicated, while atomic absorption is not suitable for the determination of a large number of elements in a single sample, as it usually requires a separate hollow-cathode lamp for each element to be determined and its sensitivity may be unsatisfactory for some elements, especially when solid samples are analysed.

The spectrographic methods based on sample dissolution in *aqua regia* and evaporation of the solution on graphite electrodes or graphite powder, followed by spectral excitation in a d.c. arc,[1,2] or solution excitation by the rotating disc technique[3] have been described in the literature. Recently Jäger described an emission spectrometric technique using a Grimm's discharge lamp.[4] As a technique suitable for solution analysis, atomic absorption has also been applied to gold analysis after dissolution of the sample in *aqua regia*.[5,6]

In view of the disadvantages of existing methods, a new emission spectrometric technique has been developed for direct analysis of solutions. A gas-stabilized low-temperature arc described elsewhere[7] has been applied to excitation of aerosol solutions. This excitation source has some characteristics that make it suitable for solution analysis: (*a*) it is sufficiently simple for routine analysis, (*b*) it shows low memory effect, as low as that found with a conventional slot-burner, and (*c*) its sensitivity is comparable to or better than that obtained with conventional flame methods.

Gold samples were dissolved and the solutions obtained analysed directly, or after the gold had been separated by extraction.

EXPERIMENTAL

Apparatus

Stabilized arc device. A slightly modified version of the arc device previously described[7] was used. A cross-section of the essential part of it is shown in Fig. 1.

The device consists of metal segments, electrically insulated and water-cooled. The arc burns through the openings in segments 4–6, between graphite anode 1 (Ringsdorf Werke RW III) and carbon cathode 9 (Ringsdorf Werke RW II); the latter is axially bored, 3 mm dia., to make possible the ignition of the arc discharge with an auxiliary graphite rod.

The openings, 3 mm dia., in segments 4 and 6 are sufficiently narrow to eliminate the influence of the irregular wandering of the cathode and anode spots on the central part of the arc column. At these points the arc column is wall-stabilized, and there is no gas flow through these openings. The sample aerosol is introduced tangentially into the cavity of segment 5, to make the gas vortex needed for stabilization of the central part of the arc column. This segment, in contrast to the others, is not water-cooled. During the arc burning, the temperature of this segment is elevated, which prevents the deposition of the aerosol drops inside its cavity. To avoid consumption of the graphite electrodes, argon shielding-streams are introduced into the sections around them.

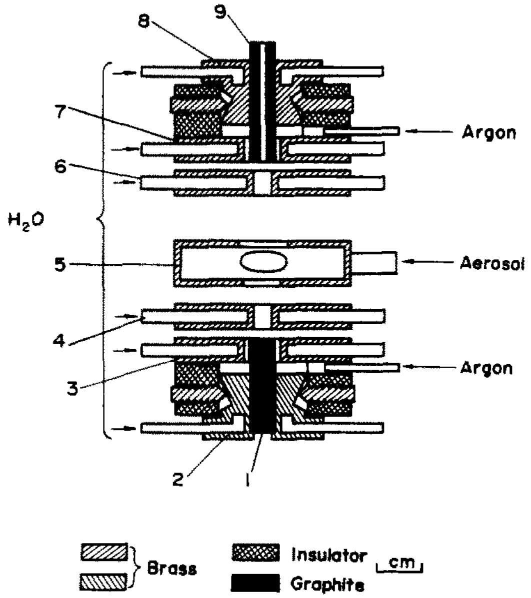

Fig. 1. Stabilized arc. 1—anode: 2—anode holder; 3, 4, 6 and 7—the metal segments, electrically insulated from one another and water-cooled; 5—the central segment, not water-cooled; 8—cathode holder; 9—cathode. The arc burns in the axial channel which consists of an opening in each segment. The analytical gap is between segments 5 and 6.

Arc-generator. The arc supply is obtained from a source based on a three-phase rectifier giving 300 V on open circuit. At a current of 6 A, the voltage drop across the electrodes was about 90 V. Small current fluctuations caused by wandering of electrode spots were avoided by electronic stabilization of the arc current.

Solution nebulizer. Solutions were aspirated into an argon stream with a chamber type nebulizer and the aerosol obtained was introduced into the cavity of segment 5. The argon flow-rate was 3 l./min and the solution uptake rate was 1·5 ml/min. The nebulizer efficiency was estimated to be 3·4%. With this nebulizer and the arc current of 6 A, the minimum concentration of potassium buffer required for obtaining low-temperature arc conditions was 0·25*M*.

Monochromator. A 2-m plane grating spectrograph PGS-2 (Carl Zeiss, Jena) with an attachment for photoelectric detection and having a single exit slit (laboratory made) was used as a monochromator. The entrance slit of the monochromator was illuminated with a three-lens system with intermediate image. For this purpose and to avoid spectral order overlapping an order-sorter (Carl Zeiss, Jena) was used. The arc portion between segments 5 and 6 (Fig. 1) was imaged on the intermediate diaphragm of the order-sorter with a 150-mm

Table 1. Limits of detection

Element	Wavelength, *nm*	Limit of detection, *μg/ml*	
		Without KCl	With KCl
Al	396·2	0·21	0·0045
B	249·7	0·013	0·027
Be	234·9	0·0077	0·021
Co	345·3	0·23	0·028
Cr	357·9	0·042	0·032
Fe	372·0	0·11	0·013
Ga	417·2	0·11	0·0073
In	451·1	0·34	0·039
Mg	285·2	0·035	0·0028
Mn	403·1	—	0·003
Ni	352·4	0·23	0·0063
Pd	340·4	0·063	0·011
Pt	265·9	1·1	0·59
Rh	345·3	0·13	0·001
Zn	213·9	0·018	—

achromatic lens. The dispersion plane of the order-sorter prism was horizontal, thus allowing the use of the full length of the entrance slit (about 14 mm).

The grating (650 lines/mm) was blazed for 590 nm. and was used in the first order for wavelengths longer than 370 nm, and in the second order for wavelengths shorter than 370 nm. The entrance and exit slits were 0·1 mm wide giving a spectral band-pass of 0·08 nm in the first order and 0·04 nm in the second order.

Light intensity measurement. A photomultiplier 1P28 (RCA) operating at 1000 V was used as a detector. The anode current was measured with a potentiometric recorder B1G1 (Carl Zeiss, Jena) which had a sensitivity of 10^{-8} A for full-scale deflection. The time constant was set to 1 sec.

Preliminary investigations

Limits of detection. Limits of detection were determined for all elements covered, with the procedure described. The limit of detection is taken to be the concentration of an element that gives a reading equal to twice the standard deviation near the blank level. The standard deviations was calculated from ten pairs of alternating sample–blank measurements.

The results obtained are shown in Table 1. Column 3 shows the limits of detection obtained by aspiration of 2% gold solution and column 4 gives the limits of detection obtained by aspiration of the solution containing 2% of gold and 0·25*M* in potassium chloride as spectroscopic buffer. It is evident that lower limits of detection are obtained for most elements in presence of potassium chloride, *i.e.*, under low-temperature conditions of arc burning. This effect is in agreement with the previous investigation of this type of the stabilized arc.[7,8]

The effect of addition of potassium buffer could be ascribed to more favourable conditions being attained for the entry of aspirated elements into the arc column and to the suppression of ionization of easily ionized elements.

For the elements of high excitation potential (*e.g.*, zinc) and for elements forming stable oxides (*e.g.*, boron and beryllium) the temperatures achieved in the low-temperature arc are not usually sufficiently high, and lower limits of detection are obtained in the absence of alkali metals as buffers.

Extraction efficiency with ether. To find optimum conditions for the separation of gold by ether extraction a radioactive tracer technique with isotopes ^{198}Au and ^{59}Fe was used. It is already known that iron can be extracted with ether at higher concentrations of hydrochloric acid, and this was the reason for investigation of iron and gold extraction at various acidities. The results are shown in Table 2. Gold is efficiently extracted with 0·5–2*M* hydrochloric acid. However, with acid concentrations higher than 1*M* the degree of extraction of iron increases. Therefore, best conditions for extraction are achieved in the range from 0·5 to 1·0*M* hydrochloric acid.

Direct analytical procedure

Two analytical procedures were used: (*a*) direct analysis of the solutions obtained by dissolving gold in *aqua regia*, and (*b*) determination of impurities in the solutions after separation of gold by ether extraction. The direct procedure will be described first.

Table 2. Extraction of Au and Fe with ether at different concentrations of HCl

[HCl], *M*	Au in ether, %	Fe in ether, %
0·1	88	0·15
0·5	98·7	0·18
1·0	98·4	0·33
2·0	98·9	1·1
3·0	97·1	2·8
4·0	97·0	26·9
5·0	96·6	56·3

Sample preparation. A gold sample (1 g) was dissolved in 5 ml of *aqua regia* and the solution obtained transferred into a 25-ml flask and made up to volume. An aliquot of this solution was mixed with an equal volume of 0·5*M* potassium chloride. For determination of most elements, the buffered solution was aspirated into the arc, but boron, berryllium and zinc were determined in a 2% solution of gold without potassium chloride addition.

Standard preparation. The standards were prepared in a similar manner to the sample. Spectrographically pure gold (Johnson–Matthey) was dissolved in *aqua regia* and a series of solutions was prepared each containing 4% of gold, and the impurities in the concentration range from 0·05 to 10 μg/ml. It was taken into account that the composition of the standard solutions should be as similar as possible to that of the solutions to be analysed. An aliquot of the solution obtained was then mixed with an equal volume of 0·5*M* potassium chloride (or distilled water) and aspirated into the arc.

Measurement. The blank and the solutions obtained as described above were aspirated with a chamber-type nebulizer and the measurement of the emission of corresponding spectral lines was simultaneously performed. Corrections for background emission were made. No internal standard was used. Analytical curves (Fig. 2) were obtained by plotting the recorder readings against the concentration on a logarithmic scale. In order to make the drawing clearer, some curves have been shifted along the intensity axis.

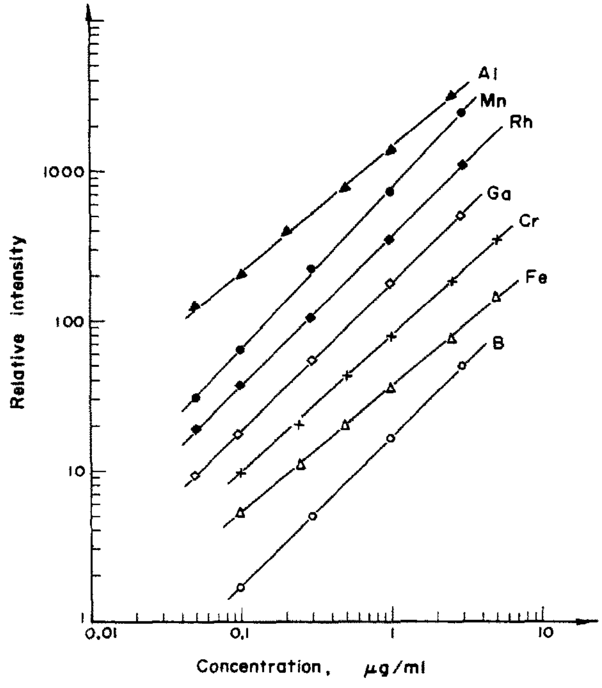

Fig. 2. Analytical curves (to make the drawing clear, some of the curves have been shifted along the intensity axis).

Analytical procedure with separation

Sample preparation. The gold (1 g) was dissolved in 5 ml of *aqua regia* and the solution evaporated nearly to dryness in order to remove nitrate; the residue obtained was dissolved in 20 ml of 1*M* hydrochloric acid. The solution was transferred into a separatory funnel, 20 ml of ether were added and after being shaken for 2 min the mixture was allowed to separate into layers. The organic phase, containing the gold, was discarded. Two more extractions, each with 10 ml of ether, were performed. The aqueous phase was evaporated to small volume, transferred to a 10-ml flask and made up to volume. An aliquot of the solution was mixed with an equal volume of 0·5*M* potassium chloride (or distilled water) and the mixture aspirated into the arc.

Standard preparation. A set of standard solutions, containing from 0·03 to 3 μg/ml of each impurity, was prepared in the same way as the sample except for the extraction being performed in the absence of the gold, in order to avoid contamination by gold impurities. The aqueous phase was evaporated to small volume and gold was added in the concentration which generally remained after the extraction procedure. Other details of the standard preparation were the same as those for the sample preparation.

Measurement. The measurement procedure was identical to that used in the direct procedure.

ANALYTICAL RESULTS

To test the extraction procedure and subsequent impurity determination standard solutions containing gold and thirteen impurity elements were prepared. The analyses were made at two impurity levels. The solutions were analysed according to the procedure described above. The results are presented in Table 3, and do not show any significant systematic deviation.

As a measure of precision relative standard deviation was used; some values are shown in Table 4.

Table 3. Recovery by the procedure

Element	Added, *μg/ml*	Found, *μg/ml*	Recovery, %
Al	0·1	0·095	95
	0·3	0·28	93
	0·3	0·27	90
B	1	0·94	94
	0·1	0·1	100
Co	0·3	0·27	90
	0·1	0·09	90
Cr	0·3	0·32	107
	1·0	1·0	100
Fe	3·0	3·1	103
	0·1	0·1	100
Ga	0·3	0·33	110
	0·1	0·11	110
In	0·3	0·31	103
	0·1	0·095	95
Mg	0·3	0·3	100
	0·1	0·11	110
Mn	0·3	0·34	113
	0·1	0·105	105
Ni	0·3	0·27	90
	1·0	1·15	115
Pd	3·0	3·0	100
	0·1	0·1	100
Rh	0·3	0·29	97
	1·0	1·0	100
Zn	1·0	1·05	105

Table 4. Precision of the determination with the stabilized arc

Element	Concentration, *µg/ml*	Standard deviation, *µg/ml*	Relative standard deviation, %
Al	0·25	0·016	6
	0·5	0·01	2
	1·05	0·016	1·5
Fe	0·25	0·005	2
	0·51	0·02	3·9
	1·00	0·02	2·0
Cr	0·255	0·008	3·1
	0·55	0·03	5·4
	1·00	0·017	1·7

The procedure developed allows quick determination of impurities in gold with satisfactory precision. The procedure employing separation of gold lowers the limits of determination, but requires a longer time and reagents of high purity.

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Zusammenfassung—Ein gasstabilisierter Bogen mit Aerosolspeisung wurde zur emissionsspektrometrischen Bestimmung von Al, B, Be, Co, Cr, Fe, Ca, In, Mg, Mn, Ni, Pd, Rh und Zn verwendet, die als Verunreinigungen in hochreinem Gold vorlagen. Zwei analytische Arbeitsvorschriften wurden verglichen: a) direktes Ansaugen gelöster Proben, die 2% Gold und 0.25*M* KCl als Puffer enthielten, b) Abtrennung der Verunreinigungen durch Extraktion von Gold mit Äther aus 1*N* HCl, anschließend Bestimmung der Verunreinigungen mit stabilisiertem Bogen. Nachweisgrenzen, Genauigkeit und Ausbeute des Extraktionsverfahrens werden angegeben.

Résumé—On a utilisé un arc stabilisé au gaz avec arrivée d'aérosol pour le dosage spectrométrique d'emission de Al, B, Be, Co, Cr, Fe, Ga, In, Mg, Mn, Ni, Pd, Rh et Zn, en tant qu'impuretés dans l'or de haute pureté. On a comparé deux techniques analytiques: (a) aspiration directe d'échantillons dissous contenant 2% d'or et KCl 0, 25*M* comme tampon, et (b) séparation d'impuretés par extraction à l'éther de l'or à partir de HCl 1*N* suivie par le dosage de l'impureté avec un arc stabilisé. On donne les limites de détection, la précision et la récupération de la technique d'extraction.

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APPLICATION OF THE ZONE-MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—VI*

A NEW APPARATUS FOR ZONE-MELTING CHROMATOGRAPHY

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Summary—An improved apparatus has been constructed for zone-melting chromatography. An essential feature of the apparatus is that the length of the molten zone can be kept constant during a zone-melting operation, by employing heating and cooling compartments which are separated from each other by double partition plates. Each compartment is heated or cooled with jets of hot or cold air. The apparatus is suitable for organic materials melting in the range between 40° and 180°. The distribution of metal ion along the column after zone melting of copper acetylacetonate in 2-methoxynaphthalene was a smooth curve. The plot of the position of maximum concentration, x_{max}, against the number of zone passes, n, gave a relationship in accordance with theoretical prediction.

A few papers have been published on the chromatographic separation of mixtures by the zone-melting technique. Peaker and Robb,[1] and Loconti and Cahill[2] applied zone-melting chromatography (ZMC) to the fractionation of polymers, and Doron and Kirschner[3] applied this method to the separation of diastereomeric mixtures. However, their experiments were irreproducible and gave poor separations. A successful application of this technique was published by Plancher, Cogswell and Latham,[4] who separated polycondensed aromatics, using induction heating, but their apparatus was expensive.

The present authors[6] have investigated the separation of mixtures of metal chelates on columns of organic solid solvents. The distribution of solutes was not reproducible owing to the inconstancy in the length of the molten zone during the operation.

The present paper reports the construction of a ZMC apparatus which can keep the molten zone length constant, and includes some preliminary experimental results.

EXPERIMENTAL

The glass tube (sample container) is held at an angle of 30° from the horizontal for convenience of operation, and is drawn upwards. Diagrams of the apparatus are shown in Figs. 1 and 2. The sample container is a Pyrex glass tube 60 cm long and 0·6 cm dia., closed at its lower end with a silicone rubber plug. The length of the molten zone is maintained at 5·0 mm. Ten heating and eleven cooling compartments are placed one above the other alternately and are separated by eleven sets of double

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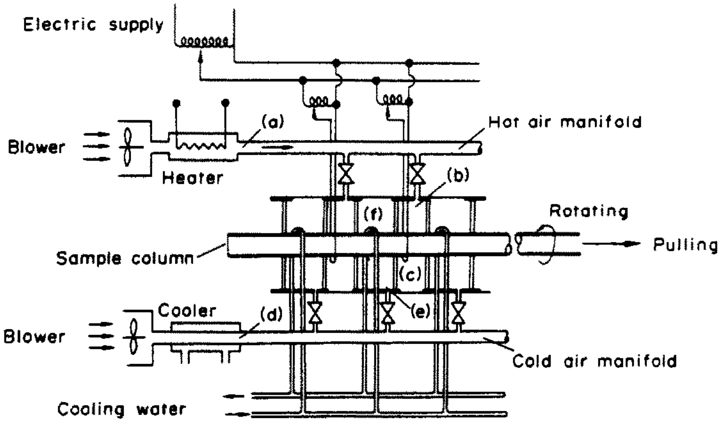

Fig. 1. Schematic diagram of ZMC apparatus.

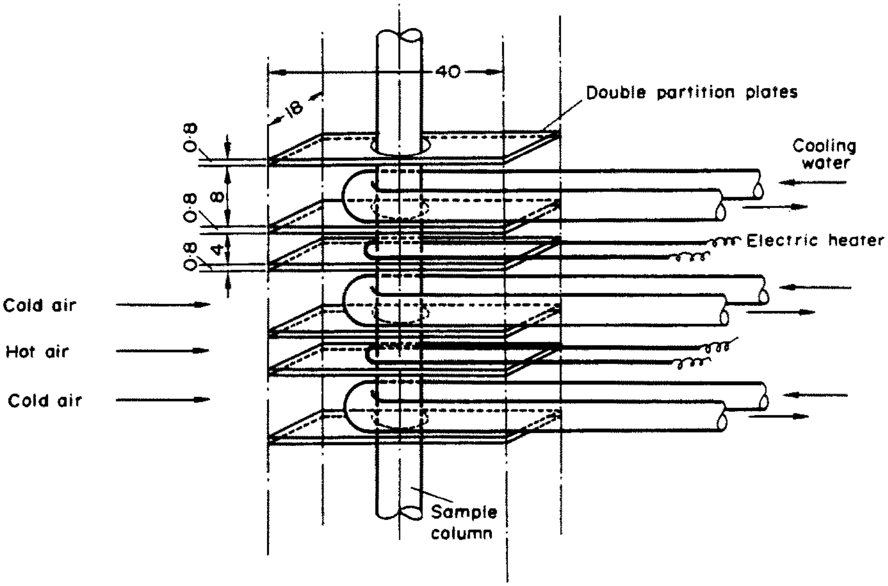

Fig. 2. Complete assembly of ZMC apparatus (dimensions in mm).

partition plates. These consist of thin brass and mica plates each of 0·2 mm thickness, 0·8 mm apart. The sample tube passes through a round hole bored at the centre of each partition plate with a clearance of 0·2 mm. Hot and cold air is introduced into the heating and cooling compartments through their manifolds at a constant flow-rate. Auxiliary heaters and coolers are built into the compartments for finer temperature control. The temperature of each compartment can be controlled independently by an individual air-flow regulator (located near the air nozzle) and a variable transformer for the auxiliary heater. The auxiliary heater and cooler are a sheathed nichrome wire ring, and a ring-shaped copper tube through which cooling water is circulated, respectively.

The sample tube is rotated at a rate of 6 rpm, so that uniform heating can be achieved.[5] The speed of zone travel can be adjusted to 49, 27, 17 and 11 mm/hr. The compartments have glass windows of width 5 mm at the centre of the front and back walls, so that the zones can be observed during an operation. The shape and length of a molten zone were determined by photography. The temperature and flow-rate of the hot and cold air as well as the power of the resistance heaters are adjusted according to the melting point of the column material. Temperature was measured by thermocouples fixed at each monitoring point, away from the walls of the apparatus.

The power supply for the entire apparatus was stabilized at 100 ± 1 V. The flow-rates of the hot and cold air were measured with a gas flowmeter (Yazaki Keiki, Model V-5) with an error of ±3%. The preparation and operation of the sample column were the same as those described previously.[6]

RESULTS AND DISCUSSION

At the first stage of our ZMC study with this new apparatus, the functions of each component were investigated under various operating conditions. The ZMC process was then applied to a system containing a single solute, copper(II) acetylacetonate, in a solid solvent, 2-methoxynaphthalene.

Insulating effect of the double partition plates

Table 1 lists the temperature measured at several points in the apparatus during the operation using 2-methoxynaphthalene (m.p. 72°) as a column material. The letters in brackets correspond to the points shown in Fig. 1.

The temperature at the point (*c*) in a hot compartment is higher than the melting point of 2-methoxynaphthalene by about 60°, and that in the cold compartment (*f*) is lower than the melting point by about 30°.

The thermal insulation efficiency of a thin brass plate, a thin mica plate and a thin brass plate covered with mica were compared, and they showed very little difference. Although the mica plate gave a slightly better effect than the metallic ones, a brass plate showed much better mechanical properties.

If a single partition plate was employed in place of the double partition plates, the temperature difference between the two points, (*c*) and (*f*), was generally less than 60° (regardless of the materials of the partition plates), and this temperature difference is not sufficient to give a successful result. With double partition plates, the gap of 0·8 mm between the two plates gives enough thermal insulation to maintain the required temperature difference of about 90°.

Constancy of zone length during operation

If the column was rotated without being raised the mean zone length was 5·18 mm with a relative standard deviation of 3·6%, when the zone length was measured every hour during a 15-hr operation. At a zone-travel speed of 49 mm/hr, the corresponding values were 5.01 mm and 4·1%, respectively, when measured every 30 min during an 8-hr operation.

Table 1. Operational conditions on a 2-methoxynaphthalene column

Point at which temperature is measured		Temperature, °C
In the hot blast generator	(*a*)*	300–400
At a hot blast nozzle	(*b*)	160–190
In the neighbourhood of the column in a hot compartment	(*c*)	about 130
In a cold blast generator	(*d*)	10–30
At a cold blast nozzle	(*e*)	20–40
In the neighbourhood of the column in a cold compartment	(*f*)	about 45

* See Fig. 1 for positions.

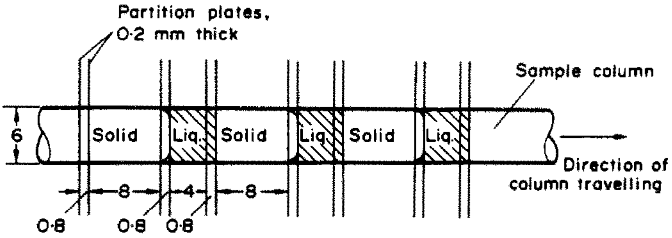

Fig. 3. Shape of the molten zone (dimensions in mm).

Shape of the molten zone

Both freezing and melting interfaces of the molten zone were flat unless the molten zone travelled. If the zone travelled at 49 mm/hr, the melting interface became slightly convex (Fig. 3) and the freezing interface was probably concave. At the lower speed of 27 mm/hr, both interfaces were flat, and remained within the gap of the double partition plates.

Temperature range of efficient operation

In order to establish the working conditions, the apparatus was operated with several organic compounds melting in the range 44–177° as column materials. The results are summarized in Table 2. The temperature of the cooling water determines the lower limit for the melting point of a column material, the upper limit being determined by the heater power.

The apparatus works satisfactorily when the temperature of the heating compartments is 40° higher than the melting point of the column material and of the cooling compartments 30° lower.

Table 2. Operating conditions for various solid solvents

		Cold blast		Hot blast		Compartment temperature, °C	
Solid solvent	m.p., °C	Velocity, *l./min*	Temp., °C	Velocity, *l./min*	Temp., °C	Cold	Hot
Lauric acid	44	116	14·0	88	95	35	55
Maleic acid	53	108	14·7	80	120	34	90
Palmitic acid	64	101	15·0	78	170	45	112
2-Methoxynaphthalene	72	80	13·5	78	180	45	130
Naphthalene	80	84	13·2	86	190	54	140
p-Dibromobenzene	87	78	13·3	83	230	60	145
Phenanthrene	101	53	24	83	230	70	145
Acetoanilide	114	39	20	78	270	75	155
Dimethylterephthalate	140	66	26	80	400	95	187
Camphor	177	38	26	60	480	145	220
Anthracene	220						

(Temperature of cooling water 13–15°C).

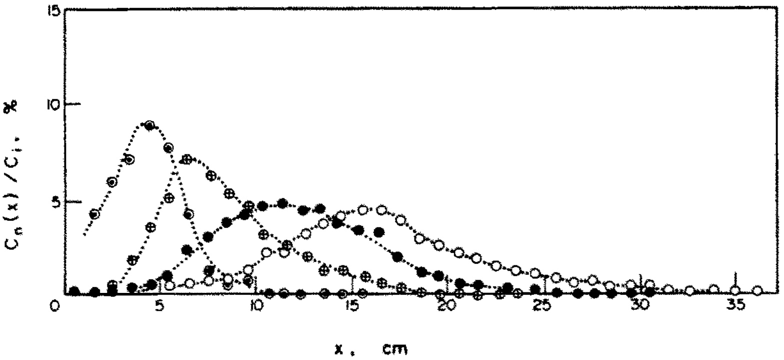

Fig. 4. Distribution of copper concentration on a 2-methoxynaphthalene column after various numbers of zone passes
Initial concentration, C_i = 1000–1500 ppm
Number of zone passes: ⊙ $n = 10$, ⊕ $n = 20$, ● $n = 30$, ○ $n = 40$.

Distribution of the solute on the column

The ZMC process was applied to the system of copper acetylacetonate and 2-methoxynaphthalene. One zone length of solid solution of the copper chelate in 2-methoxynaphthalene was placed on the top of a column of the same solvent, and the entire column was subjected to a ZMC operation. Figure 4 shows some typical examples of the distribution of a solute after the ZMC process. The concentration of the solute is shown in terms of the copper ion concentration.

The ratio of the metal concentration, $C_n(x)$, at a distance x from the column top, to the initial concentration, C_i, is plotted against the distance x.

The results shown in Fig. 4 were obtained with an initial chelate concentration, C_i, in the range 1000–1500 ppm (copper ion), and the number of zone passes was varied from 10 to 40. It is to be noted that as the number of zone passes increases, the maxima in the distribution curves shift towards the lower end of the column, while the peak height is reduced and the peak width increases.

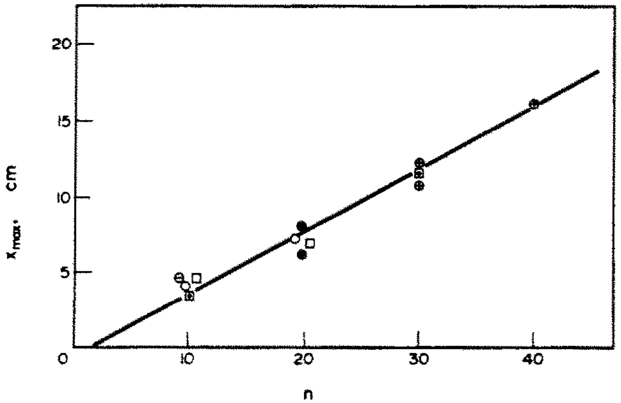

Fig. 5. Peak shifts of distribution curves
Initial concentration, C_i: ○ 1500 ppm, □ 1400 ppm, ⊕ 1300 ppm, ⊡ 1200 ppm, ⊖ 1000 ppm, ⊙ 690 ppm, ● 340 ppm

Figure 5 shows the relationship between the position of the maximum solute concentration, x_{max}, and the number of zone passes, n, observed in 12 experiments. The plot was a good straight line, which can be expressed by the equation:

$$x_{max}(n) = 0{\cdot}40n - 0{\cdot}45$$

The value of x_{max} seems to be determined only by the number of zone passes, being independent of the initial concentration. This result is in accordance with the theoretical prediction that, assuming ideal conditions,[7] the position of a chromatographic peak moves linearly with increase in the number of zone passes except near the top of the column.[8]

The present apparatus overcomes the difficulties of holding the zone length constant, and provides reproducible data in accordance with theoretical predictions.

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Zusammenfassung—Ein verbessertes Gerät zur Zonenschmelzchromatographie (ZMC) wurde konstruiert. Ein wesentliches Merkmal des Geräts ist, daß die Länge der geschmolzenen Zone während der Zonenschmelzoperation konstant gehalten werden kann. Dies wird durch die Verwendung von Heiz- und Kühlabteilen erreicht, die durch doppelte Trennwände voneinander abgeteilt sind. Jedes Abteil wird mit Strahlen von heißer oder kalter Luft geheizt oder gekühlt. Das Gerät ist für organische Stoffe geeignet, die zwischen 40° und 180° schmelzen. Die Verteilung von Metall entlang der Säule war nach dem Zonenschmelzen von Kupferacetylacetonat in 2-Methoxynaphthalin eine glatte Kurve. Die Auftragung der Stellung der maximalen Konzentration x_{max} gegen die Anzahl der Zonendurchgänge n gab eine Beziehung, die mit der theoretischen Voraussage übereinstimmte.

Résumé—On a construit un appareil amélioré pour la chromatographie par fusion de zone (ZMC). Une caractéristique essentielle de l'appareil est que la longueur de la zone fondue peut être maintenue constante durant l'opération de fusion de zone, en employant des compartiments de chauffage et de refroidissement qui sont séparés l'un de l'autre par des doubles plateaux de partage. Chaque compartiment est chauffé ou refroidi par des jets d'air chaud ou froid. L'appareil convient pour des substances organiques fondant dans le domaine compris entre 40° et 180°. Le partage de l'ion métallique le long de la colonne après fusion de zone de l'acétylacétonate de cuivre en 2-méthoxynaphtalène a été une courbe continue. Le tracé de la position de la concentration maximale, x_{max}, par rapport au nombre de passages de zone, n, a donné une relation en accord avec la prévision théorique.

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A POLAROGRAPHIC STUDY OF THE PRE-SODIUM TYPE CATALYTIC HYDROGEN WAVE EXHIBITED BY SELENOCYSTINE

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Summary—Selenocysteine, formed by reduction of selenocystine at the DME at about −0·6 V in an ammoniacal buffer, produces a pre-sodium catalytic hydrogen wave. The effects on this wave of variation of several physico-chemical parameters such as selenocystine concentration, mercury column height, buffer capacity and concentration, and ionic strength, have been studied. The results obtained all support the conclusion that the wave is of pre-sodium type. The partially protonated species of selenocysteine seem to be catalytically active. An analytical determination of selenocystine in the presence of selenocysteine, based on this study, is proposed.

Polarographic studies on the cystine–cysteine system have revealed the existence of a typical catalytic hydrogen reduction wave. As the reduction potential for cystine is relatively low ($E_{1/2} = -0{\cdot}79$ V)[1] it is reduced to cysteine at more negative potentials, and it is this which causes the catalytic waves, which may be due to: (1) catalytic hydrogen discharge of pre-sodium type; (2) catalytic pre-waves of cobalt and nickel; and (3) catalytic hydrogen discharge in the presence of cobalt or nickel ions. A review of this subject has been published by Călușaru.[2] The selenium analogues of cystine and cysteine follow similar oxidation-reduction processes to the sulphur compounds.[3] The catalytic cobalt[4] and nickel[5] pre-waves of the selenium compounds have been studied. Similar catalytic pre-waves are exhibited by the analogous sulphur compound,[6] but in contrast with sulphocystine, in the case of selenocystine the equilibria are established more rapidly. The cobalt and nickel pre-waves, well separated from the diffusion waves of the same ions, are formed without delay after the preparation of the solutions. Cobalt complexes with selenocysteine, resulting from reduction of selenocystine, do not form the catalytic hydrogen waves of the Brdička type in ammoniacal solutions, which are very characteristic in the case of the sulphur compounds.[1,2]

We have found that at very negative potentials selenocysteine forms catalytic hydrogen waves of pre-sodium type in ammoniacal and other buffers. This paper describes the results of an experimental study of this catalytic hydrogen wave.

EXPERIMENTAL

The synthesis of selenocystine has been described;[4] it is based on Painter's method[7] using serine as starting material. Only freshly preparated solutions were used, obtained by dissolution of the solid substance in water, without other solvents. The stability conditions, previously mentioned,[4] have been considered.

A type LP60 polarograph was used with cells as described by Smoler,[8] having a saturated calomel electrode as anode. The capillary constants were: $m = 2{\cdot}64$ mg/sec, $t_1 = 3{\cdot}56$ sec and $h = 56$ cm, in open circuit and $0{\cdot}1M$ ammonium chloride/$0{\cdot}1M$ ammonia as electrolyte.

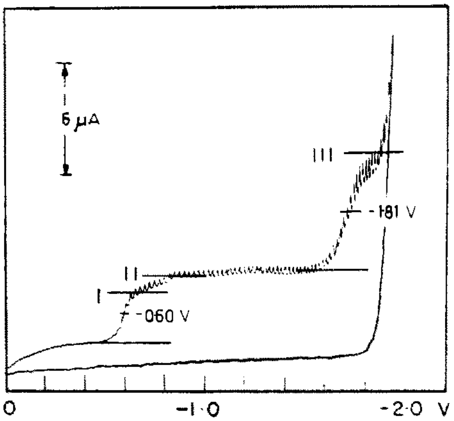


Fig. 1. Polarographic waves of selenocystine, $5 \times 10^{-4}M$, in ammoniacal buffer, NH_4Cl/NH_3, 0·1*M*. Start potential, 0 V; anode, S.C.E.

Polarography of selenocystine in absence of cobalt and nickel ions

Figure 1 shows the polarogram of a $5 \times 10^{-4}M$ selenocystine solution in ammoniacal buffer (NH_4Cl/NH_3, 0·1*M*). Several cathodic processes can be distinguished on this curve. The first wave, with half-wave potential −0·6 V corresponds to the two-electron reduction of selenocystine to selenocysteine. This wave has been described in a paper by Nygård.[3] The half-wave potential is dependent on the pH: −0·374 V at pH = 1·25 and −0·680 V at pH = 12·6. In Fig. 1 can also be seen a post-wave (between I and II) which is sometimes found in the case of other seleno-compounds.[3]

At very negative potentials a catalytic hydrogen wave of pre-sodium type[2] is formed, with half-wave potential −1·81 V. Since at the potentials greater than −0·8 V the selenocystine is completely reduced to selenocysteine, the catalytic wave is produced by this last substance, as in the case of the sulphur compounds.[2]

Effect of selenocystine concentration

In Fig. 2 the polarograms corresponding to different selenocystine concentrations in the range from $0{\cdot}5 \times 10^{-4}$ to $5 \times 10^{-4}M$ are given. The plot of the wave-height *vs.* selenocystine concentration gives a curve, tending slowly towards a limit (Fig. 3). The deviation from linearity is generally more pronounced for catalytic reactions than is indicated in Fig. 3. The difference may be explained by taking into account the enhancement of the catalytic wave[9] caused by the preceding reduction of selenocystine: as the selenocystine concentration is increased so is the height of the reduction wave which in turn enhances the catalytic wave. This effect is significant because the heights of the reduction and the catalytic waves are comparable. Therefore the current is enhanced at high selenocystine concentrations and the non-linearity of the calibration is reduced.

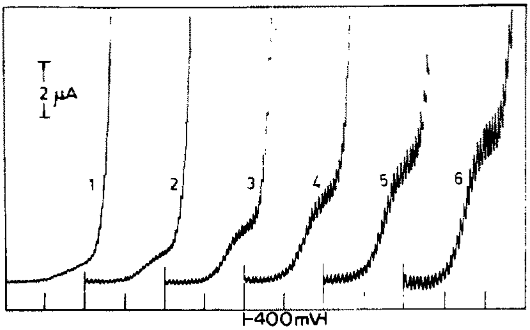


Fig. 2. Waves of catalytic hydrogen discharge of pre-sodium type in presence of selenocystine. Start potentials, −1·40 V; anode, S.C.E.; NH_4Cl/NH_3, 0·1M. Selenocystine concentration: *1* — $0{\cdot}5 \times 10^{-4}M$; *2* — $1 \times 10^{-4}M$; *3* — $2 \times 10^{-4}M$; *4* — $3 \times 10^{-4}M$; *5* — $4 \times 10^{-4}M$; *6*—$5 \times 10^{-4}M$.

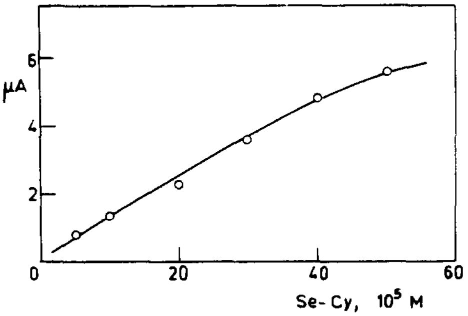


Fig. 3. Variation of the catalytic pre-sodium wave as a function of selenocystine concentration in ammoniacal buffer, NH_4Cl/NH_3, 0·1*M*.

Effect of mercury reservoir height

In contrast with diffusion-controlled waves which increase as the height of the mercury column is increased, the catalytic waves in the presence of Co^{2+} and Ni^{2+} are invariable, and the pre-sodium type waves decrease with increasing height of mercury column.[10,11]

The variation in the catalytic-wave height for selenocystine as a function of $\sqrt{h}$ is given in Fig. 4. This behaviour is very similar to that shown by cycloserine,[11] and is an important empirical indication of a catalytic pre-sodium wave.

Effect of buffer capacity

Only the proton in the catalyst molecule is discharged during the catalytic hydrogen-evolution step. After its elimination a proton from the solution takes its place in the catalyst molecule; it is generally accepted that protonation may sometimes be the rate-determining step for catalytic hydrogen discharge.[2] But the protonation rate is influenced by the buffer capacity, which is why the catalytic wave increases with the increase in the buffer capacity. This variation is considered one of the most characteristic properties of catalytic waves.

In Fig. 5 the variation of the wave height as a function of buffer capacity is given for the buffer component ratio $NH_4Cl/NH_3 = 1$. The shape of the curve is typical for a pre-sodium catalytic wave.

Effect of ammonium chloride concentration

Figure 6 shows the effect, on the height of the catalytic wave, of varying the ammonium chloride concentration at two different ammonia concentrations. Of course both the pH and the buffer capacity are altered, the latter increasing at higher ammonium chloride concentration. Another effect on the pre-sodium wave produced by variation in the ammonium chloride concentration is the modification of the half-wave potential value: at higher concentrations the shift is towards more positive potentials.

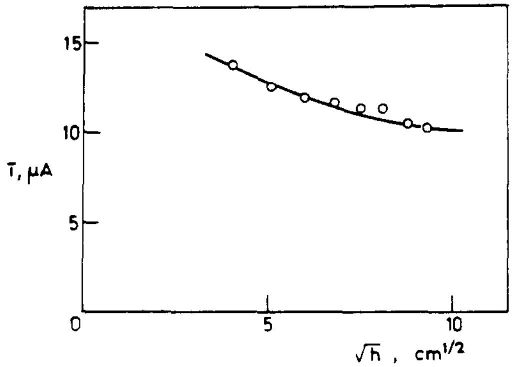


Fig. 4. Catalytic wave height *vs.* square root of mercury reservoir height. Electrolyte: NH_4Cl, 0·1*M*; NH_3, 0·01*M*; selenocystine, 5×10^{-4}*M*.

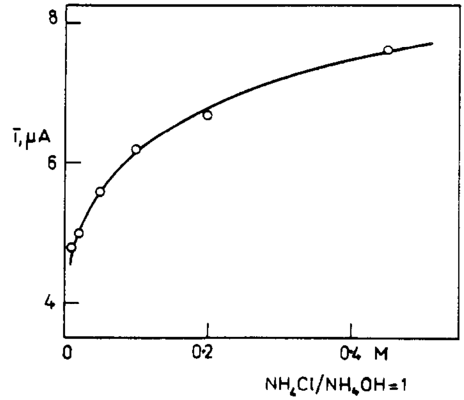


Fig. 5. Effect of the buffer capacity on the catalytic wave height. Selenocystine concentration, $5 \times 10^{-4}M$.

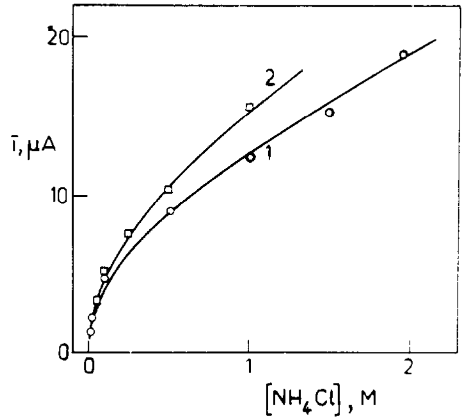


Fig. 6. Effect of NH_4Cl concentration on catalytic wave height. Electrolyte: selenocystine, $5 \times 10^{-4}M$; NH_3 : □ 0·05M; ○ 0·1M.

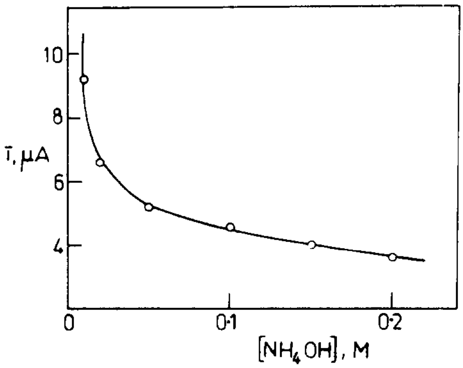


Fig. 7. Effect of ammonia concentration on the catalytic wave. Selenocystine, $5 \times 10^{-4}M$; NH_4Cl, 0·1M.

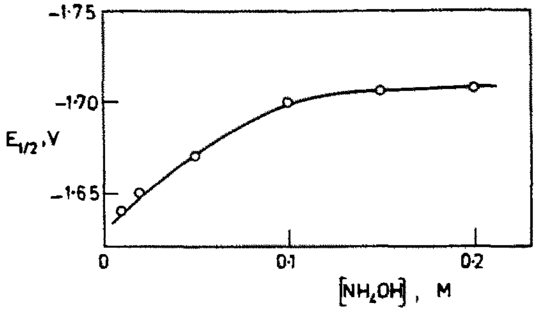


Fig. 8. Effect of ammonia concentration on half-wave potential of the catalytic wave. Selenocystine, $5 \times 10^{-4}M$; NH_4Cl, $0{\cdot}1M$.

Effect of ammonia concentration

Variation of the ammonia concentration affects both the wave height (Fig. 7) and the half-wave potential (Fig. 8) of the catalytic wave. At lower concentrations (lower pH) the wave height decreases sharply, while at higher concentrations the wave height tends towards a limiting value.

Behaviour in acid media

When an acetate buffer is used instead of the ammonium buffer and the pH value is lowered below 7, selenocystine does not form pre-sodium hydrogen waves. However, more complex catalytic waves appear in presence of certain metal ions. This problem will be dealt with in another paper.

Effect of ionic strength

Both ion-discharge and adsorption processes are modified by changes in the ionic strength. The pH value is also changed. It is therefore to be expected that changes in the strong electrolyte concentration would have a complex effect on catalytic waves where electron transfer, adsorption phenomena and protonation reactions are involved.

The effect of strong electrolyte concentration on the selenocystine pre-sodium wave is shown in Fig. 9. Several salts have been used: $NaClO_4$, LiCl, NaCl, $SrCl_2$ and $BaCl_2$. In all cases a decrease in the wave height with increase in concentration is obtained: LiCl has the weakest effect, while $SrCl_2$ and $BaCl_2$ produce the strongest. This behaviour is similar to that observed for other catalytic processes such as the catalytic nickel pre-wave[5] and the catalytic hydrogen wave in the cobalt-cycloserine system.[11]

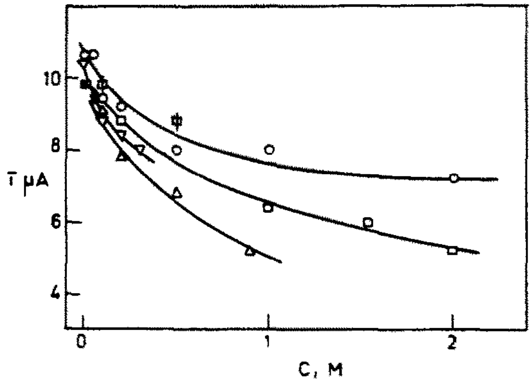


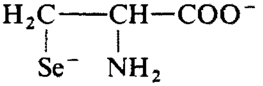
Fig. 9. Effect of the ionic strength on the catalytic wave. Electrolyte: NH_4Cl, $0{\cdot}1M$; NH_3, $0{\cdot}01M$; selenocystine, $5 \times 10^{-4}M$; □ $NaClO_4$; ○ LiCl; □ NaCl; ▽ $SrCl_2$; △ $BaCl_2$.

DISCUSSION

Although in the first paper on the polarography of selenocystine no catalytic processes were reported,[3] subsequent studies revealed several catalytic phenomena including cobalt and nickel pre-waves at very low selenocystine concentrations.[4,5] In the present paper another catalytic process, the catalytic hydrogen discharge of pre-sodium type, is reported.

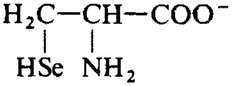
It is of special interest to compare the processes occurring with the sulphur and selenium compounds, in view of the well known role of the –SH groups in catalytic hydrogen discharge. From this point of view the main difference between sulpho- and selenocystine lies in the absence of Brdička-type catalytic waves for the selenium compound in the presence of cobalt or nickel ions and an ammonical buffer. This fact indicates that there is not a direct correlation between the metal ion pre-wave and the Brdička-wave, as has sometimes been suggested.

For the interpretation of the selenocysteine pre-sodium wave we refer to the protonated forms of this substance. As in the case of cysteine, four forms may be considered:[4]



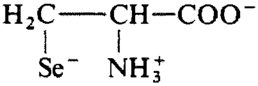
$\underset{\mathrm{Se^-}}{\mathrm{H_2C}}-\underset{\mathrm{NH_2}}{\mathrm{CH}}-\mathrm{COO^-}$

(*a*)



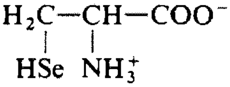
$\underset{\mathrm{HSe}}{\mathrm{H_2C}}-\underset{\mathrm{NH_2}}{\mathrm{CH}}-\mathrm{COO^-}$

(*b*)



$\underset{\mathrm{Se^-}}{\mathrm{H_2C}}-\underset{\mathrm{NH_3^+}}{\mathrm{CH}}-\mathrm{COO^-}$

(*c*)



$\underset{\mathrm{HSe}}{\mathrm{H_2C}}-\underset{\mathrm{NH_3^+}}{\mathrm{CH}}-\mathrm{COO^-}$

(*d*)

The form (*a*) is stable only in very alkaline media and the form (*d*) in acid solutions. For the equilibrium reaction between the forms (*c*) and (*d*) pK_a' was found to be 5·7 by Nygård.[3] Therefore for the pH range used in the present work it is possible to consider that mainly the forms (*b*) and (*c*) were present and responsible for the hydrogen discharge in the region of the catalytic pre-sodium wave. Taking into account the strong decrease of the wave height in concentrated ammonia solution media it is possible to consider that the form (*a*) has no catalytic effect. The decrease in wave height with increase in pH can be explained by the equilibrium displacement of the protonation reaction from the forms (*b*) and (*c*) to the inactive or less active form (*a*).

Several interpretations of the mechanism of the catalytic hydrogen discharge of pre-sodium type have been proposed.[1] More recently Mairanovskii considered the bimolecular reaction:

$$2BH \rightarrow 2B + H_2$$

as the main step in this process.[10] BH^+ represents the protonated form of the catalyst B. Březina and Kůtova[9] discussed this scheme in connection with the catalytic waves formed in the presence of an organic and inorganic depolariser. Owing to the enhancement effect on the hydrogen wave produced by the preceding reduction reaction, too close an agreement between experiment and theory cannot be expected. In the selenocystine system, studied in the present work, the preceding reaction is represented by reduction of the –Se–Se– bridge, as we have previously emphasised. There are also other factors which can affect the height of the catalytic wave, such as catalyst adsorption, electrolyte stirring at the mercury drop surface, and modification of the double-layer composition. The last of these may be achieved by changing the concentration of strong electrolyte, a technique often used in electrochemical studies. The results presented in Fig. 9 showing the decrease of the catalytic-wave height with increase in supporting electrolyte concentration are in good agreement with the behaviour of the pre-sodium wave formed in other systems.[10]

ANALYTICAL APPLICATIONS

The results of this study suggest a possible method for the determination of selenocystine in the presence of selenocysteine. From Fig. 1 the wave with $E_{1/2} = -0{\cdot}60$ V corresponds to reduction of selenocystine and may be used for a normal polarographic determination of this compound.

It is also possible to determine polarographically selenocysteine in the presence of selenocystine. For this purpose the catalytic pre-sodium wave at $-1{\cdot}81$ V must also be used. It is necessary to construct two calibration curves: (1) wave III *vs.* wave (I + II) (Fig. 1) in a solution containing selenocystine only; (2) wave (III) *vs.* concentration in a pure selenocysteine solution under the same conditions as for Fig. 1. In the sample to be analysed, containing both substances, the pre-sodium wave (III) will be higher than would correspond to a pure selenocystine solution, but by use of the wave at $-0{\cdot}60$ V and the calibration curve (1), the pre-sodium wave height corresponding to the selenocystine concentration can be determined. From the difference between the pre-sodium wave height for the sample and that predicted from calibration curve (1), the concentration of selenocysteine can be determined from the calibration curve (2).

Although the waves of cystine or cysteine interfere with the waves of the corresponding seleno-compounds, it is possible to determine qualitatively the presence of the sulphur-compounds, since they give rise to a catalytic hydrogen wave at more positive potentials (about 200 mV) in the presence of cobalt and in an ammoniacal buffer,[1,2] and the selenium compounds do not.[3-5] However, it should be pointed out that a number of other substances also give rise to pre-sodium waves,[1,2] The error in the determinations lies in the range ±2–3% for concentrations of $0{\cdot}5\text{–}6 \times 10^{-4}M$.

In view of the increasing interest in organoselenium compounds—in particular the selenocystine–selenocysteine system—this method may prove useful for control of purity of selenocysteine prepared by reduction of selencystine.

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Zusammenfassung—Selenocystein, das sich in einem ammoniakalischen Puffer bei etwa $-0{\cdot}6$V durch Reduktion von Selenocystin an der Quecksilbertropfelektrode bildet, zeigt vor der Natriumstufe eine katalytische Wasserstoffstufe. Der Einfluß der Veränderung mehrerer physikalisch-chemischer Parameter wie Konzentration von Selenocystin, Höhe der Quecksilbersäule, Pufferkapazität und -konzentration sowie der Ionenstärke auf diese Stufe wurde untersucht. Alle Ergebnisse unterstützen den Schluß, daß die Stufe vom Pränatriumtyp ist. Die teilweise protonierten Spezies von Selenocystein scheinen katalytisch aktiv zu sein. Auf Grund dieser Untersuchung wird eine analytische Bestimmung von Selenocystin in Gegenwart von Selenocystein vorgeschlagen.

Résumé—La sélénocystéine, formée par réduction de la sélénocystine à l'électrode à goutte de mercure à environ −0, 6V dans un tampon ammoniacal, produit une vague hydrogène catalytique pré-sodium. On a étudié les influences sur cette vague de la variation de plusieurs paramétres physico-chimiques tels que la concentration en sélénocystine, la hauteur de la colonne de mercure, la capacité et la concentration du tampon, et la force ionique. Les résultats obtenus sont tous en faveur de la conclusion que la vague est du type pré-sodium. L'espèce partiellement protonée de la sélénocystéine semble être catalytiquement active. On propose un dosage analytique, basé sur cette étude, de la sélénocystine en présence de sélénocystéine.

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DOSAGE MICROANALYTIQUE DU DEUTERIUM DANS LES COMPOSES ORGANIQUES

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Resumé—La méthode décrite comporte une combustion éclair du prélèvement analytique dans une chambre de combustion en silice à 950–1050°, sous courant d'oxygène de 60 ml/mn. Cette combustion en phase gazeuse est complétée par une oxydation des gaz de combustion primaires, sur oxyde de cuivre à 850°. Les produits d'oxydation porteurs d'halogènes et de soufre sont retenus sur alumine argentée à 750–800°. L'eau de combustion contenant l'oxyde et l'hydroxyde de deutérium est séparée des autres gaz de combustion sous forme de glace, dans un piège spécial, refroidi par un dispositif cryogène et pourvu de deux robinets à 5 voies qui permettent l'écoulement simultané d'oxygène et d'hydrogène. Ce dernier est utilisé comme gaz vecteur, en aval du piège. La glace est ensuite vaporisée par chauffage sous courant d'hydrogène de 30 ml/mn et la vapeur réduite par du magnésium à 600°. Le deutérium passe sous forme d'hydrure de deutérium HD au sein du courant d'hydrogène; il y est dosé par mesure différentielle de la conductibilité thermique du système gazeux. La durée d'une analyse, dans une série, est d'environ 15 minutes. La précision des résultats correspond à l'ordre de grandeur classique, en microanalyse organique.

L'idée directrice du présent travail est de mettre en œuvre les méthodes de la microanalyse organique élémentaire moderne pour les appliquer aux dosages du deutérium et, par conséquent, d'éviter de recourir à des appareils lourds et coûteux (spectromètre de masse, par exemple).

La microanalyse organique élémentaire comporte, en général, deux phases: la production de la molécule chimique quantitativement représentative de l'élément à doser, usuellement dénommée minéralisation, et le dosage proprement dit ou mesurage de la quantité de cette molécule. La méthode de mesurage susceptible d'être retenue conditionnant la minéralisation, il importe de la sélectionner en premier lieu.

Les méthodes le plus souvent utilisées, à cette fin, ont été étudiées et comparées entre elles par plusieurs auteurs.[1–6]

Le mesurage différentiel, à l'aide d'un catharomètre, de la variation de la conductibilité thermique d'un système gaz vecteur produits (de la minéralisation) en fonction de la concentration du soluté, a paru convenir à notre objectif. Son application implique la possibilité de produire, par minéralisation, une molécule deutériée appropriée et le choix du gaz vecteur correspondant.

La minéralisation par combustion dans l'oxygène d'un composé organique deutérié fournit de l'eau deutériée contenant de l'oxyde d'hydrogène H_2O, de l'oxyde de deutérium D_2O et de l'hydroxyde de deutérium HDO en équilibre suivant la réaction:

$$H_2O + D_2O \rightleftharpoons 2HDO \qquad (I)$$

Sans préjudice d'autres difficultés, les faibles différences des conductibilitiés thermiques de ces trois molécules, sont défavorables au choix de D_2O ou de HDO comme solutés mesurables.

D'aucuns ont tourné cette difficulté en réduisant les eaux deutériées en vue d'obtenir le deutérium D_2 ou son hydrure HD qui peuvent, par ailleurs, être engagés dans la réaction d'équilibre:

$$H_2 + D_2 \rightleftharpoons 2HD \qquad \text{(II)}$$

dont la constante est fort heureusement peu variable en fonction de la température;[7] les conductibilités thermiques de D_2 ou HD diffèrent, en effet, plus sensiblement de celle de H_2 que les conductibilités de D_2O et HDO de celle de H_2O.

Les principaux réducteurs utilisés pour le traitement des eaux deutériées ou de composés deutériés simples sont le magnésium,[8–11] l'uranium,[12–14] le zinc,[15] le zinc platiné,[16,17] le fer,[18–22] l'hydrure de calcium,[23–25] l'hydrure de lithium-aluminium.[25]

L'examen des publications montre, cependant, que les réducteurs cités ne sont pas tous susceptibles d'être utilisés dans le cadre de notre travail; c'est ainsi que le zinc, même platiné, donne lieu à des réductions trop lentes, que le fer nécessite d'opérer, en plusieurs étapes, sous pression réduite, que l'hydrure de calcium doit être renouvelé, entre chaque dosage et qu'en outre, il donne lieu à une réduction qui peut n'être pas quantitative;[26] quant à l'hydrure de lithium-aluminium, il est simplement mentionné mais doit, selon toute vraisemblance, être inactivé, à l'instar de l'hydrure de calcium, par formation superficielle d'oxydes; seuls le magnésium et l'uranium semblent présenter des caractéristiques appropriées à notre propre étude, sous réserve d'effectuer les réductions sous courant d'hydrogène, gaz vecteur, dont la présence, en excès, déplace la réaction d'équilibre (II) vers la formation pratiquement exlusive de HD.

Nous avons éprouvé ces caractéristiques au cours d'essais qui ont conduit aux résultats dont il est fait état ci-après.

Reduction par l'uranium

Des essais préliminaires ont fait l'objet d'un stage[27] effectué par l'un d'entre nous (Mme. D. Girard) à la Section des Isotopes du Centre d'Etudes Nucléaires de Saclay, dirigée par M. Dirian, sous l'autorité de Mme. Botter, nous permettant ainsi de bénéficier d'une expérience déjà acquise;[12,13] ces essais ont porté sur la réduction des eaux deutériées par l'uranium à 625–650°, et ont conduit à des résultats positifs encourageants, à savoir: la réduction quantitative de l'eau, la linéarité de la courbe d'étalonnage pour des masses de deutérium comprises entre 9 et 440 μg, un faible effet de mémoire et une répétabilité des résultats satisfaisante à ce stade de l'étude. Par la suite, diverses anomalies, dont les suivantes, sont apparues au cours du dosage du deutérium sur des composés organiques et des eaux deutériées: obtention, à l'enregistrement du signal du catharomètre, de deux pics et non pas, comme il était attendu, d'un seul pic correspondant à la présence exclusive de HD dans l'hydrogène (gaz vecteur), lorsque les gaz, après réduction, ont traversé un tamis moléculaire 5A; obtention de signaux différents, pour une même masse de deutérium, selon que les composés analysés sont partiellement deutériés ou perdeutériés. Ces anomalies n'ont pu être éliminées au cours d'essais portant sur l'influence des variations de paramètres tels que température et état de division de l'uranium, d'une part, débit de l'hydrogène, d'autre part. Elles nous ont conduits à envisager le remplacement de l'uranium par le magnésium. Ce dernier semblant devoir donner satisfaction, les travaux sur l'emploi de l'uranium ont été suspendus.

Reduction par le magnésium

Le magnésium a été utilisé, au cours de multiples essais, sous forme de rubans ou de copeaux. Les prélèvements analytiques d'eaux deutériées ont été introduits dans l'appareil à réduction par injection à l'aide de seringues; ils étaient caractérisés par deux paramètres: leur volume (de 0,2 à 10 μl) et le taux isotopique* des eaux deutériées† (10 taux différents). Huit cents dosages de deutérium ont pu être ainsi effectués sur les gaz de réduction des prélèvements d'eau par une même charge de 5 g de magnésium.

Il est apparu que l'emploi du magnésium permet non seulement d'obtenir les mêmes résultats que ceux qu'avait fournis initialement l'uranium (réduction quantitative, linéarité, faible effet de mémoire, répétabilité des résultats), mais en outre, lors d'une étude plus poussée, qu'il ne donne pas lieu comme celui de l'uranium, à l'apparition d'un double pic au sortir des gaz de réduction d'un tamis moléculaire 5A.

La répétabilité des résultats est satisfaisante: c'est ainsi, par exemple, que les écarts relatifs estimés à partir d'une dizaine de dosages portant sur des prélèvements d'eau de 2 μl, sont de 0,5% pour une eau d'un taux isotopique de 99,7% (masse de deutérium dans 1 μl d'eau: 0,22 mg), de ±1,5% dans une eau de taux isotopique de 10,8% (masse de deutérium dans 1 μl d'eau: 0,022 mg) et de ±2,5% dans une eau de taux isotopique de 1,6% (masse de deutérium dans 1 μl d'eau: 0,0032 mg).

Le magnésium a donc été finalement retenu, en vue du dosage microanalytique du deutérium, dans les composés organiques, fondé sur la variation de conductibilité thermique du système H_2–HD. A cette fin, les eaux, formées lors de la combustion préalable dans l'oxygène des prélèvements analytiques, sont traitées comme il est indiqué ci-après.

Principe

Le prélèvement analytique (1,5 à 10 mg) est brûlé quasi instantanément, sous courant d'oxygène d'environ 60 ml/mn, dans une chambre de combustion portée à la température de 950–1000°, suivant une technique décrite par Ingram[28] et modifiée par Fraisse.[29] Les gaz de combustion sont entraînés par l'oxygène sur une garniture d'oxyde de cuivre en fils, maintenue à 750–850°, où s'achève leur oxydation, puis sur une garniture d'alumine argentée à environ 750° et un tampon de laine d'argent à environ 720° où sont retenus les produits contenant du soufre et des halogènes (y compris le fluor). L'eau de combustion deutériée est condensée quantitativement dans un piège dit "piège à eau," refroidi à environ $-40°$, tandis que les autres gaz de combustion, tels que le dioxyde de carbone, et, dans le cas de l'analyse des composés azotés, l'azote et certains oxydes de l'azote, sont balayés vers l'atmosphère par le courant d'oxygène (le peroxyde d'azote, s'il se forme, peut cependant être retenu dans le piège).

Grâce à un système approprié à deux robinets, le piège contenant l'eau deutériée est tout d'abord isolé du tube à combustion, balayé par un courant d'hydrogène pour chasser l'oxygène présent, puis mis en communication avec le tube à réduction. Les eaux sont alors vaporisées par réchauffage du piège et entraînées par le courant d'hydrogène vers une garniture de copeaux de magnésium maintenue à la température de 600°. En présence d'un grand excès d'hydrogène (la concentration de l'eau deutériée dans

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* Taux isotopique $= \dfrac{\text{nombre d'atomes D}}{\text{nombre d'atomes H} + \text{nombre d'atomes D}} = \dfrac{n_D}{n_H + n_D}$

† Les échantillons d'eaux soumis à l'analyse ont été préparés par addition de quantités pesées d'eau lourde de taux isotopique de 99.7% à des quantités pesées d'eau naturelle distillée, les taux isotopiques des eaux deutériées ainsi préparées variant de 1.07 à 70.8%.

l'hydrogène atteint au maximum 2% en volume), l'eau deutériée qui est susceptible de contenir les molécules H_2O, D_2O et HDO en proportions variables [*cf.* réaction d'équilibre (I)] est réduite par le magnésium en donnant naissance exlusivement à H_2 et HD [*cf.* réaction d'équilibre (II)].

L'hydrure de deutérium ainsi formé est ensuite entraîné par le courant d'hydrogène vers le site de mesurage. Il traverse la cellule de mesure d'un catharomètre tandis qu'un courant d'hydrogène pur traverse la cellule de référence. La quantité de deutérium à doser est mesurée à l'aide d'un système catharomètre-pont de Wheatstone-intégrateur (ou enregistreur).*

PARTIE EXPERIMENTELLE

Appareillage

L'appareillage (figure 1) comporte 4 sections principales caractérisées par leurs fonctions: minéralisation des composés organiques, piégeage et transfert de l'eau de combustion, réduction de l'eau de combustion et mesurage. Il est complété par divers annexes et accessoires qui sont décrits ci-après.

Minéralisation des composés organiques

L'appareil de minéralisation est en tout point comparable à celui décrit par Fraisse.[29,30] Rappelons que le courant d'oxygène, issu d'un tube de gaz comprimé pourvu d'un manodétendeur, traverse, dans l'ordre, un régulateur de pression et un rotamètre (1, figure 1), préalablement étalonné; son débit est fixé entre 50 et 70 ml/mn. Il est ensuite purifié sur une garniture d'oxyde de cuivre en fil (2, figure 1) porté à 750° dans un four tubulaire suivi de tubes absorbeurs (3, figure 1) comportant une garniture d'amiante sodé (ascarite) et de perchlorate de magnésium (anhydrone).

Le tube à combustion,[30] en silice transparente, comprend une chambre, une partie tubulaire pourvue d'un ajutage latéral (4, figure 1) et un système d'introduction non représenté sur la figure (*cf.* Ingram[28] et Fraisse).[32] La chambre de combustion est portée à 1000° et la partie tubulaire contenant les réactifs (oxyde de cuivre et laine argentée) à 800°.[32]

Piégeage et transfert de l'eau de combustion

Le dispositif mis en œuvre est identique à celui décrit par Fraisse.[29] Il a ici pour objets le piégeage momentané de toute l'eau de combustion entraînée par le courant d'oxygène et le transfert ultérieur de cette eau après réchauffage, vers le site de réduction, sous courant d'hydrogène.

Rappelons qu'à cette double fin, il se compose de deux robinets A et B accouplés comme le montre la figure 2 et dont chaque clé comporte 3 voies et chaque boisseau est pourvu de 5 branches tubulaires dont trois réalisent l'accouplement, par soudage. La branche 1 raccorde le dispositif au tube à combustion (*cf.* figure 1), la branche 5 permet l'adduction du courant d'hydrogène, la branche 7 conduit les gaz, vers la sortie de l'appareil, dans l'atmosphère, et la branche 6 raccorde le système au dispositif de réduction des eaux (*cf.* figure 1).

Cet ensemble permet l'écoulement simultané des courants d'oxygène et d'hydrogène. En effet, dans un premier temps, correspondant à la combustion du prélèvement analytique et au piégeage de l'eau de combustion, le courant d'oxygène, chargé des gaz de combustion, pénètre par la branche 1, traverse la branche 3, qui constitue le piège proprement dit, et s'écoule vers l'atmosphère, par la branche 7; simultanément, le courant d'hydrogène, issu de la cellule de référence du catharomètre, entre par la branche 5, traverse les branches 4 et 6, balaie le tube à réduction et enfin la cellule de mesure du catharomètre; dans un deuxième temps, la rotation de 90° du robinet A, dans le sens inverse des aiguilles d'une montre, interrompt le courant d'oxygène tandis que le courant d'hydrogène traverse la branche dite "piège" 3 et s'écoule vers l'atmosphère; dans un troisième temps, la rotation du robinet B de 90°, dans le sens des aiguilles d'une montre, rétablit et le courant d'oxygène par les tubulures 1, 2 et 7 et le courant d'hydrogène par les tubulures 5, 4 et 6 vers la cellule de mesure. La tubulure 3, qui permet le piégeage de l'eau de combustion, comporte, à cette fin, une partie tubulaire médiane, en verre "Pyrex," garnie d'un faisceau de fils d'or, en vue d'améliorer les échanges thermiques. L'eau de combustion peut être gelée, dans ce piège, par refroidissement à l'aide d'un manchon formé de deux coquilles hémicylindriques, préalablement refroidi par immersion au sein de neige carbonique.[31] L'eau de combustion gelée peut être vaporisée par réchauffage électrique, par effet Joule, grâce à un bobinage de fil résistant en nickel-chrome.

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* L'incorporation de l'enregistreur dans l'appareil n'est nécessaire que pour l'étude proprement dite: elle devient superflue dans l'appareil de dosages en série.

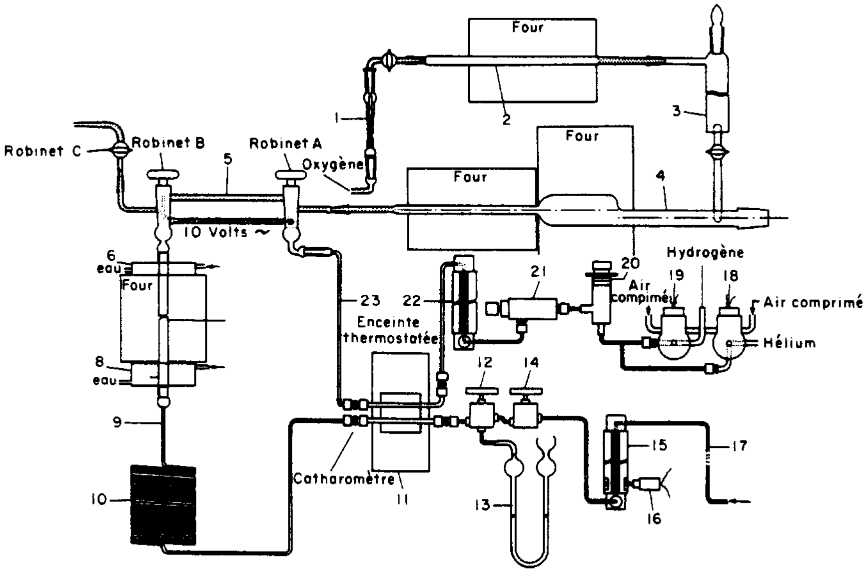

Fig. 1. Schéma de l'appareillage.

1 — Rotamètre.

2 — Tube en silice transparente, qualité étirée (diamètres: 11/8 mm, longueur: 240 mm) pourvu d'un joint conique rodé femelle RIN 00 et prolongé par un tube abducteur (diamètres: 7/2 mm, longueur: 80 mm) terminé par un joint conique rodé mâle RIN 00; longueur de la garniture d'oxyde de cuivre: 160 mm; ce tube est raccordé au rotamètre par un robinet comportant deux joints coniques rodés mâle RIN 0 et RIN 00.

3 — Tube en verre "Pyrex" (diamètres: 28/2 mm, longueur: 210 mm) pourvu d'un joint conique rodé femelle RIN 00 et d'un tube abducteur comportant un robinet et un joint conique rodé femelle RIN 0; un joint conique rodé femelle RIN 1 fermé par un bouchon conique rodé femelle RIN 1 permet l'introduction de la garniture d'amiante sodé (longueur: 100 mm) et de perchlorate de magnésium (longueur: 100 mm).

4 — Tube à combustion en silice transparente, qualité étirée.

5 — Dispositif de piégeage et de transfert des gaz.

6–8 — Réfrigérants en laiton à circulation d'eau. La température de l'eau est comprise entre 15 et 20°.

7 — Tube en alumine frittée.

9 — Raccord verre "Pyrex" — alliage Kovar-tube en acier inoxydable, pourvu d'un joint conique rodé femelle RIN 1/2.

10 — Tube retardateur en acier inoxydable (diamètres: 3,2/2 mm, longueur: 5 m).

11 — Enceinte à thermostat contenant le détecteur.

12 — Robinet à 3 voies en acier inoxydable.

13 — Manomètre à mercure en verre "Pyrex."

14 — Robinet d'arrêt.

15 — Rotamètre.

16 — Dispositif de déclenchement du système de sécurité à cellule photoélectrique et source lumineuse.

17 — Tube semi-capillaire en acier inoxydable (diamètres: 2/0,5 mm, longueur: 5 m).

18, 19 — Electrovannes refroidies par un courant d'air comprimé.

20 — *Cf.* 14.

21 — Régulateur de débit à pression différentielle.

22 — Rotamètre.

23 — Tube en acier inoxydable pourvu d'un joint conique rodé mâle RIN 00 en laiton (longueur: environ 2 m), permettant le raccordement du détecteur au dispositif de piégeage.

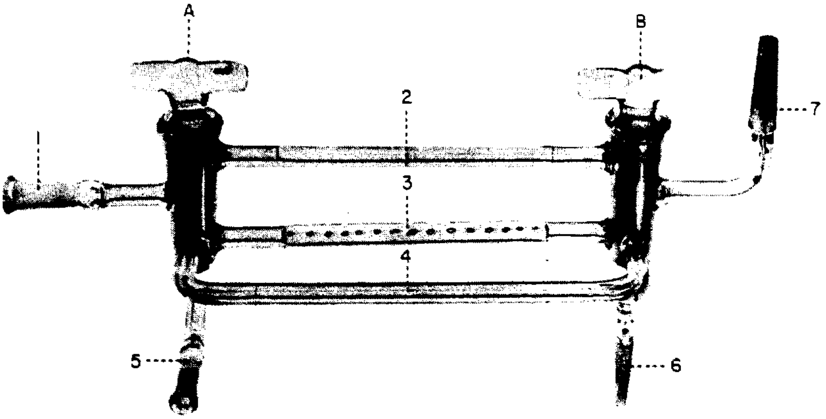

Fig. 2. Dispositif de piégeage et de transfert de l'eau de combustion.

Réduction de l'eau de combustion

L'eau de combustion gelée puis vaporisée dans le piège est entraînée sous courant d'hydrogène jusqu'au dispositif de réduction.

Celui-ci comprend un tube en alumine frittée Desmarquet AF 975 (1, figure 3) pourvu, à chaque extrémité, d'un joint conique rodé mâle permettant son raccordement au piège, d'une part, et à la cellule de mesure, d'autre part; les joints coniques rodés sont graissés avec de la graisse Apiezon H et fixés par des ressorts métalliques sous tension. Le tube à réduction comporte une garniture de 5,5 g de magnésium en copeaux (5, figure 3) qui constitue une colonne de 250 mm. Il est placé dans un four tubulaire de 360 mm de longueur qui permet d'obtenir une température stable comprise entre 580 et 600° sur toute la longueur de la garniture de magnésium (*cf.* Fraisse et Levy).[31] La température du four est repérée à l'aide d'un thermo-couple platine–platine rhodié à 10% disposé verticalement dans le tube laboratoire du four. Afin d'éviter un détassement de la garniture de magnésium provoqué par la formation d'oxyde de magnésium pulvérulent, le tube à réduction est placé verticalement; un petit tampon de toile de nickel-chrome (6, figure 3) permet de maintenir la garniture dans la zone de température convenable. La proximité du four et des joints coniques rodés graissés peut être la cause de fuites; pour maintenir l'étanchéité, deux réfrigérants, à circulation d'eau (2_1, 2_2, figure 3), en laiton, formés chacun de deux coquilles hémicylindriques, sont placés autour du tube d'alumine, à chaque extrémité du four.

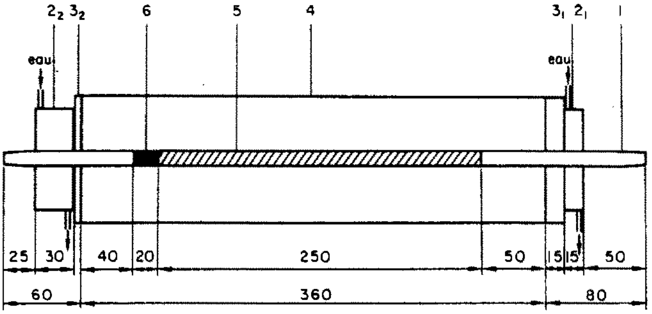

Fig. 3. Dispositif de réduction (cotes en mm).

1 — Tube en alumine frittée (diamètres 12/8 mm, longueur: 500 mm) pourvu à chaque extrémité d'un joint conique rodé mâle RIN 1/2.

2 — Réfrigérant en laiton à circulation d'eau formé de deux coquilles creuses hémicylindriques, serrées autour du tube en alumine.

2_1 — Réfrigérant supérieur (épaisseur: 15 mm).

2_2 — Réfrigérant inférieur (épaisseur: 30 mm).

3 — Plaque d'amiante assurant un isolement thermique entre le four et les deux réfrigérants.

4 — Four tubulaire.

5 — Garniture de magnésium (hauteur: 250 mm).

6 — Tampon de toile de nickel-chrome (hauteur: 20 mm).

Mesurage

L'appareil utilisé est un détecteur (catharomètre), du type Pretzel 9285 (GOW-MAC Instruments Company, Madison, New Jersey, U.S.A.), à quatre cellules dont les filaments, en tungstène rhénié W2X constituent les quatre branches d'un pont de Wheatstone. Ce dernier est alimenté par un courant stabilisé fourni par une alimentation du type 40-05C (GOW-MAC).

La variation de l'écart de conductibilité thermique entre l'hydrogène pur et l'hydrogène chargé d'hydrure de deutérium produit dans le tube à réduction donne lieu à la variation de la tension de déséquilibre du pont en fonction du temps. L'integration correspondante est effectuée, à l'aide d'un intégrateur électronique ou électromécanique, auquel peut être adjoint un enregistreur potentiométrique. Le détecteur est placé dans une enceinte thermostatique dont la régulation de température est assurée à un dixième de degré près. L'hydrogène issu d'un tube de gaz comprimé pourvu d'un manodétendeur traverse, dans l'ordre, une électrovanne, (19, figure 1) dont le rôle est précisé ci-après, un robinet d'arrêt, type Ugine V3 (DAM-SETARAM, Lyon, France), permettant la fermeture de l'appareil en période d'arrêt prolongé (20, figure 1), un régulateur de débit à pression différentielle type 8844 (Brooks Instr. N.V. Veenendaal, Pays-Bas) (21, figure 1) et un rotamètre (22, figure 1) pour le repérage du débit. La connexion des appareils est réalisée par des tubes d'acier inoxydable de diamètre 2 et 3,2 mm directement brasés ou assemblés par raccords "Swagelock." Le courant d'hydrogène traverse ensuite les deux premières cellules du catharomètre (11, figure 1) dont les filaments sont les résistances de référence du pont de Wheatstone, avant de pénétrer dans le dispositif de piégeage de l'eau de combustion (5, figure 1), par l'intermédiaire d'un tube en acier inoxydable (23, figure 1) puis, successivement, dans le tube à réduction (7, figure 1) et dans les deux autres cellules du catharomètre dont les filaments sont les résistances de mesure du pont de Wheatstone. Le raccordement du tube à réduction au catharomètre est assuré par un serpentin retardateur (10, figure 1) qui est réalisé en tube d'acier inoxydable terminé par un tube de raccord métal-verre (9, figure 1); *il a pour object de retarder d'environ 1 mn 30 s l'arrivée, dans les cellules de mesure, de l'hydrure de deutérium entraîné par le courant d'hydrogène*; ce laps de temps permet au pont de Wheatstone d'atteindre à nouveau son équilibre momentanément rompu lors du balayage du piège, par l'hydrogène, vers l'atmosphère (*cf. Piégeage et transfert de l'eau*).

A la sortie des cellules de mesure, le courant d'hydrogène traverse un robinet à trois voies (12, figure 1), auquel est raccordé un manomètre à mercure (13, figure 1), un robinet d'arrêt permettant la fermeture de l'appareil (14, figure 1), un rotamètre (15, figure 1), et enfin un tube semi-capillaire, en acier inoxydable, (17, figure 1), dont la fonction est de créer une perte de charge suffisante, en sortie de l'appareil, et ainsi, de minimiser l'influence des variations de pertes de charge au sein de l'appareil, sur le débit d'hydrogène. Un dispositif de sécurité (Crawford Fitting Co., Cleveland, U.S.A.), asservi au débit du courant d'hydrogène, complète l'appareil; il permet la substitution d'un courant d'hélium au courant d'hydrogène. A cette fin, une cellule photoélectrique (16, figure 1) reçoit le faisceau lumineux émis par une lampe à travers le tube du rotamètre (15, figure 1). L'interruption accidentelle du courant d'hydrogène donne lieu à la chute de la bille du rotamètre, ce qui provoque la coupure du faisceau lumineux et le déclenchement du système de sécurité, à savoir, la fermeture de l'électrovanne (19, figure 1) qui coupe l'arrivée de l'hydrogène dans l'appareil et, simultanément, l'ouverture d'une autre électrovanne (18, figure 1) qui le fait balayer par un courant d'hélium. En cours d'analyse, le système de sécurité est mis hors circuit.

Réactifs

Minéralisation. — Oxygène de qualité N 45 ("Air Liquide").

— Oxyde de cuivre en fil tamisé (module 29-31, norme NF XII-501) calciné à l'air (Prolabo n° 23 150).

— Amiante sodé (8–20 mesh): Ascarite (Arthur H. Thomas Company, Philadelphia, Pa., U.S.A.).

— Perchlorate de magnésium (10–20 mesh): Anhydrone (G. Frederick Smith Chemical Co., Colombus, Ohio, U.S.A.).

— Alumine argentée. La préparation est effectuée suivant le mode opératoire décrit par Zimmermann[32] pour la ponce argentée.

Matières premières:

— Alumine "Alcel" en grains de 1 mm environ (Desmarquet, France),

— Nitrate d'argent pur cristallisé.

— Argent vierge en fils (diamètre: 0,05 mm) (Lyon-Alemand, France).

— Graisse Apiezon H (Apiezon Products Ltd., London).

— Lut de Krönig préparé en fondant ensemble une partie de cire blanche et quatre parties de colophane, puis coulé sous forme de bâtonnets.

Réduction. — Hydrogène de qualité U ("Air Liquide").

— Hélium de qualité U ("Air Liquide").

— Magnésium à 99% en copeaux de 0,5 mm d'épaisseur (Schuchardt), ces copeaux sont coupés en morceaux d'environ 5 mm de côté.

Mode opératoire

Mise en condition de l'appareil. — Régler le débit du courant d'oxygène à 60 ± 10 ml/mn.

— Régler le débit de l'hydrogène à 30 ± 2 ml/mn. Ce débit est mesuré à la sortie du tube semi-capillaire (17, figure 1) avec un débitmètre à film de savon.

— Contrôler l'étanchéité du circuit de l'hydrogène: à cette fin, fermer le robinet d'aval (14, figure 1); il en résulte une augmentation de pression dans l'appareil provoquant, dans le manomètre (13, figure 1), une dénivellation d'environ 300 mm de mercure; attendre l'équilibre et fermer le robinet d'amont (20, figure 1). Si l'appareil est étanche, la dénivellation doit rester constante.

— Rétablir le courant d'hydrogène.

— Régler l'intensité de chauffage des filaments du détecteur à 150 mA.

— Mettre en fonctionnement l'enregistreur et l'intégrateur. Lorsque l'équilibre du pont de Wheatstone est atteint, l'appareil est prêt à fonctionner.

Afin de réduire au minimum le temps de mise en condition de l'appareil, le circuit de mesure est laissé constamment sous courant d'hydrogène, les fours restant sous tension. Lors d'arrêts prolongés (plusieurs jours), les fours sont laissés sous tension et l'appareil, sous pression d'hydrogène, est isolé par la fermeture des robinets prévus à cette fin (14 et 20, figure 1).

Détermination du coefficient d'étalonnage

La mesure de la quantité de deutérium qui traverse le catharomètre implique un étalonnage préalable. Pratiquement cet étalonnage est effectué à partir de substances-types, à teneurs connues en deutérium, pour l'ensemble des opérations du dosage (minéralisation, piégeage, mesurage) et pour un appareil donné.

Plusieurs paramètres contribuent à modifier l'étalonnage de l'appareil: débit, pression, vieillissement des réactifs. Avant chaque série d'analyses, il est nécessaire de procéder à l'analyse de plusieurs substances-types telles que: l'anthracène-D_1: $D\% = 1{,}18$; l'anthracène-D_{10}: $D\% = 10{,}52$; le polyéthylène perdeutérié: $D\% = 24{,}67$. Chaque substance-type fournit une valeur du coefficient k d'étalonnage qui se calcule d'après la formule:

$$k = \frac{m\,.\,C}{100S},$$

dont les symboles sont définis ci-après:

S: signal numérique fourni par l'intégrateur, proportionnel à la masse du deutérium contenue dans la substance-type.

m: masse du prélèvement analytique (exprimée en milligramme).

C: teneur centésimale en deutérium de la substance-type.

La moyenne des valeurs trouvées est adoptée comme coefficient d'étalonnage; l'écart entre les valeurs extrêmes du rapport k ne doit pas excéder 10^{-6} mg de deutérium par unité de comptage de l'intégrateur. Du fait de l'existence d'un effet de mémoire (*cf.* "Discussion", il convient de faire précéder toute série de mesures du coefficient d'étalonnage ou de dosages par une analyse préliminaire complète effectuée sur une substance deutériée (pesée ou non) et comportant toutes les opérations des dosages (minéralisation, piégeage, mesurage).

Analyse proprement dite

Dans une série, certaines opérations analytiques viennent s'imbriquer dans les déterminations successives. Ainsi, les opérations ci-après doivent avoir été effectuées pendant la détermination précédente: la nacelle contenant le prélèvement analytique (1,5 à 10 mg) préalablement pesé a été disposée dans l'hélice de platine du poussoir (*cf.* Ingram[28]), le manchon de refroidissement a été placé sur le piège à eau proprement dit (3, figure 2) et les robinets A et B du dispositif de piégeage et de transfert de l'eau ont été mis dans les positions qui permettent, d'une part, au courant d'oxygène issu du tube à combustion de traverser successivement les tubulures 1, 3, 7 (figure 2), d'autre part, au courant d'hydrogène, les tubulures 5, 4 et 6 et le circuit de mesure.

Mode opératoire proprement dite. — Introduire le poussoir magnétique dans la chambre de combustion de façon que la nacelle contenant le prélèvement analytique se trouve au point le plus chaud; régler à zéro un chronomètre.

— Au temps $t = 3$ mn: tourner le robinet A (figure 2) de 90° dans le sens inverse des aiguilles d'une montre; le piège proprement dit (3, figure 2), dans lequel l'eau de combustion est condensée (glace), est alors purgé de toute trace d'oxygène par le courant d'hydrogène.

Dans le même temps, retirer le poussoir magnétique de la chambre de combustion et le replacer dans le logement prévu à cet effet (*cf.* Ingram[28]), le refroidir par soufflage extérieur d'air comprimé ou par ventilation.

— Au bout de 30 s: tourner le robinet B (figure 2) dans le sens des aiguilles d'une montre: le courant d'hydrogène parcourt à nouveau le circuit de mesure. L'interruption du courant d'hydrogène dans le catharomètre déséquilibre le pont de Wheatstone et il est nécessaire d'attendre environ 2 mn pour que l'équilibre soit rétabli.

— Au temps $t = 5$ mn 30 s: enlever le manchon de refroidissement et mettre sous tension la résistance chauffante du tube à condensation.

— Au temps $t = 12$ mn: introduire un nouveau prélèvement analytique dans l'hélice de platine du poussoir et placer le manchon de refroidissement sur le piège à eau proprement dit.

— Au temps $t = 15$ mn: tourner les robinets B puis A, de façon à faire suivre aux courants d'oxygène et d'hydrogène les mêmes voies qu'au début de l'analyse et introduire immédiatement la nouvelle nacelle dans le four.

Le pesage du prélèvement a été effectué pendant le déroulement du dosage précédent.

DISCUSSION

Effet de mémoire

Un effet de mémoire se constate en procédant au dosage du deutérium sur un composé organique enrichi en deutérium, de teneur en deutérium élevée, et connue, et en le faisant suivre de celui d'un composé organique non enrichi. Il est évalué numériquement par le calcul du rapport

$$E = \frac{S_0}{S_D} \times 100,$$

dans lequel S_0 et S_D sont les nombres, affichés par l'intégrateur, correspondant respectivement aux dosages du deutérium dans le composé non enrichi et dans le composé enrichi. L'expérience montre que la valeur du rapport E, faible lors de la mise en service d'une nouvelle charge de magnésium (inférieure ou égale à 1%) croît progressivement au fur et à mesure de son vieillissement; elle atteint 2% après 160 analyses, 3% après 250 analyses et 5% après 400 analyses. Cette augmentation autorise à penser que l'effet de mémoire se situe au niveau de la charge de magnésium et est vraisemblablement lié à une adsorption chimique (formation d'un hydroxyde de magnésium) ou physique sur la magnésie.

Maintenance de l'appareil

Afin de maintenir l'appareil en parfait état de fonctionnement, il est recommandable de ne pas attendre l'épuisement des réactifs et la dégradation des matériaux pour procéder à leur remplacement. Le tube à combustion et ses garnitures sont renouvelés systématiquement tous les mois; toutefois, l'analyse de composés organiques contenant des quantités importantes d'halogène ou de soufre peut conduire à un renouvellement plus fréquent.

La garniture de magnésium est renouvelée dès que la valeur de l'effet de mémoire dépasse 3%. Le tube en alumine peut être réutilisé plusieurs fois après nettoyage avec une solution d'acide nitrique à 50% suivi d'un rinçage à l'eau distillée et d'un séchage. Dans ces conditions, l'influence de l'effet de mémoire est négligeable lorsque les masses en deutérium de deux prélèvements analytiques successifs, varient du simple au double ou inversement. En conséquence, il est souhaitable de grouper les produits soumis à l'analyse d'après leurs teneurs en deutérium.

Influence du debit d'hydrogène—durée d'une analyse

Le débit du courant d'hydrogène doit être tel que soient suffisants:

— le temps de contact des corps réagissants (eau de combustion, hydrogène, magnésium), d'une part,

— l'excès d'hydrogène assurant la conversion quantitative de l'eau, deutériée en hydrure de deutérium, d'autre part.

Un débit de 30 ml/mn concilie ces deux conditions. Il lui correspond une durée d'analyse d'environ 16 mn par dosage, dans une série.

Intégration

L'allure des variations de la tension de déséquilibre du pont de Wheatstone est très différente suivant qu'elles correspondent à l'analyse de composés organiques perdeutériés ou dont les taux isotopiques sont élevés ou faibles. *A priori*, il était permis de penser que, quels que soient les composés analysés, leur eau de combustion étant condensée par piégeage avant tout traitement, sa vaporisation et son élution simultanée par l'hydrogène suivies de sa réduction par le magnésium conduiraient à l'obtention de pics sensiblement gaussiens, de surfaces proportionnelles à la quantité d'hydrure de deutérium à doser. Or, si les composés perdeutériés ou les composés à taux isotopiques élevés fournissent effectivement de tels pics, il n'en est pas de même pour les composés à faibles taux isotopiques. En effet, dans ce dernier cas, l'hydrure de deutérium résultant de la réduction des eaux par le magnésium se trouve dilué dans un très grand volume d'hydrogène de sorte que les enregistrements obtenus présentent des paliers plus ou moins longs mais dont les hauteurs maximales ne varient que de quelques dixièmes de millivolts, suivant l'importance des prélèvements analytiques, pour un courant d'alimentation du pont de Wheatstone de 150 mA.

Il en résulte que le choix de l'intégrateur à employer est très important; c'est ainsi que certains intégrateurs très perfectionnés, couramment utilisés en chromatographie, ne sont pas les mieux adaptés à nos besoins et qu'il est préférable de mettre en œuvre des appareils qui, après l'amplification des signaux du pont de Wheatstone, donnent lieu à un comptage électromécanique proportionnel.

Domaine d'application de la méthode

L'application de la méthode décrite permet le microdosage du deutérium dans les composés organiques contenant les éléments suivants: hydrogène, oxygène, azote, halogènes (dont le fluor) et soufre. Le défaut de substances-types deutériées contenant ces différents éléments nous a conduits à expérimenter leurs effets sur le dosage du deutérium par addition de composés organiques porteurs de ces éléments aux prélèvements analytiques de composés deutériés.

Pesage des prélèvements analytiques

Les prélèvements analytiques sont pesés sur microbalance Mettler M5. Les composés organiques solides stables sont pesés en nacelle de platine. Les liquides sont prélevés en ampoules de verre " Pyrex " dont le corps, d'environ 2 mm de diamètre intérieur et 10 mm de longueur, est prolongé par deux capillaires d'environ 10 mm. L'emploi de ces ampoules a été décrit par Fraisse.[30] (Rappelons que dans le cas des composes liquides stables, à faible tension de vapeur, l'un des capillaires de l'ampoule, qui contient le prélèvement analytique pesé, est brisé, avant son introduction dans l'hélice de platine rhodié de la tige-support du tube à combustion, tandis que dans le cas des composés volatils, l'ampoule, dont les deux capillaires restent scellés, est introduite telle quelle dans la chambre de combustion où elle éclate.)

RESULTATS ET CONCLUSION

La méthode décrite a été éprouvée avec succès par l'analyse de composés organiques perdeutériés ou partiellement deutériés. Les résultats obtenus sont reportés dans le tableau 1 qui montre, simultanément, l'ordre de grandeur des masses des prélèvements analytiques; leur précision a l'ordre de grandeur classique en microanalyse.

En vue de mettre en évidence l'influence de plus grandes variations du taux isotopique $n_D/(n_D + n_H)$ sur les résultats de dosage du deutérium, nous avons effectué de multiples déterminations sur des mélanges en proportions variables d'anthracène-D_1 (D% = 1,18) et de substances-types perdeutériées (anthracène-D_{10}, phénanthrène-D_{10}, acénaphtène-D_{10}, polyéthylène perdeutérié). Sur de multiples mélanges dont les taux isotopiques ont varié d'environ 0,03 à 0,60 aucun effet n'a été constaté: les résultats de dosage du deutérium conservent, en effet, la même précision que ceux du tableau 1.

L'Etude de l'influence de la présence d'hétéroéléments (N, Cl, I, F) ou de la présence simultanée de certains d'entre eux (N + Cl, N + S, N + Cl + S) sur les résultats de dosage du deutérium nous a conduits à effectuer nombre de déterminations sur des mélanges d'anthracène-D_{10} et de composés porteurs de ces hétéroéléments (urée, hexaméthylènetétramine, acétamide, nicotinamide, pyramidon, hydroxyquinoléine, chlorure de picryle, sulfanilamide, dichlorodinitrobenzène, chloroacétamide, chlorure de *S*-benzyle isothiouronium, acide iodobenzoïque, acide trifluorobenzoïque). Sur ces mélanges aucun effet de la présence desdits hétéroéléments n'a été constaté; les résultats de dosage du deutérium conservent encore la même précision que ceux du tableau 1.

Le dosage du deutérium, dans des prélèvements analytiques contenant des quantités de deutérium très différentes, montre qu'en deçà de 60 µg de deutérium, les résultats manquent de reproductibilité et sont entachés d'une erreur systématique par excès; cette erreur est vraisemblablement due à deux causes: d'une part, à un défaut de linéarité du catharomètre, et, d'autre part, à un signal trop faible. Ces remarques sont également valables lorsque les masses de deutérium sont supérieures à 1 mg. En conséquence, nous avons limité le domaine d'application de la méthode au dosage de masses de deutérium comprises entre 60 et 500 µg, ce qui conduit à des prélèvements analytiques variant de 1,5 à 6 mg pour des teneurs centésimales en deutérium courantes. Pour des composés organiques dont les teneurs en deutérium sont inférieures à 1%, les masses des prélèvements analytiques peuvent être portées à 10 mg.

Tableau 1. Dosage du deutérium dans divers composés organiques, solides ou liquides

		D%				D%	
Composés	*m**, *mg*	Calculé	Trouvé	Composés	*m**, *mg*	Calculé	Trouvé
Anthracène-D_1	5,880	1,18	1,20	Polyéthylène perdeutérié	0,924	24,67	24,72
	10,183		1,18		1,103		24,80
	7,997		1,16		1,258		24,65
Anthracène-D_{10}	3,225	10,52	10,54	Nitrobenzène-D_5 (liq.)	2,881	7,86	7,78
	2,025		10,38		3,988		7,75
	2,352		10,55		4,055		7,88
Phénanthrène-D_{10}	1,813	10,65	10,80	Pyridine-D_5 (liq.)	3,189	11,90	12,02
	1,043		10,84		2,265		11,72
	2,094		10,52		1,839		12,08
Acénaphtène-D_{10}	2,711	12,17	12,30	Toluène-D_8 (liq.)	2,481	15,73	15,63
	2,818		11,94		1,251		15,58
	2,239		12,07		3,921		15,89

* Masse du prélèvement analytique.

Dans ces conditions, la précision du dosage du deutérium dans les composés organiques est tout à fait comparable à celle obtenue par la mise en œuvre de méthodes décrites dans la littérature[6] (densimétrie, spectrométrie infra-rouge et spectrométrie de masse). En outre, la méthode microanalytique décrite est simple et fiable et l'appareillage mis en oeuvre n'exige pas un investissement élevé.

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Summary—A simple method is described for the microdetermination of deuterium in organic compounds. It involves a flash combustion of the weighed sample in a hot empty chamber at 950–1050° and swept by oxygen at 60 ml/min. Together with this combustion in the gaseous phase, an oxidation of the primary combustion gases on cupric oxide at 850° is necessary. Oxidation products containing halogens and sulphur are retained on silvered alumina at 750–800°. Combustion water containing deuterium oxide and hydroxide is frozen out from the combustion gases in a special trap with two five-way stop-cocks which make possible the simultaneous flow of oxygen and hydrogen: the latter is used as a carrier-gas in the apparatus from the trap downwards. The frozen water is then vaporized by heating in a hydrogen flow of 30 ml/min and reduced on magnesium at 600°. Deuterium is obtained as deuterium hydride in hydrogen: it is measured versus pure hydrogen, with a thermal conductivity detector. A determination within a series can be completed in 15 min. The precision of the results is that obtained in classical organic microanalysis.

Zusammenfassung—Eine einfache Methode zur Mikrobestimmung von Deuterium in organischen Verbindungen wird beschrieben. Dabei wird die gewogene Probe in einer heißen leeren Kammer bei 950–1050° schnell verbrannt und mit 60 ml/min Sauerstoff ausgespült. Zusammen mit dieser Verbrennung in der Gasphase ist eine Oxidation der Primärverbrennungsgase über Kupfer(II)oxid bei 850° notwendig. Halogen- und schwefelhaltige Oxidationsprodukte werden an Silber auf Aluminium-oxid bei 750–800° zurückgehalten. Das Verbrennungswasser, das Deuteriumoxid (D_2O) und -hydroxid (HDO) enthält, wird aus den Verbrennungsgasen in einer Spezialfalle ausgefroren. Diese trägt zwei Fünfweghähne, die das gleichzeitige Fließen von Sauerstoff und Wasserstoff ermöglichen; letzterer wird in der Apparatur stromabwärts von der Falle als Trägergas verwendet. Das ausgefrorene Wasser wird dann durch Erwärmen in einem Wasserstoffstrom von 30 ml/min verdampft und bei 600° über Magnesium reduziert. Man erhält Deuterium als Deuterium-hydrid in Wasserstoff; es wird mit einem Wärmeleitfähigkeitsdetektor gegen reinen Wasserstoff gemessen. Eine Bestimmung innerhalb einer Serie kann in 15 min erledigt werden. Die Genauigkeit der Ergebnisse ist die der klassischen organischen Mikroanalyse.

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SHORT COMMUNICATIONS

USE OF VITREOUS CARBON AS A WORKING ELECTRODE IN COULOMETRIC TITRATION OF POTASSIUM HYDROGEN PHTHALATE

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Previous work has shown that vitreous carbon may be used to make a working electrode for electrogenerated bromine titrations.[1] The present paper describes the use of a vitreous carbon electrode for the coulometric generation of hydroxyl ions in the titration of potassium hydrogen phthalate (chosen as titrand because it is obtainable at a specified purity of 100·0 ± 0·1% and has been titrated coulometrically with high precision, using a platinum working electrode[2]).

It was not considered necessary to repeat the platinum electrode work, but it was considered of value to compare the current-potential curves obtained with platinum and vitreous carbon cathodes. As the presence of dissolved gases such as carbon dioxide leads to positive errors, the effect on the current-voltage curves of displacing it with nitrogen was examined.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade, unless stated otherwise. Potassium hydrogen phthalate solution was prepared by dissolving about 5 g of solid, accurately weighed and previously dried at 110° for 1 hr, and diluting to 500 ml in a grade-A flask at 20°. A 1-ml portion of this solution (0·04855M) was added by grade-A pipette to the titration cell for each titration, and was equivalent to 9·915 mg of solid and required 4·684 C for coulometric titration.

Apparatus and titration procedure

A Thorn coulometric titrator TE 110 was used to provide a constant current of 5 mA. The current values were determined during each titration by measuring the potential drop across a 50-Ohm (±0·05%) resistor to 0·1 mV with a Beckman Research pH meter. The mean current was 4·993 mA, with variations up to 0·1%.

The titration cell was a 50-ml Pyrex beaker. The vitreous carbon cathode was a 3-mm dia rod, grade V25, supplied by Le Carbone (Great Britain) Limited. The active surface area exposed to the catholyte solution was about 1 cm^2. The counter-electrode was a coil of 130 cm of 28-swg pure silver wire, and separated from the cathode solution by a sintered-glass disc, porosity 4. The anolyte and catholyte solutions were both 1M potassium chloride, with volumes of 1·5 and 30 ml respectively. The catholyte solution was stirred with a magnetic stirrer.

Titration end-points were indicated by the colour change of one drop of 0·5% methanolic phenolphthalein solution (added as indicator) from colourless back to a standard pink corresponding to a solution of pH 8·5 and an absorbance at 555 nm of 0·04 in a 2·5-cm cell. A correction was applied for the indicator blank. It was found possible after a 'blank' titration to determine up to eight successive 1-ml aliquots of 0·05M potassium hydrogen phthalate before the end-point colour change became indistinct.

For the determination of current-potential curves a platinum foil electrode (area 0·91 cm^2) and a vitreous carbon electrode (area 0·87 cm^2) were used, placed close to a saturated calomel electrode, and their potentials were measured with the high-impedance potentiometer of the Thorn coulometer (range 0–2 V). The current-potential curves were obtained in phthalate, phosphate and borate buffer solutions with pH values of 3·7, 6·5 and 9·0 respectively, in the presence of dissolved carbon dioxide and oxygen from the atmosphere, or while 'White Spot' nitrogen gas was bubbled through a coarse glass frit into the solution. Each buffer solution was made 1M in potassium chloride. The solutions were stirred magnetically.

RESULTS AND DISCUSSION

Current–voltage curves

Figures 1 and 2 demonstrate that, compared with platinum, vitreous carbon has an overpotential for the overall electrochemical reaction. The passage of nitrogen through the solution alters the potential of either the platinum or the vitreous carbon for a given current density. It is thus probable that any dissolved oxygen is reduced. Although this reaction involves hydrogen ions according to the equation.

$$O_2 + 4H^+ + 4e = 2H_2O,$$

the effect would be unnoticed in the titration results discussed in the next paragraph.

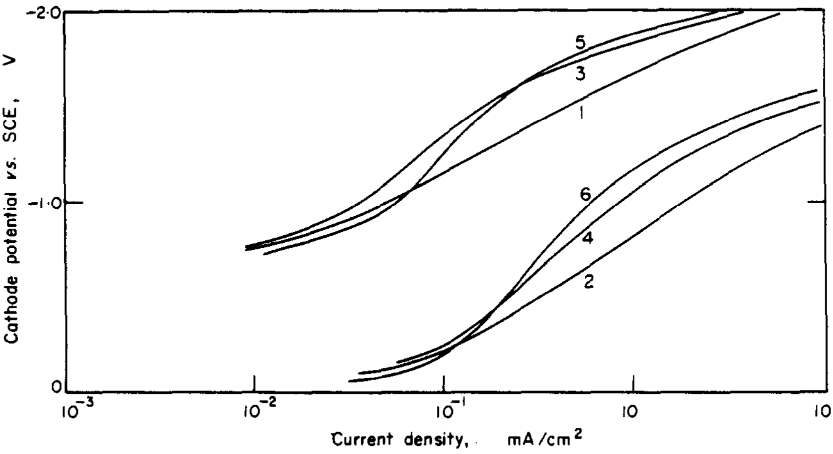

Fig. 1. Current-voltage curves for vitreous carbon and platinum as working cathodes in the generation of hydroxyl ions. Carbon dioxide present.
1, vitreous carbon pH 3·7; 2, platinum pH 3·7; 3, vitreous carbon pH 6·5; 4, platinum pH 6·5; 5, vitreous carbon pH 9·0; 6, platinum pH 9·0.

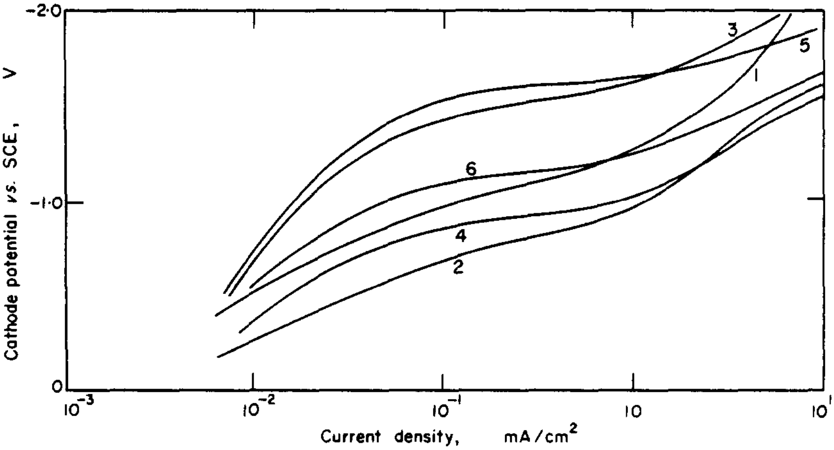

Fig. 2. Current-voltage curves for vitreous carbon and platinum as working cathodes in the generation of hydroxyl ions. Nitrogen gas bubbled through the solution to remove dissolved oxygen. Curves numbered as in Fig. 1.

Titration results

When no attempt was made to remove dissolved carbon dioxide there was an overall mean error of +0·6%; when nitrogen gas was bubbled through the solution the blank value was reduced by a factor of two, suggesting that a volatile acidic component had been removed (Table 1). There was a mean error of −0·4%, but a decrease in precision (the relative standard deviation increased from 0·3 to 0·8%).

Table 1. Coulometric titrations of 1-ml aliquots of 0·04855*M* potassium hydrogen phthalate (equivalent to 9·92 mg of solid)

CO_2 *present*									
Titration time, *sec*	32	940	945	939	946	945	945		
Found, *mg*	Blank	9·93	9·99	9·92	10·00	9·99	9·99		
	Mean 9·97 mg				Error +0·6%				
	Relative standard deviation 0·3%								
CO_2 *displaced by* N_2									
Titration time, *sec*	15	927	931	933	937	932	945		
Found, *mg*	Blank	9·80	9·84	9·86	9·91	9·87	10·01		
	Mean 9·88 mg				Error −0·4%				
	Relative standard deviation 0·8%								
N_2 *atmosphere* (series C)									
Titration time, *sec*	27	939	934	934	936	941	929	936	936
Found, *mg*	Blank	9·92	9·87	9·87	9·89	9·95	9·82	9·89	9·89
	Mean 9·89 mg				Error −0·3%				
	Relative standard deviation 0·4%								

It was thought that the loss in precision could be due to loss of titrand in the form of a fine spray caused by nitrogen bubbling. To avoid this and still reduce carbon dioxide absorption during the titration, experiments were done with an atmosphere of nitrogen maintained over the surface of the titrand. Table 1 shows the results from one such series and Table 2 a summary of results from three series. The latter table shows a mean error of −0·2% and a mean relative standard deviation of 0·4%.

Table 2. Coulometric titration of 9·92 mg of potassium hydrogen phthalate, nitrogen atmosphere

Series	A	B	C
No. of results	7	8	8
Mean found, *mg*	9·91	9·88	9·89
Relative standard deviation, %	0·5	0·3	0·4
Error, %	−0·1	−0·4	−0·3

In view of the expected error in measuring the volume of the potassium hydrogen phthalate solution titrated, locating the end-point and measuring of the quantity of electricity used, Table 2 shows that vitreous carbon behaves satisfactorily as a working cathode for the coulometric titration of potassium hydrogen phthalate.

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Summary—The use of a vitreous carbon electrode as a cathode in the amperostatic coulometric titration of aqueous potassium hydrogen phthalate solution is described. It is shown that 10 mg of the phthalate can be titrated with a precision better than 0·5%. Current-voltage curves for platinum and vitreous carbon cathodes show that there is an overpotential on the latter relative to the former.

Zusammenfassung—Die Verwendung einer glasigen Kohlenstoffelektrode als Kathode bei der amperostatisch-coulometrischen Titration von wäßriger Kaliumhydrogenphthalatlösung wird beschrieben. Es wird gezeigt, daß 10 mg Phthalat mit einer besseren Genauigkeit als 0.5% titriert werden können. Stromspannungskurven für Platin- und glasige Kohlenstoffkathoden zeigen, daß relativ zu den ersteren an den letzteren eine Überspannung auftritt.

Résumé—On décrit l'emploi d'une électrode en carbone vitreux comme cathode dans le titrage coulométrique ampérostatique d'une solution aqueuse de phtalate acide de potassium. On montre qu'on peut titrer 10 mg de phtalate avec une précision meilleure que 0, 5 %. Les courbes intensité-tension pour les cathodes de platine et de carbone vitreux montrent qu'ily a une surtension sur la seconde par rapport à la première.

Talanta, Vol. 20, pp. 684–688. Pergamon Press, 1973. Printed in Great Britain

SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTION OF Cu(II) AND Cu(I) WITH 1-ISONITROSO-(1,2,3,4)-TETRAHYDROPHENAZINE

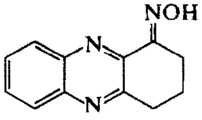
(*Received* 12 *October* 1972. *Accepted* 14 *December* 1972)

Many authors[1–7] have studied the capability of some substituted phenazines of forming chelates with metal ions, mainly the mono and dioxyphenazines. In this paper the reactions of Cu(II) and Cu(I) with 1-isonitroso-(1,2,3,4)-tetrahydrophenazine (HITF) are studied. The reagent is specific for Cu(I) determination.

EXPERIMENTAL

Reagents

We prepare HITF according to Cookson.[8]



HITF

After crystallization from ethanol it melts at 213°. It is slightly soluble in neutral medium, but we may obtain an $8 \times 10^{-3}M$ solution at pH 9, which is stable for over one month if kept in the dark and out of contact with air.

The solutions of the metal ions studied were prepared from the perchlorates.

HITF acid–base equilibrium

HITF in the range of pH between 0 and 12 shows three acid-base forms in equilibrium (Fig. 1). Between pH 2 and 10 the free base (HITF) is stable and characterized by two peaks at 257 and 350 nm. The anion $(ITF)^-$ is formed at pH >10, showing peaks at 262 and 375 nm with the respective isosbestic points at 262 and 308 nm. The $(H_2ITF)^+$ cation appears at pH <2 and has peaks at 260 and 380 nm with isosbestic points at 294 and 358 nm.

Solutions at pH $<0{\cdot}5$ are not stable: the $(H_2ITF)^+$ decomposes rapidly, as may be found from absorbance curves of solutions kept for some hours in acid medium and afterwards brought to the pH range for existence of the free base.

The plots of absorbance against pH, at the wavelengths of the peaks of the three forms are given in Fig. 2. The dissociation constants at ionic strength adjusted to $0{\cdot}1M$ with sodium perchlorate are, at $25 \pm 0{\cdot}2°$,

$$pK_{a_1} = 1{\cdot}7 \text{ for } (H_2ITF)^+ \rightleftharpoons HITF + H^+$$

and

$$pK_{a_2} = 10{\cdot}25 \text{ for } HITF \rightleftharpoons (ITF)^- + H^+.$$

Zusammenfassung—Die Verwendung einer glasigen Kohlenstoffelektrode als Kathode bei der amperostatisch-coulometrischen Titration von wäßriger Kaliumhydrogenphthalatlösung wird beschrieben. Es wird gezeigt, daß 10 mg Phthalat mit einer besseren Genauigkeit als 0.5% titriert werden können. Stromspannungskurven für Platin- und glasige Kohlenstoffkathoden zeigen, daß relativ zu den ersteren an den letzteren eine Überspannung auftritt.

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EXPERIMENTAL

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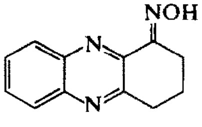

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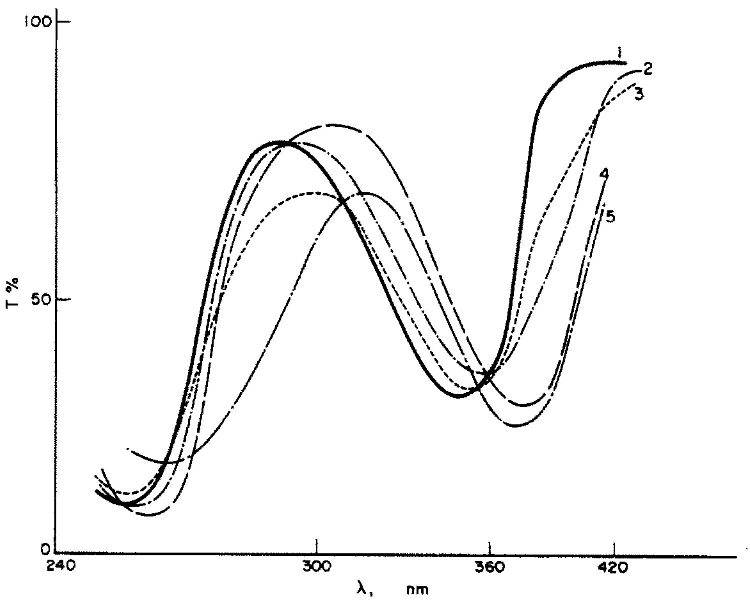

Fig. 1. Transmittance curves of $4 \times 10^{-5} M$ HITF as a function of pH.

1 = pH 7,90	4 = $HClO_4$ 0,10 *M*
2 = pH 1,22	5 = pH 11,90
3 = pH 9,84	

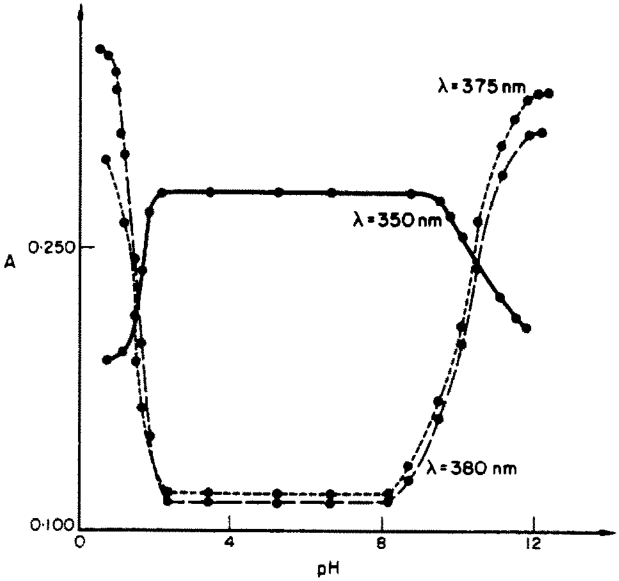

Fig. 2. pH/absorbance plots for $2{\cdot}8 \times 10^{-5} M$ HITF

$\lambda_{375\ nm}$; $\varepsilon_{ITF^-} = 1{\cdot}20 \times 10^4$ l.mole^{-1} . cm^{-1}.
$\lambda_{380\ nm}$; $\varepsilon_{H_2ITF^-} = 1{\cdot}40 \times 10^4$ l.mole^{-1} . cm^{-1}.
$\lambda_{350\ nm}$; $\varepsilon_{HITF} = 9{\cdot}20 \times 10^3$ l.mole^{-1} . cm^{-1}.

the second equilibrium being calculated from the absorbance at 375 nm and the first from that at 350 and 380 nm. Chloride and phosphate buffers were used. The constants were calculated both by the direct method and graphically.

Reaction between HITF and Cu(II)

We studied spectrophotometrically the reaction between HITF and Cu(II) at different pH values both for excess of HITF and excess of Cu(II). In both cases we found formation of a single complex with a peak at 400–405 nm and 1 : 2 composition (Cu : ITF) (Yoe-Jones method). The complex formation starts at pH >4.

The transmittance of HITF solutions at constant concentration with increasing quantities of Cu(II) added, at pH 5, is given in Fig. 3: the peaks at 400–405 and the isosbestic point at 365 nm are shown. The equilibrium constant for formation of the chelate was determined by the Sommer method.[9,10] For the reaction

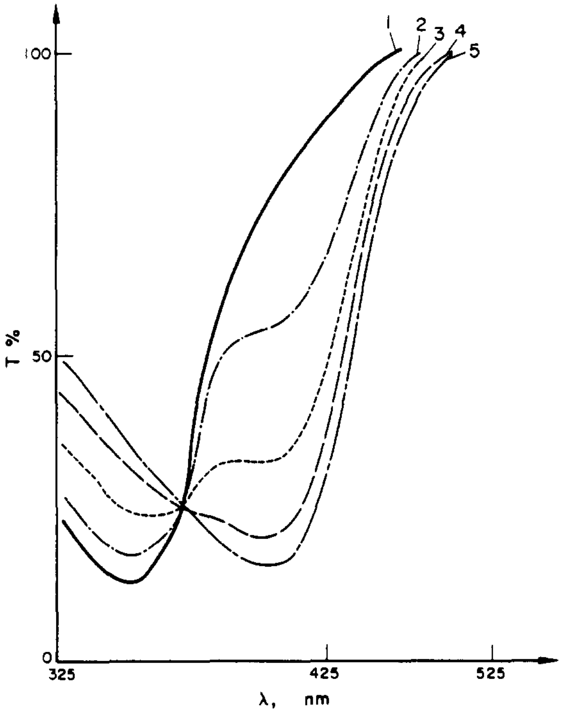

Fig. 3. Transmittance curves for 1 × $10^{-4}M$ HITF containing Cu(II) at pH 5.

[Cu]: (1) 0, (2) 1·2 × $10^{-5}M$, (3) 2·5 × $10^{-5}M$, (4) 4 × $10^{-5}M$, (5) 6 × 10^{-5} and 7 × $10^{-5}M$.

$$\mathrm{Cu(II)} + 2\mathrm{HITF} \rightleftharpoons \mathrm{Cu(ITF)_2} + 2\mathrm{H}^+,$$

we obtained, at $\mu = 0{\cdot}1M$ ($NaClO_4$) and temperature 25° ± 0·2°, $\log \beta_2{}^* = -0{\cdot}7$, where

$$\beta_2{}^* = [\mathrm{Cu(ITF)_2}][\mathrm{H}^+]^2/[\mathrm{Cu(II)}][\mathrm{HITF}]^2.$$

Taking $\beta_2 = [\mathrm{Cu(ITF)_2}]/[\mathrm{Cu(II)}][\mathrm{ITF}^-]^2 = \beta_2{}^*/K_{a_2}{}^2$, we have $\log \beta = 19{\cdot}8$. Plotting the pH-dependence of $\log\{\Delta A/(\varepsilon_{\mathrm{CuL_2}}[\mathrm{Cu(II)}]_t - \Delta A)\}$ (where $[\mathrm{Cu(II)}]_t$ is the total copper(II) concentration, $\Delta A = A - \varepsilon_L C_L$, A being the absorbance), we obtain a straight line with slope 1·96. The chelate may be extracted into carbon tetrachloride. For the chelate $\varepsilon = 9{\cdot}85 \times 10^3$ l.mole^{-1} . cm^{-1}.

Reaction between Cu(I) and $(HITF)^+$

Copper(I) chloride solutions in $10^{-2}M$ hydrochloric acid become deep red on addition of an excess of ligand; in air they quickly discolour and turn yellow, depending on the pH, and give the same spectra as those for Cu(II) and HITF. In the presence of the maximum amount of ligand soluble in acid media (not more than $2{\cdot}5 \times 10^{-4}M$) and in a nitrogen atmosphere, the solutions are stable for a longer time. Reducing agents such as hydrazine, hydroxylamine and ascorbic acid keep the red solution stable for some hours. For the reduction of Cu(II) to Cu(I) these reagents show the same efficacy: we prefer ascorbic acid, as under our conditions it does not interfere in any way with HITF whereas the other two reducing agents give small variations in the spectra of the reagents after a few hours.

We have analysed spectrophotometrically at different pH values solutions of Cu(II) in 0·1% ascorbic acid [*i.e.*, of Cu(I)] containing at least a 10-fold excess of HITF. At pH >1 the solution gives a peak at 505 nm, the absorbance of which increases with pH up to a maximum value of $1{\cdot}08 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ at pH >2. According to the Yoe-Jones and Job methods the complex has a 1 : 2 metal : ligand ratio. The conditional stability constant of the complex stable in the presence of 0·1% ascorbic acid and at $\mu = 0{\cdot}1M$ (sodium sulphate-sulphuric acid) has been calculated at pH = 3 from the ε value and absorbance at 1 : 2 molar ratio of metal to ligand, and is $\log \beta_2 = 9{\cdot}75$.

Analysis of the ascending part of absorbance/pH curves (with ligand in excess) gives for the reaction

$$2(H_2ITF)^+ + Cu(I) \rightleftharpoons Cu(HITF)_2^+ + 2H^+,$$

at $\mu = 0{\cdot}1M$ (Na_2SO_4-H_2SO_4) and 0·1% of ascorbic acid, $\log \beta_2^* = 6{\cdot}3$. Taking

$$\beta_2 = [Cu(HITF)_2^+]/[Cu(I)][H_2ITF^+]^2,$$

we have $\log \beta_2 = 9{\cdot}7$. The straight line $\log A(1 + K_{a_1}/[H^+])^2/(\varepsilon_{Cu(I)L_2} . [Cu]_t - A)$ gives a slope of 2·05.

Preparation of Cu(I) complex

The red complex was isolated from perchloric acid medium; 111 mg of HITF were dissolved in the minimum quantity of sodium hydroxide and the solution was diluted to 250 ml with water. Then a copper(II) solution in perchloric acid was added to give a 1 : 2 metal : ligand ratio, followed by 2·5 ml of $10^{-2}M$ ascorbic acid and the solution was brought to pH 4 with perchloric acid. The solution was left in a nitrogen atmosphere and the precipitate formed was filtered off and washed (all operations under nitrogen).

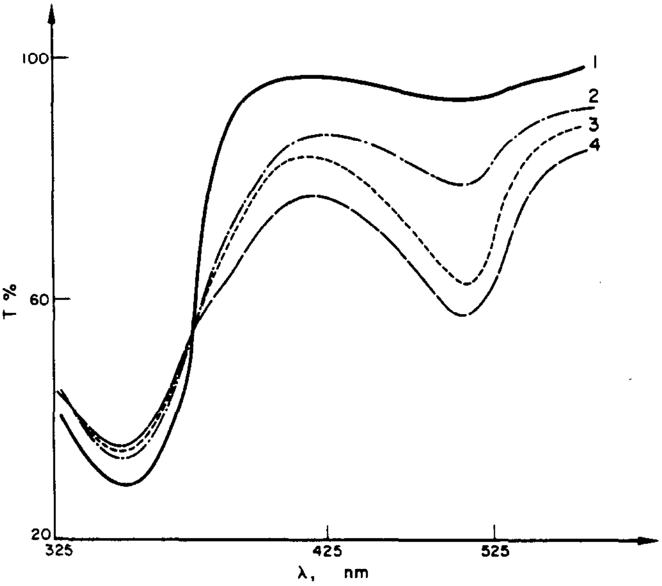

Fig. 4. Transmittance curves for $4{\cdot}8 \times 10^{-5}M$ HITF and copper at pH = 4, in presence of 0·1% of ascorbic acid.

[Copper]: (1) $2 \times 10^{-6}M$, (2) $9 \times 10^{-6}M$, (3) $1{\cdot}7 \times 10^{-5}M$, (4) $2{\cdot}2 \times 10^{-5}$ and $3 \times 10^{-5}M$.

After drying at 100–110° a red-brown product was obtained, m.p. >340°. It was very stable and soluble in water with difficulty. In 20% ethanol solution it gave the same spectrum as the solutions of Cu(II) + ITF + ascorbic acid previously described.

The copper(I) in these solutions quickly oxidizes to Cu(II) so the spectrum becomes the same as for HITF because Cu(II) at pH <3·8 does not react with ITF in this ratio (1 : 2). The analysis of the complex is in agreement with $Cu(HITF)_2 . ClO_4$. Found: Cu = 10·6%; N = 14·2%; Cl = 6·0%; calc.: Cu = 10·79%; N = 14·27%; Cl = 6·01%. The existence of the ion $Cu(HITF)_2^+$ was confirmed by electrophoresis.

Quantitative determinations

It is possible to use HITF as an analytical reagent for quantitative determination of Cu(I), with few interferences, at 505 nm, pH 3–4, in presence of 0·1% ascorbic acid. The lowest measurable limit is $2 \times 10^{-6}M$ (0·12 ppm), the highest $5 \times 10^{-5}M$ (because of the slight solubility of the ligand at the pH used) With aqueous alcohol solutions of reagent we may use HITF concentrations up to $5 \times 10^{-4}M$ in 20% ethanol and copper is measurable up to $10^{-4}M$. Ca(II), Zn(II), Cr(III), Al(III), Mg(II), Mo(VI), V(V), W(VI), Fe(III) do not interfere even at concentrations 100 times that of copper. Cd(II), Pd(II), Sn(II) and Ni(II) do not interfere if their concentrations are not more than 30 times that of the copper.

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Summary—The reactions of Cu(II) and Cu(I) with 1-isonitroso-(1,2,3,4)-tetrahydrophenazine (HITF) have been studied spectrophotometrically. Both ions form complexes with metal/ligand ratio 1 : 2. The complex of Cu(I) and ITF can be used for copper determination in the range $2–50 \times 10^{-6}M$, and has been separated as the perchlorate in crystalline form. The spectrophotometric characteristics and the equilibrium constants for the ligand and for the complexes are reported.

Zusammenfassung—Die Reaktionen von Cu(II) und Cu(I) mit 1-Isonitroso-(1,2,3,4)-tetrahydrophenazin (HITF) wurden spektrophotometrisch untersucht. Beide Ionen bilden Komplexe mit dem Metall : Ligand-Verhältnis 1 : 2. Der Komplex von Cu(I) und ITF kann im Bereich $2–50 \cdot 10^{-6}M$ zur Kupferbestimmung verwendet werden und ist als Perchlorat in kristalliner Form abgetrennt worden. Die spektrophotometrischen Eigenschaften und die Gleichgewichtskonstanten des Liganden und der Komplexe werden mitgeteilt.

Résumé—On a étudié spectrophotométriquement les réactions de Cu (II) et Cu (I) avec la 1-isonitroso (1,2,3,4)-tétrahydrophénazine (HITF). Les deux ions forment des complexes avec un rapport métal/ligand 1 : 2. Le complexe du Cu (I) avec l'ITF peut être utilisé pour le dosage du cuivre dans le domaine $2–50 \times 10^{-6}M$, et a été séparé à l'état de perchlorate sous forme cristalline. On rapporte les caractéristiques spectrophotométriques et les constantes d'équilibre pour le ligand et pour les complexes.

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SPECTROPHOTOMETRIC MICRODETERMINATION OF HYDROXYTRIAZENES*

(*Received* 1 *August* 1972. *Accepted* 2 *September* 1972)

In an earlier paper,[1] a spot test for hydroxytriazones was reported. It has now been made quantitative.

EXPERIMENTAL

Procedure

Take 2·5 ml each of glacial acetic acid solutions of α-naphthylamine ($5 \times 10^{-3}M$) and hydroxytriazene ($\sim 5 \times 10^{-4}M$) in a beaker, add 5·0 ml of glacial acetic acid to prevent precipitation on dilution, and 10·0 ml of water. Adjust the pH to the desired value with 5*M* sodium hydroxide. Heat the solution over a water-bath at 65–70° for 30 min, cool and make up to 25 ml with water. Measure the absorbance at 535 nm, using a 1·0-cm cell and α-naphthylamine solution as blank.

RESULTS AND DISCUSSION

Properties and general characteristics of the 3-hydroxy-1,3-diphenyltriazene (HDPT) *α-naphthylamine complex*

The absorption spectra of HDPT and its α-naphthylamine complex are shown in Fig. 1. The absorption becomes constant after 3 hr and remains constant for 24 hr. A wavelength of 535 nm was selected for the measurement of the complex, because HDPT exhibits no absorbance at this wavelength. The reaction can be

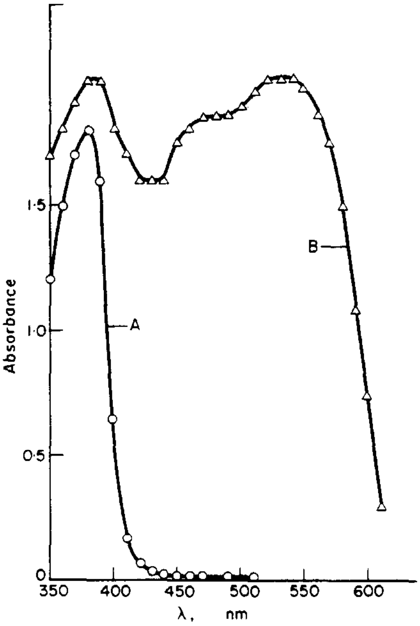

Fig. 1. Absorption spectra of (A) $1 \times 10^{-3}M$ HDPT (3-hydroxy-1,3-diphenyltriazene) and (B) $1 \times 10^{-3}M$ HDPT + $1 \times 10^{-2}M$ α-naphthylamine.

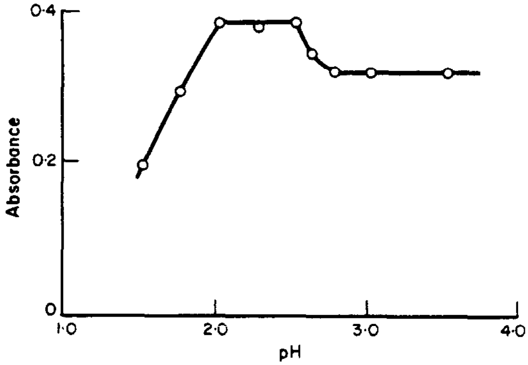

Fig. 2. Effect of pH on absorbance of $5 \times 10^{-5}M$ HDPT + $5 \times 10^{-4}M$ α-naphthylamine.

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* Presented at the International Congress on Analytical Chemistry, Kyoto, Japan, 3–7 April 1972.

completed more rapidly by heating the solution at 65–70° for 30 min. For complete colour development at least a tenfold molar excess of α-naphthylamine is required. The influence of hydrogen-ion concentration is shown in Fig. 2; the optimum pH range for the determination of HDPT is 2·0–2·5.

Beer's law is obeyed up to $2 \times 10^{-4}M$ HDPT. The Sandell sensitivity is 0·028 $\mu g/cm^2$ for an absorbance of 0·001, the molar absorptivity $7{\cdot}5 \times 10^3$ $l.mole^{-1}.cm^{-1}$. A continuous-variation study showed that HDPT and α-naphthylamine react in 1 : 1 molar ratio.

Other hydroxytriazenes

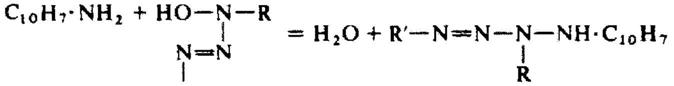
The results of similar investigations for the other hydroxytriazenes studied are reported in Table 1.

Table 1.

Compound	m.p. °C	Colour of complex	Beer's law, *ppm*	pH	Sandell's sensitivity $\mu g/cm^2$
$C_6H_5N(OH).N{=}N{-}C_6H_5$	127	Pale yellow	0·4–400	2·0–2·5	0·028
$C_6H_5N(OH).N{=}N{-}C_6H_4.COOH(p)$	184	Pale yellow	0·2–13	2·3–2·5	0·022
$C_6H_5N(OH).N{=}N{-}C_6H_4.Cl(o)$	78·5	Light greenish yellow	0·25–90	3·0–4·3	0·066
$C_6H_5N(OH).N{=}N{-}C_6H_4.Cl(p)$	148	Light greenish yellow	0·75–20	2·1–2·5	0·035
$C_6H_5N(OH).N{=}N{-}C_6H_4.Br(p)$	154	Light green	0·6–18	2·5–2·8	0·022
$CH_3N(OH).N{=}N{-}C_6H_5$	69	White	1·5–90	2·3–3·2	0·076
$C_2H_5N(OH).N{=}N{-}C_6H_5$	44·5	White	1·0–53	2·4–2·7	0·066
$C_3H_7N(OH).N{=}N{-}C_6H_5$	61	White	3·6–11	2·2–2·3	0·21
$p\text{-}CH_3.C_6H_4N(OH).N{=}N{-}C_6H_4.Cl(o)$	101	Pale yellow	4·6–130	2·5–3·0	0·23

DISCUSSION

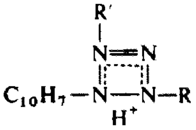
The pink colour formed by HDPT and other hydroxytriazenes by reaction with α-naphthylamine may be explained in the following manner. It is proposed that HDPT forms a condensation product with α-naphthylamine with elimination of one molecule of water, forming a tetrazene or a cyclic tetrazene:



$$C_{10}H_7{\cdot}NH_2 + HO{-}\underset{\substack{|\\ N=N\\ |\\ R'}}{N}{-}R = H_2O + R'{-}N{=}N{-}\underset{\substack{|\\ R}}{N}{-}NH{\cdot}C_{10}H_7$$

Tetrazene *A*

or



Cyclic tetrazene *B*

Our attempts to isolate the pink compound were not successful. However, it would be reasonable to assume that the product has structure *B*. Our suggestion is supported by the fact that Maccoll[2] on the basis of valence-bond theory predicted the absorption maximum of 1,2,3,4-tetrazene to be 530 nm, which may be compared with the 535 nm found by us.

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Summary—A method is reported for the determination of hydroxytriazenes, based on development of a pink colour by the reaction of hydroxytriazenes with α-naphthylamine. The method is general and can be used for the determination of any hydroxytriazenes.

Zusammenfassung—Ein Verfahren zur Bestimmung von Hydroxytriazenen wird angegeben; es beruht auf der Entwicklung einer Rosafärbung durch die Reaktion von Hydroxytriazenen mit α-Naphthylamin. Die Methode ist allgemein und kann zur Bestimmung jedes beliebigen Hydroxytriazens verwendet werden.

Résumé—On rapporte une méthode pour le dosage d'hydroxytriazènes, basée sur le développement d'une coloration rose par la réaction des hydroxytriazènes avec l'α-naphtylamine. La méthode est générale et peut être utilisée pour le dosage d'hydroxytriazènes quelconques.

Talanta, Vol. 20. pp. 691–694. Pergamon Press, 1973. Printed in Great Britain

ATOMABSORPTIONSSPEKTRALPHOTOMETRISCHE (A.A.S.) BESTIMMUNG VON CHROM IN ELEKTRODENKOKS

(*Eingegangen am* 13. *November* 1972. *Angenommen am* 28. *Januar* 1973)

Zur Kontrolle des Gehaltes von Chromverunreinigungen in für Elektroden hergestellten Koks wurde von uns eine A.A.S. Bestimmungsmethode ausgearbeitet. In der Literatur wurden einige Chrombestimmungsmethoden beschrieben, bei denen das Chrom meist in verdünnten wäßrigen Lösungen vorlag.[1–5] Die Bestimmung des Chroms im Elektrodenkoks ist verbunden mit Untersuchungen von Matrix- und Mediumeinflüssen, da infolge von Aufschlußprozessen relativ konzentrierte Salzlösungen zum Einsatz kommen müssen.

EXPERIMENTELLER TEIL

Geräte

Verwendet wurde ein Eigenbau-Atomabsorptionsspektralphotometer, welches aus folgenden Teilen bestand:

Spiegelmonochromator SPM 2 mit Quarzprisma	(VEB C. Zeiss, Jena)
Sekundärelektronenvervielfacher M12 FQS 35	(VEB C. Zeiss, Jena)
Kompensationsbandschreiber G 1 B 1	(VEB C. Zeiss, Jena)
Hochspannungsversorgungsgerät für SEV	(PGH Statron)
Vorkammerringspaltzerstäuber	(Eigenbau)
gekühlter Schlitzbrenner (120 mm)	(Eigenbau)
Hohlkathodenlampe	(Eigenbau)
Kathode Chromstahl (Cr 25%)	
Neondruck 4 Torr	

Als optimale Bedingungen ergaben sich für die Chrombestimmung: Wellenlänge: 357,9 nm, Lampenstrom 20 mA, Spaltbreite 0,15 mm, Acetylen: 70 l./h (90 mm WS), Luft: 50 l./h (3,9 at), Zusatzluft: 200 l./h, brennstoffreiche, reduzierende Flamme, Lösungsverbrauch 2,6 ml/min, Strahlendurchgang: 8 mm oberhalb des Brenners.

Reagenzien

Standard-Chromlösungen: Cr 1 g/l. $Cr(NO_3)_3$,
$CrCl_3$,
$K_2Cr_2O_7$.

Schwefelsäure *p.A.*, Kaliumhydrogensulfat *p.A.*

Bestimmungsvorschrift

In einem Quarztiegel werden 5 bis 10 g Koks (je nach Aschegehalt) eingewogen und im Muffelofen, durch den ein Luftstrom von 25 l./h geleitet wurde, bei 800° 8–12 Stunden langsam verascht. Von der erhaltenen Koksasche werden 5 mg in Anlehnung an einen Aufschluß für Ton und Kaolin[6] in einem Quarzreagensglas mit 100 mg Kaliumhydrogensulfat bis zur klaren Schmelze geglüht (*ca.* 1,5 min). Die abgekühlte,

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ERGEBNISSE UND DISKUSSION

Untersuchung wäßriger Chromlösungen

Lösungen von Chrom(III)-chlorid, Chrom(III)-nitrat und Kaliumdichromat(VI), die gleiche Chrommengen enthalten, liefern gleiche Extinktionswerte. Zwischen 0 und 20 μg/ml Chrom ergibt sich ein etwa linearer Anstieg der Extinktion, ab 20 μg/ml ist eine deutliche Krümmung der Eichgeraden zur Konzentrationskoordinate feststellbar.

Einfluß von Schwefelsäure auf die Chromabsorption

Die Steilheit der Eichkurven nimmt mit zunehmender Schwefelsäurekonzentration ab (siehe Tabelle 1). Etwa 20 Prozent der Extinktionsabnahmen sind auf die Vergrößerung der Viskosität der schwefelsauren gegenüber der wäßrigen Lösung, die eine verminderte Zerstäubungsgeschwindigkeit und ein anderes Tröpfchenspektrum zur Folge hat, zurückzuführen. Der größere Teil der Extinktionsabnahme wird verursacht durch eine verminderte Konzentration der Chromatome im Plasma infolge der gegenüber Chrom(III)-chlorid und Chrom(III)-nitrat schwereren Verdampfbarkeit von Chrom(III)-sulfat.

Tabelle 1. Abhängigkeit der Absorption von den Schwefelsäure- und Kaliumhydrogensulfatkonzentrationen

[H_2SO_4], *M*	[$KHSO_4$], *mg/ml*	*M*	Extinktionseinheiten pro 10 μg
0,00	—	—	0,208
0,25	—	—	0,175
0,5	—	—	0,170
0,75	—	—	0,163
1,0	—	—	0,156
—	0	0,00	0,211
—	50	0,37	0,197
—	100	0,75	0,180
0,00	0	0,00	0,208
0,5	0	0,5*	0,173
0,5	50	0,87*	0,201
0,5	100	1,25*	0,189

* Gesamtsulfatkonzentration.

Einfluß des Kaliumhydrogensulfates

Der Aufschluß der Koksasche mit Kaliumhydrogensulfat bietet den Vorteil, daß nach Lösen der Schmelze in Schwefelsäure die Kieselsäure ausflockt und die Chrombestimmung nicht stört. Die Abnahme der Absorption ist zurückzuführen auf die Sulfatanionen. Es ist jedoch festzustellen, daß der Einfluß des Kaliumhydrogensulfates geringer als der der Schwefelsäure bei gleicher Sulfatkonzentration ist. Setzt man zu schwefelsauren Lösungen Kaliumhydrogensulfat zu, so erhöht sich trotz erhöhter Sulfationenkonzentration die Absorption. Die Ursache für die Erhöhung der Extinktion ist einmal das leicht ionisierbare Kaliumatom (Erhöhung der Chromatomkonzentration im Plasma infolge Zurückdrängung der Chromionisation). Da jedoch nach Woodward bei 2550° nur 0,3% der Chromatome ionisiert vorliegen,[7] kann die Ionisationsverminderung nicht der einzige Grund für die Extinktionszunahme sein. Eine zweite Ursache sehen wir in den veränderten Verdampfungsbedingungen. Kaliumhydrogensulfat verdampft relativ leicht, außerdem gibt es bei höheren Temperaturen zuerst Wasser, dann Schwefeltrioxid ab. Die im Kaliumhydrogensulfat befindlichen Chrom(III)-sulfat-oder Chrom(III)-oxid-Partikel liegen dadurch feiner verteilt vor und verdampfen ebenfalls schneller. Dies führt zur Erhöhung der Chromatomkonzentration im Plasma. Mit zunehmender Kaliumhydrogensulfatkonzentration nimmt die Chromatomkonzentration wieder ab. Dies ist auf die schlechtere Verdampfung relativ großer Teilchen zurückzuführen, die bei höheren Salzkonzentrationen vorhanden sind.

Einfluß von Begleitelementen

Neben Siliziumdioxid enthält die Koksasche zwischen 5 und 10% Eisen, Calcium und Aluminium, 1 und 2% Magnesium, 0,1 und 0,5% Titan und Mangan und unter 0,1% Zink, Vanadin, Nickel, Kupfer bei einem Chromgehalt von 0,1 bis 1%.

Es ist bekannt, daß Eisen(III)-ionen und Aluminiumionen—besonders in reduzierenden Flammen—die Absorption durch Chromatome stark vermindern.[8,9] Dies wird auf die Bildung von schwer verdampfbaren Mischoxiden vom Spinelltyp zurückgeführt. Rubeska[10] verwendet Ammoniumchlorid zur Behebung dieses Einflusses. Hurlbut und Chriswell[11] beschreiben eine Verminderung dieses Einflusses durch Natriumsulfat und Husler[12] unterdrückt die Absorptionsbeeinflussung durch 10 mg K^+ pro ml (als KCl). In rein wäßrigen, eisenfreien Lösungen erzielt er hiermit sogar eine Absorptionssteigerung. Dies stimmt mit unserem Ergebnis über den gegenüber Schwefelsäure verminderten Einfluß des Kaliumhydrogensulfates überein.

Bei unseren Untersuchungen stellten wir fest, daß die genannten Begleitelemente keinen Einfluß auf die Absorption durch Chromatome hatten. Die Ursache für dieses Verhalten sehen wir darin, daß sich beim Verdampfen des Lösungsmittels Wasser in der Flamme feste Teilchen bilden, die vorwiegend aus Kaliumhydrogensulfat bzw. Kaliumpyrosulfat bestehen. Die sofortige Bildung von Mischoxiden ist dadurch behindert.

Aufstellung einer Eichkurve und Genauigkeit des Verfahrens

Zur Aufstellung einer Eichkurve wurden Lösungen hergestellt, die $1N$ an Schwefelsäure waren, 0, 1, 2, ... 20 µg Chrom und 100 mg Kaliumhydrogensulfat pro ml enthielten. Es wurden jeweils 10 Lösungen eines Chromkonzentrationswertes untersucht. Die erhaltenen Werte wurden mittels der Ausgleichsrechnung in eine Geradenfunktion umgewandelt. Um festzustellen, ob der Funktionsansatz ($y = ax + b$) Berechtigung besitzt, wurden erstens die Werte zwischen 0 und 10 µg/ml, zweitens die Werte zwischen 10 und 20 µg/ml und drittens die Werte zwischen 0 und 20 µg/ml ausgeglichen. Die a-Werte betrugen 0,0202, 0,0195 bzw. 0,0198.

Daraus geht hervor, daß die Gesamtgerade eine kleine Krümmung aufweist. Ermittelt man die Standardabweichungen der Teilgeraden, so liegen diese mit 0,008 niedriger als die Standardabweichung der Gesamtgeraden von 0,010. Die Nachweisgrenze, nach dem 3σ-Kriterium ermittelt, beträgt 0,4 µg/ml. Der Variationskoeffizient an der Nachweisgrenze liegt bei ±47%, bei 1 µg/ml bei ±26%, bei 10 µg/ml bei ±4% und bei 20 µg/ml bei ±2%. Der gemessene Blindwert ist auf Lichtstreuung zurückzuführen.

Tabelle 2. Ergebnisse der atomabsorptionsspektralphotometrischen Bestimmung von Chrom in Elektrodenkoks (5-g Proben)

Koks Art	dotiertes Chrom		Chrom* gefunden pro 5 mg Asche, µg	Chrom		Abweichung, %
	µg	bezogen auf Koks, ppm		gegeben Dotier. und Grundwert, ppm	gefunden ppm	
1	—	—	4,1	—	7,5	—
1	41,7	8,3	9,5	15,8	16,1	+2
1	125,0	25,0	17,9	32,5	32,3	−0,6
2	—	—	3,8	—	5,7	—
2	3,4	0,7	4,4	6,4	6,9	+7
2	13,4	2,7	9,4	8,4	9,9	+18
3	—	—	6,4	—	11,1	—
3	38,7	7,7	10,8	18,8	18,6	−1
3	92,7	19,3	17,2	30,4	30,5	+0,3
3	145,3	29,1	24,2	40,2	40,0	−0,5

* Durchschnittswert von 3 Ascheaufschlüssen, deren Variationskoeffizient zwischen 5 und 14 Prozent lag.

Überprüfung der Anwendbarkeit des Verfahrens

Da kein garantiert chromfreier Koks vorhanden war, und Chromspuren außerdem die unangenehme Eigenschaft besitzen, durch Adsorption an Glaswänden u.ä. zu verschwinden, mußte das Verfahren durch die Zusatzmethode überprüft werden.

Zur Überprüfung wurde Koks homogenisiert, in mehrere Teile geteilt, in Quarzbechergläser eingewogen und z.T. mit unterschiedlichen Chrommengen, die in einem Methanol–Wasser-Gemisch (zur besseren Benetzung des Kokses) gelöst waren, versetzt. Unter einem IR-Strahler wurde zur Trockne eingedampft und der Koks nach der gegebenen Vorschrift verascht. Es wurden jeweils drei Parallelbestimmungen mit je 5 mg Asche durchgeführt. Aus der Tabelle 2 ist ersichtlich, daß kein Chrom verloren geht und eine gute Übereinstimmung zwischen den vorgegebenen und gefundenen Chrommengen erzielt wurde.

Es ergibt sich, daß die Methode bei einer Einwaage von 10 g Koks bei einem Aschegehalt von mindestens 0,15% und der Voraussetzung, daß zur Erhöhung der statistischen Sicherheit und Verbesserung des Vertrauensbereiches Dreifachbestimmungen durchgeführt werden, für die Bestimmung von 0,1 bis 2 ppm Chrom bezogen auf Koks anwendbar ist. Erhöht sich der Aschegehalt sehr stark, so vermindert sich die Nachweisgrenze, da mehr als 10 mg Asche pro Aufschluß nicht eingewogen werden können.

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Summary—A method is described for the determination of chromium in electrode-grade coke in the range 0·1–2 ppm (or 1–20 μg/ml in solution). The limit of detection is 0·4 μg/ml, the standard deviation is 0·008 absorbance units and the sensitivity is 0·02 absorbance units per μg. The influence of sulphuric acid and potassium hydrogen sulphate concentrations is discussed.

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In a previous paper[1] we described the synthesis and properties of bipyridylglyoxal dithiosemicarbazone (BGT) and its reactions with some cations. We have now applied the reagent to photometric estimation of iron.

The reaction of BGT with transition metal ions is complex, and not only the thiosemicarbazone group plays a part. The reagent has two 'ferroin' groups and its reactivity with the transition metals, especially iron, is remarkable.

Zur Überprüfung wurde Koks homogenisiert, in mehrere Teile geteilt, in Quarzbechergläser eingewogen und z.T. mit unterschiedlichen Chrommengen, die in einem Methanol–Wasser-Gemisch (zur besseren Benetzung des Kokses) gelöst waren, versetzt. Unter einem IR-Strahler wurde zur Trockne eingedampft und der Koks nach der gegebenen Vorschrift verascht. Es wurden jeweils drei Parallelbestimmungen mit je 5 mg Asche durchgeführt. Aus der Tabelle 2 ist ersichtlich, daß kein Chrom verloren geht und eine gute Übereinstimmung zwischen den vorgegebenen und gefundenen Chrommengen erzielt wurde.

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The reaction of BGT with transition metal ions is complex, and not only the thiosemicarbazone group plays a part. The reagent has two 'ferroin' groups and its reactivity with the transition metals, especially iron, is remarkable.

The complexes formed by Fe(II) and Fe(III) with BGT and picolinaldeyde thiosemicarbazone (PAT)[2] are similar. Both reagents give a red colour with Fe(II) at pH 1–3, characteristic of 'ferroin' complexes, but the BGT complex is the more stable, and allows the photometric estimation of iron in acid solution.

EXPERIMENTAL

Reagents

BGT solutions in ethanol. 0·1 and 0·25%.

Standard solutions of Fe(II) and Fe(III) sulphates.

Buffer solutions. Acetic acid/sodium acetate, pH 5·0; ammonia/ammonium chloride, pH 10·0; potassium hydrogen phthalate/hydrochloric acid, pH 2·5.

Ascorbic acid.

All reagents were analytical grade.

Procedures

Homogeneous medium. Samples were prepared in 50-ml volumetric flasks by taking 100–800 μg of iron, 10 ml of 0·1 or 0·25% reagent solution, 0·1 g of ascorbic acid, 20 ml of buffer solution, and diluting to volume with water. After 1 hr, the absorbances were measured against a reagent blank.

Extraction. The complex was developed as above in 100-ml separatory funnels, with ammonia/ammonium chloride buffer. After 30 min, the mixture was extracted four times with 5-ml portions of chloroform and the organic extracts were diluted to 25 ml. After 1 hr the absorbance was measured against a reagent blank similarly prepared.

RESULTS AND DISCUSSION

Formation of the iron complexes

BGT forms a yellow chelate with Fe(III), the solution of which is stable and has λ_{max} at about 400 nm. The reagent forms strongly coloured complexes with Fe(II), which absorb between 500 and 600 nm; the formation of these complexes is strongly pH dependent. Because of the position of the absorption bands we have attached more importance to the ferrous complexes.

To ensure that the iron remained in the lower oxidation state we used ascorbic acid; in the absence of reducing substances, the Fe(II) complexes are transformed slowly into the Fe(III) complex.

Influence of pH and solvent. A red-violet iron(II) complex is formed in acid solution (pH < 2·5, λ_{max} 550 nm) and a green-blue in alkaline solution (pH > 6; λ_{max} 610 nm). At intermediate pH both complexes occur. The range of pH in which either complex is formed is influenced by the alcohol concentration in the solution. Owing to the lower dielectrical constant of the solvent, the complexes are more stable and their colours are purer in ethanol, but in the analysis of most samples the formation of insoluble products may be expected if ethanol is used, and it is preferable to dilute the samples with water.

Redox behaviour. The aerial oxidation of the ferrous complex takes about 45 min for 7 ppm of Fe(II) at pH 2·5 or 5·0 and is slower at higher pH.

On addition of H_2O_2 an orange colour appears with a new absorption band, which is not stable, at 475 nm. The oxidation is slow and does not stop at the ferric complex. In alkaline medium the oxidation is slower, but the system is equally unstable.

The ferric complex is completely reduced by ascorbic acid (0·2 g) in about an hour, at pH 2·5 or 5·0.

Stability of the ferrous complexes. The absorbance is constant within 1% over a period of 5 hr, irrespective of pH (2·5–9), and alters by not more than 3% within 24 hr, whether ethanol or water is used for dilution. In ethanol, at pH 1·5, the complex is so stable that ascorbic acid need not be added.

Stoichiometry. The metal–reagent ratio for the ferrous complexes was determined by Job's method at two wavelengths. For the red-violet complex (pH 2·5) it is 1 : 2; for the green-blue complex (pH 5·0–10·0) it is 1 : 1. The same result was obtained for the extraction systems.

Analytical applications of the ferrous complexes

Red-violet complex. The optimum conditions for the homogeneous medium procedure are 10 ml of 0·25% reagent, 0·2 g of ascorbic acid, and 20 ml of phthalate buffer, pH 2·5, with measurement at 550 nm against a reagent blank, after 1 hr. Beer's law is obeyed over the range 2–9 ppm of Fe(II). The molar absorptivity is $5{\cdot}58 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. The relative error (95% confidence level) is 1·4%.

With a 6 ppm of Fe(II), 6 ppm of Ni, Cu or Pt(IV) give errors not above 8%; Co(II) may be present only up to 12 ppm; 100 ppm of Zn, Pb, Al, Be, Mg, Ca, Ba, UO_2(II) and V(V) give errors < 4%.

Green-blue complex. The optimal conditions for homogeneous medium are 15 ml of 0·4% reagent solution, 0·2 g of ascorbic acid and 20 ml of ammonia/ammonium chloride buffer, pH 10·0, and measurement at 610 nm. Beer's law is obeyed from 2 to 7·5 ppm of Fe(II). The molar absorptivity is 7.14×10^3 $\text{l.mole}^{-1}.\text{cm}^{-1}$. The relative error (95% confidence level) is 0·5%.

For 4 ppm of Fe(II) there is less than 2·5% error with 12 ppm of Ni, Co(II), Pt(IV), Mn(II) and Ce(IV); there is no interference from 25 ppm of Au(III), 50 ppm of Zn or Ba, and 100 ppm of Pb, Al, Be, Mg and Ca; 100 ppm of UO_2(II) or V(V) interfere seriously.

Extraction of the green-blue complex into chloroform reduces the interferences. The absorbance is measured at 630 nm. Salting-out agents do not improve the extraction. The extracted complex is stable for at least 5 hr. Beer's law is obeyed from 2 to 8 ppm of Fe(II). The molar absorptivity is $6{\cdot}60 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. For 3·7 ppm of Fe(II) the error is $< 2{\cdot}5\%$ with 200 ppm of Li, Na, K, Rb, Mg, Ca, Sr, Ba, Zn, Sn(II), La, V(V), Cr(VI), Os(IV), Pt(IV) and Mo(VI). Up to 100 ppm of Cd may be present. Errors are below 4% for 16 ppm of Cu(II) or Ni, 32 ppm of Co(II), 100 ppm of Hg(I) and 200 ppm of Al or Mn(II); Ag(I) is reduced to elemental silver.

DISCUSSION

In acid medium, pH 2·5, BGT behaves like the ferroin reagents. In basic medium, pH 10·0, it forms with Fe(II) a chelate with four pentagonal rings partially conjugated, agreeing with the formulae proposed by French and Blanz,[3,4] with the sulphur atom taking part in the co-ordination.

The complexes may be stabilized indefinitely by addition of a reducing agent. Ascorbic acid or hydroquinone may be used, but not hydroxylamine, which displaces the thiosemicarbazone groups, giving rise to the oxime (*cf.* ref. 5). Sodium sulphite cannot be used either, probably because of to its ability to add to carbonyl groups and double bonds, and hence destroy the chromophore groups of the reagent.

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Summary—Bipyridylglyoxal dithiosemicarbazone reacts with iron(II) or (III). The Fe(III) complex is yellow (λ_{max} 400 nm). Fe(II) forms a red-violet 1 : 2 complex at pH 2·5 (λ_{max} 550 nm) and a green-blue 1 : 1 complex at pH 5–10 (λ_{max} 590–610 nm). Both ferrous complexes can be oxidized to the ferric complex; this reaction is reversible. The quantitative application of the ferrous complex has been studied.

Zusammenfassung—Dipyridylglyoxaldithiosemicarbazon reagiert mit Eisen(II) oder -(III). Der Fe(III)-Komplex ist gelb (λ_{max} 400 nm). Fe(II) bildet bei pH 2·5 einen rotvioletten 1 : 2-Komplex (λ_{max} 550 nm) und bei pH 5–10 einen grünblauen 1 : 1-Komplex (λ_{max} 590–610 nm). Beide Eisen(II)-Komplexe können zum Eisen(III)-Komplex oxidiert werden; diese Reaktion ist reversibel. Die quantitative Verwendung des Eisen(II)-Komplexes wurde untersucht.

Résumé—La bipyridyglyoxal dithiosemicarbazone réagit avec le fer (II) ou (III). Le complexe de Fe (III) set jaune (λ_{max} 400 nm). Fe (II) forme un complexe 1:2 rouge-violet à pH 2, 5 (λ_{mex} 550 nm) et un complexe 1:1 vert-bleu à pH 5–10 (λ_{max} 590–610 nm). Les deux complexes ferreux peuvent être oxydés en complexe ferrique; cette réaction est réversible. On a étudié l'application quantitative du complexe ferreux.

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DICHLORAMINE-T AS A NEW OXIDIMETRIC TITRANT IN NON-AQUEOUS AND PARTIALLY AQUEOUS MEDIA—II*

POTENTIOMETRIC DETERMINATION OF HYDROQUINONE, HYDRAZINE, OXINE, CINNAMIC ACID, Sn(II), Sb(III), Tl(I) AND FERROCYANIDE

(*Received* 21 *September* 1972. *Revised* 31 *January* 1973. *Accepted* 8 *February* 1973)

In an earlier communication, potentiometric determinations of ascorbic acid, iodide, arsenic(III) and iron(II) with dichloramine-T (DCT) in glacial acetic acid medium were described. The behaviour of DCT towards eight other reductants, *viz.* hydroquinone, hydrazine, oxine, cinnamic acid, Sn(II), Sb(III), Tl(I) and ferrocyanide has now been examined.

* Part I: *Talanta*, 1972, **19**, 347.

Extraction of the green-blue complex into chloroform reduces the interferences. The absorbance is measured at 630 nm. Salting-out agents do not improve the extraction. The extracted complex is stable for at least 5 hr. Beer's law is obeyed from 2 to 8 ppm of Fe(II). The molar absorptivity is $6{\cdot}60 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. For 3·7 ppm of Fe(II) the error is $< 2{\cdot}5\%$ with 200 ppm of Li, Na, K, Rb, Mg, Ca, Sr, Ba, Zn, Sn(II), La, V(V), Cr(VI), Os(IV), Pt(IV) and Mo(VI). Up to 100 ppm of Cd may be present. Errors are below 4% for 16 ppm of Cu(II) or Ni, 32 ppm of Co(II), 100 ppm of Hg(I) and 200 ppm of Al or Mn(II); Ag(I) is reduced to elemental silver.

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* Part I: *Talanta*, 1972, **19**, 347.

EXPERIMENTAL

The apparatus and DCT solutions were the same as described earlier.[1] Solutions of hydroquinone, oxine and cinnamic acid were prepared in glacial acetic acid as well as in water, whereas standard solutions of the remaining reductants were prepared in water only, and all were standardized by the usual methods.[2] All reagents were of analytical or guaranteed reagent grade.

Determination of hydroquinone

The experiments with aqueous hydroquinone solutions corresponded to titrations in aqueous-organic medium and those with glacial acetic acid solutions to titrations in purely non-aqueous medium, sufficient acetic anhydride being added to remove water when necessary.

Direct titration with DCT gave no potential break, and the reverse titration, though giving a potential break, gave very premature end-points with variable stoichiometries. The addition of perchloric acid was tried for reasons explained earlier,[1] but did not do any good. However, addition of a little potassium bromide made the direct titration successful. Further, small amounts of water were found to be necessary.

Recommended procedure. Take 5 ml of the sample solution and add 5–10 ml of glacial acetic acid, about 0·5 g of finely powdered potassium bromide and about 2 ml of water (if not already present). Titrate with DCT solution from a microburette. (Potential break 300 mV per 0·1 ml of 0·1*N* oxidant.)

Table 1. Potentiometric titrations with dichloramine-T

Reductant	Taken, *mmole*	DCT consumed, *meq.*	$\frac{\text{DCT (equiv)}}{\text{Reductant (mole)}}$	Reductant found, *mmole*	Error %
Hydroquinone	0·2999	0·5998	2·000	0·2999	0·0
	0·3599	0·7163	1·990	0·3582	−0·5
	0·5380	1·073	1·995	0·5365	−0·3
Hydrazine	0·1287	0·5163	4·012	0·1290	+0·2
	0·1574	0·6273	3·986	0·1568	−0·4
Oxine	0·3590	1·438	4·005	0·3594	+0·1
	0·4307	1·724	4·002	0·4309	+0·1
	0·4695	1·878	4·000	0·4695	0·0
Cinnamic acid	0·1039	0·2078	2·000	0·1039	0·0
	0·1444	0·2885	1·998	0·1443	−0·1
	0·1650	0·3302	2·001	0·1651	+0·1
Sn(II)	0·1626	0·3242	1·994	0·1621	−0·3
	0·3253	0·6530	2·007	0·3265	+0·4
Sb(III)	0·2267	0·4539	2·002	0·2270	+0·1
	0·2900	0·5790	1·996	0·2896	−0·1
Tl(I)	0·1614	0·3225	1·998	0·1613	−0·1
	0·2260	0·4516	1·998	0·2258	−0·1
Ferrocyanide	0·2203	0·2223	1·009	0·2223	+0·9
	0·3525	0·3521	0·9988	0·3521	−0·1
	0·3965	0·3983	1·005	0·3983	+0·5

Determination of hydrazine

Direct titration with DCT gave belated end-points owing to the slowness of the reaction. This could be remedied by addition of perchloric acid (5 ml of 70% solution). Addition of acetic anhydride completely spoils the titration, possibly because of acetylation of hydrazine. Addition of potassium bromide gave faster equilibration of the potential.

Recommended procedure. To 5 ml of hydrazine solution add 5 ml of 70% perchloric acid solution and 0·5 g of potassium bromide, and about 2 ml of water (if not already present). Titrate with DCT (potential break 300 mV per 0·1 ml of 0·1*N* oxidant).

Determination of oxine

Direct titration gave no potential break, which is not surprising in view of the lack of any simple oxidation mechanism under these conditions. Addition of perchloric acid did not help. Oxine is conventionally determined by bromination.[2] Hence, the possibility of potentiometric titration in presence of bromide was explored and found to work. The presence of perchloric acid is unnecessary. Acetic anhydride should not be added, because of possible complications caused by acetylation of the oxine.

Recommended procedure. To 5 ml of the sample solution containing not more than 0·5 mmole of oxine, add 5–10 ml of glacial acetic acid, 0·5 g of potassium bromide and 2 ml of water (if not already present). Titrate with DCT (potential break 100 mV per 0·1 ml of 0·1*N* oxidant).

Determination of cinnamic acid

Direct or reverse titrations were unsuccessful in either non-aqueous or mixed media, except when bromide was also present. Potential equilibration was very slow, but could be speeded up by addition of 5 ml of conc hydrochloric acid.

Recommended procedure. To 5 ml of cinnamic acid solution add 10 ml of 10% aqueous potassium bromide solution and 5 ml of conc hydrochloric acid. Titrate slowly with DCT (potential break 200 mV per 0·1 ml of 0·1*N* oxidant).

Determination of Sn(II), Sb(III) and Tl(I)

Direct titration worked for Sn(II) and Sb(III), though attainment of steady potentials was slow, but not for Tl(I). Addition of perchloric acid made no difference, but bromide improved matters. The presence of a small amount of water made attainment of steady potentials faster. It is advantageous to have an atmosphere of carbon dioxide during titration of Sn(II), but it is not essential if the titration is done fast enough. In the titration of Tl(I) a white precipitate of TlBr forms on addition of bromide but dissolves during the titration as it is converted into $TlBr_3$.

Recommended procedure. To 5 ml of the reductant solution add 0·5 g of potassium bromide and 2 ml of water (if not already present). Titrate with DCT. Potential breaks per 0·1 ml of 0·1*N* oxidant are: Sn(II), 400 mV; Sb(III) or Tl(I) 200 mV.

Determination of ferrocyanide

Direct titration in non-aqueous medium was unsuccessful except in the presence of potassium bromide and a small amount of water.

Recommended procedure. To 5 ml of the aqueous ferrocyanide solution add 0·5 g of potassium bromide and titrate with DCT (potential break 400 mV per 0·1 ml of 0·1*N* oxidant).

RESULTS AND DISCUSSION

Typical results are presented in Table 1. The equivalence points were obtained from potentiometric titration curves and were checked by calculations employing the Hostetter–Roberts equation.[3] Under the condition specified, DCT oxidizes hydroquinone to quinone, hydrazine to nitrogen, Sn(II) to Sn(IV), Tl(I) to Tl(III), Sb(III) to Sb(V), cinnamic acid to dibromocinnamic acid and oxine to dibromo-oxine.

All the titrations proceed smoothly only in presence of Br^-. It is conceivable that Br_2, formed as an intermediate product by the oxidation of Br^- by DCT, could act as a catalyst.

$$4Br^- + RNCl_2 + 2H^+ \longrightarrow RNH_2 + 2Br_2 + 2Cl^-$$

$$Br_2 + [Red] \longrightarrow 2Br^- + [Ox].$$

In the case of oxine and cinnamic acid, bromine produced *in situ* may be looked upon as a reactant, since the final products here are bromo-derivatives.

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Summary—Potentiometric titration procedures are described for the determination of hydroquinone, hydrazine, Sn(II), Sb(III), Tl(I), oxine, cinnamic acid and ferrocyanide, with dichloramine-T dissolved in glacial acetic acid.

Zusammenfassung—Zur Bestimmung von Hydrochinon, Hydrazin, Sn(II), Sb(III), Tl(I), Oxin, Zimtsäure und Ferrocyanid mit Dichloramin-T in Eisessig werden potentiometrische Titrationsvorschriften beschrieben.

Résumé—On décrit des techniques de titrage potentiométrique pour le dosage d'hydroquinone, hydrazine, Sn (II), Sb (III), Tl (I), oxine, acide cinnamique et ferrocyanure, avec la dichloramine-T dissoute en acide acétique glacial.

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THIN-LAYER CHROMATOGRAPHIC METHOD FOR SEPARATION AND DETERMINATION OF PAPAVERINE AND ITS OXIDATION PRODUCTS

(*Received* 16 *October* 1972. *Accepted* 31 *January* 1973)

Many investigators have tried to determine why the colour of papaverine hydrochloride in ampoules often changes with time from colourless to yellow. Some authors have attributed this change to the presence of papaveraldine, the hydrochloride of which is known to be yellow; this was proved by paper chromatographic separation of the components in a coloured sample.[1,2] Pawelczyk and Hermann[3] showed that in coloured samples eight unidentified compounds were present besides papaverinol and papaveraldine.

The separation of papaverine from other alkaloids, either from opium tincture or different pharmaceutical preparations, by TLC has been investigated from 1960 onwards.[4-23] Only paper chromatographic methods were reported for the separation of papaverine, papaverinol and papaveraldine.[1-3,24] Separation of papaverine from papaverinol was achieved by 2-dimensional chromatography on alumina.[25]

A review of the published work shows the need for a rapid and sensitive method for the estimation of papaverine in opium extracts and in drugs, with special attention paid to elimination of interference by the oxidation products of the alkaloids. The main object of this work was to develop a TLC method for the separation of papaverine, papaverinol and papaveraldine so that any of these compounds could be easily determined by a spectrophotometric and/or polarographic method.

EXPERIMENTAL

Materials

Papaverine base. Prepared from a solution of papaverine hydrochloride in water by addition of dilute ammonia solution,[26] and recrystallized from an alcohol-ether mixture.[27] M.p. 147°.

Papaverinol base. Prepared according to Čtvrtnik and Sapara[28] and recrystallized from ethanol. M.p. 137-8°.

Papaveraldine base. Prepared by the method of Menon[29] and recrystallized from benzene. M.p. 210°.

All reagents used were of analytical reagent grade. Methanol and chloroform were redistilled before use.

Plates, adsorbent and solvent system

The plates, 20 × 20 × 0·3 cm, covered with a 0·25-mm thickness of fluorescent silica gel G, were activated at 110°, then developed at room temperature (25°) in a chamber saturated with the solvent (chloroform saturated with ammonia). The filter-paper lining of the chamber was soaked with ammonia solution.

The dried developed plates were either viewed under ultraviolet light (254 nm), or sprayed with Dragendorff's reagent[30] which gave the spots an orange colour.

Reference solutions

Papaverine (10 mg) was dissolved in 1 ml of glacial acetic acid, followed by 2 ml of hydrochloric acid (sp.gr. 1·18). Papaverinol and papaveraldine were treated similarly. The reference mixture contained 5 mg of each compound in 3 ml of the acid solution.

Methods

Spectrophotometry. Calibration curves were constructed by using 2-14 μl of a solution of 45 mg of papaverine in 2·5 ml of glacial acetic acid and 5 ml of hydrochloric acid for chromatography. Each spot was removed as well as an equivalent area of the blank, and all were quantitatively transferred to separate

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The absorbances of the methanol solutions were measured at 253·7 and 311 nm for papaverine, 253·4 and 312 nm for papaverinol and 247·0 and 332 nm for papaveraldine. Beer's law was obeyed between 0·4 and 12·0 μg/ml at the shorter wavelength, which was chosen for further work because at this wavelength the molar absorptivities were higher. The means from five different experiments for each compound were used to prepare the standard curves.

Polarography. According to the literature, papaverine can only be polarographically reduced in a quaternary ammonium base medium.[31-33] Moreover, the catalytic wave of papaverine interferes completely with the reduction wave in acid medium and prevents the use of the reduction wave for quantitative analysis. Naturally the same would apply for papaverinol. On the other hand, papaveraldine can be polarographically reduced in different buffers and at different pH values, since the carbonyl group conjugated with the rings is the group to be reduced.[32-35]

The chromatography and extraction were done as before. Gelatin solution (0·2%, *ca.* 0·1 ml) was added to act as maximum suppressor, the volume was made up to 10 ml with Britton-Robinson buffer, composed of 0·04*M* solutions of phosphoric, acetic and boric acids, adjusted to pH 4·1 with 0·2*M* sodium hydroxide. the solution was transferred to the polarographic cell, and deaerated for 2 min with pure nitrogen. The polarogram was recorded starting at −0·4 V *vs.* SCE. The half-wave potential of papaveraldine was −0·645 V, in close agreement with the reported values for the pH range 4–6.[32,34] The wave height was a linear function of papaveraldine concentration over the range 0·6–24 μg/ml.

Ampoule analysis

The papaverine hydrochloride ampoules tested contained 30 mg of the compound in 1 ml of solution. The contents of a 1-ml ampoule were made up to 5 ml with acetic-hydrochloric acid mixture (1 : 2) and 10 μl were applied to the TLC plate; the rest of the procedure was as above.

The method was practicable for the detection of down to 1% of papaveraldine in aged ampoules.

RESULTS AND DISCUSSION

The R_f values of the compounds were: papaverine 0·53, papaverinol 0·44 and papaveraldine 0·63. The precision and accuracy of the method were calculated from the results for five analyses of known mixtures (Table 1).

Table 1

Compound	Weight taken per 5 ml of acid soln., *mg*	Relative std. devn., %	Systematic error, %*
Papaverine	3·0	2·4	+0·7
	9·0	2·3	−0·2
	24·0	0·1	+0·1
Papaverinol	3·0	3·8	−0·6
	9·0	1·5	−0·6
	21·0	1·0	+0·7
Papaveraldine (spectrophotometric)	3·0	1·7	+1·4
	12·0	1·3	−0·4
	21·0	0·6	−0·1
Papaveraldine (polarographic)	3·0	1·2	−0·9
	12·0	0·4	0
	21·0	0·6	+0·2

* Difference between mean found and amount taken, relative to amount taken.

The results indicate that papaveraldine is preferably determined polarographically. The conventional methods for papaverine determination depend upon its extraction before its determination; papaverinol and papaveraldine could easily be extracted along with papaverine and hence be determined with it, especially if a spectrophotometric method was used.

The papaverine must be separated from its oxidation products before its determination, if interferences are to be overcome. The TLC method given here is very rapid, suitable for this purpose, and is sensitive and reproducible.

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Summary—A method is presented for the separation of papaverine, papaverinol and papaveraldine by TLC on silica gel with chloroform saturated with ammonia as the solvent system. The spots are extracted with absolute methanol and each compound determined spectrophotometrically in $1M$ hydrochloric acid. Papaveraldine is also determined polarographically in Britton–Robinson buffer, pH 4·1, after its separation and elution. The method is rapid and sensitive and permits the determination of papaverine, after its extraction from drugs, without interference by papaverinol and papaveraldine.

Zusammenfassung—Ein Verfahren zur Trennung von Papaverin, Papaverinol und Papaveraldin durch Dünnschichtchromatographie auf Kieselgel mit ammoniakgesättigtem Chloroform als Lösungsmittelsystem wird vorgelegt. Die Flecken werden mit absolutem Methanol extrahiert

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und jede Verbindung spektrophotometrisch in 1 *M* Salzsäure bestimmt. Papaveraldin wird auch nach seiner Abtrennung und Elution polarographisch in Britton-Robinson-Puffer pH 4,1 bestimmt. Die Methode ist rash und empfindlich und erlaubt die Bestimmung von Papaverin nach dessen Extraktion aus Drogen ohne Störung durch Papaverinol und Papaveraldin.

Résumé—On présente une méthode pour la séparation de la papavérine, du papavérinol et de la papavéraldine par chromatographie en couche mince sur gel de silice avec le chloroforme saturé d'ammoniaque comme système solvant. Les taches sont extraites au méthanol absolu et chaque composé est déterminé spectrophotométriquement en acide chlorhydrique 1 *M*. La papavéraldine est aussi déterminée polarographiquement en tampon Britton-Robinson, pH 4,1, après ses séparation et élution. La méthode est rapide et sensible et permet le dosage de la papavérine, après son extraction de médicaments, sans interférence du papavérinol et de la papavéraldine.

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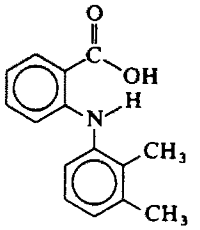
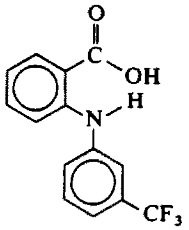
NATIVE FLUORESCENCE OF ANALGESICS DERIVED FROM *N*-PHENYLANTHRANILIC ACID

(*Received* 18 *January* 1973. *Accepted* 31 *January* 1973)

Certain *N*-phenylanthranilic acid derivatives such as mefenamic acid (**I**), flufenamic acid (**II**), and meclofenamic acid (**III**) are used as analgesics and anti-inflammatory agents. The investigation of the fluorescences of these compounds, in the present work, showed that all three demonstrate native fluorescence in organic solvents. This property could be useful for their detection and determination.



(I)



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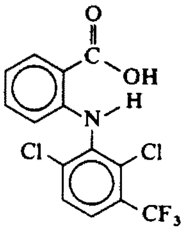

(III)

Table 1. Fluorescence data for mefenamic, flufenamic and meclofenamic acids

Drug	Solvent	Wavelength combination,* *nm*	Limit of detection, *M*
Mefenamic acid	Dioxan	350/440	$\sim 5 \times 10^{-7}$
	Ethanol†	—	—
	Chloroform	365/460	$\sim 10^{-6}$
Flufenamic acid	Dioxan	334/410	$\sim 3 \times 10^{-7}$
	Ethanol†	—	—
	Chloroform	340/430	$\sim 2 \times 10^{-7}$
Meclofenamic acid	Dioxan	334/390	$\sim 10^{-5}$
	Ethanol	340/410	$\sim 5 \times 10^{-6}$
	Chloroform	340/406	$\sim 2 \times 10^{-7}$

* Wavelengths of maximum excitation/emission.
† Fluorescence in this solvent is too weak to be analytically useful.

und jede Verbindung spektrophotometrisch in 1 *M* Salzsäure bestimmtl Papaveraldin wird auch nach seiner Abtrennung und Elution polarographisch in Britton-Robinson-Puffer pH 4,1 bestimmt. Die Methode ist rash und empfindlich und erlaubt die Bestimmung von Papaverin nach dessen Extraktion aus Drogen ohne Störung durch Papaverinol und Papaveraldin.

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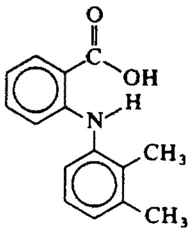
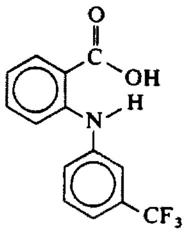


(I)



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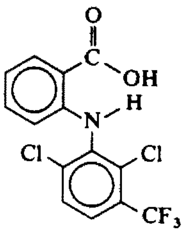

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Meclofenamic acid	Dioxan	334/390	$\sim 10^{-5}$
	Ethanol	340/410	$\sim 5 \times 10^{-6}$
	Chloroform	340/406	$\sim 2 \times 10^{-7}$

* Wavelengths of maximum excitation/emission.

† Fluorescence in this solvent is too weak to be analytically useful.

Fluorimetric methods have been reported for these drugs,[1,2] based upon the conversions of the substituted *N*-phenylanthranilic acids into substituted acridones with concentrated sulphuric acid or into substituted *N*-phenyl-4-oxo-1,2-dihydro-3,1,4-benzoxazines with formaldehyde. In the first of these reactions, two isomeric trifluoromethyacridones, with differing fluorescence properties, may be formed from (**II**), thereby further complicating analysis. In our opinion, fluorimetric analyses of (**I**)-(**III**) by means of their native fluorescences are simpler, quicker and as sensitive, as, or in some cases, more sensitive than the fluorimetric methods entailing fluorogenic derivative-formation reactions.

The fluorescence was investigated in distilled water, 0·1*N* sodium hydroxide, 0·1*N* sulphuric acid, dioxan, 95% ethanol and chloroform. The drugs showed fluorescence only in organic solvents having a low dielectric constant. The limit of detection was taken as that concentration which gave a signal equal to twice the value for a solvent blank under identical instrumental conditions. Fluorescence spectra were taken on a Baird-Atomic Fluorispec, Model SF-1. The drug substances were obtained from Parke Davis Company, Detroit, Michigan. The results are summarized in Table 1.

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Summary—The native fluorescence of mefenamic, flufenamic and meclofenamic acids is more useful for determination of these drugs than is the fluorescence of the derivative substituted acridones and benzoxazines obtained from these drugs by treatment with sulphuric acid or formaldehyde respectively.

Zusammenfassung—Die Eigenfluoreszenz von Mefenaminsäure (2,3-Dimethyldiphenylamin-2'-carbonsäure), Flufenaminsäure (3-Trifluormethyldiphenylamin-2'-carbonsäure) und Medofenaminsäure ist zur Bestimmung dieser Drogen von größerem Nutzen als die Fluoreszenz der davon abgeleiteten substituierten Acridone und Benzoxazine, die man aus den genannten Drogen durch Behandlung mit Schwefelsäure bzw. Formaldehyd erhält.

Résumé—La fluorescence native des acides méfénamique, flufénamique et méclofénamique est plus utile pour le dosage de ces produits pharmaceutiques que ne l'est la fluorescence des acridones et benzoxazines substituées dérivées obtenues à partir de ces produits pharmaceutiques par traitement à l'acide sulfurique ou au formaldéhyde respectivement.

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HOW TO WRITE A PAPER ON ATOMIC-ABSORPTION SPECTROMETRY

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Summary—The present situation in the preparation of new papers on atomic-absorption spectrometry is discussed. The different types of papers published in this field are reviewed, and details given of the topics that *must* be dealt with in writing such papers. Particular attention is given to experimental papers dealing with new instrumentation, study of the analytical behaviour of analytes, and new procedures for specific analytical applications.

Perhaps one of the abilities most difficult to teach scientists is the ability to write their own scientific papers. They will learn how to search for new scientific information, to develop new working procedures, and to invent new devices to perform the work better, but they will have a hard time when the moment of writing down findings, methods or disclosures comes.

The final version of a paper should contain all the necessary information which has to be submitted to the attention of readers, but, at the same time, the contents should be concise without losing clarity, organized without losing the personality of the author, and visually attractive without losing text in favour of a multiplicity of graphs, tables, diagrams and photographs. Very few scientific papers reach maximum performance in all these characteristics, even if the title and subject attract the attention of readers, and they are read and used. The other papers, even when printed, are seldom read, referred to and used. They fall in the category of average printed and forgotten papers, with no other life than the space of a few pages in a journal, a few lines in an index, and a few entries in one or several journals of reviews and abstracts, waiting there for some reader, some day, in the years to come.

In former times (perhaps until the last decades of the first half of this century) journal space was not a grave problem because the number of writers was not so high. Later, a slow increase in the number of journals without much increase in the number of pages available, and an overwhelming increase in the number of writers, led to establishment of selective policies in terms of *interest of the subject*, *novelty of the contribution*, *extent* (the cold measurement of number of printed lines or number of pages of the manuscript), *and usefulness of conclusions derived from the contribution.*

The time for short papers came: short contributions, short communications, preliminary communications, short papers, notes, letters to the editor (many letters were never followed by a formal paper). Patterns were established to give all the information in a standardized manner, within narrow presentation limits for each precast section: *Introduction*, *Experimental*, *Results* and *Conclusions.* References were reduced in extent (even the names of the journals were abbreviated), and condemned to small print, at the end or in footnotes. The number of figures and tables was reduced to a minimum and two columns of text were used instead of one, three instead of two. Summaries were kept short and only a few key words were given, if any at all.

Time (time to read) was also a decisive factor. Multiplicity and plurality of papers made the task of readers difficult. There was too much to read and not enough time to do it. The number and extent of index publications increased; collections of abstracts appeared everywhere; lists of titles of current papers were printed; organized retrieval services were established.

In this situation, from time to time, a new field, a new method, a new technique comes and demands printed space in journals to explain to the scientific world that this innovation exists, what it is, how it works, and how it may be applied. The pressure of print restrictions relaxes a bit: general papers, informative papers, even 'popular' science papers appear, later followed by collective papers, reviews, updating contributions, compilation articles, none containing much that is new, but just putting things together. At this point books begin to appear, which will also be compilations, but with the old, traditional, and always appreciated taste of a book (comprehensive, clear, organized, and collecting the references; easy to read; giving a lot of information, at hand, on the desk, in a single volume).

There comes a moment at which readers again go to journals to search for general papers to update a little their collection of reprints, photocopies and books. They have been learning and increasing their knowledge, and consider that they are saturated up to some given level, and their attention decreases. But production of papers by writers does not decrease or stop. It increases (applications, modifications, small features, more or less brilliant improvements). More and more papers are printed on the new subject, which enters in its turn into the established system. Once in a while a new review article appears, but is so often a condensed collection of names and reference numbers. Readers wait for some new book that does not repeat the same concepts already read in the earlier ones, and which might actually be considered as *new*. The task of looking for titles, abstracts, and computer-retrieved lists and summaries once again arrives.

In atomic-absorption spectrometry (AAS) this type of cycle has occurred and is going on at present.

By examining *from outside* the development of AAS it is easy to see that the method has reached some kind of a plateau of performance with slight modifications due to specific improvements introduced from time to time. This status influences the applicability of the method as an established analytical method, fully accepted today, and also influences the trends in the AAS literature by leading to an increase in the number of papers dealing with new studies on analytical response of analytes and on specific applications.

If at this point the question arises of *how to write a paper on AAS*, any writer finds himself again inside the narrow circle of imposed limitations: novelty of contribution, scope, and positive gains derived from the experimental effort to be communicated. Many papers are presented orally at meetings, symposia and conferences, and only a few of them are seen later in printed form. Why? Lack of novelty? Simply rejected because they were too long? Poor positive contributions to the established method? Too commercial in aspect, remote from the academic pattern of a scientific communication? Some kind of prejudice because in the 70's the AAS methods can no longer be considered as recently invented?

Will this situation not discourage new and old writers from preparing and submitting the written presentation of new and valuable experimental findings just because they are afraid that their contributions might be rejected? Does this situation not jeopardize the rights of readers to have access to new findings encountered through the honest and patient work of some AAS scientist in some hidden corner of the world?

Rejection is not necessarily the result of prejudice on the part of editors and editorial boards. The fundamental reason should rather be sought in the contents and presentation of each paper.

To write is difficult. To write in scientific terms is still more difficult. Courses in universities, colleges and commercial enterprises, seminars, lectures, as well as several books on scientific writing do not seem to have done the job properly. Contents and presentation of papers are still poor, and frequently on the borderline of rejection.

If at this point the question of *how to write a paper on AAS* is raised, it is necessary to consider that today is not yesterday. The contents of papers not only have to satisfy generally established standards, but have also to offer the information which is actually needed today.

To write a paper on AAS it is necessary to have a good knowledge of AAS, a good knowledge of scientific writing, and some kind of feeling for and knowledge of what is really needed or desired by potential readers interested in AAS topics.

This article will be devoted to the third aspect, the most vital one today, perhaps. No lessons on AAS are given here, since AAS has been fully and clearly discussed in several articles and a few books. No lessons are going to be given here about scientific writing since many others have dealt with this. No attempts will be found to give instructions about personal style or grammar (and any errors in this paper are undoubtedly the editor's fault!). First of all, style in writing is such a personal characteristic that any attempt to standardize it is against the precious freedom of a scientist to express himself in his own way. Trying to include rules of grammar can only lead to repetition of concepts given and discussed by well-known authorities. In any case, a good editor will see to it that grammar is correct and ambiguity avoided.

Concepts and topics pertaining to AAS are not defined or discussed here because they have been explained in detail in the author's book *Atomic-Absorption Spectroscopy.*[1]

The author has preferred not to illustrate the discussion by reproducing sections of articles in the current literature and does not include references to examples, because whichever good examples are given many other worthy papers have to be ignored, and this type of discrimination seems unfair. On the other hand, if one or two are shown as bad examples, this is very discouraging for their authors. A few references to the author's papers are included, not because they should be considered as examples, but because they describe topics mentioned in this contribution and not described in the above-mentioned book.

The matter of nomenclature in AAS deserves more than a paragraph in a review article. This is a matter of vital importance. Fortunately committees of specialists in AAS are preparing recommendations on nomenclature on behalf of I.U.P.A.C. and other organisations. The reader interested in this topic should consult the collections of recommendations prepared by these groups of scientists.

DIFFERENT TYPES OF PAPERS

Not all papers on AAS can be considered in the same way. Many categories of papers are printed in scientific journals. The main categories are summarized in Table 1, and will be discussed below.

Table 1. Papers on atomic-absorption spectrometry

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1. *Review Papers*
    - 1.1. General papers.
    - 1.2. Recent advances.
    - 1.3. Reviews on selected fields.
2. *Theoretical Papers*
3. *Experimental Papers* (Normal and short communications)
    - 3.1. On instrumentation.
    - 3.2. On individual analytes.
    - 3.3. On specific sample applications.
    - 3.4. On aids to the flame photometrist.

Review papers

Readers expect to find review papers exhaustive, *i.e.*, compilations prepared to save them the trouble of going to the library to look for details of a general subject or of a definite field of that subject. This is not the reality. There is too much to review. Review papers and articles, unfortunately, are also limited in space, and that means, immediately, limitation in information. Review papers try to be small-size books of a few pages only, with similar organization to that used for books, but with encapsulated contents.

The main weaknesses in review papers are that: (*a*) they are too personalized, much more than books are, according to the taste and inclinations of the author; (*b*) references are hardly exhaustive (some selection criteria are used by the author); (*c*) references are handled in the standard way, eliminating the title of journal articles (readers can perhaps form an idea of the contents from a passing mention in the text, but cannot obtain more without reading an abstract or the original); (*d*) procedures, modifications and applications are announced in single-sentence style, with or without mentioning the author in the text, and accompanied by a single or multiple reference entry, sometimes even less than that—no text, just a place in a large summary table, where reference numbers are included in the last column; and (*e*) lack of comments, comparisons, evaluations, or criticisms, and only some plain information letting the reader know that some work has been done.

Selection criteria greatly decrease the interest of a review article. The main selection criteria used by authors are as follows.

Topic. The author leaves untouched some areas which may be of interest to readers in order to give more space to areas of his own particular interest. Consequently references corresponding to the omitted areas do not appear.

Language. The author eliminates many interesting papers because they are written in Japanese, Russian, Italian, *etc.* The fact that the author has difficulty in reading these languages does not mean that all readers will have the same language limitation.

Commercial literature. Many interesting contributions appear in journals supported by commercial enterprises. That the commercial enterprises are profit-oriented is irrelevant; these scientific contributions have an informative and formative value that should not be eliminated and ignored.

Country of origin. Valuable contributions may come from any country, even if the research media available are not so advanced as those used in leading scientific research countries.

Accessibility. No limitation should be imposed on the supposition that certain publications are not easily accessible to readers (unless they are government or industrial classified papers or special proprietary methods or reports). It might be understood that some information was not accessible to the writer at the time of preparation of the manuscript, but it should at least be mentioned for the convenience of the reader. The present author has tried successfully the idea of including the addresses of authors whose work was included in the review, in the collection of periodic reviews published in the Spanish journal *Información de Química Analítica.* This has allowed many readers from Spain and Spanish-speaking countries to obtain reprints and copies of papers of inaccessible journals.

Some of these defects are found, paradoxically, in some books, where bibliographic references are accumulated in some chapters, leaving the reader the heavy task of going to the library even to discover the titles of a collection of papers and the real contents of each one of them.

General papers, in principle, should begin at the beginning, from fundamentals and theory to the particularities of analytical applications. Although this was useful at the very beginning, it is not so now, when most analysts are aware of fundamentals and generalities on instrumentation and operation. Even those not so well informed will prefer to go to books, where wider information is supposed to be found. However, from time to time, authors have again to prepare general reviews from the beginning to the end, as complete subject contributions, since these manuscripts are scheduled to be included as specialized chapters in multi-author books. Maximum care should be devoted to the preparation of such general papers or specific chapters to avoid unnecessary repetition of topics already dealt with many times before.

If for some reason the paper cannot be exhaustive and the text (and, thus, references) must be kept within limits, topics could be chosen from the following ideas.

(*a*) Books, general reviews and special reviews.

(*b*) Up-to-date bibliographies.

(*c*) Theoretical contributions which have solved or explained some key aspects of the method.

(*d*) Studies of particular aspects (errors, precision, sensitivity, *etc.*)

(*e*) Major developments in instrumentation which have produced a significant change in the general philosophy of the method.

(*f*) Major techniques which extend the method (nitrous oxide–acetylene flame, graphite furnace, evolution methods, Delves cup, among others), opening new applications, especially if involving some changes in the general philosophy of the method.

(*g*) Significant contributions to knowledge of the behaviour of analytes, including interferences.

(*h*) Significant contributions in the field of sample analysis, including new approaches to sample preparation (new single or multi-element extractions for instance).

At the present stage of development of AAS, reviews of recent advances would be much appreciated, since they give an up-to-date view of the latest developments in instrumentation, specialized techniques, sample preparation procedures, applications, *etc.* Some care is necessary in the preparation of the introduction in such reviews in order to help the reader to make a smooth transition from known areas—or areas supposed known—to the new ones.

The rapid increase of new contributions to the field makes it very difficult to prepare good reviews on developments and advances, especially in the field of applications. The most recently published applications will not reach the writer in time and will not be mentioned in the review. Others will not be mentioned because of selection criteria (mainly on account of space limitation). This is why the most appreciated reviews will be those restricted to selected fields (*e.g.*, instrumentation, trace analysis, environmental analysis, biological analysis, non-flame methods). All the available space can be used for a very restricted topic and information will be not so 'dry' as it usually is in review papers, and the author, if a specialist in that area, will try to offer as much as is available and known without rejecting or simply ignoring too many papers.

Theoretical papers

Theoretical papers have been, are, and will be one of the most valuable kinds of paper on AAS because they explain and justify by mathematical expressions all phenomena involved in the method: spray characteristics, influence of geometry of burners in flame stability, flame equilibria, formation and decay of absorbing species, and so many other important and basic topics which need to be known, and knowledge of which really makes AAS considered a part of Analytical Science, and not just a simple analytical art.

Many advances used today in AAS laboratories are due to theoretical studies by prominent AAS scientists, whose papers help each day in the understanding of a diversity of phenomena encountered by users of AAS in laboratory work. These contributions are the builders of AAS as an analytical method. However, the number of users of AAS as an 'analytical tool' can be counted by thousands, and the flame specialists involved in theoretical studies represent a much smaller number. Users, in general, cannot find an immediate and direct benefit from these contributions in planning the routine determination of a given analyte in a given type of sample. They look for procedures, experimental conditions and working recipes, *i.e.*, something that normally is not found in theoretical papers. Readers of theoretical papers are not numerous, and some papers are not used to full advantage, since they receive the attention only of other specialists, some manufacturers searching for clues to improve instrumentation, and beginners interested more in theoretical aspects at academic level than the everyday use of AAS as an applicable analytical methodology to solve specific problems.

Theoretical papers have one or more of the following purposes.

(*a*) To study fundamentals of atomization processes.

(*b*) To study fundamentals of aerosol formation processes.

(*c*) To study equilibria in flames, including compound formation, ionization phenomena and distribution of absorbing species.

(*d*) To study spectral aspects related to atomic lines (profiles, oscillator strengths, broadening effects and related topics).

(*e*) To study flame characteristics.

(*f*) To study optical characteristics which may lead to future improvements of the optical system.

(*g*) To study electronic characteristics which may lead to future improvements in the electronic and detection systems.

(*h*) To study factors involved in spectral emitters.

Not many suggestions can be given for preparation of theoretical papers, except to advise that concepts, mathematical treatments and conclusions be made as clear as possible, so as to attract readers who are users of AAS, thus avoiding the danger that these interesting contributions will be read only by specialists. Not only the equations and mathematical derivations should be given but also some indication of how to use the findings in practice.

Some papers might be classified as theoretico-practical papers, because without going into a deep theoretical treatment they try to study some particular phenomena, processes, or analytical characteristics on the basis of experimental data. Examples are papers on sensitivity in AAS, concentration range, concentration and dilution processes, computer handling of data, accuracy, precision, selectivity, addition methods, errors in AAS work. Not many suggestions can be given for this type of contribution either, since many of them are a consequence of long experience of the author in AAS and contain a treatment of an important field of AAS from another angle. It might be desirable, however, that such treatments should be sufficiently general for many users to be able to take advantage of the findings, new approaches and recommendations.

Experimental papers

Experimental papers form the majority of AAS papers appearing in scientific journals and are the most searched for by users, who try to find in them other colleagues' experiences, new results, new methodologies, and always some practical recommendations that may be used in their own analytical problems.

Analytical chemists and chemical analysts search for new papers primarily in terms of the *analyte and medium* or *analyte and sample type* they are concerned with, and only secondarily in terms of *method. Medium* in this case is the prepared subsample containing the analyte under the conditions to be used for measurement by the instrument. Thus the concern may be in the one case with chromium in very acid solutions or calcium in the presence of phosphate, and in the other case be lead in pottery, zinc in serum or iron in brass. When such a paper has been found it will be searched to find *how* to do the determination. It frequently happens that instrumentation innovations are sought to solve some given analyte/medium or analyte/sample problem, and then experimental papers dealing with new instrumentation developments (instruments and/or accessories) and new procedures (element or sample applications) are constantly searched for and read. Papers of this kind are expected to be exhaustive in the treatment of a specific subject because they are *specific papers on a single subject.*

Experimental papers, in general, have one or more of the following purposes.

(*a*) To look for the most convenient atomization process for a given analyte (increase of sensitivity, thus lowering the concentration limits and eliminating the conditions giving low release of absorbing species).

(*b*) To look for the most convenient instrumental operating conditions (trying to lower the noise, decrease identification concentration limits, improve linearity, control the contribution of the shape of the emission lines from the source, *etc.*)

(*c*) To search for, study and control factors which can contribute to disturbance of precision and accuracy, especially those factors classified as physical and chemical interferences.

(*d*) To search for, study and test the treatment of samples that is necessary to bring the analytes in a suitable form to the instrument in order to achieve better sensitivity, accuracy and precision.

Papers presented under a title which refers to the study of the analytical behaviour of a given element, with no attempt to determine it in specific samples, will be expected to fulfill purposes (*a*), (*b*) and (*c*) in part or in full.

GENERAL ORGANIZATION

If the intention of this paper is to discuss the contents of papers, leaving aside personal style, perfection of grammar, and limitations normally imposed by journals, it seems that recommendations should be given about what to include in the final manuscript. However, it is necessary to consider that any planning of a paper is preceded by planning to do the experimental work and by the laboratory work necessary to accumulate information and results. It has been advised many times that when the moment of writing comes, the writer should begin by writing the experimental part, then the discussion, and at the end the conclusions and introduction.

On the other hand, this paper might be expected to be a collection of suggestions on how to conduct research in AAS. In practice, both aspects must necessarily go hand in hand. Recommendations for the contents of a paper can be used as recommendations on experimental areas which have to be studied in the laboratory.

The various instructions to authors that are given by journals are generally agreed that any experimental contribution should be cast in four main sections.

(*a*) Introduction.
(*b*) Experimental.
(*c*) Results.
(*d*) Conclusions.

By fusion of (*b*) and (*c*) we arrive at the three main parts of any oral or written communication.

(*a*) *Opening* (Introduction).
(*b*) *Body* (Experimental + Results, and corresponding discussion).
(*c*) *Close* (Conclusions).

This is an accepted distribution of manuscripts, recommended and followed everywhere, with slight variations in wording, subheadings, and contents of each subsection. Subheadings and subsections are a great help, since some authors include recommendations before or after conclusions, discussions interspersed with or separate from results, notes in the text as separate subsections, statistical treatment of data as results or as discussions, and descriptions of computer programmes as part of the experimental section or as an appendix. Footnotes and references are addenda to the various parts of the paper.

The space available has then to be distributed between these three main parts and the best way found for imparting the necessary information to readers. The space distribution for experimental papers on instrumentation and applications might be as shown in Fig. 1.

Although the relative lengths of the three sections may be varied, the main fraction of available space should be devoted to the *body* (Experimental + Results). Depending on the nature of the paper, the main differences in distribution of space will be in the *opening* and *close*. If possible a climactic order should be observed in the general presentation of the paper: (*a*) background, (*b*) statement of the problem, (*c*) description of the equipment, (*d*) discussion of the experimental procedure, (*e*) statement of results, (*f*) discussion of results, and (*g*) conclusions. This order maintains the attention of the reader *in crescendo* through the paper.

Since readers will look for different types of information in papers devoted to instrumentation and in papers devoted to applications, different presentations should be followed by the writer as discussed in the following subsections. Recommendations

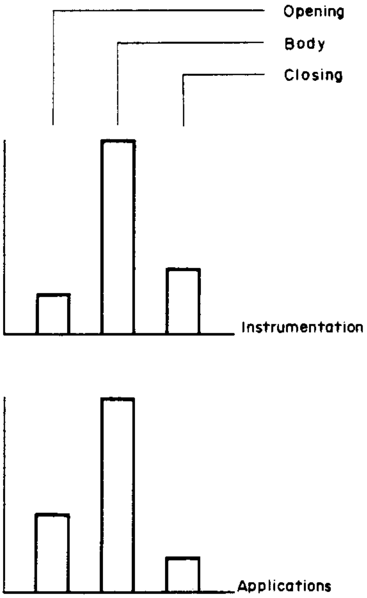

Fig. 1. Distribution of space devoted to different main sections in papers on instrumentation and applications.

included here can never be taken as fixed rules. Some flexibility is necessary. Some parts may be omitted completely, especially if some of the information has been given in earlier contributions and is still valid.

Papers on instrumentation

The author's attention should be focused on presenting the information in such a way that readers should even be able to construct the instrument or instrumental accessories described. This especially applies to home-made instrumentation. It does not normally apply to commercial instrumentation, which is readily available, but papers describing the performance of commercial instruments should provide the readers with enough results to help them to judge the real value of the instrumentation described.

Appropriate contents of a paper on instrumentation might be as follows.

Introduction. A short introduction. Advantages of the instrument or accessory should not be presented here, but later, after enough data have been given to be used as a basis for discussion. The introduction may include: unsolved problems with present instrumentation; need for new instrumentation; basic criteria used to develop new instrumentation; advance notice of tests done to solve other problems with the newly developed instrumentation.

Experimental + Results. As this is the body of the paper, it is necessary to use a logical order rather than a chronological exposition of tests performed. This helps to avoid backwards and forwards references to the text. Headings should be used as a help, but not as indispensable items in the understanding of the text. In this section, the author should explain what may be deduced from tables and graphs without expecting the reader to extract this information for himself. These recommendations are valid for all types of experimental papers, whether dealing with instrumentation or not. This section should include the following.

(*a*) Description of the instrument.
  Construction of the instrument (not recommended as standard for papers dealing with commercial instruments). Drawings and photographs might be included here.
  Description of principal parts.
  Commercially available parts used, if any.
  Functioning. Block diagrams and electronic diagrams might be included here.
  Specifications.
  Controls. Range of controls.
  Installation.

(*b*) Chemicals and solutions.

(*c*) Analytical performance.
  Operating conditions. All settings given and justified, if necessary.
  Linearity (graphs).
  Precision (repeatability and reproducibility). Recordings and tables can be included here.
  Accuracy (tables).
  Sample handling (concentration range, work at low concentration levels, sensitivity, concentration limits, tables).
  Versatility.
  Speed in analysis.
  Cost per unit analysed, if necessary.
  Practical examples (graphs or tables).

Conclusions. A long section is advisable here. Conclusions in this case should state clearly the significant and new information included in the text. They should state decisions taken and justify them, if they were based on the results obtained. They should clearly indicate the nature of additional work necessary if the results obtained show the need for new research projects. These rules also apply to other kinds of experimental papers. Conclusions, in the case of papers on instrumentation should include the following.

Capabilities (sensitivity, accuracy, precision, speed handling, versatility and reliability).
Resolution of present problems.
Advantages over similar existing instrumentation, if advisable (in the case of commercial instruments ethics may dictate avoidance of comparisons).
Future possible developments.

Papers on individual analytes

This type of paper should be written in such a way that readers can reproduce the work described, even with different instrumentation, since well-oriented laboratory work can be presented in a manner that lets an intelligent reader make the necessary adjustments to suit his own situation. The contents of a paper on individual analytes might be as follows.

Introduction. A long introduction may be helpful, because it could contain an advance review of the new procedures and tests at the same time as giving an idea of other authors' work. This lets the reader compare prior contributions with the new work. The introduction might contain:

Reasons for studying the problem.
Bibliographic revision (as short as possible).
Summary of results achieved by other authors.
Experimental planning.

Experimental + Results. This section should contain:

(*a*) Solutions and instrumentation.
  Chemicals.
  Solutions (stock and working solutions).
  Instrument (home-made or commercial).
  Auxiliary equipment.
  Experimental conditions.

(*b*) Tests.
  Linearity (graphs).
  Precision (repeatability and reproducibility). Recordings and graphs can be included here.
  Accuracy. Recovery tests (tables).
  Sensitivity. Concentration limits (tables).
  Selectivity. Interferences. Possible correction of interferences.

(*c*) Discussion.
  Advantages of conditions proposed.
  Inconveniences.
  Possible modifications.

Conclusions. In this type of paper, conclusions may be short.
Achievements.
Applicability of conditions proposed.

Papers on specific sample applications

In this case also the author should try to prepare the paper so as to allow the reader to reproduce the findings by following the sample preparation and practical procedures advised, with due adjustment for differences in instrumentation. The contents of these papers should be as follows.

Introduction. Again long enough to let the reader judge earlier work along with the new. The introduction might contain:
Fundamentals of the study.
Bibliographic review (as short as possible).
Summary of results achieved by other authors.
Reasons for looking for a new method.
Preliminary tests (briefly described).
Experimental planning.

Experimental + Results. This section should include:

(*a*) Solutions and instrumentation.
  Chemicals.
  Solutions (Stock and working solutions).
  Instrument (home-made or commercial).
  Auxiliary equipment.
  Experimental conditions.

(*b*) Preliminary tests (including analytical behaviour of the analyte). Linearity (graphs).

Optimum concentration range (working concentration range).
Precision (repeatability and reproducibility). Recordings and graphs may be introduced here.
Accuracy. Recovery tests (tables). Standardized samples (tables). Certified analysed samples (tables). Addition method (tables).
Sensitivity. Concentration limits (tables).
Selectivity. Interferences (due to the matrix; due to sample preparation).
Correction of or compensation for interferences.

(*c*) Subsequent tests.
Final reproducibility tests (tables).
Comparison with other methods (tables).
Collaborative work (tables).
Statistical treatment of results (tables).

(*d*) General discussion.
Advantages.
Inconveniences.
Modifications introduced as improvements.
Applicability to other types of similar samples.

(*e*) Recommended procedure.
Sample treatment.
Preparation of standards and blanks.
Instrumental procedure. Recommended settings.
Automation techniques (if applicable).
Data handling.

Conclusions. A short section devoted to conclusions might contain:
Usefulness of the method.
Agreement with other methods.
Agreement in collaborative work (if done).
Other samples to which the method can be applied.

Short notes, aids to the flame photometrist, and similar short contributions

Normally it is advised to present the manuscript without the headings and subdivisions which are standard in full papers. However, a summarized introduction will help, as well as some indispensable references. The body of the contribution might be a summarized version of what would appear in a full paper. The directions already given may be applied here. Recommendations, if any, should be strictly limited to emphasize some points of the procedure, attachment or modification described. If a full paper is to follow, dealing with the same subject, this should be indicated, with the name of the journal in which it will appear (if known). Photographs, graphs and/or tables, if really necessary, should be kept to a minimum. The laboratory work for a short paper probably follows the same steps used for a full paper. In preparation of the manuscript only the really important topics and results should be chosen.

AUXILIARY SECTIONS OF THE PAPER

Only a few comments will be made here on these sections. References will not be discussed, because every journal has its own style which is clearly specified and easily discovered by inspection.

Abstracts and summaries

These should be not too general, but informative, more than a list of topics, and less than an introduction. They should be prepared by thinking that reading them might be a substitute for reading the paper itself. Actually summaries and abstracts often help to decide whether the paper should be read or not. Busy readers will use it to extract the specific information given. If the reader has the time to read the paper, abstracts and summaries may help him to follow the text more intelligently. It is best not to repeat the title in the summary or abstract, and to keep it short (50–150 words, with a maximum of 250, if necessary). The use of complete sentences is also advised. They may include results if these are principal findings. They should not mention projected work for the future or parts of the project planned but not accomplished in the laboratory work.

In the case of experimental papers, they should list the analytes studied and/or samples tested, if they have not been announced in the title. Significant working conditions should be mentioned. The same applies to data on sensitivity, accuracy and precision if they are significant or representative.

Key words

A list of key words is required by some journals. If such a list has to be prepared, the reader should place himself in the situation of a person looking for the information contained in the paper, and include all words he might be searching for when consulting the index.

Words contained in the title should be included. Analytes, samples, flames, preconcentration (if used), extraction (if used) and words related to main steps of the experimental procedure should be included. Also words such as flame, atomic-absorption, spectrometry, spectroscopy, spectrophotometry should be added, plus related words and words of higher and lower rank in connection with topics described or discussed.

If the author does not wish to use key words he should choose an appropriate journal.

Acknowledgements

If any person helps the author in the preparation of the paper (laboratory work and/or manuscripts), the author should mention this person. It is so nice to give thanks. In any case, giving thanks does not decrease the recognition due to the author or authors. Any assistant who has done the major part of the practical work should be considered as a co-author.

COMMENTS ON SPECIFIC TOPICS IN EXPERIMENTAL PAPERS

A few comments will be added here on some topics included in the lists given above for different types of experimental papers. These comments refer to particular details that should be included in the experimental sections to give the reader better information. Consequently, they cover information that it would be advisable to obtain from the experimental work, and that should be included in the planning of the work.

If all this information is included it may make the paper too long. If some of it is already available in other publications it can be omitted if the necessary references are given. The author should carefully judge what to transfer from the laboratory to the manuscript by thinking of what the reader would like to find in a new contribution.

Solutions

With the exception of some special techniques in which the sample is fed into the instrument in solid or gaseous form, in most cases liquid samples and subsamples are used. Detailed information on solutions used should be given.

Chemicals used to prepare solutions, and their purity.

Type of water used for dilution (demineralized, doubly demineralized, distilled).

Solvents other than water.

Acids (reagent grade or specially purified). Residual acids in solution.

Salinity of solutions, in terms of solid contents in salt form.

Additives (alcohols, surfactants, *etc*., and order of addition). Concentrations added.

Releasing and protecting agents. Concentrations added.

Buffers (chemical and spectral). Concentrations added.

Temperature of solutions brought to the instrument (at room temperature or preheated).

Viscosity (especially applicable to syrups, oils and oil solutions).

Stability of solutions. It should be clearly stated when solutions should be freshly prepared, if solutions should be kept in the dark, and if they should be kept under refrigeration.

Working conditions

A clear statement of working conditions is of capital importance, even if readers may have to try the procedures with another type of instrumentation. Even more, two instruments of the same manufacturer's model may show slight differences, and in this case also a careful checking of conditions is mandatory.

Information desired is as follows.

Emission system

Lamp (make, single or multi-element).

Lamp current. Lamp current will influence the quality of the emission spectrum.

Atomization system

Burner (type, cold or hot operation).

Spray rate (in ml/min). Its influence on sensitivity.

Flame (gases, and quality: lean, rich).

Gases (quality, at room temperature or preheated).

Flow-rates (in metric units).

Pressures (in metric units). If the instrument is calibrated in terms of set pressures, some indication of flow-rates will be advisable.

Rotation of the burner.

Burner elevation (in mm). Related to flame profiles and sensitivity.

Number of light-passes through the flame.

Selection system

Slit-width (in mm) if only slit-width is known as an operational setting.

Nominal spectral band-pass (in nm) if known. It is more useful than the slit-width to operators using other instrumentation.

Analytical wavelength (in nm). If lines other than those which permit the operator to achieve the maximum sensitivity are used in the work, the author should explain why.

Photodetection and reading system

Time constant (in sec). Related to noise level.

Scale expansion. Related to real signal size.

Phototube. Different multiplier phototubes may be used and explanations should be given if a particular one is used.

Dynode voltage. If the instrument is double-beam type, probably the dynode voltage is automatically adjusted. However, a knowledge of its value gives a basis for evaluating the noise level.

Linearity tests

Some journals do not print straight-line calibration or working curves. Equations representing these curves are useful, especially if the fit has been calculated (manually or by computer) by the method of least squares. Non-linear curves may give a good idea of the tendency of response of standards. Simple lines can be used, but lines with experimental points shown are more significant, as they show the distribution of experimental readings. It is even more useful if the range of variability is marked for each experimental point with vertical lines limited by the limits of spread.

Authors should try to avoid exaggeration of scales, if searching for a way of showing better signal/concentration response. As a matter of fact, the size of the scale unit does not change the sensitivity at all.

Ways used to improve linearity should be explained (instrumental curvature correction or rotation of burner, even if in this way some sensitivity is lost).

Repeatability and reproducibility

Tests should be done with freshly prepared solutions. These tests are important to give an impression of the reliability of the methods described. Information needed is:

Number of readings.

Standard deviation.

Relative standard deviation.

Range.

Relative spread of results (%).

A number representing relative standard deviation (or coefficient of variation) has not much meaning for instance, unless the reader knows the number of readings examined and the formula used for their interpretation.

Sensitivity

A lot of confusion exists about reporting of sensitivity values in AAS. According to the well-established principles of analytical chemistry, sensitivity is nothing else but a relation between signal and concentration (response/stimulus). Thus sensitivity cannot be a concentration and cannot be expressed in concentration units of any kind. Sensitivity is related to the slope of a calibration or response curve. Concentration limits can be expressed in concentration units. For this reason, sensitivity level has often been numerically represented by means of the corresponding concentration limit (in ppm or any other concentration unit) necessary to obtain an absorption signal of 1% absorption. Sensitivity in this case should be understood as not equal to the concentration limit, but functionally related to it.

Details on sensitivity are necessary in AAS papers since sensitivity can be varied by a series of factors (among them: lamp current, flame conditions, slit-width, spray rate, elevation of the burner). If studied, it should be mentioned in the paper, and it is best to check it in order to be able to report it.

A study of the sensitivity as a function of burner elevation has given origin to flame profiles. Planar flame profiles correlate the variation of signal (sensitivity is correlated with signal at a given concentration) and burner elevation. Three-dimensional flame profiles correlate signal, burner elevation and concentration, showing surface variations along wide ranges. If available, they should be reported.

Calculation of identification concentration limits. If these are calculated, conditions of scale expansion and time constant (noise suppression used) should be reported to be sure that the reader will have some confidence in the values reported. If some particular criterion is used to define the limits, this should be clearly stated. This refers especially to the so-called 'detection limits.' Signals can be much better identified if limits are given as concentrations producing signals equal to four standard deviations ($4s$). Concentration limits reported in this way seem to be higher (worse) than those reported as a function of $2s$. This is only an apparent difference, since s remains the same and it is the interpretation that is different. Values calculated on the basis of $4s$ are more realistic.

Interferences

Results of interference studies will be most appreciated if they correspond to widely varied conditions. Any species expected to produce interferences should be tested, if the report is intended to be complete.

Several cases may be distinguished.

(*a*) *Single concentration of analyte/single concentration of interferent.* This case produces single results. It might be useful in cases of almost constant sample composition.

(*b*) *Multiple concentrations of analyte/single concentration of interferent.* This case corresponds to invariability of matrix with variable contents of analyte. Curves or tables can be used to report interference effects.

(*c*) *Single concentration of analyte/multiple concentration of interferent.* Studies corresponding to this combination are useful to calculate limiting ratios of interferent/analyte at which interference begins. Curves or tables are useful for presenting results.

(*d*) *Multiple concentration of analyte/multiple concentration of interferent.* This is the most complete case, and gives a complete picture of the general system. Representation may be complicated if graphs are preferred.

1. Families of curves can be used, the variable parameter being the concentration of interferent or the concentration of analyte.
2. Three-dimensional representations can be used, such as those published by Ramírez-Muñoz and Roth.[2] On one axis the signals are given, and the other axes are used for concentration of analyte and concentration of interferent. Authors using this type of representation will show the reader a surface representing distribution of the variation of the interference phenomena.
3. Sensitivity diagrams can also be used, as proposed by Ramírez-Muñoz.[3] Sensitivity is calculated for each analyte concentration at given interferent concentration. A planar representation is obtained in which the variation of sensitivity is shown as a function of the concentration of interferent.

Authors should be careful when reporting interference results, to give a clear indication of the level at which interferences really begin to be noticed. As a general rule, interference does not exist if error encountered and supposed due to interferences is consistently less than $2s$ calculated for the absorbance values for a pure solution (analyte without interferent component).

A particular case that might be reported is the simultaneous effect of both an interferent and a releasing agent. This pattern can be represented in three dimensions, as described by Ramírez-Muñoz[3] and called *space diagrams.*

Both high and low concentrations of interferents should be studied, since an interferent may act as an enhancing agent at one concentration and a suppressant at another. Concentration ratios of interferent to analyte should cover the ranges likely to be met with in practice.

CONTRADICTIONS AND DISCREPANCIES

Contradictions and discrepancies are frequent in experimental papers on AAS. They arise from different causes.

(*a*) Use of different instruments.
(*b*) Use of different operating conditions, even with identical instruments (flame conditions, burner elevation, hollow-cathode lamp, among other causes).
(*c*) Different ways of controlling or overcoming interferences.
(*d*) Different nature of standards and final prepared subsamples.
(*e*) Different criteria used in presenting results (especially sensitivity values).
(*f*) Different nomenclatures.
(*g*) Lack of clarity in the description of test done and in the discussion of results achieved.
(*h*) Misinterpretations.

The existence of discrepancies and contradictions has always made difficult the task of the reader when trying to choose a method for his own problem, and it has always made very difficult the task of a reviewer when preparing a review paper, if he intends to be critical and not only informative. As a result of this situation, some authors of reviews limit themselves to presenting the information available without discussing the reason for discordant findings by different researchers.

Misinterpretation is a cause which cannot be excluded. Scientists are subject to human errors, as other professionals are, and these errors can be reflected in their findings and discussions. Fortunately many errors are discovered by editors and referees through their patient and careful reading, study and reconsideration of manuscripts. If any error escapes through this fine and delicate scientific filter (and if not corrected by a later note), it will remain for ever in some page of some journal, always prepared to produce confusion and doubts in present and future readers.

Readers should be prepared to use their own judgement to read newly printed papers discriminatingly in order to discover—and perhaps to forgive—these involuntary errors. Anyway, mistakes of today are open doors for new researchers of tomorrow, who with more preparation, better work and more knowledge, will discover the truth. Books and bound volumes of journals get outdated, and are complemented by new contributions.

This general phenomenon, which is essential as an inherent part of the active life of science, must also occur in AAS, since that has been a part of scientific knowledge for several years. If this renewal of ideas, concepts and methods did not exist, AAS would have become a static scientific field. Fortunately, AAS is alive, changes, grows and improves.

CONCLUSIONS

Given that the author may use a personal writing style, and that the paper will be prepared according to rules established by the chosen journal the contents of a new paper on AAS should be carefully planned to satisfy the needs of contemporary readers for information. This is especially so with experimental papers which present improvements in instrumentation, studies of the analytical behaviour of particular analytes, or the application of the method to a given analytical system.

Since thousands of analytical chemists and chemical analysts are today using atomic-absorption spectrometers and may be supposed to already have the necessary knowledge about fundamentals and usage of the method, new papers should go directly to facts, conditions, procedures, results, and justified recommendations. Information given should be clear enough, not only to be understood, but to be repeated and adopted, if found convenient. Lack of details may lead to rejection of the paper by some sector of readers. If necessary, procedures should be presented in recipe style so as to reach even semi-skilled laboratory operators (professionals will understand why, and will forgive any excess of detail). On the other hand, lack of detail may lead to unnecessary duplication of effort if readers have to repeat the investigation to discover how to do some kind of work.

More freedom is allowable in reviews and theoretical contributions, but even in this case, the personal taste or preference of authors should be subordinated to the demands of readers. These papers should be *useful*, not a mere presentation of references or equations. They should be critical if reviewing and applicable to practice if studying theoretical aspects.

Readers today are more demanding because they know more. Writers should not write just for pleasure, but to satisfy other people's needs, and to help their colleagues in atomic-absorption work, offering them clear information, well-tested results, and reproducible working procedures.

Writers should understand that if they are granted the privilege of publication of their manuscripts, they do not receive this opportunity as a personal favour, but as a serious responsibility: the responsibility of serving the new—and every day increasing—atomic-absorption analytical population.

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Zusammenfassung—Es wird der derzeitige Stand bei der Abfassung neuer Publikationen über Atomabsorptionsspektrometrie diskutiert. Es wird eine Übersicht über die verschiedenen Typen von Arbeiten auf diesem Gebiet gegeben und einzelne Gesichtspunkte angegeben, die in solchen Arbeiten behandelt werden *müssen*. Besonderer Wert wird auf experimentelle Publikationen gelegt, die sich mit neuen Instrumenten befassen, mit dem analytischen Verhalten von Analyten und neuen Arbeitsvorschriften für spezielle analytische Anwendungen.

Résumé—On discute de la situation présente dans la préparation de nouveaux mémoires sur la spectrométrie d'absorption atomique. On passe en revue les différents types de mémoires publiés dans ce domaine et l'on donne des détails sur les questions dont il *doit* être traité lors de la rédaction de tels mémoires. On porte une attention particulière aux mémoires expérimentaux traitant d'instrumentation nouvelle, d'étude du comportement analytique d'analytes, et de nouvelles techniques pour des applications analytiques spécifiques.

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THE PERFORMANCE CHARACTERISTICS OF ANALYTICAL METHODS—III*

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Summary—The range of concentrations covered by an analytical method is an important performance-characteristic, and suggestions are made for definition of this range. The ability to detect small concentrations are also considered, and it is suggested that the standard deviation of blank determinations be quoted as the performance-characteristic relevant to the power of detection.

This part of the series is concerned with the range of concentrations† covered by an analytical method. This range is an important performance-characteristic but there appears to be no general agreement on how its upper and lower limits should be defined. As with other performance-characteristics, this lack of agreement leads to difficulty in comparing analytical methods. The purpose of this part is to consider these limits and to suggest how they should be defined. An important aspect of these considerations is the detection of small concentrations; this problem is also discussed and a recommendation is made on the definition of a relevant performance-characteristic.

Upper limit of the concentration range

However the upper limit is defined, it may usually be increased by: (1) simply diluting the sample; (2) using a less sensitive response parameter (*e.g.*, a less intense spectral line in emission spectrography). This first part[1] of this series stressed the need for complete and unambiguous specification of all experimental conditions for an analytical method, and on this basis it is better to regard approaches (1) and (2) as leading to different, though related, analytical methods. Accordingly, the following discussion is concerned solely with the upper concentration limit of a completely-specified method. Of course, should special considerations arise when approaches (1) or (2) are used, they should be mentioned in the published paper describing the method.

There are several ways in which the upper limit can be defined, for example:

(*a*) the greatest concentration specified for preparing the calibration curve;
(*b*) the concentration above which a theoretical relationship between analytical response and concentration ceases to hold;

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* Part II—*Talanta*, 1970, **17**, 31.

† For simplicity, throughout this paper analytical results are spoken of as in units of concentration; the arguments apply equally if other units (*e.g.*, mass, volume) are used.

(*c*) the greatest concentration allowing a defined relative standard deviation to be achieved;
(*d*) the greatest concentration for which quantitative tests of the precision and bias of analytical results have been made.

Of these possibilities, (*a*) is in itself quite arbitrary and (*b*) is not universally applicable, because analytical methods can be valuable even when the calibration curve follows no theoretical relationship. Possibility (*c*) seems more useful but it also suffers from the need for some arbitrary decision on the relative standard deviation to be used. Therefore (*d*) is preferred because it involves no arbitrary elements, it represents a simple factual statement based on experimental evidence, and it also implies no claim that stated performance-characteristics remain constant at concentrations greater than the maximum tested experimentally. This last aspect is important as the precision and bias of analytical results may depend markedly on the concentration of the determinand. For example, results from absorptiometric methods may show negative bias that increases rapidly with increasing concentration of the determinand when large proportions of the chromogenic reagent are consumed by reaction with other species present in the sample. Precision (as measured by standard deviation) often worsens rapidly with increasing concentration of the determinand above some value, *e.g.*, in absorptiometric and emission spectrographic methods.

Therefore, when performance-characteristics are being defined, it is recommended that the upper limit of the concentration range of an analytical method should be the greatest concentration for which detailed investigations have been made of the precision and bias of analytical results. Of course, methods may well allow perfectly acceptable results to be obtained in particular applications at greater concentrations, but this is irrelevant. Performance-characteristics must be based on quantitative evidence, and adoption of the recommendation above would not prevent analysts from considering use of methods at concentrations greater than the stated upper limit.

Lower limit of the concentration range

The lower limit can also be defined in several ways, for example:

(*a*) the smallest concentration that can be detected;
(*b*) the smallest concentration specified for preparing the calibration curve;
(*c*) the smallest concentration that can be determined with a defined relative standard deviation;
(*d*) the concentration below which a theoretical relationship between analytical response and concentration ceases to hold;
(*e*) the smallest concentration for which quantitative tests of the precision and bias of analytical results have been made.

Of these possibilities, (*a*), (*b*) and (*c*) all involve arbitrary decisions; (*a*) because, as will be seen later, a statistical confidence level must be chosen, and (*c*) because the relative standard deviation must be chosen. Possibility (*d*) is undesirable for the same reason as when the upper limit was considered. Thus possibility (*e*) is preferred because it contains no arbitrary elements, and it represents again a simple factual statement based on experimental evidence.

Therefore, in defining performance-characteristics, it is recommended that the lower limit of the concentration range of an analytical method should be the smallest concentration for which detailed investigations have been made of the precision and bias of analytical results. When this definition is used, the lower limit will often be zero when the experimental design for estimating precision is as recommended in the second part[2] of this series. It is important to note that this definition does not imply that the method allows infinitely small concentrations to be detected and measured. The range of a method, defined as above, merely states the range of concentrations over which experimental tests of precision and bias have been made. Other considerations are required to define the smallest concentration that can be determined, and this topic is discussed in the next section.

Detection of small concentrations

There are two important aspects* of the detection of small concentrations: (1) the criterion used by an analyst to decide whether or not a particular analytical result justifies a claim that the determinand has been detected; (2) the smallest concentration that an analyst can claim to be capable of detecting. Such parameters have been and are determined in a variety of ways. For example, an analyst may decide (when an absorptiometric method is involved) that analytical results equivalent to absorbances less than 0·01 are so unreliable as not to justify reporting a positive result. This type of approach, although still in rather widespread use, has been increasingly recognized as subjective and ambiguous, and there now seems to be growing acceptance of the need to use statistical considerations in defining parameters such as the limit of detection.

Sillars and Silver[4] are the first authors known to me to introduce (in 1944) statistical concepts to determine the smallest concentration that could be regarded as significantly different from zero. They suggested that this concentration be called 'the significance range,' and even briefly suggested that this concept could be applied to any analytical measurement. Although the precise statistical techniques used by these workers were incorrect, the general approach was clear but was not taken up as a means of generally defining parameters such as the limit of detection. Kaiser[5] appears to have first used statistical concepts for a general definition of the limit of detection of spectrographic methods. Later, Kaiser and Specker[6] suggested the same approach for all analytical methods, and since their papers there have been many contributions to the subject by different authors. In this paper, there is no need to trace the historical development of the concepts; useful reviews have been given by Kaiser[7,8] and by Currie,[9] who stresses the large number of different definitions and terms that have been proposed.

The statistical approach is summarized below because it will be used as the basis for a suggestion on how aspects (1) and (2) above should be quantified in a unified statement of performance-characteristics. This suggestion does not need detailed knowledge of the methods of statistical inference and significance testing; the papers by Kaiser[7,8] and Currie[9] should be consulted by those requiring more detail.

Criterion of detection. To illustrate the need for a statistical approach, consider an analytical method in which the final result is obtained by subtracting the result for a blank determination from the results for a sample. Even if the sample contains none of the determinand, it does not follow that the analytical result will be zero. The random errors of sample and blank determinations will cause the results from repeated

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* Roos[3] appears to have been the first to distinguish these.

analyses of such a sample to vary both in sign and magnitude. Thus, a positive result is not alone sufficient to justify the analyst in claiming to have detected the determinand. However, as the magnitude of a positive analytical result increases relative to the size of the random errors, so it becomes more and more likely that the sample contains the determinand. Therefore, some criterion is required for deciding when a result is sufficiently large to justify a claim for detection of the determinand. Such a criterion must clearly be based on the magnitude of the random errors, and must therefore be deduced statistically.

Suppose that portions of a homogeneous sample are analysed, and that the sample contains none of the determinand. Assuming that the analytical results are free from bias, they will be distributed about zero. If the nature of this distribution is known, the probability of obtaining a result greater than some particular value can be evaluated. For example, if the results follow a normal distribution with a standard deviation, σ_0, 5% of the results will, on average, exceed the value $1{\cdot}65\sigma_0$.* Thus, if a result just greater than $1{\cdot}65\sigma_0$, is obtained, there is less than a 5% probability that it came from a sample with zero concentration of the determinand. In other words, there is at least a 95% probability that the sample contained the determinand at a concentration greater than zero, *i.e.*, the determinand has been detected (95% confidence level). Thus, if an analyst were satisfied with a confidence level of 95%, he would use the parameter $1{\cdot}65\sigma_0$ as the criterion to judge whether or not he was justified in claiming to have detected the determinand. Following Roos,[3] the term 'criterion of detection' seems an admirable term for this concept and it is recommended for general use. The 'criterion of detection' corresponds to the critical level, L_c, in the terminology used by Currie.[9]

This method of defining a criterion is quantitative and objective, and is preferable to arbitrary definitions based on subjective decisions such as the number of scale divisions that can easily be read on an instrument or some intuitive notion of the reliability of results.

To calculate the criterion of detection for any particular application, three parameters must be known: (1) the confidence level required by the analyst; (2) the type of frequency distribution followed by results for samples with zero concentration of the determinand; (3) the standard deviation of the distribution (or an estimate of this parameter). The first parameter will, in general, vary from one application to another for two reasons. First, different analytical requirements may call for different confidence levels. Secondly, greater confidence levels than would otherwise be necessary may be used to counteract uncertainty caused by lack of precise knowledge of the nature of the frequency distribution. There is, therefore, no valid reason why any one confidence level should be used universally. Thus the many proposals that have been made to define the criterion of detection as a fixed multiple of the standard deviation seem both undesirable and unnecessary. It is recommended therefore that the criterion of detection should not be regarded as a fundamental performance-characteristic. The safest and least ambiguous technique for reporting performance is to quote information relevant to parameters (2) and (3) above. Any analyst may then make any calculations he wishes from such data.

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[*] The use of the term $1{\cdot}65\sigma_0$ may be unexpected by those accustomed to associating 95% confidence limits with the term $1{\cdot}96\sigma_0$. The factor 1·65 arises because we are concerned only with the chance of a result exceeding a certain value. Thus, from the properties of the normal distribution, 10% of results, on average, fall outside the range $\pm 1{\cdot}65\sigma_0$. The distribution is symmetrical, so 5% of results exceed $+1{\cdot}65\sigma_0$ and 5% are less than $-1{\cdot}65\sigma_0$.

Evaluation and reporting of parameters (2) and (3) is considered in more detail after the next section.

Limit of detection. The second aspect of the detection of small concentrations is the smallest concentration that the analyst can expect to detect with a given degree of confidence. This concentration, again following Roos,[3] may be termed the 'limit of detection' which corresponds to the 'detection limit, L_D' in the terminology used by Currie.[9] The difference between the criterion and limit of detection can be illustrated by considering the analysis of a sample having a true concentration, C_c, equal to the criterion of detection. In this situation (and assuming a symmetrical frequency distribution of results), results exceeding the criterion would be obtained, on average, on 50% of occasions. The analyst would therefore have 50% confidence in claiming that he is able to detect a concentration C_c. To achieve a greater confidence, the analyst would have to quote a greater concentration so that the chance of obtaining a result less than C_c is reduced. This greater concentration is the limit of detection, C_L, and can again be calculated statistically. For example, if the standard deviation is independent of concentration and the frequency distribution is symmetrical, C_L is twice C_c if the analyst requires equal confidence levels for the criterion and limit of detection.

It should be emphasized that concentrations smaller than the limit of detection will sometimes be detected, *i.e.*, the results will exceed the criterion of detection. In this sense, the term 'limit of detection' is rather misleading for it suggests that smaller concentrations will not be detected. However, without marked expansion of the term, it is impossible to convey in one simple title all the statistical and analytical implications. Accordingly, no alternative term is suggested.

To calculate the limit of detection, one must know the same three parameters stated above for the criterion of detection. For the same reasons, it is also recommended that the limit of detection should not be regarded as a performance-characteristic. As with the criterion of detection, all that is necessary is to quote information on the nature and standard deviation of the frequency distribution followed by analytical results.

Defining the random error at low concentrations. The nature of the frequency distribution followed by analytical results at low concentrations is important in that it affects the quantitative interpretation of standard deviation as a measure of the ability to detect low concentrations. The frequency distribution should therefore be regarded as a performance-characteristic. Unfortunately, rather large numbers of results are required to define frequency distributions closely, and analysts will seldom have sufficient results to allow this. In this situation, it seems reasonable at present* to assume that the normal distribution is followed at least until contrary evidence is obtained. Experimental results should therefore be analysed statistically to decide whether or not they are consistent with the assumption of a normal distribution.†

As discussed above, the standard deviation relevant to the criterion of detection is that for a sample containing none of the determinand and analysed exactly as described

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* Future investigations may indicate that a log normal or some other type of distribution is more generally useful in considering the detection of small concentrations. Until such evidence is available, there seems no point in generally assuming any distribution other than the normal, the properties of which are well documented and easily interpreted.

† When sufficient experimental results are available to allow other types of distribution to be distinguished, the relevant distribution should be quoted as the performance-characteristic. For example, Hobbs and Smith[10] have reported a log normal distribution at small concentrations when certain emission spectrographic methods were used.

by the analytical method. The standard deviation relevant to the limit of detection can be estimated if the dependence of precision on concentration of the determinand is known. These two standard deviations will often be essentially the same, and the remaining discussion rests on the basis that the standard deviation at zero concentration is the fundamental performance-characteristic requiring definition and evaluation. There are a few practical points of importance in the experimental design and interpretation of results for the estimation of this parameter.

It follows directly from the above that the required standard deviation should be estimated from the results of repeated analyses of a sample containing essentially none of the determinand and analysed exactly as described in the method for normal samples; the sample used for this purpose should reproduce all those properties of normal samples affecting precision. Departures from these principles, though sometimes making for convenience, should be avoided whenever possible for two main reasons. First, the sample matrix may have an important effect on precision. For example, in gas-chromatographic techniques, the random noise of the base-line when only carrier-gas is flowing may not be a valid measure of the precision obtained when samples are injected into the chromatographic column. Secondly, the method of computing analytical results from the observed analytical response may markedly affect the estimates of precision. Thus, the method itself must be very exactly defined and must be rigorously followed; otherwise the interpretation of the quoted standard deviation will be ambiguous. This aspect is particularly important for analytical systems for which the response is observed on a chart-recorder. The length of time for which a sample is analysed and the method used to compute a result from a length of recorder-trace showing random variations may both have marked effects on the calculated standard deviation.* The method must therefore describe both these aspects very clearly and precisely.

In many analytical methods, blank determinations are specified as a means of determining the analytical response corresponding to zero concentration of the determinand. Thus, repeated analysis of blanks is a suitable means of estimating the standard deviation at zero concentration provided the sample and technique used for the blank satisfy the principles in the preceding paragraph. Thus, the standard deviation of blank determinations is of fundamental interest in the detection of small concentrations. When methods do not specify a blank determination or the sample and/or technique for the blank differ from those for normal samples, consideration should be given to obtaining results from special samples and/or determinations aimed at estimating the standard deviation obtained when the normal analytical technique is applied to samples with zero concentration of the determinand.

As discussed in Part II, the standard deviation of a set of analytical results will usually tend to increase as the period of time in which the results were obtained increases. This will often be particularly true for blank determinations which can be subject to systematic changes with time that do not affect analytical results for samples. Part II described the concept of within- and between-batch variations, and this concept is also usefully applied to the blank. Which of the corresponding standard deviations is relevant depends on the method. For example, if the method prescribes a blank determination

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* In passing, it is worth noting that the rather common practice of defining the limit of detection for certain techniques solely in terms of the peak-to-peak noise of the trace on a recorder-chart takes no account of the reduction of the effect of random errors by the averaging process used in computing a result from a length of recorder-trace.

with every batch of sample determinations, only the within-batch standard deviation is of direct interest because variations of the blank between batches will have no effect on analytical results. On the other hand, if a blank determination is not made in every batch, then it is the total standard deviation, σ_t,* that is of importance. By following the experimental design and analysis of results given in Part II, σ_w, σ_b, σ_t can all be estimated and quoted, and this approach is generally recommended. In this experimental design, any samples used for the blank must contain a sufficiently small concentration of the determinand for the estimated standard deviations to apply to zero concentration. So long as this is so, the presence of the determinand in the blank is unimportant. If it is impossible to obtain samples complying with this condition, it is best, in quoting performance-characteristics, merely to quote the experimentally-measured standard deviations and not to quote for zero concentration any estimates obtained by extrapolation.

CONCLUSIONS

In quotation of performance-characteristics of analytical methods, the range of a method should be defined by stating the smallest and greatest concentrations for which experimental tests of precision and bias have been made.

In connection with the ability to detect small concentrations, the precision of blank determinations is of fundamental importance. It is suggested that it be assumed that blank determinations follow the normal distribution until evidence to the contrary is obtained. On this basis, it is necessary only to quote experimental estimates of the standard deviation of blank determinations. The experimental design suggested in Part II is generally recommended for estimating precision, and the within-batch, between-batch and total standard deviations of the blank should all be quoted as performance-characteristics.

Acknowledgements—I should like to acknowledge the valuable discussions with many of my colleagues and, in particular, with Mr. I. R. Morrison.

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Zusammenfassung—Der durch eine analytische Methode erfaßte Konzentrationsbereich ist eine wichtige Kenngröße für ihre Leistungsfähigkeit. Zur Abgrenzung dieses Bereichs werden Vorschläge gemacht. Die Möglichkeit des Nachweises kleiner Konzentrationen wird ebenfalls betrachtet; es wird vorgeschlagen, die Standardabweichung der Blindbestimmungen innerhalb eines Postens als die für die Leistungsfähigkeit des Nachweises wesentliche Kenngröße anzugeben.

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* $\sigma_t^2 = \sigma_w^2 + \sigma_b^2$,
Where σ_w = within-batch standard deviation, σ_b = between-batch standard deviation, so that σ_t is the standard deviation of any result in any batch.

Résumé— Le domaine de concentrations couvert par une méthode analytique est une importante caractéristique de performance, et l'on fait des suggestions pour la définition de ce domaine. On considère aussi la faculté de déceler de petites concentrations, et l'on suggère que l'écart type de déterminations de témoins soit fourni en tant que caractéristique de performance correspondant au pouvoir de détection.

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GRAPHICAL ANALYSIS OF THE FORMATION FUNCTION—I

THE REAL CROSS-OVER POINT

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Summary—From a mathematical treatment, it has been proved that a family of formation curves shows a real cross-over point in the following cases: (*a*) a mixture of mononuclear complexes BA, $BA_2 \ldots BA_N$ and polynuclear complexes of general formula $(B_qA_p)_n$, provided that $p/q < N$; (*b*) a mixture of homonuclear complexes B_QA_p, where Q is constant, and mononuclear complexes shows at least one cross-over point if the maximum value for p is smaller than NQ and at least two cross-over points if NQ lies between the minimum value and the maximum value for p. Curves calculated for three different examples are in perfect agreement with the theory.

The formation function Z is a versatile tool in identifying the complex species present in solution and determining their stability constants,[1,2] especially in studying mononuclear complexes and polynuclear complexes of the 'core + links' type $B(A_tB)_n$, where B is the metal ion and A the ligand. However, in the case where neither coinciding curves nor a family of equidistant formation curves are found, it is not easy to interpret the experimental results by means of a graphical analysis. In this series of papers a number of special shapes of the family of Z $(\log a)_B$ curves (where a is the concentration of uncombined A and the total metal ion concentration B is constant) will be discussed in order to enhance the possibility of interpreting the formation function. This is important when nothing is known about the composition of the complexes in solution, since difficulties may arise when the experimental results are treated by a computer programme based on a least-squares procedure. In that case it is convenient to have at least some idea about the possible composition of the complexes present.

A special form of the formation function is encountered when the Z $(\log a)_B$ curves show a cross-over point: all formation curves intersect at one point. We can distinguish between a real cross-over point and a pseudo cross-over point, *i.e.*, when all formation curves intersect one another in so small a range that this can hardly be distinguished from a single point. In this paper only the real cross-over point will be discussed. The main question that will be answered is what is the composition of the complexes that gives rise to a cross-over point? There is some controversy in the literature about this question. The cross-over point in acid-base systems, called the isohydric point by Carpéni,[3,4] would according to this author[5] be found at a acid–base ratio equal to $(Z/n)_m$, Z being the charge of the ion, n the number of atoms of the central element in the most probable species and m an integer. A similar relation is given by MacBryde.[6] On the other hand Byé[7] and Souchay[8] are convinced that the cross-over point is due to equilibria between species of two different degrees of condensation. Rossotti and Rossotti[1] reported that an equilibrium of mononuclear complexes BA_n and a set of $B_Q A_p$ complexes, with constant Q and varying p, can give a cross-over point.

MATHEMATICAL TREATMENT

There are two conditions for a cross-over point. (*a*) $(\partial Z/\partial B)_a = 0$ for a fixed value of Z and a finite value for a. B is the total concentration of metal ion, and a the free ligand concentration. (*b*) The sign of $(\partial Z/\partial B)_a$ must change at the cross-over point.

Z can be expressed as:

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^{q-1} a^p}{1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p}, \tag{1}$$

where b is the concentration of free metal ion and β_{qp} is the stability constant of $B_q A_p$, defined as

$$\beta_{qp} = \frac{[B_q A_p]}{b^q \cdot a^p}.$$

The mass-balance equation with respect to B is given by

$$B = b + \sum_q \sum_p q\beta_{qp} b^q a^p. \tag{2}$$

From equation (2) the following equation can be obtained:

$$\left(\frac{\partial b}{\partial B}\right)_a = 1 \Big/ \left(1 + \sum_q \sum_p q^2 \beta_{qp} b^{q-1} a^p\right). \tag{3}$$

Differentiation of equation (1) and insertion of equation (3) into the expression obtained gives

$$\left(\frac{\partial Z}{\partial B}\right)_a = \frac{\left[\sum_q \sum_p (q-1)(p-Zq)\beta_{qp} b^{q-2} a^p\right]}{\left(1 + \sum_q \sum_p q^2 \beta_{qp} b^{q-1} a^p\right)\left(1 + \sum_q \sum_p q\beta_{qp} b^{q-1} a^p\right)}. \tag{4}$$

The denominator of equation (4) is always positive, so the sign of the numerator will determine the sign of $(\partial Z/\partial B)_a$, and therefore the function ψ_A is defined as:

$$\psi_A = \sum_q \sum_p (q-1)(p-Zq)\beta_{qp} b^{q-2} a^p. \tag{5}$$

If only mononuclear complexes are present, ψ_A will be zero for all values of Z: all formation curves will coincide. ψ_A will also be zero for polynuclear complexes $B_q A_p$ for a fixed value of Z, if the ratio p/q is constant and equal to that fixed value. However, when only polynuclear complexes exist in solution, this value of Z will be obtained for an infinite value of a. If there are also a number of mononuclear complexes BA, BA_2 . . . BA_N and N is greater than p/q, Z will be equal to p/q for a finite value of a. Moreover ψ_A and consequently $(\partial Z/\partial B)_a$ will be positive for Z smaller than p/q, and negative for Z greater than p/q. This means that all conditions for a cross-over point are fulfilled. Thus a system composed of mononuclear complexes BA, BA_2, . . . BA_N and a series of polynuclear complexes with formula $(B_q A_p)_n$ will always give a cross-over point, provided that N is greater than p/q. Mononuclear complexes with one polynuclear complex can be considered as a special case of the system described above and will give a cross-over point if $N > p/q$.

When a series of mononuclear complexes BA_n coexists with a series of homonuclear complexes $B_Q A_p$, there is also a possibility of a cross-over point, as discussed by Rossotti and Rossotti.[1] The function ψ_A then becomes

$$\psi_A = (Q - 1)b^{Q-2} \sum_p (p - QZ)\beta_{Qp} a^p. \tag{6}$$

Let the functions ψ_Q and ψ_M be defined as:

$$\psi_Q = \frac{\sum_p p\beta_{Qp} a^p}{Q \sum_p \beta_{Qp} a^p}, \tag{7}$$

$$\psi_M = \frac{\sum_n n\beta_{1n} a^n}{1 + \sum_n \beta_{1n} a_n}. \tag{8}$$

It can easily be proved that according as ψ_M is smaller than, equal to or greater than ψ_Q, Z will also be smaller than, equal to or greater than ψ_Q.

The functions ψ_M and ψ_Q are continuous and increasing with increasing a, except when only one polynuclear complex is present. ψ_M tends from zero for very small values of a to N for very large values of a. ψ_Q goes from $p_{\min}/Q$ to $p_{\max}/Q$, $p_{\min}$ and $p_{\max}$ being respectively the minimum and the maximum value for p. The following cases can be differentiated.

(*a*) $p_{\max}/Q < N$. The functions ψ_M and ψ_Q will always have at least one intersection point for a finite value of a. At that point ψ_Q will be equal to ψ_M and thus equal to Z, and ψ_A will be zero. If a is smaller, ψ_Q will be greater than ψ_M and consequently Z will be smaller than ψ_Q, and ψ_A positive. At higher a, ψ_Q will be smaller than ψ_M, Z will be greater than ψ_Q, and ψ_A negative. So the conditions for a cross-over point are fulfilled. The value for Z where the cross-over point will be found, lies between $p_{\min}/Q$ and $p_{\max}/Q$ and is dependent on the values of the stability constants.

(*b*) $p_{\min}/Q > N$. There exists no intersection point between ψ_M and ψ_Q and consequently no cross-over point will be found.

(*c*) $p_{\min}/Q < N < p_{\max}/Q$. It is possible that ψ_M and ψ_Q do not intersect one another. In this case no stable mononuclear complexes are present. Otherwise at least two intersection points will be found. The same reasoning holds as for case (*a*) with the result that $(\partial Z/\partial B)_a$ will be positive before the first intersection point, zero at it, negative between the two intersection points, zero at the second intersection point and positive after the second intersection point, *etc*. The two cross-over points will be found between $p_{\min}/Q$ and N and their positions will be dependent on the values of the stability constants. The formation curves tend to $p_{\max}/Q$.

It should be noted that it is not necessary, in studying complex systems showing a cross-over point, to keep the total metal ion concentration constant.

THEORETICAL CURVES

Theoretical curves were calculated by using the computer programme ALTH written in Fortran IV. This programme calculates and plots the $Z(\log a)_B$ curves obtained from the equations

$$B - b - \sum_q \sum_p q\beta_{qp} b^q a^p = 0, \tag{9}$$

$$Z = \frac{\sum_q \sum_p p\beta_{qp} b^q a^p}{B}. \tag{10}$$

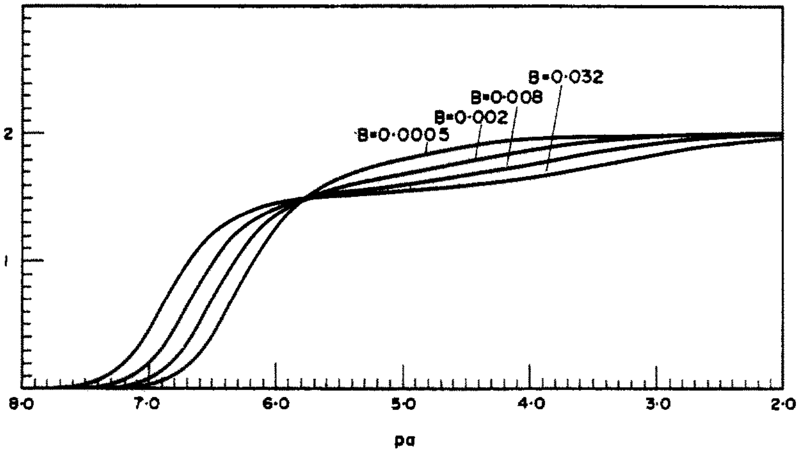

Fig. 1. Theoretical curves for four complexes; BA_2, B_2A_3, B_4A_6, B_6A_9. Log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,3} = 22{\cdot}0$; log $\beta_{4,6} = 34{\cdot}0$; log $\beta_{6,9} = 46{\cdot}0$.

The most efficient method for solving this problem is to start with various given values for B and a, for an appropriate set of values of β_{qp}, solving equation (9) for b by means of a "*regula falsi*" method, and calculating Z from the given values for B and a and the calculated value of b. Instead of a, pa = $-\log a$ was varied, since this gives a more regular spread of the points of the formation curve. At the beginning of the programme a search was made for an upper limit for pa by starting with a high value (*e.g.*, 20) and reducing it successively by 1 until the calculated Z value was greater than 0·01. This pa value, increased by 1, was chosen as the start value for pa, which was then systematically changed over a range of 6 or 7 units.

A large number of $Z(\log a)_B$ curves were calculated for various sets of possible complexes. Three examples are given here. In Fig. 1 the formation curves for a mixture of a mononuclear complex and polynuclear complexes B_2A_3, B_4A_6 and B_6A_9 are shown. The cross-over point falls exactly at a Z value of 1·5. Varying the constants does not

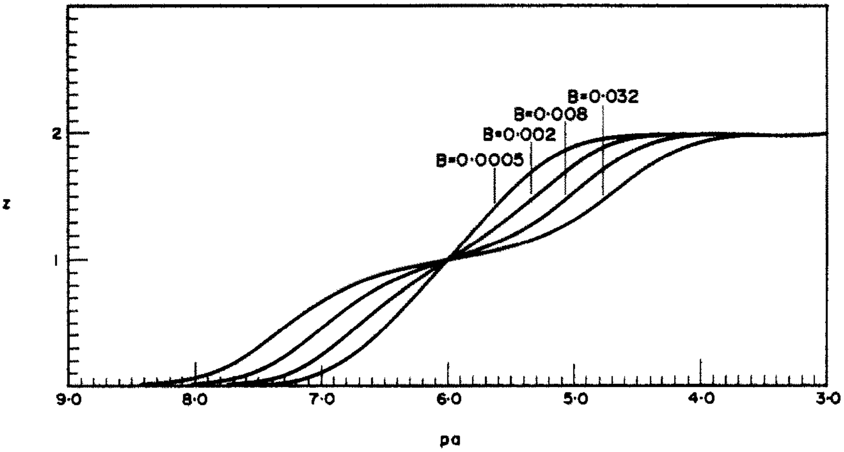

Fig. 2. Theoretical curves for three complexes; BA_2, B_2A_2, B_2A_3. log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,2} = 16{\cdot}0$; log $\beta_{2,3} = 18{\cdot}0$.

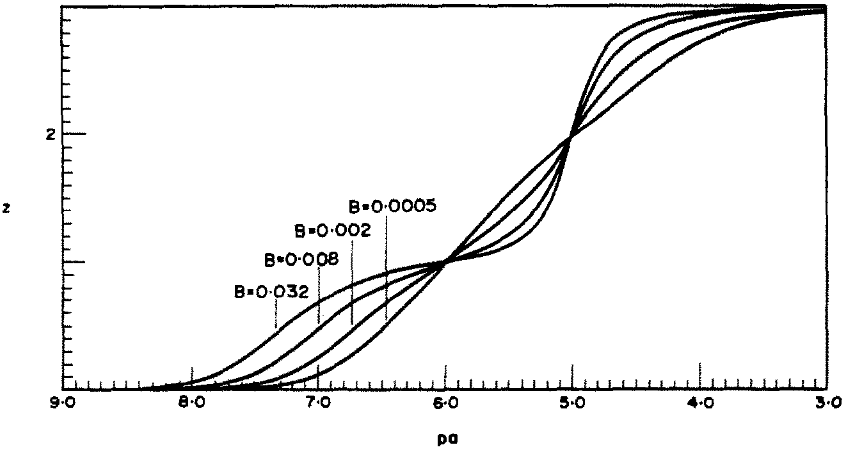

Fig. 3. Theoretical curves for three complexes; BA_2, B_2A_2, B_2A_6. Log $\beta_{1,2} = 12{\cdot}0$; log $\beta_{2,2} = 16{\cdot}0$; log $\beta_{2,6} = 36{\cdot}0$.

change the place of the cross-over point. In Fig. 2 an example of a cross-over point encountered with a mixture of mononuclear complexes and homonuclear complexes with $N > p_{\max}/Q$ is given. A cross-over point is found as predicted by the theory. An example with two cross-over points is shown in Fig. 3 for a mixture of one mononuclear complex BA_2 and two polynuclear complexes B_2A_2 and B_2A_6.

The calculations and plots were performed by means of an IBM 360/30.

Acknowledgement—The authors wish to thank Prof. Z. Eeckhaut for helpful discussions.

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Zusammenfassung—Aus einer mathematischen Verhandlung wird bewiesen daß, in den folgenden Fällen, eine Schar Bildungskurven einen echten "cross-over" Punkt vorzeigt:

(*a*) Eine Mischung von mononuklearen Komplexen BA, BA_2 ... BA_N und polynuklearen Komplexen $(B_q A_p)_n$ unter der Bedingung daß $p/q < N$.

(*b*) Eine Mischung von mononuklearen Komplexen und homonuklearen Komplexen $B_Q A_p$ mit konstantem Q. Wenn der Höchstbetrag für p kleiner ist als $N.Q$ gibt es wenigstens einen "cross-over" Punkt. Liegen die $N.Q$ Werte zwischen dem Mindeswert und dem Maximumwert von p dann sind wenigstens zwei "cross-over" Punkte vorhanden.

Theoretische Kurven werden für drei verschiedene Beispiele berechnet. Die Übereinstimmung mit der Theorie ist vollkommen.

Résumé—On a démontré mathématiquement qu'un réseau de courbes de formation possède un point isohydrique réel dans les cas suivants:

(*a*) Un mélange de complexes mononucléaires BA, BA_2 ... BA_N et de complexes polynucléaires $(B_q A_p)_n$, à condition que $p/q < N$.

(*b*) Un mélange de complexes homonucléaires $B_Q A_p$, Q étant constant, et de complexes mononucléaires possède au moins un point isohydrique quand la valeur maximale de p est plus petite que $N.Q$ et au moins deux points isohydriques quand la valeur de $N.Q$ se situe entre la valeur minimale et la valeur maximale de p.

Les courbes théoriques, calculées pour trois exemples, correspondent parfaitement avec la théorie.

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DETERMINATION OF TRACES OF ZINC BY FLUORIMETRICALLY INDICATED COMPLEXOMETRIC TITRATIONS

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Summary—Zinc forms fluorescent complexes with 8-hydroxyquinoline-5-sulphonic acid (HQS) in the pH region 7–10. The stability of these complexes is such that two different titration procedures are possible: the titration of zinc with HQS and the titration of zinc with EDTA in the presence of HQS. For both procedures the choice of the titration conditions is described. Also two separation procedures for zinc are described, especially suitable in connection with the EDTA titration. The practical results show that zinc in concentrations larger than $10^{-6}M$ (0·05 μg/ml) can be titrated with good precision.

In a previous paper[1] we derived some new formulae relating the fluorescence intensity to the concentration of the fluorescent species. From these formulae conditions have been derived for which the fluorescence intensity is linearly dependent on the concentration. In this paper it will be shown how these conditions can be fulfilled in practice. First, however, the relevant chemical equilibria will be discussed. In doing so, formulae will be given in which L denotes HQS, and Y represents EDTA. Unless otherwise stated, values for the stability constants are taken from Sillén and Martell.[2] Conditional constants, *etc.*, will be represented according to the conventions used by Ringbom.[3]

Chemical equilibria

HQS is a dibasic acid. The stability constants of the acidic forms are given by $\log K_1 = 8{\cdot}4$ and $\log K_2 = 3{\cdot}8$. HQS can therefore occur in three different forms: H_2L, HL and L (charges are omitted). Figure 1 shows a distribution diagram for the three forms as a function of pH.

HQS forms two complexes with zinc, of composition ZnL and ZnL_2. The stability constants for the complexes are given by $\log K_1 = 7{\cdot}5$ and $\log K_2 = 6{\cdot}8$. In Fig. 2 the conditional constants $K_1' = K_{M'L(ML)}$, $K_2' = K_{(ML)L'(ML_2)}$ and $\beta_2' = K_1' . K_2'$ are given as functions of pH. It should be noted that $\alpha_{Zn(buffer)}$ is not taken into account. As can be seen from Fig. 2 the conditional constants have a maximum at pH 8·8. Titration of zinc with HQS is therefore preferably carried out at this pH.

The chemistry of the system containing zinc, HQS, EDTA and buffer is best described graphically. This can be done by using diagrams such as were introduced by Kragten.[4,5]

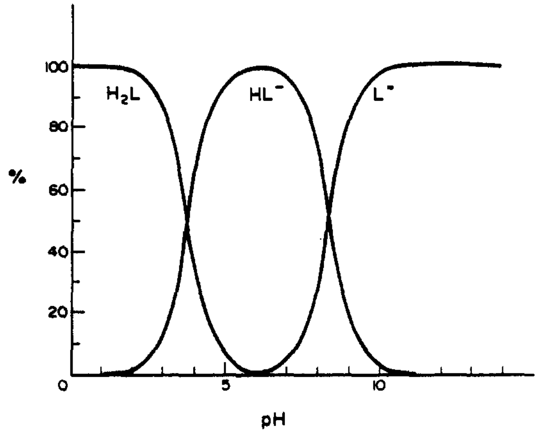

Fig. 1. The relative abundance of the forms of HQS as a function of pH ($\log K_1 = 8{\cdot}35$; $\log K_2 = 3{\cdot}84$).

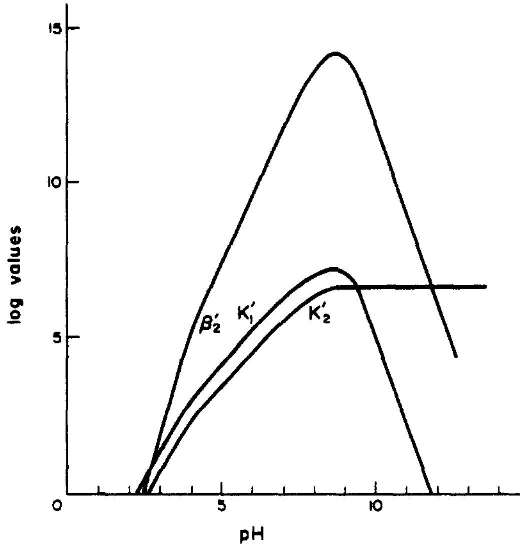

Fig. 2. The conditional stability constants of the complexes of Zn^{2+} with HQS ($\log K_1 = 7{\cdot}5$; $\log K_2 = 6{\cdot}8$).

The following quantities are plotted *vs.* pH (Fig. 3).

1. Log $K_{ZnY'(ZnY)}$. Side-reactions of Zn are not included.
2. Log $\alpha_{Zn(X_i)}$. The side-reaction coefficients for the side-reactions of zinc with X_i. Also the total side-reaction coefficient is plotted as log α_{Zn}.
3. Log $\chi_2 = \log C_L{}^2 \cdot \beta_{ZnL'(ZnL_2)}$. C_L is the analytical concentration of HQS.
4. $\text{Log}\,{}^{L}_{2}K = \log \dfrac{K_{ZnY'(ZnY)}}{\chi_2}$.

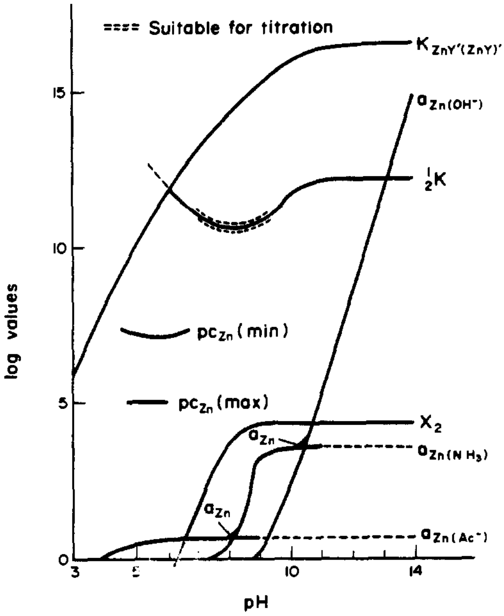

Fig. 3. The chemistry of the system Zn^{2+}/HQS/EDTA/buffer. Conditions: $C_L = 10^{-5}M$; $[NH_3] = 0{\cdot}1M$; $[Ac^-] = 0{\cdot}1M$. Values needed for the construction of this diagram were taken from Sillén and Martell[2] and from Ringbom.[3]

Titration of zinc with EDTA with end-point indication by means of the complexes of zinc with HQS is feasible, if near the equivalence point either ZnL or ZnL_2 predominates, and if some other conditions are fulfilled. It can be shown that the type of titration in which ZnL_2 predominates allows the determination of much lower zinc concentrations than the type in which ZnL predominates. The conditions which should be met in this case are, according to Kragten:[5]

$$\log \chi_2 - \log \alpha_{Zn} > 1. \tag{1}$$

$$\log C_{Zn} - \log {}^L_2K > 3{\cdot}5. \tag{2}$$

$$\log K_{(ZnL)L'(ZnL_2)} \cdot C_L > 1. \tag{3}$$

$$C_L > C_{Zn}. \tag{4}$$

Conditions (1) and (2) are necessary to obtain an end-point with a systematic error smaller than 0·5 %. Conditions (3) and (4) are necessary to ensure that ZnL_2 predominates over ZnL in the vicinity of the equivalence point. The pH values for which conditions (1) and (2) are fulfilled are indicated in Fig. 3. Also, the lowest and the highest zinc concentrations that can be titrated are plotted as pC_{Zn}(min) and pC_{Zn}(max).

EXPERIMENTAL

Apparatus

Absorption spectra were recorded with a Unicam SP700 spectrophotometer and a Honeywell recorder, or plotted manually from measurements on a Zeiss PMQ II equipped with an M4Q III monochromator. Excitation and fluorescence spectra were obtained with a Jobin et Yvon type Bearn spectrofluorimeter. The light source was an Osram XBO150W/1 high-pressure xenon arc. A Goerz Servogor RE 511 recorder was used.

Some titrations were performed manually on the Jobin et Yvon spectrofluorimeter. For most titrations, however, a semiautomatic equipment was used, consisting of the Zeiss PMQ II spectrophotometer with M4Q III monochromator and ZFM4 fluorescence attachment, a Hanau St 41 mercury vapour lamp in combination with interference filters as a light-source, a Philips PM8000 recorder with a stepping motor in place of the original motor, a Metrohm E 457 burette, also equipped with a stepping motor, and a unit for synchronizing the motors of the burette and the recorder, developed by Poppe.[7]

Reagents

Chemicals of reagent grade were used throughout.

Optical data

Knowledge of the optical properties of the components present during the titration is necessary for the choice of excitation wavelength and wavelength of fluorescence measurement. This knowledge also serves another purpose: it has been shown[1] that the relation between fluorescence intensity and concentration of a fluorescent compound is linear only if the absorbance of the sample is constant both at the excitation wavelength and at the wavelength of fluorescence measurement. If the absorbance at either wavelength is not constant during the titration, deformation of the titration graph occurs, which results in a systematic titration error. As the magnitude of this error is related to the change in absorbance, and accordingly to the concentration of the substance to be titrated, knowledge of the optical properties serves in this case to set an upper concentration limit at which titration is still possible with an acceptable systematic error.

In the wavelength region from 300 to 650 nm, Zn, EDTA, ZnY and the (ammonia) buffer do not absorb significantly. Therefore, only the absorption spectra of HQS (in the forms H_2L, HL and L), ZnL and ZnL_2 need be given. The absorption spectra of ZnL and ZnL_2 cannot be measured separately. Therefore, the spectra of two different mixtures of zinc with HQS were taken. From the known stability constants the compositions of these mixtures were computed. At any wavelength this resulted in two equations both containing ε_{ZnL} and ε_{ZnL_2}. These equations were then solved for ε_{ZnL} and ε_{ZnL_2}. The absorption spectra of L, ZnL and ZnL_2 are identical, but at any wavelength the molar absorptivity of ZnL_2 is twice the molar absorptivity of ZnL, and that of L (Fig. 4). This kind of behaviour of oxinates has been reported before.[8–10] HQS does not exhibit fluorescence in any of its forms (in aqueous media). Therefore, in Fig. 5 excitation and fluorescence spectra are given for ZnL and ZnL_2 only. The excitation and fluorescence spectra of ZnL and ZnL_2 were separated in the same way as the absorption spectra of ZnL and ZnL_2. From the known absorbances and the excitation and fluorescence spectra it can be found that the ratio of the fluorescence efficiencies of ZnL and ZnL_2 is $\Phi_{ZnL} : \Phi_{ZnL_2} = 1 : 0{\cdot}9$. This ratio differs from the one found by Bishop:[11] $\Phi_{ZnL} : \Phi_{ZnL_2} = 0 : 1$, but it is comparable to the findings of Ballard:[12] $\Phi_{ZnL} : \Phi_{ZnL_2} = 1 : 1$.

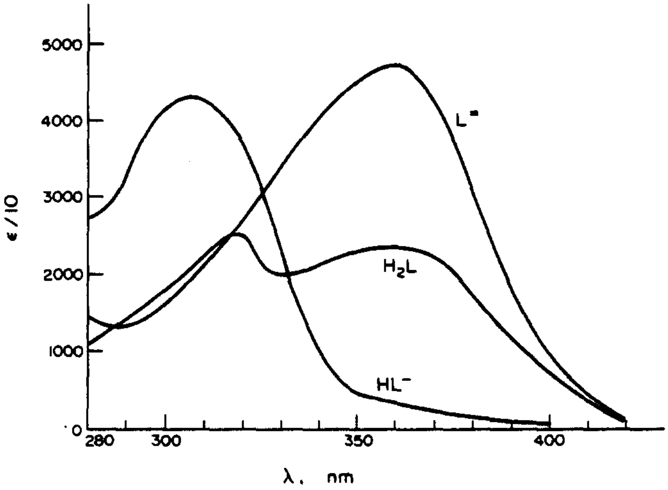

Fig. 4. The absorption spectra of HQS, ZnL and ZnL_2. Conditions: H_2L, pH = 2; HL^-, pH = 6·2; L^{2-}, pH = 10. The spectra of $10^{-4}M$ and $5 \times 10^{-5}M$ ZnL_2 are identical with that of $10^{-4}M$ L.

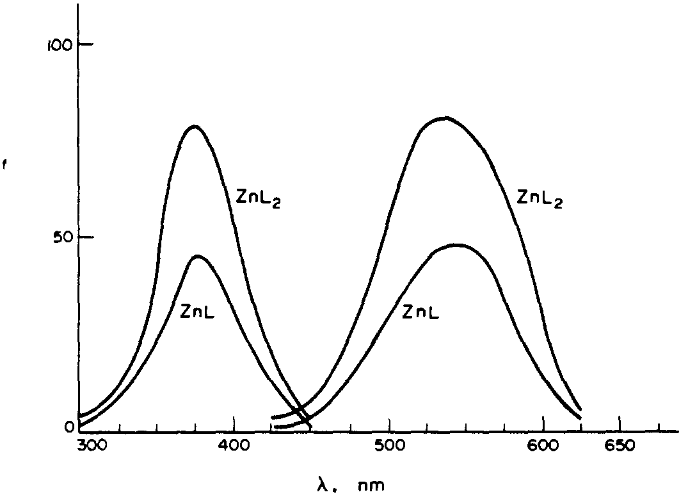

Fig. 5. The excitation and fluorescence spectra of ZnL and ZnL_2 (uncorrected). For I_f an arbitrary scale is used.

The titration of zinc with HQS

This titration is based on the reactions (charges are omitted):

$$Zn + L \rightleftharpoons ZnL \qquad (5)$$

$$ZnL + L \rightleftharpoons ZnL_2 \qquad (6)$$

As both ZnL and ZnL_2 exhibit fluorescence the end-point indication depends on both. Since HQS is added, the absorbance of the sample at the excitation wavelength changes during the titration. Zn, ZnL, ZnL_2 and L do not absorb at the wavelength of fluorescence measurement. Therefore the measured fluorescence intensity can be written as:

$$I_{fl} = k\{[ZnL] + 0{\cdot}9[ZnL_2]\}\,.\,f(A_{ex}) \qquad (7)$$

where k is a constant and $f(A_{ex})$ is a function of the absorbance at the excitation wavelength. A discussion of this function is given elsewhere.[1,6]

Two limiting cases can now be distinguished.

1. At low concentrations of zinc the factor $f(A_{ex})$ in (7) is nearly constant during a titration. Therefore, the lowest concentration of zinc that can successfully be titrated is determined by the values for the stability constants for reactions (5) and (6). For a more complete discussion of this limit see Freese and den Boef.[13]
2. At higher concentration of zinc the influence of $f(A_{ex})$ on the titration graph becomes appreciable: extrapolation of the quasilinear branches yields false results.

From computer computations[6] it appears that the lower limit for the concentration of zinc is about $5 \times 10^{-6}M$, and the upper limit (for the apparatus used, and with excitation at 365 nm) is about $10^{-5}M$ for a systematic error of 1% in the end-point. Both values were computed for pH 8·8.

Procedure. A 10-ml sample, containing 1–15 μg of zinc and buffered to pH 8·8, is transferred by pipette into a cell. The cell is placed in the fluorimeter, and the sample is titrated with HQS. Excitation is at 365 nm, the fluorescence is measured at 520 nm.

The results of typical titrations are reported in Table 1. The results are accurate over the concentration range from $2 \times 10^{-6}M$ (1·268 μg) to $10^{-5}M$ (6·34 μg). This range is slightly larger than the predicted range, the lower concentration limit being lower than predicted. It seems that the conditional stability constants for the zinc complexes are somewhat larger than those calculated from the values given in the literature. This effect can be seen even more clearly if a computed titration graph is compared with an experimental graph.

Zinc has also been titrated with HQS in the presence of a number of other metal ions. It was found that nearly all these metals interfered with the determination of zinc (14 metals tested, only a 5-fold excess of calcium did not interfere). It must therefore be concluded that as a test for the theory of end-point indication by fluorescence the titration has been successful, the upper concentration limit being accurately predicted, but that the titration has rather little practical value.

Table 1. Results of the titration of zinc with HQS

Zn taken, μg	Zn found, μg*	Zn found, μg†	Difference, %§	Relative std. devn., %‡	No. of detns.
0	1·14			4·0	6
0·634	1·41	0·27	−57	3·6	3
1·268	2·40	1·26	−0·6	1·6	5
3·17	4·35	3·21	+1·2	2·5	5
6·34	7·55	6·41	+1·1	0·7	5
9·51	10·44	9·30	−2·3	1·2	6
12·68	13·40	12·26	−3·3	0·9	5
15·85	16·07	14·93	−5·8	0·7	5

* Before correction for blank.
† After correction for blank.
§ Relative to Zn taken.
‡ Relative to the uncorrected value of Zn found.

The titration of zinc with EDTA in the presence of HQS

Zinc can be titrated with EDTA according to

$$Zn + Y \rightleftharpoons ZnY.$$

This reaction is not self-indicating, and an indicator has to be added. We have investigated the use of HQS as the indicator. It is necessary that one of the complexes of HQS with zinc should predominate in the titration system. This condition is most easily fulfilled for the complex ZnL_2. A titration is then feasible, if conditions (1)–(4) are fulfilled. Condition (1) is fulfilled for a certain minimum value C_L of the concentration of HQS, which depends on α_{Zn} and therefore on the buffer. An ammonia/ammonium salt buffer of pH 8·8 is chosen, with $[NH_3] = 0{\cdot}1M$. Condition (1) is then satisfied if $\log C_L > -5{\cdot}1$. Titrations can be performed with $C_{HQS} = 10^{-5}M$. With this value of C_L condition (3) is also satisfied. Conditions (2) and (4) are fulfilled if $10^{-7}M < C_{Zn} < 10^{-5}M$.

A peculiarity of the indication reaction is that the absorbance of the sample is constant during the titration (changes in volume being neglected), because the absorptivity per mole of ligand is the same for L, ZnL and ZnL_2, and the total concentration of HQS is fixed. Therefore, the fluorescence intensity is linearly related to the concentration of the zinc complex.

Procedure. To a sample add pH 8·8 buffer and HQS. Take a 10-ml aliquot in a cell and place the cell in the fluorimeter. Titrate with EDTA, measuring the fluorescence at 520 nm, with excitation at 365 nm.

The results of titrations in the absence of other ions are given in Table 2. Owing to the rather high blank, titrations of less than 0·634 μg of zinc ($10^{-6}M$) would have been quite inaccurate. Such titrations were therefore not attempted.

Table 2. Titration of zinc with EDTA in the presence of HQS

Zn taken, μg	Zn found, μg*	Zn found, μg†	Difference, %§	Relative std. devn., %‡	No. of detns.
0	0·48			3·0	15
0·634	1·14	0·66	+4·1	3·1	15
1·268	1·74	1·26	−0·6	1·0	15
3·17	3·64	3·16	−0·3	1·2	15
6·34	6·82	6·34	0·0	1·5	15

* Before correction for the blank.
† After correction for the blank.
§ Relative to Zn taken.
‡ Relative to the uncorrected value for Zn found.

The results of titrations in the presence of various ions are given in Table 3. All titrations were performed on samples containing 1·268 μg of zinc ($2 \times 10^{-6}M$). From Table 3 it is apparent that the zinc titration is not very selective. To improve the selectivity the zinc should be separated from the interfering ions. Two separation schemes have been investigated:[6] separation by means of anion-exchange in a medium containing a high concentration of iodide,[14] and extractive separation with dithizone in carbon tetrachloride.[15]

Separation by means of ion-exchange

Several metal ions, notably Hg(II), Pb, Cd, Tl(I), Bi and Cu(II), form iodo-complexes with a negative charge. Zinc does not form such complexes in aqueous media. It is therefore possible to separate zinc from the iodo-complexes by using an anion-exchanger.

Procedure. Prepare a 10 × 200 mm column of Dowex 1-X2. Bring the resin into the iodide form by passing 100 ml of 0·1*M* potassium iodide through the column. To a sample containing 5–50 μg of zinc add 1·5 g of potassium iodide, 0·1 g of ammonium acetate and 0·1 g of sodium thiosulphate. Dilute to 100 ml. Pass this solution through the column. Reject the first 25 ml of the eluate, and collect the remainder for either further separation with dithizone, or, if no further separation is needed, for titration of a 10-ml aliquot. Regenerate the column by passing successively 100 ml of 2*M* nitric acid, 100 ml of distilled water and 100 ml of 0·1*M* potassium iodide through it.

Several samples were subjected to this separation procedure. They did not need further separation. The results obtained are given in Table 4.

Separation by means of dithizone

Several metal ions, notably Cu(II), Ag and Hg(II), are completely extracted from aqueous solution at pH 1 by dithizone in carbon tetrachloride. Bi(III) is partially extracted. Zinc is not extracted under these conditions. At pH 5, and in the presence of 2*M* iodide, Zn, In(III) and Sn(II) (partially) are extracted by dithizone in carbon tetrachloride.[6] The following extraction scheme therefore suggests itself: extraction at pH 1; extraction at pH 5 in the presence of 2*M* iodide; stripping at pH 1 from the second extract. The last two steps could be repeated to ensure a complete separation of zinc with appropriate phase-volume ratios if a concentration step is desired. After the final stripping the pH of the sample is adjusted to 8·8 with ammonia and a 10-ml portion is titrated. Typical results are given in Table 5.

Table 3. Titration of zinc with EDTA in the presence of HQS and diverse ions

Foreign ion (X)	C_X/C_{Zn}	Zn found,	Difference,		Relative std. devn.,	No. of detns.
		μg*	μg†	%§	%‡	
Cu(II)	2·5	1·17	−0·10	−7·9	6·4	9
Cu(II)	5·0	1·12	−0·15	−11·8	5·9	9
Ni(II)	2·5	0·97	−0·30	−23·6	2·5	9
Co(II)	5·0	1·18	−0·09	−7·1	3·2	9
Fe(III)	2·5	1·01	−0·26	−20·5	5·9	9
Cr(III)	5·0	1·14	−0·13	−10·5	8·0	9
Ag(I)	2·5	1·08	−0·19	−15·0	2·9	9
Ba(II)	2·5	1·84	+0·56	+44	6·4	9
Ca(II)	2·5	1·53	+0·26	+20·5	9·3	6
Mg(II)	2·5	¶				3
Cd(II)	1·0	2·51	+1·24	+97	4·8	3
Na(I)	10^5	1·28	+0·01	+0·8	3·0	9
K(I)	10^5	1·29	+0·02	+1·6	3·2	9
HPO_4^{2-}	500	1·26	−0·01	−0·8	4·9	9
F^-	500	1·29	+0·02	+1·6	4·1	9
I^-	10^6	1·27	0·0	0·0	2·8	18
Cl^-	10^5	1·29	+0·02	+1·6	3·1	18
CO_3^{2-}	500	1·24	−0·03	−2·4	4·3	9
$Cd:I^-$	$1:10^6$	1·74	+0·47	+37	9·7	3

* After correction for blank.

† Between Zn found and Zn taken.

§ Relative to Zn taken.

‡ Relative to Zn found.

¶ No equivalence point could be obtained

Table 4. Results for separation by ion-exchange

Zn taken, μg*	Foreign ion (X)	C_X/C_{Zn}	Zn found, μg†	Zn found, μg§	Difference, %‡	Relative std. devn., %¶	No. of detns.
0	—	—	0·70	—	—	2·5	16
6·34	—	—	7·05	6·35	+0·2	0·7	27
6·34	Cd(II)	10	6·99	6·29	−0·8	0·5	9
6·34	Cd(II)	100	7·11	6·41	+1·1	0·6	9
6·34	Cd(II)	500	7·85	7·15	+12·8	0·5	3
6·34	Cd(II)#	500	7·09	6·39	+0·8	0·8	9
6·34	Pb(II)	1	6·90	6·20	−2·2	0·9	9
6·34	Pb(II)	10	7·80	7·10	+12·0	1·2	3
6·34	Pb(II)#	10	6·98	6·18	−2·5	0·4	9
6·34	Pb(II)#	100	7·34	6·64	+4·7	2·5	6
6·34	Hg(II)	10	7·13	6·43	+1·4	0·8	9
6·34	Hg(II)	100	7·05	6·35	+0·2	0·6	9
6·34	Hg(II)	500	7·02	6·32	−0·3	0·6	9
6·34	Cu(II)	1	7·08	6·38	+0·6	0·3	9
6·34	Cu(II)	10	7·04	6·34	0·0	0·1	9
6·34	Cu(II)	50	7·05	6·35	+0·2	0·2	9
6·34	Cu + Hg + Pb + Cd	10 + 100 + 10 + 100	7·00	6·30	−0·6	0·4	9

* Amount of zinc present in aliquot titrated.
† Before correction for blank.
§ After correction for blank.
‡ Relative to Zn taken.
¶ Relative to the uncorrected value of Zn found.
\# Samples passed through the column twice.

Table 5. Results for extractive separation with dithizone

Zn taken, μg	Foreign ion (X)	C_X/C_{Zn}	Zn found, μg*	Zn found, μg†	Difference, %§	Relative std. devn., %‡	No. of detns.
0	—	—	0·85	—	—	3·7	9
0·634	—	—	1·47	0·62	−2·2	2·8	9
1·268	—	—	2·12	1·27	+0·2	2·5	9
3·17	—	—	3·98	3·13	−1·3	2·9	9
6·34	—	—	7·12	6·27	−1·1	1·9	9
6·34	Ca(II)	1000	7·21	6·36	+0·3	0·9	9
6.34	Mg(II)	1000	7·09	6·24	−1·6	2·0	9
6.34	Pb(II)	10	7·00	6·15	−3·0	3·6	9
6·34	Cu(II)	10	7·15	6·30	−0·6	0·4	9
6·34	Cd(II)	10	9·22	8·37	+32	0·8	9
6·34	Cu(II) + Pb(II)	50 + 50	6·42	5·57	−12·2	6·2	9

* Before correction for blank.
† After correction for blank.
§ Relative to Zn taken.
‡ Relative to the uncorrected value of Zn found.

CONCLUSIONS

Samples containing 0·5–5 μg of zinc per 10-ml aliquot can be titrated successfully with EDTA in the presence of HQS at pH 8·8. Many metal ions interfere in this titration, but the interferences can be eliminated by a separation with an anion-exchanger [Cd, Pb, Hg(II), Cu(II)], or by an extraction procedure using dithizone. If the dithizone separation is used, an enrichment of the sample should be possible. However, this possibility was not investigated.

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Zusammenfassung—Zink bildet mit 8-Hydroxychinolin-5-sulfonsäure (HQS) im pH-Bereich 7–10 fluoreszierende Komplexe. Die Stabilität dieser Komplexe ist derart, daß zwei verschiedene Titrationsmethoden möglich sind: die Titration von Zink mit HQS und die Titration von Zink mit EDTA in Gegenwart von HQS. Für beide Methoden wird die Wahl der Titrationsbedingungen beschrieben. Ferner werden zwei Abtrennverfahren für Zink beschrieben, die in Verbindung mit der EDTA-Titration besonders geeignet sind. Die praktischen Ergebnisse zeigen, daß Zink in Konzentrationen über 10^{-6}M (0,05 μg/ml) mit guter Genauigkeit titriert werden kann.

Résumé—Le zinc forme des complexes fluorescents avec l'acide 8-hydroxyquinoléine 5-sulfonique (HQS) dans la zone de pH 7–10. La stabilité de ces complexes est telle que deux techniques de titrage différentes sont possibles: le titrage du zinc par HQS et le titrage du zinc à l'EDTA en la présence de HQS. On décrit le choix des conditions de titrage pour les deux techniques. On décrit aussi deux techniques de séparation pour le zinc, particulièrement adaptées en liaison avec le titrage à l'EDTA. Les résultats pratiques montrent que le zinc en concentrations supérieures à $10^{-6}M$ (0,05 μg/ml) peut être dosé avec une bonne précision.

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A STUDY OF THE COMPOSITION AND PROPERTIES OF THE ION-ASSOCIATION COMPLEX OF RHODAMINE B WITH SILICOMOLYBDIC ACID, WITH A VIEW TO ITS ANALYTICAL APPLICATION

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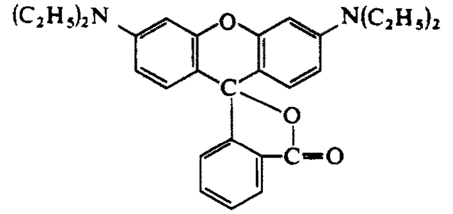
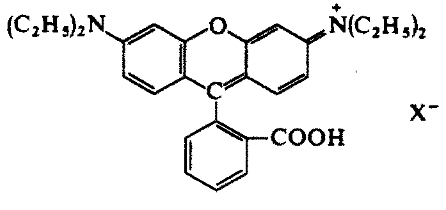
Summary—The composition of the ion-association complex of Rhodamine B with silicomolybdate has been examined by Job's method and spectrophotometric titration. The ratio of Rhodamine B to silicon in the complex is 4 : 1. The same ratio is obtained by analysis of the crystalline complex. The composition of the complex is identical in aqueous medium, an organic solvent (ethanol) and in the crystalline state ($(C_{28}H_{30}N_2O_3)_4SiMo_{12}O_{40}$). The complex is stable in the organic solvent and has its absorption maximum at 555 nm and a molar absorptivity of 5×10^5 l.mole^{-1}cm^{-1}. The complex can be advantageously used for the determination of silicon.

Basic xanthone dyes, including Rhodamines, are monovalent cations which occur in the form of salts in aqueous solution. They tend to form ion-pairs (ion-association complexes) with metal-complex anions and are advantageously used for separation and extractive-photometric determination of a number of elements. According to Kuznetsov[1] Rhodamine B forms ion-association complexes only with anions of molecular weight above 200, *e.g.*, WO_4^{2-}, $SbCl_6^-$, $Zn(SCN)_4^{2-}$, $AuCl_4^-$, $TlCl_4^-$, CdI_4^{2-}, heteropoly complexes. These complexes are extractable with organic solvents, *e.g.*, benzene, toluene, isopropyl ether, while the excess of the dye usually remains in the aqueous phase. According to Noelting and Dziewonski[2] Rhodamine B occurs in two principal forms:



the lactone form



RHX salt

Ramette and Sandell[3] showed that in aqueous solutions other forms occur, *i.e.*, R° (a colourless lactone form), R^{+-}, RH^+, RH_2^{2+}, RH_3^{3+}. The equilibrium between these forms is dependent on pH. Colourless solutions of Rhodamine B in benzene and ether contain the lactone form R°, which in polar solvents, *e.g.*, alcohol, acetone, water, shows a strong tendency to open the lactone ring, forming a violet amphoteric form R^{+-} at pH 4–13. At pH < 4 the carboxyl group is protonated, giving RH^+. At pH 0–1 an amino nitrogen atom is protonated, giving the orange RH_2^{2+}. The further protonated yellow form RH_3^{3+} occurs only in concentrated sulphuric or perchloric acid medium.

According to Blyum *et al.*[4,5] the optical properties of compounds of a given dye with various anions are dependent only on the amount of the dye combined with the anion, and on its molar absorptivity, and are similar to those of an aqueous solution of the dye containing mainly the univalent form RH^+. This suggests that only the univalent form of Rhodamine B, RH^+, can react with anion complexes. It follows then that the presence of this form of Rhodamine B is indispensible for the formation of ion-association compounds with anions in solutions.

In the formation of an ion-association complex the interaction between the cation of the dye and the anion of the solvent (water) diminishes considerably, resulting in precipitation of the compound formed.

We have dealt earlier[6,7] with the determination of trace amounts of silicon as the silicomolybdic acid complex with Rhodamine B. The high molar absorptivity of this complex seemed to be interesting enough to justify further investigation of its analytical properties and composition.

EXPERIMENTAL

Reagents

Standard silicon solutions, 10^{-2}, 10^{-3} *and* $10^{-4}M$.

Sodium molybdate (analytical reagent grade) *solutions*, 0·1 *and* 0·012*M* (pH 1·3).

Rhodamine B solutions, 10^{-3} *and* $10^{-4}M$. Prepared from dye recrystallized from ethanol.

Nitric acid (spectrally pure), 5*M*.

Water. Redistilled in quartz apparatus.

Preparations

The Rhodamine B silicomolybdate complex (RB–Si–Mo) in aqueous solution. Sodium molybdate solution (0·012*M*, 1 ml) was added to a 10-ml volumetric flask containing sodium silicate solution. The contents were mixed and after 10 min, 1 ml of 5*M* nitric acid was added. The mixture was diluted to 8 ml, a suitable amount of Rhodamine B (RB) solution was added and the solution diluted to the mark and mixed. The absorbance was measured 10 min later.

Separation of RB–Si–Mo by flotation. An aqueous solution of the complex was prepared as above, and 1 or 2 ml (according to the silicon concentration) transferred to a separatory funnel; 2 ml of di-isopropyl ether were added and the mixture was shaken for 15 sec. The RB–Si–Mo complex precipitated as a thin layer on the phase boundary. The aqueous phase was separated, and the ether and adhering precipitate were washed with 2 ml of water. The water was separated, the ether removed, and the precipitate was dissolved in ethanol. For determination of uncombined Rhodamine B the absorbance of the aqueous solution and washings was measured at 555 nm (λ_{max} for RB) in 1-cm cells.

Crystalline RB–Si–Mo. Sodium silicate solution (0·01*M*, 20 ml) and 200 ml of 0·024*M* sodium molybdate were transferred to a 1-litre separatory funnel. After 10 min, 100 ml of 5*M* nitric acid and 400 ml of 0·01*M* RB were added, and the solution was diluted to 1 litre and shaken vigorously. A violet precipitate of RB–Si–Mo was formed. After 15 min 50 ml of di-isopropyl ether were added and the mixture was shaken for 15 sec. The complex accumulated at the phase boundary. The aqueous phase was separated and the ether phase plus precipitate was washed several times with water to remove uncombined RB completely. The precipitate was filtered off and dried at 110° to constant weight.

RESULTS AND DISCUSSION

Absorption spectra

The spectra of the complex and of Rhodamine B in ethanol solution are shown in Fig. 1, and those for aqueous media are shown in Fig. 2. The spectrum of the complex in aqueous medium is very similar to the spectra of crystals of Rhodamine B and the complex deposited on quartz plates. This suggests that in aqueous solution, even before precipitation,

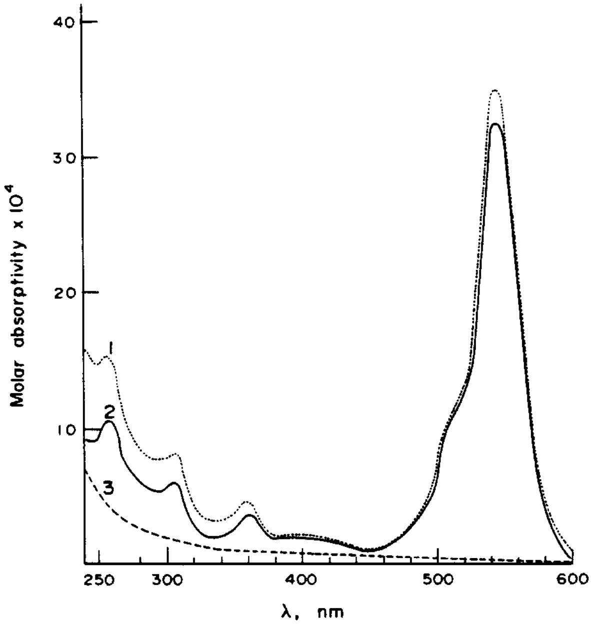


Fig. 1. Absorption spectra

1—crystalline complex in ethanol, [RB-Si-Mo] = $1{\cdot}39 \times 10^{-6}M$;
2—RB in ethanol, [RB] = $5{\cdot}6 \times 10^{-6}M$;
3—Si-Mo in ethanol, [Si] = $1{\cdot}5 \times 10^{-6}M$, [Mo] = $18 \times 10^{-6}M$.

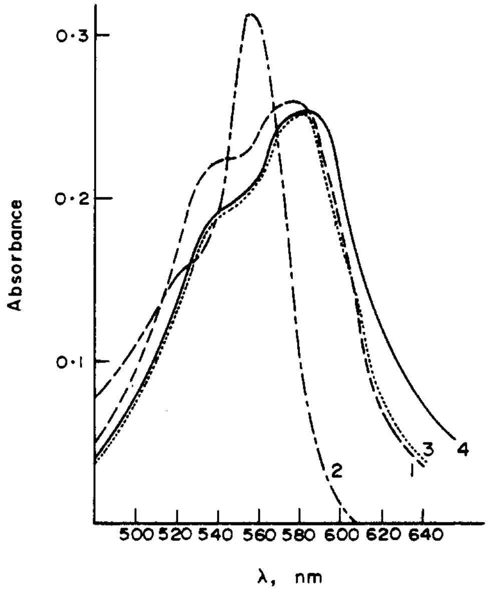


Fig. 2. Absorption spectra

1—complex in aqueous solution (0·5M HNO_3), [Si] = $2 \times 10^{-6}M$, [RB] = $8 \times 10^{-6}M$, [Mo] = $1{\cdot}2 \times 10^{-3}M$;
2—RB in aqueous solution (0·5M HNO_3), [RB] = $8 \times 10^{-6}M$; reference water;
3—crystalline RB;
4—crystalline complex.

the complex forms agglomerates of a structure similar to that of the crystalline material. If just enough alcohol to prevent precipitation is added to this solution the spectrum of the complex becomes identical in shape with that of Rhodamine B. This fact confirms the suggestion.

Composition of the RB–Si–Mo complex

Job's method and spectrophotometric titrations were used to determine the composition of the complex. The absorbance of free Rhodamine B in the aqueous solution was measured after separation of the complex by flotation.

All the Job and titration curves show an apparent combining ratio of Si : RB = 1 : 6. However, the shape of the Job curve indicates that interfering reactions occur and reduce the effective concentration of Rhodamine B, resulting in a shift of the maximum. This type of interference was discussed by Asmus.[8] Taking into account that at the break-point of the curves about 20% of the Rhodamine B is not combined in the complex but remains in the aqueous solution, and that some Rhodamine B in the lactone form dissolves in di-isopropyl ether during the flotation process, the ratio Si : RB must be corrected. When this is done the ratio Si : RB is about 1 : 4.

Analysis of crystalline RB–Si–Mo for molybdenum by the thiocyanate method,[9] silicon by the molybdenum blue method[10] and carbon, hydrogen and nitrogen by microanalysis, gave the results Mo 32·15%, Si 0·78%, C 37·1%, H 3·5%, N 3·1%. $(RB)_4SiMo_{12}O_{40}$ requires Mo 32·10%, Si 0·78%, C 37·45%, H 3·43%, N 3·12%.

The composition is further confirmed by the congruence of the visible-region absorption spectra of ethanol solutions of RB and of the complex (Fig. 1), the molar concentration of RB being four times that of the complex (calculated on the basis of the postulated composition).

Properties of RB–Si–Mo

The best solvents for the RB–Si–Mo complex are alcohols and ketones, but they cannot be used for extraction of the complex because Rhodamine B is also extracted. Ethers and hydrocarbons (*e.g.*, xylene, hexane, cyclohexane) do not dissolve the complex but can be used for flotation of the precipitate from water.

The spectrum of the dry crystalline complex dissolved in ethanol is identical with that of an ethanol solution of Rhodamine B (Fig. 1) and has its absorption maximum at 543 nm, but is shifted towards shorter wavelengths relative to the spectrum of the complex dissolved in ethanol directly after flotation from aqueous solution (Fig. 3, curve 6) which has its absorption maximum at 555 nm. This shift is connected with the dependence of the spectra of the complex and of Rhodamine B on pH. The effect of nitric acid on the shape of the spectra is shown in Fig. 3. Small amounts of nitric acid ($5M$, 0·05 ml) shift λ_{max} of the RB solution from 543 to 555 nm, and also increase the absorbance. A slightly larger amount of acid (0·2–1 ml) causes only a slight decrease in absorbance (curves 2, 3). At very large amounts of the acid (curve 4) the univalent form of Rhodamine B begins to pass into the bivalent form (curve 5).

The molar absorptivity of the dry complex dissolved in ethanol is $3{\cdot}6 \times 10^5$ $l.mole^{-1}.cm^{-1}$ (at λ_{max} 543 nm) and of Rhodamine B $8{\cdot}3 \times 10^4$. The value for the complex is slightly higher than that expected from the composition ($4 \times 8{\cdot}3 \times 10^4$). This may be because free Rhodamine B in ethanol occurs partly in the lactone form. Slight acidification increases the molar absorptivities to $4{\cdot}6 \times 10^5$ and $1{\cdot}1 \times 10^5$ $l.mole^{-1}.cm^{-1}$ respectively, suggesting a shift of the equilibrium from R° to RH^+.

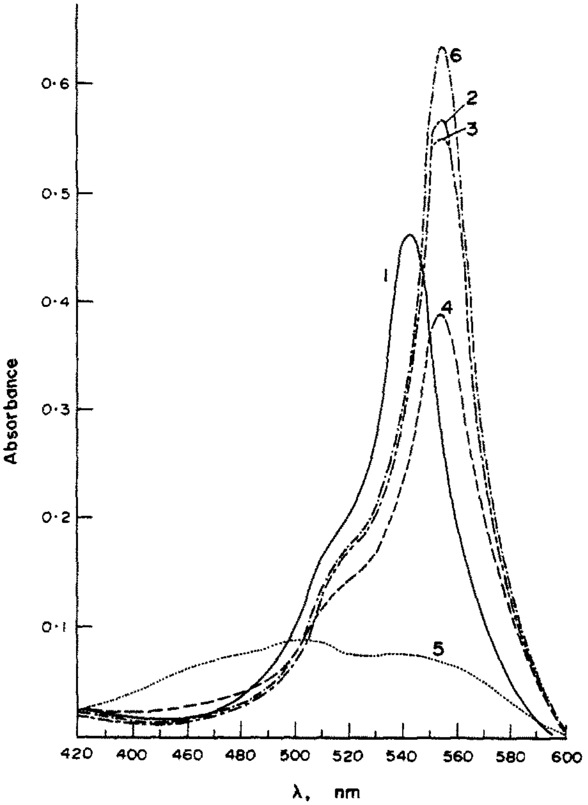


Fig. 3. The effect of nitric acid on the spectrum of RB in ethanol, [RB] = $5{\cdot}6 \times 10^{-6}M$. 1—RB in ethanol; 2–5—RB in ethanol after addition of $5M$ HNO_3: 2—0·05 ml; 3—1 ml; 4—5 ml; 5—8 ml; 6—complex dissolved in ethanol directly after separation from aqueous solution formed in the presence of excess of RB, [Si] = $1{\cdot}3 \times 10^{-6}M$.

The molar absorptivity of the complex produced under optimum analytical conditions and dissolved in ethanol directly after separation by flotation is 5×10^5 $l.mole^{-1}.cm^{-1}$ (λ_{max} 555 nm). The complex is formed in acid aqueous medium and contains only the intensely coloured form RH^+. Moreover it is presumably solvated with acid molecules, which protect it from the influence of ethanol.

The identity of the spectra of crystalline RB–Si–Mo and Rhodamine B dissolved in ethanol implies that an ionic bond occurs between RB and silicomolybdate and that the structure of the dye molecule is not affected by the formation of the complex. The similarity of the spectra of crystalline RB–Si–Mo dissolved in acidified ethanol and of the complex dissolved in ethanol directly after flotation suggests identical structure and composition of the complex in the solution and in the crystalline form.

The sharp break-points on the spectrophotometric titration curves and the Job curves suggest that the complex is very stable.

In view of these and earlier results[7] the RB–Si–Mo complex can be advantageously used for determination of traces of silicon, by two methods.

(1) The complex RB–Si–Mo formed under optimum conditions of acidity (0·5M nitric acid) in the presence of an excess of RB is separated by flotation with di-isopropyl ether, and dissolved in ethanol, and its absorbance at 555 nm is measured.

(2) Silicon can be determined directly by measurement of the absorbance of an aqueous solution of the complex at 590 nm, where absorption by RB is insignificant. Because of the low solubility of the complex this method can only be used for the determination of Si at concentrations below 30 ng/ml.

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Zusammenfassung—Die Zusammensetzung des Ionenassoziationskomplexes von Rhodamin B mit Silicomolybdat wurde nach der Job'schen Methode und durch spektrophotometrische Titration untersucht. Das Verhältnis Rhodamin B: Silicium im Komplex beträgt 4 : 1. Dasselbe Verhältnis erhält man durch Analyse des kristallinen Komplexes. Die Zusammensetzung des Komplexes ist dieselbe in wäßrigem Medium, einem organischen Lösungsmittel (Äthanol) und im kristallinen Zustand ($(C_{28}H_{30}N_2O_3)_4SiMo_{12}O_{40}$). Der Komplex ist in dem organischen Lösungsmittel stabil und hat ein Absorptionsmaximum bei 555 nm mit dem molaren Extinktionskoeffizienten $5 . 10^5$ l mol^{-1}cm^{-1}. Der Komplex kann mit Vorteil zur Siliciumbestimmung verwendet werden.

Résumé—On a examiné la composition du complexe d'association ionique de la Rhodamine B avec le silicomolybdate par la méthode de Job et le titrage spectrophotométrique. Le rapport entre la Rhodamine B et le silicium dans le complexe est 4 : 1. Le même rapport est obtenu par analyse du complexe cristallin. La composition du complexe est identique en milieu aqueux, dans un solvant organique (éthanol) et à l'état cristallin ($(C_{28}H_{30}N_2O_3)_4SiMo_{12}O_{40}$. Le complexe est stable dans le solvant organique et a son maximum d'absorption à 555 nm et un coefficient d'absorption molaire de 5×10^5 l.mole^{-1} cm^{-1}. Le complexe peut être avantageusement utilisé pour le dosage du silicium.

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EVALUATION OF A CARBON-ROD ATOMIZER FOR ROUTINE DETERMINATION OF TRACE METALS BY ATOMIC-ABSORPTION SPECTROSCOPY

APPLICATIONS TO ANALYSIS OF LUBRICATING OIL AND CRUDE OIL*

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Summary—A carbon-rod atomizer (CRA) fitted with a 'mini-Massmann' carbon rod was evaluated for routine analysis of petroleum and petroleum products for trace metal content by atomic-absorption spectroscopy. Aspects investigated included sensitivity, detection limit, effect of solvent type, and interferences. The results of analysis of oil samples with this technique were compared with those obtained by other techniques. Metals studied were silver, copper, iron, nickel, and lead. Sensitivity and detection limit values obtained with the CRA were similar to those obtained with the carbon-filament atomizer. Strong 'solvent effects' were observed as well as interference by cations. On the basis of this study, design changes for the CRA are suggested, with the object of minimizing 'solvent effects' and interferences, increasing the atomization efficiency, and increasing the residence time of the atomic vapour in the optical path of the instrumental system.

The development and application of non-flame atomization techniques utilizing carbon rods or tube furnaces of various designs have yielded a powerful tool for trace-metals analysis which overcomes many of the limitations imposed by flame atomization in atomic spectroscopy.[1–27] Non-flame atomizers generally give better sensitivities and detection limits than do conventional flame techniques. Also, such devices provide a reducing atmosphere created by the graphite rod of the atomizer, an inert gas (argon or nitrogen) sheath enveloping the sample-cell cavity, and a high rod temperature (up to 3000°).[8] Kirkbright has reviewed the earlier development of these devices.[1]

The various tube furnace designs, as developed by L'vov,[2] Massmann,[3–4] and Woodriff,[20] are in general more sensitive, achieve lower detection limits, and are less prone to interferences than the geometrically simpler 'mini-Massmann" carbon-rod atomizer (CRA) and 'West-type' carbon-filament atomizer (CFA) configurations. However, because of the complexity of the furnace designs, more stringent power and instrumentation requirements, and the increased time needed for analytical measurements, more emphasis for routine applications has been placed on the simpler and easier to use CRA and CFA.

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West and co-workers[11–19] developed the CFA and studied its applicability to a wide range of metals, using atomic-absorption and fluorescence spectroscopy. They found that, in general, there was no change in sensitivity for copper, silver, zinc, cadmium, iron, and lead with changes in complexing agents or salts, and for metal complexes extracted into organic solvents. A number of cations were found to interfere, but the extent of the interference could be reduced by restricting the place of measurement to the area immediately above the graphite rod. Amos *et al.*,[7] studied the clinical application of a CFA and found interferences; these were reduced by the addition of a hydrogen diffusion flame about the carbon rod.

Matoušek and Stevens[6] applied a CRA to biological systems. They used standard solutions of about the same composition as that of the samples, thereby compensating for interferences and also allowing for similar penetration of the standard and the sample into the graphite rod. Rosen,[25] and Kubasik, Volosin and Murray[26,27] have demonstrated the applicability of a CRA to the routine determination of lead in whole blood.

Brodie and Matoušek[8] demonstrated the applicability of a CRA to analysis of synthetic lubricating oils for various metals, using aqueous standards, but the rod had to be pretreated with xylene to prevent penetration of the aqueous solutions into the rod. Bratzel and Chakrabarti[10] applied a CRA to the analysis of various petroleum products for lead; the sensitivity for lead was the same for the different solvents employed and no interference was noted from 100-fold amounts (relative to lead) of a number of cations. Winefordner and co-workers,[22–24] reported the use of a CFA for the routine determination of 'wear' metals in used engine oils. Solutions of organometallic compounds in neutral base oil were used as standards. The results showed a high correlation coefficient with average values obtained by up to fifty U.S. military laboratories by flame atomization. Alder and West[17] reported the determination of silver and copper in lubricating oils, using organometallic standards in neutral base oil.

In the analysis of used lubricating and reciprocating oils for wear metal content, discrepancies in results[28,29] are usually attributed to the metal being present in particulate rather than in dissolved form.[30,31] Golden[32] and Taylor *et al.*,[33] have studied the effect of various instrumental factors, including flame temperature and composition, as well as the effect of particle size, on the efficiency of nebulization and atomization of particulates containing iron, copper, magnesium, chromium, and lead. In general, they found that the particle size was important and, for iron, the fuel-to-air ratio. Solutions of organometallic standards proved satisfactory as reference solutions only when the particle size was small and the particulates could therefore be atomized in a flame to a degree similar to that of dissolved metal species. The use of high-temperature and low-velocity flames as well as of the standard-addition technique solved some, but not all, of the problems. Winefordner and co-workers[24] reported that a better atomization efficiency and correlation coefficient were obtained when a hotter flame was used.

Because of the advantages (better sensitivity and detection limit and smaller sample volume) of the CRA over flame techniques, and of the promise of minimal solvent and interference effects, a CRA was evaluated for its applicability to routine trace analysis for metals in petroleum matrices. Our earlier work[10] with the CRA on lead in petroleum samples was expanded and extended to silver, nickel, copper and iron. Samples analysed were used jet-engine lubricating oil and crude oil. The metals chosen ranged from lead (easy to atomize) to nickel (difficult to atomize); iron was chosen because of its anomalous behaviour in a flame.[33] Effects of various solvents (xylene, MIBK, butyl acetate, carbon tetrachloride, and 40% v/v nitric acid) were studied. The 40% v/v nitric acid medium was chosen because no pretreatment was required to prevent penetration of the solvent into the carbon rod.[10] Both calibration curves and the standard-addition technique were used. Sensitivity and detection limit were determined for each metal, and compared with those determined by the same or similar techniques. The applicability of the CRA to routine analysis of oil samples was evaluated, and design modifications were suggested to overcome problems and limitations encountered in application to trace metals in general.

EXPERIMENTAL

Apparatus

The instrumentation was that used previously.[6–10,25,26] An Elektronik 194 (Honeywell) fast-response millivolt recorder was used to register the absorbance signals detected with an R-213 photomultiplier tube. The CRA was sheathed with argon to prevent entry of atmospheric air. There was provision for bleeding hydrogen into the argon line to provide a small hydrogen diffusion flame around the CRA. The monochromator slit-width was 0·100 mm, corresponding to a spectral bandpass of 0·33 nm. The atomic-absorption lines used for analysis were 328·07 nm (Ag), 324·75 nm (Cu), 248·33 nm (Fe), 232·00 nm (Ni), and 283·31 nm (Pb).

Standards and reagents

The following standards of known metal content were used: silver nitrate (Anachemia Chemicals, Ltd., Montreal, Quebec), nickel cyclohexanebutyrate (Ni-CHB) (Eastman Organic Chemicals, Rochester, New York 14650), nickel naphthenate (Harshaw Chemical Company, Cleveland, Ohio), lead cyclohexanebutyrate (Pb-CHB) (Eastman), tetraethyl lead (TEL) (Ethyl Corporation, New York, New York 10017), tris(1-phenyl-1,3-butadione)iron (Fe-TPB) (Eastman), copper cyclohexanebutyrate (Cu-CHB) (Eastman). Tri-iso-octyl phosphorothioate (TOTP) (Mobil Chemical, 801 East Main Street, Richmond, Virginia 23208) of analytical reagent grade purity was used as the complexing agent for the preparation of the organosilver standard. The 40% v/v nitric acid solutions of the metals were prepared from the pure metals. Other reagents used were analytical-reagent grade. Distilled water was demineralized before use. The crude oil samples were supplied by Imperial Oil Ltd. (Montreal, Quebec), and the used U.S.A.F. jet-engine lubricating oils by Dr. J. D. Winefordner (Department of Chemistry, University of Florida, Gainesville, Florida 32601).

Preparation of standard solutions

Nickel naphthenate and TEL were diluted directly with the appropriate solvent. Ni-CHB, Pb-CHB, Cu-CHB, and Fe-TPB were dissolved in the appropriate solvent. Silver nitrate was dissolved directly in the appropriate organic solvent with about 10% v/v of TOTP added; the silver was then present in solution as a stable TOTP complex.[34,35] The appropriate solvents are shown in Table 1. All stock solutions were prepared to be about 500 μg/ml; dilutions were made immediately before use.

Table 1. Effect of solvent on absorbance signals (coefficient of variation 5%)

Metal, *μg/ml*	Compound or complex	Absorbance relative to 1·00 for MIBK					
		40% HNO_3, peak height	Xylene		CCl_4		Butyl acetate, peak height
			Peak height	Integration	Peak height	Integration	
Ag, 0·173	NO_3-TOTP	—	0·79	0·88	0·46	0·95	—
Cu, 1·88	CHB	1·05	0·62	0·62	1·31	1·12	—
Fe, 1·12	TPB	1·06	0·74	0·75	0·76	0·73	—
Ni, 1·78	CHB	0·78	0·86	0·94	1·16	1·16	—
Pb, 0·202	TEL	1·05	1·00	1·04	1·56	1·48	0·73

Carbon rod operating conditions: argon-sheath gas flow = 1 l./min, hydrogen diffusion gas flow = 0·5 l./min, sample volume = 2 μl.

Procedure

An argon flow for 1·0 l/min and a hydrogen flow of 0·5 l/min were used for all studies; the flow-rates were not critical. The oil samples required no preparation except dilution with xylene when the metal concentration was too high. Calibration curves were prepared by use of synthetic standards of the appropriate metal, and the standard-addition technique was also used. A 2-μl sample was placed in the sample cell of the CRA and subjected to the dry, ash, and atomize cycle, typical cycle-times being dry—10 sec, ash—15 sec, atomize—2 sec. The time and voltage settings in the cycle are dependent on the solvent, the sample matrix, and the metal determined. The voltage was adequate to ensure complete removal of the sample in one firing. The peak height was generally taken as the measure of the absorbance signal but sometimes the absorbance signal was integrated. Although duplicate determinations gave satisfactory agreement, from 4 to 6 determinations were performed on each solution; the relative standard deviations for the standards and the samples were less than 5%. Solvent blanks showed no signal. Correction, by means of a hydrogen-lamp source, for molecular absorption and/or scattering was found to be unnecessary under optimum experimental conditions for both the samples and the synthetic standards.

RESULTS AND DISCUSSION

Solvent effect

A comparison of the absorbance signals when different solvents were used is presented in Table 1.

Brodie and Matoušek[8] observed that aqueous solutions of silver, aluminium, copper, chromium, magnesium, nickel, lead, vanadium and zinc could be used as standards for analysis of synthetic oil samples. Aggett and West,[15] in their atomic-absorption studies with the CFA, found no change in the signals for silver, cadmium, copper, lead and zinc, whether the metals were extracted as complexes into benzene, chloroform, carbon tetrachloride or MIBK, or analysed directly as aqueous solution. However, our studies with the CRA indicate a rather large 'solvent effect' which is much the same whether the peak-height or the integrated absorbance is measured. The absorbance signals for xylene and MIBK solutions are generally similar in shape and peak half-width (indicating similar times of atomization) but that for carbon tetrachloride is broader and generally occurs later in the atomization cycle than that for xylene or MIBK, indicating a slower rate of vaporization and atomization. The variation in integrated peak area with change of solvent indicates a definite solvent effect, perhaps due to different degrees of penetration by the solvent (and hence, the analyte) into the porous carbon rod when the sample is placed on the rod, and the relative ease of release as vapour from the pores. This penetration by solvent may be eliminated by impregnating the rod with an immiscible solvent,[8,25,26] or by using non-porous pyrolytic graphite.[1,2,27] The absence of a solvent effect with the CFA[11] is probably largely due to the design, which allows a relatively large beam of radiation to pass higher above the carbon filament, thereby allowing more time for the drying, ashing, and atomization processes to become complete. However, with the CRA, the radiation passes through a 1·5-mm hole in the rod, and the incident beam is small and at a lower height above the sampling area, allowing less time for these processes; therefore, the larger the degree of solvent penetration the smaller the amount of vaporized sample available for analysis. Thus, with the CRA there exists a solvent penetration effect. This was minimized by Brodie and Matoušek,[8] by injecting the sample into the carbon rod during the drying cycle, *i.e.*, while the rod was warm so that the solvent evaporated quickly before significant penetration, or by impregnating the rod with xylene before injecting the sample into the cold carbon rod and then following the usual cycle of operation.

Salt effect

The sensitivity for lead had already been found to be the same for Pb-CHB and TEL dissolved in xylene.[10] In the present study solutions of Ni-CHB and nickel naphthenate were also found to give equal sensitivities. These results are in agreement with those of Brodie and Matoušek[8] for aqueous solutions of metal nitrates or sulphates and for organometallic salts in oils, with the CRA. They also agree with those of West and co-workers[15,19] for various metal chelates and organometallic compounds in organic solvents and metal ions in aqueous solution, with the CFA; however, West and co-workers reported that results with organometallic compounds are low unless carefully controlled pyrolysis precedes the atomization.

Sensitivity and detection limit

The sensitivities (weight of metal giving 1% absorption) for MIBK medium are given in Table 2 along with those reported by Matoušek and Stevens for an identical system, by West and co-workers for a CFA, and by L'vov for his graphite furnace. In general, the sensitivities obtained with a CRA or a CFA are similar; small differences may be attributed to difference in design and instrumental components. However, these results are significantly poorer than those obtained by L'vov, by a factor of at least ten. The L'vov furnace appears to possess a higher atomization efficiency, probably because of its design, in which the sample is confined long enough within a cell in a highly reducing atmosphere for equilibrium to be attained; also the sample cell is made of or lined with pyrolytic graphite, which is impervious to solvent, thereby allowing the sample solution to remain on the surface of the cell, and the temperature attained is higher, so the atomization is more complete.

Detection limits (defined as signal : root-mean-square noise = 2) for MIBK medium are also presented in Table 2 and compared with those of Brodie and Matoušek for an almost identical system, and those obtained with a CFA. The CFA and the CRA give similar sensitivities and detection limits, and neither has a clear advantage.

Interferences

The effect of addition of 100- and 1000-fold w/w ratios of other cations is presented in Table 3. In several cases, the interference of 100-fold amounts of foreign species

Table 2. Sensitivities and detection limits (*g*) (operating conditions as in Table 1)*

	This study		CRA		CFA		Furnace	
Metal	S	LD	S	LD	S	LD	S	Wavelength, *nm*
Ag	1×10^{-12}(9)	2×10^{-14}(9)	—	2×10^{-13}(8)	1×10^{-12}(11) 13×10^{-12}(17)	1×10^{-12}(7) 2×10^{-11}(15)	1×10^{-13}(1, 2)	328·07
Cu	4×10^{-11}	1×10^{-11}	2×10^{-11}(6)	1×10^{-11}(8)	3×10^{-11}(1) 22×10^{-12}(17)	2×10^{-11}(7) 5×10^{-11}(15)	6×10^{-13}(1, 2)	324·75
Fe	2×10^{-11}	9×10^{-12}	9×10^{-11}(6)	—	3×10^{-12}(19)	1×10^{-11}(7) 6×10^{-12}(19)	1×10^{-12}(1, 2)	248·33
Ni	9×10^{-11}	2×10^{-11}	—	1×10^{-11}(8)	$9{\cdot}5 \times 10^{-11}$(18)	2×10^{-10}(18)	9×10^{-12}(1, 2)	232·00
Pb	1×10^{-11}(10)	2×10^{-12}(10)	5×10^{-12}(6)	5×10^{-12}(8)	7×10^{-12}(1)	2×10^{-11}(7) 4×10^{-10}(15)	2×10^{-12}(1, 2)	283·31

* S = sensitivity; LD = limit of detection; references are given in parentheses.

Table 3. Effect of foreign cations on absorbance signals (xylene as solvent, operating conditions as in Table 1)

			Relative absorbance in presence of foreign cations added in ratio shown†									
			Ag		Cu		Fe		Ni		Pb	
Metal*	Concentration, μg/ml	Absorbance of analyte alone	100	1000	100	1000	100	1000	100	1000	100	1000
Ag	0·120	0·209			1·23	1·08	1·71	1·12	1·30	1·18	1·01	0·92
Cu	2·25	0·343	1·46	—			1·67	—	1·30	—	1·00	—
Fe	1·12	0·278	1·33	—	—	—			1·28	—	0·99	—
Ni	2·24	0·162	0·98	—	1·08	—	1·10	—			1·02	1·11
Pb	0·202	0·120	0·91	0·60	0·92	0·68	0·91	—	1·13	0·65		

* Compounds used are given in Table 1.

† Relative to value of 1·00 for each metal solution with no foreign cations added. Coefficient of variation, 5%, calculated from $s = \frac{100}{\bar{x}} \sqrt{\frac{\sum (\bar{x} - x_i)^2}{(n-1)}} \%$.

is greater than that of 1000-fold amounts. There may therefore be more than one source or type of interference, acting in opposition, so that the observed effect is the resultant of these interferences.

Alkemade[36] classified interferences in flames into two categories. The first includes all effects based on the formation of a chemical compound by the analyte with the concomitant in the condensed phase, resulting in signal depression or enhancement. The second includes all effects based on occlusion of the analyte in a less volatile matrix (resulting in signal depression) or dispersion in a more volatile matrix (resulting in signal enhancement). This interpretation may be used as a basis for discussing the interferences observed with the CRA. With the CRA, the times at which the analyte and the concomitant are vaporized depend on the relative rates of their vaporization, and if the concomitant is vaporized significantly faster than the analyte, there should be no interference provided the analyte is dissociated in a time which is small compared with its residence time. For example, lead, as TEL which is more volatile, would be expected to produce little interference with less volatile systems, and this was borne out experimentally (Table 3).

The general enhancement by a 100-fold amount of interferent may be due to a chemical reaction in the condensed phase before atomization (the first category above), or the presence of the foreign species (the concomitant) may affect the penetration of the sample into the carbon rod, resulting in an effect similar to the solvent effect discussed above.

The relative volatility of the five species studied is Pb > Ag > Fe > Cu > Ni. On the basis of volatility alone, a sample dispersed in a volatile lead matrix should give a larger absorbance signal, and a sample dispersed in a nickel matrix a smaller signal. However, enhancement due to the dispersion of the analyte in a more volatile matrix (the second category above) has not been observed, possibly because of the simultaneous existence of other opposing and competing factors.

Measurements on the atomic vapour produced in the sample cell of the CRA and the CFA indicate that relatively low vapour temperatures may exist,[37] that equilibrium is not attained, and that occlusion of the analyte metal is a distinct possibility. The absorbance

Table 4. Analysis of oil samples

Sample	Metal	This study*	FAF-FAE†	FAA§
68-1	Ag	0·83 ± 0·09	—	0·5 ± 0·2
70-2A	Ag	0·96 ± 0·11	2·1 ± 0·6	0·6 ± 0·5
70-3A	Ag	0·45 ± 0·04	2·6 ± 0·2	0·2 ± 0·2
Guanipa	Ag	≤ 0·0001	—	—
T.V. 102	Ag	≤ 0·0001	—	—
68-1	Cu	11·5 ± 0·2	—	4·6 ± 0·9
70-2A	Cu	7·2 ± 0·1	8·2 ± 1·9	2·2 ± 0·6
70-3A	Cu	6·2 ± 0·1	6·6 ± 1·6	1·0 ± 0·1
Guanipa	Cu	0·24 ± 0·03	—	—
T.V. 102	Cu	0·38 ± 0·04	—	—
68-1	Fe	29·2 ± 1·2	—	13·9 ± 2·4
70-2A	Fe	38·4 ± 1·2	13·8 ± 1·9	20·3 ± 2·3
70-3A	Fe	20·1 ± 1·6	8·3 ± 0·8	9·1 ± 1·8
Guanipa	Fe	2·6 ± 0·2	—	—
T.V. 102	Fe	1·6 ± 0·1	—	—
68-1	Ni	1·6 ± 0·1	—	1·0 ± 0·4
70-2A	Ni	1·3 ± 0·1	—	0·8 ± 0·7
70-3A	Ni	0·61 ± 0·04	—	0·5 ± 0·3
Guanipa	Ni	27·9 ± 2·0	—	—
T.V. 102	Ni	58·7 ± 5·0	—	—
68-1	Pb	11·9 ± 0·3	—	10·8
70-2A	Pb	4·4 ± 0·1	—	2·4 ± 1·3
70-3A	Pb	3·7 ± 0·1	—	2·2 ± 1·0
Guanipa	Pb	0·31 ± 0·02	—	—
T.V. 102	Pb	0·17 ± 0·02	—	—

* The figures shown as ± are standard deviations. For samples 68-1, 70-2A and 70-3A concentration is in μg/ml; for Guanipa and T.V. 102 it is in μg/g.

† FAF = flame atomic-fluorescence; FAE = flame atomic-emission. Values for 70-2A and 70-3A from refs. 28 and 29; for 68-1 from refs. 28 and 38.

§ FAA = flame atomic-absorption.

signals are a complex function of the nature and concentration of the analyte and the concomitants, the geometry of the sample cell (determining the residence time and the concentration of atoms), and the temperature of the vapour phase.

Analysis of samples

The results of analysis of used jet-engine lubricating oils (68-1, 70-2A, and 70-3A) and of Venezuela crude oils (Guanipa and T.V. 102) for trace-metals content are shown in Table 4 and compared with those obtained by flame atomic-fluorescence, atomic-emission and atomic-absorption techniques. Calibration curves were used in the analysis, but because of the pronounced interferences and the solvent effect, sample 70-3A was also analysed for silver, iron, copper and lead, and 68-1 for iron, by the standard-addition technique. Results obtained by the two methods agreed within 10%; the coefficient of variation for each determination was also about 10%. The effect of physical properties of the liquid samples and of foreign species in the samples was minimized by dilution with xylene.

The interferences reported in Table 3 were not noticeable because the species were either not present or at too low a concentration; at any rate their effect was below the level of the statistical variation. The dilution with xylene may have assisted in this, and also produced samples of uniform matrix, much easier to handle by syringe, and gave better precision (the precision was significantly better than that of the results of other workers reported in Table 4).

Agreement of our results with those of others is as good as can be expected in view of the reported behaviour of particulates in analytical systems.[32,33] In general, our values are equal to or higher than those of others. The higher values may indicate that the atomization of particulates is more complete with the CRA than with conventional flames, especially since the results obtained by standard addition and by calibration curve (prepared with synthetic standards) agree.

Analyses of the crude oils by independent techniques are not available. However, with the CRA no effect should be expected from the bulk of the sample matrix, because of its complete removal during the drying and ashing cycles before atomization. Also, on the basis of the salt effects found in this and other studies,[10,15] the form in which the metal exists in the crude oil sample should be unimportant. Therefore, it may be considered that these values are acceptable measures of the metal content of these oils, and that the CRA is applicable to this type of sample.

CONCLUSIONS

Both the CFA and the CRA give comparable sensitivities and detection limits. The CFA offers advantages over the CRA in that there are apparently no solvent or salt effects, but it also has a disadvantage: the temperature of the atomic vapour above the carbon filament is relatively low,[37] probably because the sample cell is more open to the ambient atmosphere, and provides less contact area with the incandescent carbon. The CRA, on the other hand, generates a higher atomic vapour temperature (although the temperature of the carbon itself is about the same for both atomizers) because the sample cell is surrounded by the incandescent carbon; the design also produces a more reducing atmosphere. However, the small diameter of the sample cell limits the sample size, the sensitivity, and the detection limit.

This study has demonstrated the applicability of the CRA to the analysis of used oil samples for wear metal content and of crude oil samples, by use of either synthetic standards or the standard-addition technique; however, the present design of the CRA (Model 61) has limitations, and certain modifications are suggested.

Solvent effects and interferences may be avoided by proper choice of construction material for the carbon rod and of the dimensions of the sample cell. The spectrographic grade graphite used to make the carbon rod is generally porous and exhibits different porosity toward different solvents, although there is no correlation between the analytical signal, the surface tension, viscosity, or density of the solvents used. The use of non-porous pyrolytic graphite for construction of the sample cell should reduce the magnitude of the effects observed in this study. Pyrolytic graphite would also prevent diffusion of atomic vapour through the walls of sample cells, thereby enhancing sensitivity. Also, redesign of the CRA sample cell to accommodate a larger sample and to provide longer sample residence time in the optical path should reduce solvent and interference effects. Preheating the sheathing gas should also result in a higher atomic vapour temperature and hence a more favourable equilibrium position. Such changes would provide a system more similar to the graphite tube furnace, which would give a higher atomization efficiency while retaining the simplicity and advantages of the CRA.

Since the completion of these studies, the manufacturer of the CRA has marketed a new model (Model 63) of the CRA incorporating the modifications suggested above, thereby removing some of the limitations of the earlier CRA (Model 61).

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Zusammenfassung—Die Eignung einer Kohlestab-Atomquelle (CRA) mit einem "Mini-Massmann"-Kohlestab zur Routineanalyse von Petroleum und Petroleumprodukten auf ihren Gehalt an Spurenmetallen durch Atomabsorptionsspektroskopie wurde beurteilt. Geprüft wurden Empfindlichkeit, Nachweisgrenze, Einfluß der Lösungsmittelart und Störungen. Mit diesem Verfahren erhaltene Analysenergebnisse von Ölproben wurden mit auf andere Weise erhaltenen verglichen. Die untersuchten Metalle waren Silber, Kupfer, Eisen, Nickel und Blei. Mit dem

CRA erzielte Empfindlichkeiten und Nachweisgrenzen waren ähnlich denen, die mit einer Kohlefaden-Atomquelle erhalten wurden. Es wurden starke "Lösungsmitteleffekte" und Störungen durch Kationen beobachtet. Auf Grund dieser Untersuchung werden Konstruktionsänderungen am CRA vorgeschlagen, um "Lösungsmitteleffekte" und Störungen möglichst klein zu halten, die Ausbeute an Atomen zu erhöhen und die Verweilzeit des atomaren Dampfes im Lichtweg des Instruments zu erhöhen.

Résumé— On a évalué un atomiseur à tige de carbone (CRA) équipé d'une tige de carbone "mini-Massmann" pour l'analyse de routine du pétrole et de produits pétroliers pour la teneur en métaux à l'état de traces par spectroscopie d'absorption atomique. Les aspects étudiés comprennent la sensibilité, la limite de détection, l'influence du type de solvant et les interférences. On a comparé les résultats d'analyse d'échantillons d'huile par cette technique avec ceux obtenus par d'autres techniques. On a étudié les métaux suivants: argent, cuivre, fer, nickel et plomb. La sensibilité et les valeurs limites de détection obtenues avec le CRA ont été similaires à celles obtenues avec l'atomiseur à filament de carbone. On a observé de forts "effets de solvant" ainsi que des interférences par cations. Sur la base de cette étude, on suggère des modifications de conception pour le CRA, avec pour but de réduire au minimum les "effets de solvant" et les interférences, d'accroître l'efficacité d'atomisation, et d'accroître le temps de séjour de la vapeur atomique dans le trajet optique du système instrumental.

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APPLICATION OF AN OXYGEN-SHIELDED AIR–ACETYLENE FLAME TO ATOMIC SPECTROSCOPY

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Summary—A burner has been designed which provides an oxygen-shielded air–acetylene flame for atomic-absorption work. The chemical reducing properties of the oxygen-shielded flame operated under fuel-rich conditions are enhanced by the higher C : O ratio obtainable in the flame and by the higher flame temperature just above the reaction zone. The flame is inherently essentially free from the risk of flashback, and is offered as an alternative to the nitrous oxide–acetylene flame for use with certain types of equipment and for particular applications.

Previous work with premixed oxygen–acetylene flames[1–5] has shown such systems to offer a high temperature and a chemically reducing environment, and therefore to be very suitable for the purposes of analytical atomic spectroscopy. The properties of high temperature and reducing nature mean that the oxygen–acetylene flame is particularly suited to the determination of those elements capable of forming oxides that are thermally stable in the vapour phase, as well as to specific cases where chemical interference effects may be encountered. Although these inherent advantages have been successfully employed for both atomic emission and absorption studies,[1–4] its high burning velocity and corrosive nature[6] have tended to restrict any widespread application of the premixed flame.

The present work describes a burner capable of shielding a premixed air–acetylene flame from the atmosphere by a laminar oxygen flow. Thus oxygen rather than air entrainment occurs at the base of the flame, to give an oxygen-supported diffusion zone. Preliminary studies carried out with this flame show it to have a temperature maximum in excess of 2900 K, and to be chemically reducing in nature. Some degree of comparison has accordingly been made between the oxygen-shielded flame and its premixed counterpart (although such a comparison can never, of course, be absolute, owing to the differing mechanisms of nitrogen entrainment operative in the two systems). Since the burner described in this communication permits only oxygen entrainment, rather than premixing the reactant gases, the problems of corrosion and flashback associated with the premixed flame are automatically overcome. Thus the technique of oxygen-shielding is felt to offer a practicable method of applying the analytically useful characteristics associated with oxygen–acetylene combustion for the purposes of atomic spectroscopy without suffering the operating hazards of the premixed flame.

At the present time, the nitrous oxide–acetylene flame is generally used in preference to oxygen-supported flames, since it provides a high temperature and good chemical reducing characteristics leading to good atomization efficiency, and hence useful analytical sensitivity, for all but the most stable refractory-oxide-forming samples.[7,8] At the same time, the nitrous oxide–acetylene flame has a very much lower burning velocity than the oxygen–acetylene flame, and can therefore be more readily supported on the long-path burners required for atomic-absorption spectroscopy. However, the nitrous oxide–acetylene flame has recently been shown to have a maximum burning velocity of 285 cm/sec,[9] considerably exceeding the 150 cm/sec of the air–acetylene flame, and giving rise to a risk of flashback during operation.[9] The burning velocity of the oxygen-shielded flame was not observed to differ drastically from that of the air–acetylene flame, and the risk of flashback during its operation is therefore regarded as minimal. Thus, for example, it was found in the present studies that the shielded flame could be directly extinguished with complete safety even at very reduced gas flow-rates, a procedure which could not be attempted with nitrous oxide–acetylene under any circumstances with the burner described. In view of this, and since the oxygen-shielded flame offers other potential advantages, such as the capacity to utilize long-path burners and the elimination of a high CN background, as well as a significantly greater economy of operation, the system is felt to warrant an examination as a possible alternative to the nitrous oxide–acetylene flame for the purposes of analytical spectroscopy.

EXPERIMENTAL

Apparatus

The experiments were done with a Varian A A 5 spectrometer. The apparatus was operated in a fully conventional manner for both flame-emission and atomic-absorption work, with the exception of the burner and nebulizer assembly. The standard burner was replaced by the shielded unit described below. The A A 5 nebulizer was used in conjunction with the shielded burner, but was removed from its housing and coupled to the burner *via* a 6-in. length of $\frac{3}{8}$-in. bore "Tygon" tube. The separation of burner and nebulizer thus achieved permitted the water and oxygen inlets of the burner to be mounted clear of the optical rail of the spectrometer, facilitating the mechanical lay-out of the system.

The solutions required both for temperature measurements and for the atomic-absorption studies below were made up in water, from either the metal chloride or by dissolution of the metal itself in a minimum of hydrochloric acid. The atomic-absorption studies were carried out with standard Varian hollow-cathode lamp sources, operated at the recommended lamp-currents and monochromator slit-widths for the individual elements, except where otherwise stated. The lamps were electronically modulated at 285 Hz; a Hamamatsu R213 photomultiplier was used for detection.

Burner design

The burner used is shown in Fig. 1. A burner slot 4·0 cm in length and 0·34 mm in width was used to permit stabilization of either air–acetylene or nitrous oxide–acetylene flames under a variety of conditions. The burner was constructed from $\frac{1}{16}$-in. brass sheet, to provide good heat conduction from the edges of the slot, and was water-cooled. The internal joints of the burner were sealed with silver solder; the outer joints (around the oxygen shield) were sealed with epoxy resin. The oxygen shielding-gas was passed around the outer part of the cooling jacket and directed horizontally across the top of the burner head by suitably positioned steel deflecting plates (Fig. 1). Observation of the enhancement of the $CO + O_2$ continuum in the outer zone of the flame due to oxygen-shielding showed oxygen entrainment to begin at the base of the primary reaction zone. The entrained oxygen did not appear to penetrate to the reaction zone itself, and entrainment is therefore considered to be confined to the outer region of the flame. Observation following smoke injection into the shielding gas showed no visible turbulence of the oxygen flow at the point of entrainment despite the changes of flow direction induced by this design; hence it was assumed that flame turbulence due to turbulence of the shielding gas was of minor importance only. Correct positioning of the deflecting plates was, however, necessary; for the present purposes their position was established empirically at the alignment giving visually optimum flow conditions.

The oxygen shielding-gas was passed through a bed of ceramic chips to smooth the initial flow. Ceramic was used rather than, for example, crimped steel strip, which could be oxidized in a manner analogous

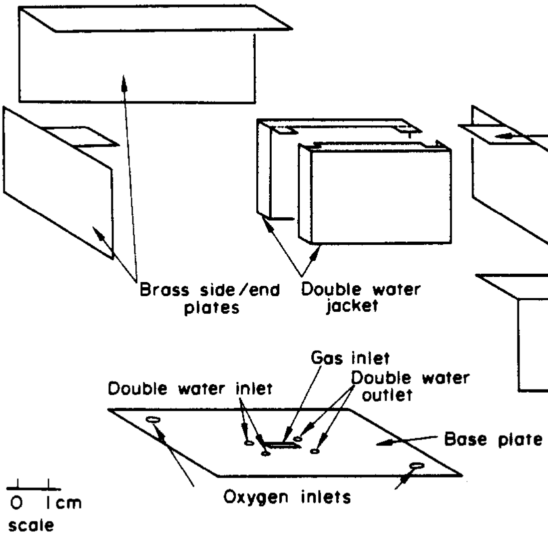

Fig. 1. The oxygen-shielded burner.

to that used in a "thermal lance," an effect which was observed to occur in the event of a local overheating of the burner, and one which necessitated the provision of the adequate cooling precautions, already mentioned, for the burner head itself.

RESULTS

Effect of oxygen-shielding on flame temperature and composition

Figure 2 shows the vertical temperature profiles of the air–acetylene flame, observed at increasing oxygen-shielding flow-rates. The profiles were measured through the centre of the flame, from a point just above the reaction zone to a maximum height of 3·0 cm, where air entrainment effectively reduced the flame temperature back to the non-shielded level. The temperature measurements were done on fuel-rich flames, at an air flow-rate of 5·6 l/min,* and with the acetylene flow adjusted so that emission from luminous carbon particles was just apparent. Flame temperatures were determined by the two-line method, using the iron emission lines at 373·33 and 374·95 nm for temperatures between 2400 and 2600 K, and the lines at 383·42 and 392·03 nm at higher temperatures.[10] The maximum temperature increase thus observed was 520 K, occurring at a point 1·6 cm above the reaction zone. The two main effects responsible for this temperature increase are thought to be (1) the increased rate of reaction in the diffusion zone, due to the increased rate of oxygen entrainment, and (2) the exclusion of atmospheric nitrogen, with its associated cooling effect on the flame as a result of molecular dissociation *etc.*

The effect of oxygen-shielding on flame composition is illustrated by Fig. 3, which shows the dependence of the acetylene flow-rate needed to give a flame that was just luminous, on oxygen flow-rate. The experimental conditions were the same as for the temperature studies. Figure 3 shows that the fuel-rich (luminous) limit of the reactant gas composition can be raised to a previously unattainable carbon to oxygen (C : O) ratio by shielding the flame. This can be attributed either to oxygen entrainment at the base of the flame, causing an increased fuel combustion rate, or else to an enhancement of the effective C : O ratio which can be maintained by the flame, owing to the increased

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* All flow-rates are quoted for 20°C and 1 atmosphere pressure.

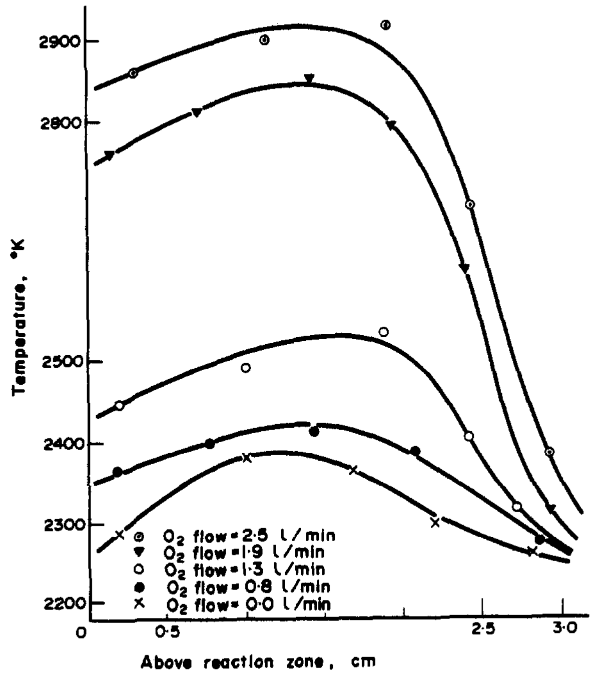

Fig. 2. Effect of oxygen-shielding on flame temperature.

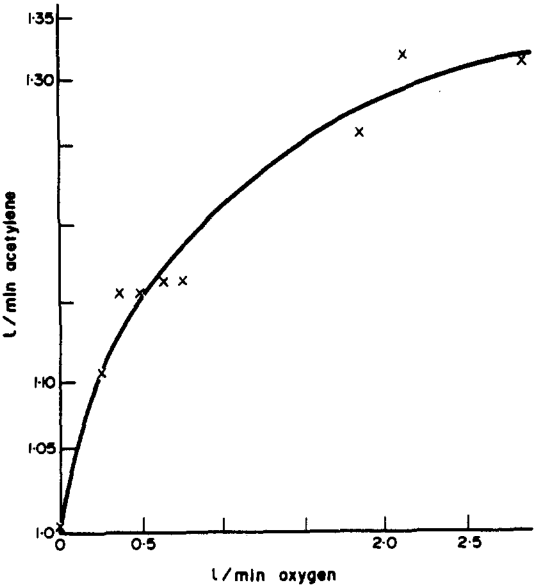

Fig. 3. Dependence of fuel flow on oxygen-shielding.

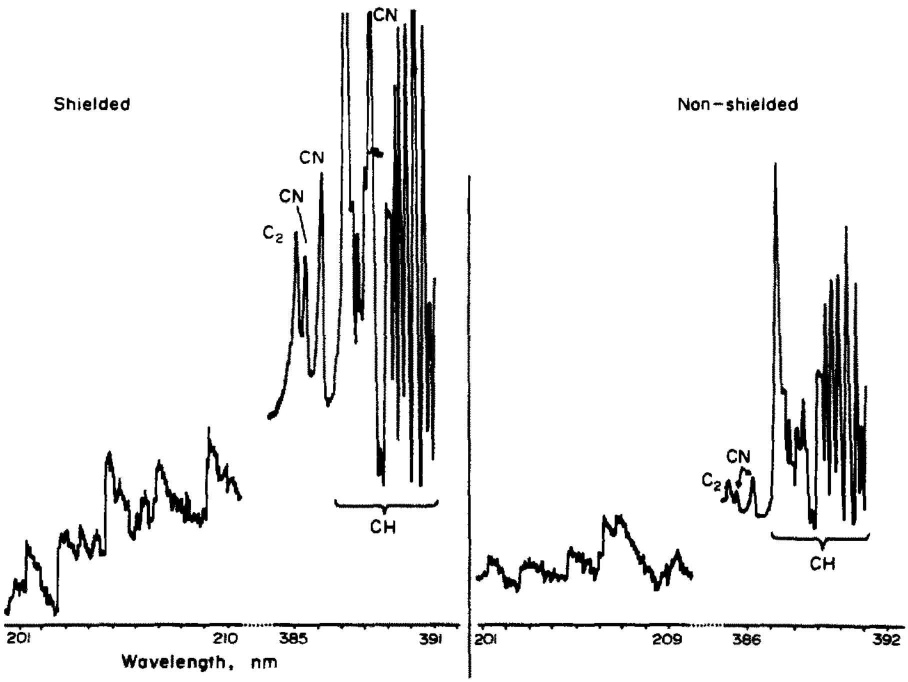

Fig. 4. Spectra of the reaction zone of the shielded and non-shielded flames.

flame temperature after shielding. Under the experimental conditions described here it is considered that the latter mechanism is dominant, for reasons which are discussed at greater length below.

Figures 2 and 3 show "oxygen saturation" of the flame to be achieved at a flow-rate of about 2·5 l/min. Except where otherwise stated, the oxygen flow-rate was therefore preset to this value during all subsequent experiments. However, since both the flame temperature and composition showed only a slight dependence on oxygen flow-rate at this level, and gas turbulence did not become apparent until much higher flow-rates were used, the adjustment was not considered critical and slight variations in oxygen delivery rate could readily be tolerated.

Effect of oxygen-shielding on flame background

Figure 4 shows the spectra of the reaction zones of shielded and non-shielded air–acetylene flames. Regions of the spectrum shown are those covering the CO 'fourth positive' bands between 200·0 and 210·0 nm, and the C_2, CH and CN bands between 385·0 and 393·0 nm. Both spectra were observed with fixed air and acetylene flow-rates of 5·6 and 1·0 l/min, a shielding flow of 2·5 l/min, and with a monochromator slit-width of 20 μm. The spectra show slight enhancement of the CO 'fourth positive' bands, and strong enhancement of C_2, CH and CN emission, within the shielded flame. Similar enhancement effects were also observed outside the spectral regions shown in Fig. 4, for the other bands of the Deslandres–D'Azambuja system and for the CH band heads between 415·2 and 421·6 nm. These enhancement effects are again in accordance with the increased C : O ratio of the shielded flame, deduced from Fig. 3 (see below).

For the purposes of analytical spectroscopy, the flame background of the diffusion

Table 1.

		Sensitivity for 1% absorption, C_S, *ppm*			
Element	Line, *nm*	unshielded	shielded	C_2H_2–N_2O (shielded burner)	C_2H_2–N_2O (ref. 8)
Sn†	224·6	4·1	2·9*	2·8	2·5
Al	309·3	>1000	5·7*	1·6	1·0
Fe	248·3	0·21	0·36	—	—
Cr	357·9	0·29	0·62	—	—
Pb	217·0	0·38	0·69	—	—
Ca	422·7	2·2	0·58*	0·24	0·03
Sr	460·7	4·8	0·65*	0·33	0·06
Mg	285·2	0·012	0·014	0·082	0·02

* A luminous flame was found to give optimum sensitivity for these elements.

† Perkin–Elmer lamp, part no. 303-6074, was used. Lamp current and monochromator slit-width were 12 mA and 17 μm respectively.

A 1000-ppm potassium solution was used as an ionization suppressant for Al, Ca and Sr determinations.

zone rather than that of the primary reaction zone is of major interest. This was found to be dominated by the OH and CH bands between 306·4 and about 325 nm, and by the $CO + O_2$ continuum at wavelengths longer than about 200 nm.[11] The spectra of both the shielded and non-shielded flames are thus qualitatively very similar within the diffusion zone. However, both band and continuum emission showed a maximum intensity increase of about 30-fold in the shielded flame, which must be expected to lead to generally greater noise levels in any analytical application of the latter system.

Preliminary atomic-absorption studies in the oxygen-shielded flame

Figure 3 indicated that the C : O ratio of the reactant gases of the flame is increased by oxygen-shielding. This in turn suggested that the chemical reducing properties of the shielded flame should be enhanced in comparison with those of its non-shielded counterpart.[12] This effect, together with the temperature enhancement shown by Fig. 2, implied that the shielded flame could offer some of the analytical advantages mentioned originally with regard to the premixed oxygen–acetylene flame. Some preliminary studies have accordingly been made, to compare the atomic-absorption sensitivity for both refractory- and non-refractory-oxide-forming elements in the shielded and non-shielded air–acetylene flames, together with the corresponding results obtained with a nitrous oxide–acetylene flame.

For comparative work between the shielded and non-shielded flames, all experimental conditions were kept constant except for the oxygen and acetylene flow-rates. The former was set to 2·5 l/min, when required, and the latter was adjusted to give the optimum sensitivity for the element concerned during any particular determination. A constant air flow of 5·6 l/min was used, and all readings were made at a fixed height in the flame, just above the primary reaction zone. Hence a direct comparison between the shielded and non-shielded flames could be obtained without the necessity of allowing for factors such as the short path-length of the burner, mechanical variations in nebulizer efficiency *etc.* Sensitivity measurements for the nitrous oxide–acetylene flame were obtained at a nitrous oxide flow-rate of 5·6 l/min, and a small correction was made for the associated

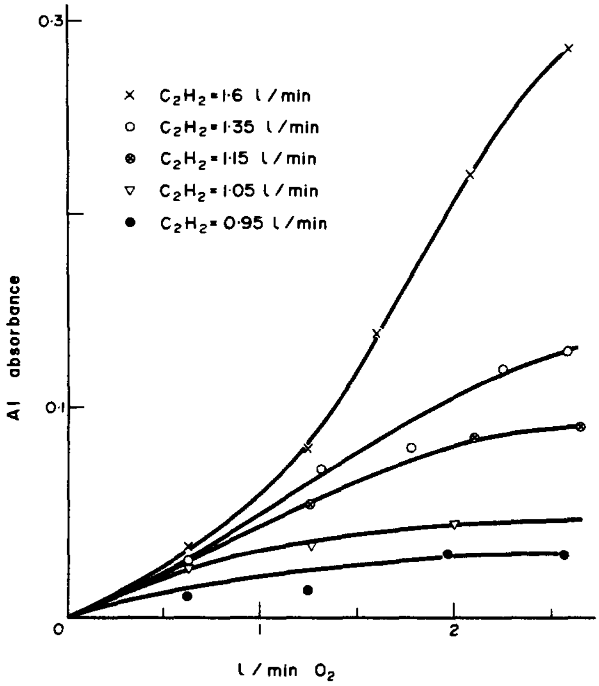

Fig. 5. Variations of Al absorption with fuel and shielding-gas flow-rates.

change in nebulization rate; the fuel flow and burner position were set for maximum absorbance for each element. The results thus obtained are given in Table 1.

The results in Table 1 showed that enhanced sensitivities for elements normally forming oxides stable in the vapour phase could be obtained by using a luminous oxygen-shielded flame. It thus appears that in practice the chemical reducing properties of the shielded flame can be increased by this means to an even greater extent than is suggested by Fig. 3, and this is considered to be due to the initially enhanced temperature of the shielded flame. Thus the initial temperature enhancement in the shielded flame permits the temperature drop associated with the use of a luminous flame to be more readily tolerated in terms of flame atomization efficiency than is the case with the conventional non-shielded air–acetylene flame. The magnitude of the effect is indicated by Fig. 5, showing the effect of fuel flow on the absorption of a 25-ppm aluminium solution in a luminous flame with various shielding flow-rates.

Table 2.

		Change of signal, %	
Element	Interfering ion	Unshielded flame	Shielded flame
Ca	PO_4^{3-}	−16	0
Ca	Al	−27	−6
Fe	SiO_3^{2-}	−43	0
Cr	Fe^{3+}	−53	0
Cr	V^{5+}	−14	−2
Mg	Al^{3+}	−9	0

In addition to the observations described above, a number of common analytical interference effects observed with the conventional air–acetylene flame have also been examined with the shielded flame. The experimental conditions used were those described for the sensitivity determinations above. In each case, the calibration curve from C_s to $3C_s$ (see Table 1) was examined in the presence of a 1000-ppm concentration of the interfering ion, for both the shielded and non-shielded flames, and the change of slope noted. The results thus obtained are given in Table 2.

DISCUSSION AND CONCLUSIONS

It is considered from Figs 3–5, and from the atomic-absorption studies, that the fuel-rich oxygen-shielded flame offers an inherently more chemically reducing environment than does its non-shielded counterpart. This increase of chemical reducing character can probably be attributed directly to the enhanced flame temperature, since it is already known that the C : O ratio of premixed flames measured at the luminous limit increases as the flame temperature is increased by some external means such as pre-heating the reactant gases.[13–15] This conclusion is further supported by the enhanced radical emission from the primary reaction zone, as shown in Fig. 4, observations again suggesting that the results shown in Fig. 3 represent a true increase in C : O ratio at the luminous limit of the flame rather than, for example, deep oxygen entrainment from the shielding gas.

The enhancement of analytical sensitivity for elements such as Al, Sn, Ca, Sr, relative to conventional air–acetylene flames, together with the suppression of chemical interferences also observed, is felt to demonstrate the analytically useful nature of the oxygen-shielded flame as an atom reservoir. In absolute terms, the sensitivities obtained for these elements in all the flames examined were poor, presumably reflecting the rather inefficient nebulizer system used with this burner for reasons of mechanical convenience. Comparison of analytical sensitivity obtained in the shielded flame with the corresponding results for a nitrous oxide–acetylene flame shows the latter flame to be generally superior, particularly in the case of aluminium, a result possibly indicating the inner zone of the shielded flame to be inherently less reducing than that of the nitrous oxide–acetylene flame. Thus it is considered from the present results that a nitrous oxide–acetylene flame is preferable to the shielded air–acetylene flame if optimum analytical sensitivity is to be attained, although it might be possible to improve the performance of the latter by utilizing larger burner heads, to give both a longer absorption path and greater efficiency of aerosol transport to the flame. It is, however, further considered, in view of the advantages of the shielded flame discussed previously, that under conditions where optimum analytical sensitivity is not a dominant requirement the shielded flame may offer a useful alternative to a nitrous oxide–acetylene flame in analytical situations which have hitherto more usually required the latter flame to be employed.

Acknowledgement—The author is indebted to the National Research Council of Canada for a grant in support of this work.

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Zusammenfassung—Es wurde ein Brenner konstruiert, der eine mit Sauerstoff abgeschirmte Luft–Acetylen-Flamme für Atomabsorptionsarbeiten liefert. Die chemischen Reduktionseigenschaften der mit viel Brennstoff betriebenen, mit Sauerstoff abgeschirmten Flamme werden verstärkt durch das höhere C : O-Verhältnis, das man in der Flamme erhalten kann, und durch die direkt oberhalb der Reaktionszone höhere Flammentemperatur. Die Flamme ist ihrem Wesen nach praktisch frei von der Gefahr des Zurückschlagens; sie wird für bestimmte Instrumententypen und für besondere Anwendungen als Alternative zur Lachgas–Acetylen-Flamme angeboten.

Résumé—On a conçu un brûleur qui fournit une flamme air–acétylène protégée de l'oxygène pour le travail d'absorption atómique. Les propriétés réductrices chimiques de la flamme protégée de l'oxygène produite dans des conditions riches en combustible sont accrues par le rapport C : O plus élevé obtenu dans la flamme et par la température de flamme plus élevée juste au-dessus de la zone de réaction. Cette flamme est par inhérence essentiellement exempte du risque de retour de flamme et est présentée comme une alternative à la flamme protoxyde d'azote–acétylène pour l'emploi avec certains types d'équipement et pour des applications particulières.

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SHORT COMMUNICATIONS

COMPUTER PROGRAMME FOR CALCULATION OF ELECTRIC DIPOLE MOMENTS FROM MEASUREMENTS IN SOLUTION

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Although the Debye equation[1,2] was derived for molecules in the vapour phase, few compounds are sufficiently volatile and stable to permit the appropriate electric permittivity measurements to be made over adequate temperature and pressure ranges. Most reported electric dipole moments are consequently derived from measurements made upon a series of dilute solutions in a non-polar solvent. In such a solvent it may be assumed[3,4] that the polarization of the solvent is independent of the solute concentration and that extrapolation to zero solute concentration eliminates any solute–solute interaction. The dipole moment obtained may still differ somewhat from the true vapour phase value, however, because of solute–solvent interactions.

The procedure normally employed is that associated with Halverstadt and Kumler[5] in which a series of dilute solutions with weight fractions W_2 are prepared, their electric permittivities (E), specific volumes (V), and refractive indices (N) measured, and the limiting slopes at zero weight fraction of the plots of E, V, and N^2 against W_2 found. These slopes will be labelled α, β and γ respectively.

The specific solute polarization (p_2) at infinite dilution is given by the expression

$$p_2 = \frac{3V_1}{(E_1 + 2)^2}\alpha + \frac{(E_1 - 1)}{(E_1 + 2)}(V_1 + \beta)$$

where the subscripts 1 and 2 indicate the solvent and solute respectively. The distortion polarization may be equated to the specific refraction r_2 for Na(D) radiation (sometimes taken to be $1{\cdot}05\, r_2$, $1{\cdot}10\, r_2$, or $1{\cdot}15\, r_2$) and is given by an analagous equation, *viz.*

$$r_2 = \frac{3V_1}{(N_1^2 + 2)^2}\gamma + \frac{(N_1^2 - 1)}{(N_1^2 + 2)}(V_1 + \beta)$$

With this approximation the specific orientation polarization is $p_2 - r_2$ and the dipole moment μ is given by

$$\mu = \left[\frac{9kT}{4\pi L} M_2(p_2 - r_2)\right]^{1/2}$$

$$= 0{\cdot}12812(TM_2(p_2 - r_2))^{1/2} \text{ debye}$$

where L is the Avogadro constant, M_2 the solute molecular weight, T the absolute temperature and k Boltzmann's constant. Within experimental error it is generally found in dilute solutions that

$$E = E_1 + \alpha W_2 \tag{1}$$

but if the solute associates or dissociates then

$$E = E_1 + \alpha W_2 + \alpha' W_2^2 \tag{2}$$

is a better representation of the dependence of the experimental results on the weight fraction; analagous expressions hold for the dependence of V and N^2 on W_2.

When it is realized that measurements are made with up to six significant figures on 5–10 solutions it will be appreciated that the computation involved is considerable.

COMPUTER PROGRAMME

The computer programme, written in ALGOL, consists of four nesting blocks.

I (Statement number 0). Data relevant to the solvent and temperature employed are read and certain constants evaluated.

II (Statement number 20). Data for the solutions are read, dielectric constants are calculated from capacity measurements, and specific volumes are calculated from pyknometer weights. The experimental values are printed.

```
STATEMENT
NO.

  0    ‘BEGIN’‘REAL’CONST1,CONST2,CONST3,CONST4,CONST5,
  1    ES,VS,NS,MS,T,M2,X1,X2,X3,X4;
  1    ‘INTEGER’X,I;
  2    SELECT INPUT(1);
  4    SELECT OUTPUT(2);
  5    ES ← READ; VS ← READ; NS ← READ; MS ← READ; T ← READ;
 10    X1 ← READ; X2 ← READ; X3 ← READ; M2 ← READ; X ← READ;
 15    CONST1 ← (ES − 1)/(ES + 2); CONST2 ← 3 * VS/(ES + 2) ↑ 2; CONST3 ← (NS ↑ 2 − 1)/(NS ↑ 2 + 2);
 18    CONST4 ← 3 * VS/(NS ↑ 2 + 2) ↑ 2; CONST5 ← 0.012812 * SQRT(T + 273.15);
 20    ‘BEGIN’‘REAL’‘ARRAY’W[1:X],E[1:X],V[1:X],
 20    N[1:X],NN[1:X],C[1:X + 2];
 20    ‘REAL’A,B,CO,CA,WE,WS,Y,Z;‘INTEGER’J;
 22    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’W[I] ← READ; B ← 1;
 26    ‘FOR’I ← 1‘STEP’1‘UNTIL’X + 2‘DO’C[I] ← READ;
 28    CO ← (C[1] * ES − C[2])/(ES − 1); CA ← C[1] − CO;
 30    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’E[I] ← (C[I + 2] − CO)/CA;
 32    WE ← READ; WS ← READ; Y ← (WS − WE) * VS;
 35    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’‘BEGIN’Z ← READ; V[I] ← Y/(Z − WE)‘END’;
 39    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’‘BEGIN’N[I] ← READ;
 42    ‘IF’N[I] > 0‘THEN’NN[I] ← N[I] ↑ 2‘ELSE’NN[I] ← N[I]‘END’;
 43    ‘IF’ABS(MS − 78) > 1‘THEN’‘GOTO’ S1‘ELSE’WRITETEXT(‘(‘BENZENE’)’); ‘GOTO’L3;
 45    L1: ‘IF’ABS(MS − 88) > 1‘THEN’‘GOTO’L1‘ELSE’WRITETEXT(‘(‘DIOXAN’)’); ‘GOTO’L3;
 47    S1: ‘IF’ABS(MS − 84) > 1‘THEN’‘GOTO’S2‘ELSE’WRITETEXT(‘(‘CYCLOHEXANE’)’);
 48    ‘GOTO’L3; S2: ‘IF’ABS(MS − 154) > 1‘THEN’‘GOTO’L3‘ELSE’WRITETEXT(‘(‘CARBON
 49    ‘(‘1S’)’TETRACHLORIDE’)’);
 50    L3: WRITETEXT(‘(‘‘(‘1C’)’TEMPERATURE’(‘2S’)’’)’); PRINT(T,2,1);
 52    WRITETEXT(‘(‘‘(‘2C’)’SOLUTE’(‘1C’)’MW’(‘2S’)’’)’); PRINT(M2,3,3);
 54    WRITETEXT(‘(‘‘(‘1C’)’W’(‘10S’)’E’(‘8S’)’V’(‘9S’)’N’)’);
 55    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’‘BEGIN’NEWLINE(1);
 58    PRINT(W[I],1,6); PRINT(E[I],1,4); PRINT(V[I],1,5); PRINT(N[I],1,5)‘END’;
 62    ‘BEGIN’‘PROCEDURE’LSF(A,INT,SLOPE,P,K);
 63    ‘VALUE’A; ‘REAL’‘ARRAY’A; ‘REAL’INT,SLOPE,P,K;
 66    ‘BEGIN’‘REAL’C,D,E,F,G,H,SUM; C ← D ← E ← F ← G ← SUM ← 0;I ← 1;
 69    NEXT: ‘IF’A[I] < 0‘THEN’‘GOTO’LAST‘ELSE’
 69    C ← C + A[I]; D ← D + 1; E ← E + W[I]; F ← F + A[I] * W[I]; G ← G + W[I] ↑ 2; LAST: I ← I + 1;
 75    ‘IF’I < X + 0.2‘THEN’‘GOTO’NEXT‘ELSE’
 75    H ← D * G − E ↑ 2; INT ← (C * G − F * E)/H; SLOPE ← (D * F − C * E)/H; I ← 1;
 79    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’‘BEGIN’‘IF’A[I] > 0‘THEN’
 81    SUM ← SUM + (INT + SLOPE * W[I] − A[I]) ↑ 2‘ELSE’‘END’;
 82    K ← 0.6745 * SQRT((D * SUM)/((D − 2) * (D * G − E ↑ 2))); P ← SQRT(SUM/(D − 1))‘END’;
 83    ‘PROCEDURE’LSF2(A,INT,SLOPE,AL1,P,K);
 85    ‘VALUE’A; ‘REAL’‘ARRAY’A; ‘REAL’INT,SLOPE,AL1,P,K;
 88    ‘BEGIN’‘REAL’N,B,C,D,F,G,H,L,SUM,R,MA1,MA2.MA3.MA4;
 88    N ← B ← C ← D ← F ← G ← H ← L ← SUM ← 0;I ← 1;
 91    LA1: ‘IF’A[I] < 0‘THEN’‘GOTO’LA2‘ELSE’N ← N + A[I]; B ← B + 1; C ← C + W[I];
 94    R ← W[I] ↑ 2; D ← D + R; F ← F + A[I] * W[I]; G ← G + W[I] * R; L ← L + R ↑ 2; H ← H + A[I] * R;
100    LA2: I ← I + 1; ‘IF’I < X + 0.2‘THEN’‘GOTO’LA1‘ELSE’
101    MA1 ← D * L − G ↑ 2; MA2 ← C * L − G * D; MA3 ← C * G − D ↑ 2; MA4 ← B * MA1 − C * MA2 + D * MA3;
105    INT ← (N * MA1 − F * MA2 + H * MA3)/MA4; MA1 ← C * H − D * F; MA2 ← B * H − D * N; MA3 ← B * F − C * N;
109    SLOPE ← (D * MA1 − G * MA2 + L * MA3)/MA4; AL1 ← (C * MA1 − D * MA2 + G * MA3)/(−MA4);
111    ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO’‘BEGIN’‘IF’A[I] > 0‘THEN’
113    SUM ← SUM + (INT + SLOPE * W[I] + AL1 * W[I] ↑ 2 − A[I]) ↑ 2‘ELSE’‘END’;
114    K ← 0.6745 * SQRT((B * SUM)/((B − 2) * (B * D − C ↑ 2))); P ← SQRT(SUM/(B − 1))‘END’;
115    ‘PROCEDURE’REJECT2(Q,R,S,U,INT,SLOPE,AL1,P,K);
117    ‘VALUE’R,S; ‘REAL’‘ARRAY’Q; ‘REAL’R,S,U,INT,SLOPE,AL1,P,K;
120    ‘BEGIN’‘INTEGER’J; ‘REAL’INC,MAX1,MAX2,NO1,NO2,U1,U2,U3,U4,U5;
121    MAX1 ← 0; J ← 1;
124    LA8: ‘IF’Q[J] < 0‘THEN’‘GOTO’LA7‘ELSE’INC ← ABS(R + S * W[J] + U * W[J] ↑ 2 − Q[J]);
125    ‘IF’INC > MAX1‘THEN’‘GOTO’LA5‘ELSE’
125    ‘IF’INC > MAX2‘THEN’‘GOTO’LA6‘ELSE’‘GOTO’LA7;
126    LA5: MAX2 ← MAX1; NO2 ← NO1; MAX1 ← INC; NO1 ← J; ‘GOTO’LA7;
131    LA6: MAX2 ← INC; NO2 ← J; LA7: J ← J + 1;
134    ‘IF’J < X + 0.2‘THEN’‘GOTO’LA8‘ELSE’J ← NO2; Q[J] ← − Q[J];
136    ‘IF’X4 > 1‘THEN’LSF2(Q,U1,U2,U3,U4,U5)‘ELSE’LSF(Q,U1,U2,U4,U5);
137    Q[J] ← − Q[J]; J ← NO1; Q[J] ← − Q[J];
140    ‘IF’X4 > 1‘THEN’LSF2(Q,INT,SLOPE,AL1,P,K)‘ELSE’
140    ‘BEGIN’LSF(Q,INT,SLOPE,P,K);AL1 ← U3 ← 0‘END’;
143    ‘IF’P > U4‘THEN’‘BEGIN’Q[J] ← − Q[J]; Z ← J ← NO2; Q[J] ← − Q[J];
147    INT ← U1; SLOPE ← U2; AL1 ← U3; P ← U4; K ← U5‘END’‘ELSE’Z ← J‘END’;
151    ‘BEGIN’‘REAL’E1,ALPHA,A1,PE,TE,V1,BETA,B1,PV,TV,NN1,GAMMA,G1,PNN,TNN,K,
152    DM,RD,TP,OP,P,INT,SLOPE,AL1,N1,PSE,PSV,PSNN;
152    TE ← TV ← TNN ← A1 ← B1 ← G1 ← Y ← 0;
154    ‘IF’X1 > 1‘THEN’LSF2(E,E1,ALPHA,A1,PE,PSE)‘ELSE’LSF(E,E1,ALPHA,PE,PSE);
```

```
STATEMENT
NO.

155         ‘IF’X2 > 1‘THEN’LSF2(V,V1,BETA,B1,PV,PSV)‘ELSE’LSF(V,V1,BETA,PV,PSV);
156         ‘IF’X3 > 1‘THEN’LSF2(NN,NN1,GAMMA,G1,PNN,PSNN)
156         ‘ELSE’LSF(NN,NN1,GAMMA,PNN,PSNN);
157         REPEAT: WRITETEXT(‘(“(‘3C12S’)‘RESIDUALS’(‘1C1S’)’E
157         ‘(‘10S’)‘V’(‘10S’)‘NN’(‘1C’)”)’);
158         ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO“BEGIN“IF’E[I] < 1‘THEN’SPACE(11)‘ELSE’
160         PRINT(E1 + ALPHA * W[I] + A1 * W[I] ↑ 2 − E[I],2,5);
161         ‘IF’V[I] < 0‘THEN’SPACE(11)‘ELSE’PRINT(V1 + BETA * W[I] + B1 * W[I] ↑ 2 − V[I],2,5);
162         ‘IF’NN[I] < 1‘THEN“GOTO’L‘ELSE’PRINT(NN1 + GAMMA * W[I] + G1 * W[I] ↑ 2 − NN[I],2,5);
163         L: NEWLINE(1)‘END’;
164         WRITETEXT(‘(“(‘1C’)‘PROBABLE’(‘2S’)‘ERRORS’(‘1C’)”)’);
165         PRINT(0.6745 * PE,2,5); PRINT(0.6745 * PV,2,5); PRINT(0.6745 * PNN,2,5);
168         WRITETEXT(‘(“(‘2C’)‘INTERCEPTS’(‘1C’)”)’);
169         PRINT(E1,2,4); PRINT(V1,3,5); PRINT(NN1,2,5);
172         WRITETEXT(‘(“(‘1C’)‘SLOPES’(‘1C’)”)’);
173         PRINT(ALPHA,2,3); PRINT(BETA,4,3); PRINT(GAMMA,4,3);
176         NEWLINE(1); ‘IF’X1 > 1‘THEN’PRINT(A1,6,0)‘ELSE’SPACE(9);
178         ‘IF’X2 > 1‘THEN’PRINT(B1,8,0)‘ELSE’SPACE(11); ‘IF’X3 > 1‘THEN’PRINT(G1,8,0);
180         RD ← M2 * (CONST4 * GAMMA + CONST3 * (V1 + BETA));
181         TP ← M2 * (CONST4 * ALPHA + CONST1 * (V1 + BETA));
182         OP ← TP − RD; ‘IF’OP < 0‘THEN“BEGIN’B ← DM ← 0; ‘GOTO’L9‘END’
185         ‘ELSE’DM ← CONST5 * SQRT(OP);
186         A ← M2 * (CONST4 * PSE + CONST1 * PSV); B ← CONST5 * SQRT(OP + A); L9:
188         WRITETEXT(‘(“(‘2C’)‘POLARIZATIONS’(‘1C’)‘DISTORTION’)’); PRINT(RD,4,2);
190         WRITETEXT(‘(“(‘1C’)‘TOTAL’)’); PRINT(TP,9,2);
192         WRITETEXT(‘(“(‘1C’)‘ORIENTATION’)’);PRINT(OP,3,2);
194         WRITETEXT(‘(“(‘2C’)‘DIPOLE’(‘2S’)‘MOMENT’)’);
195         PRINT(DM,2,3); WRITETEXT(‘(‘ERROR’)’); PRINT(ABS(B − DM),2,3);
198         TE ← TE + 0.3; TV ← TV + 0.3; TNN ← TNN + 0.3; Y ← Y − 0.1;
202         ‘IF’(X + 10 * Y) < 3.2‘THEN“GOTO’L10‘ELSE’
202         ‘IF’TE > 1‘THEN“GOTO’VOLUME‘ELSE’X4 ← X1;
203         REJECT2(E,E1,ALPHA,A1,INT,SLOPE,AL1,P,K); ‘IF’P > (1 + Y) * PE
204         ‘THEN“BEGIN’TE ← 2; E[Z] ← − E[Z]; ‘GOTO’VOLUME‘END“ELSE’
207         E1 ← INT; ALPHA ← SLOPE; A1 ← AL1; PE ← P; PSE ← K;
212         VOLUME: ‘IF’TV > 1‘THEN“GOTO’REFRACTION‘ELSE’X4 ← X2;
213         REJECT2(V,V1,BETA,B1,INT,SLOPE,AL1,P,K);‘IF’P > (1 + Y) * PV
214         ‘THEN“BEGIN’TV ← 2; V[Z] ← − V[Z]; ‘GOTO’REFRACTION‘END“ELSE’
217         V1 ← INT; BETA ← SLOPE; B1 ← AL1; PV ← P; PSV ← K;
222         REFRACTION: ‘IF’TNN > 1‘THEN“GOTO’TEST‘ELSE’X4 ← X3;
223         REJECT2(NN,NN1,GAMMA,G1,INT,SLOPE,AL1,P,K); ‘IF’P > (0.9 + Y) * PNN
224         ‘THEN“BEGIN’TNN ← 2; NN[Z] ← − NN[Z]; ‘GOTO’TEST‘END“ELSE’
227         NN1 ← INT; GAMMA ← SLOPE; G1 ← AL1; PNN ← P; PSNN ← K;
232         TEST: ‘IF’TE < 1‘THEN“GOTO’REPEAT‘ELSE“IF’TV < 1‘THEN“GOTO’REPEAT‘ELSE’
232         ‘IF’TNN < 1‘THEN“GOTO’REPEAT‘ELSE’NEWLINE(2);
233         L10: WRITETEXT(‘(“(‘2C11S’)‘INCREMENTS’(‘1C6S’)‘6’(‘10S’)‘4’(‘7S’)‘5
233         ‘(‘7S’)‘5’(‘1C’)‘W’(‘1S’)‘X’(‘1S’)‘10’(‘5S’)‘E’(‘1S’)‘X’(‘1S’)‘10
233         ‘(‘2S’)‘V’(‘1S’)‘X’(‘1S’)‘10’(‘2S’)‘N’(‘1S’)‘X’(‘1S’)‘10’)’);
234         N1 ← SQRT(NN1);
235         ‘FOR’I ← 1‘STEP’1‘UNTIL’X‘DO“BEGIN’NEWLINE(1);
238         PRINT(W[I] * 10 ↑ 6,5,0); PRINT((ABS(E[I]) − E1) * 10 ↑ 4,6,0);
240         PRINT((ABS(V[I]) − V1) * 10 ↑ 5,5,0), PRINT((N[I] − N1) * 10 ↑ 5,5,0)‘END’
241         ‘END“END“END“END’
```

III (Statement number 62). This block contains three procedures.

(*a*) *Procedure LSF*. A least-squares method is used to fit the experimental quantities to a linear dependence on solute weight fraction [equation (1)]. The residuals, equal to the differences between calculated and experimental values, are tabulated, and the probable errors, the intercepts (E_1, V_1 and N_1^2), and the slopes (α, β and γ) are printed.

(*b*) *Procedure LSF 2*. This performs the same function as the procedure LSF but for a quadratic dependence upon W_2 [equation (2)]. The parameters α', β' and γ' are printed below the values of α, β and γ.

(*c*) *Procedure REJECT 2*. The effect of ignoring in turn the experimental points which give the two largest residuals in the least-squares method is examined and the one which produces the greatest reduction in the probable error is rejected.

IV (Statement number 151). This final block controls the calculation and the printing of the results. The calculation is repeated with up to three experimental values of E, V and N rejected for each and the investigator must then decide which result to accept, based upon the residuals, the improvement in the probable errors, and the number of solutions employed.

Finally a table is printed of the increments in the experimental values of the solutions above the last set of intercepts E_1, V_1 and N_1 at zero weight fraction.

The dipole moment is based upon taking the specific distortion polarization as equal to the specific refraction r_2 at the wavelength employed; if it is desired to take it as xr_2 then statement 180 should be altered to read

```
RD = x * M2 * (CONST4 * GAMMA + CONST3 * (V1 + BETA));
```

The error quoted for the dipole moment is based upon the extreme values obtained by using ($\alpha \pm$ probable error in α) and ($\beta \pm$ probable error in β) in place of the gradients α and β.

Data

The deck of data cards should be punched as follows.

1. *Solvent data*

ES, VS, NS, MS, T,. The electric permittivity, specific volume, refractive index and molecular weight of the solvent and the temperature in °C.

2. *Linear or quadratic relationships*

X1, X2, X3,. For a linear relationship [equation (1)] of the measured properties E, V and N^2 respectively against W_2 these have values <1 but for a quadratic relationship [equation (2)] they must be >1.

3. *Solution data*

M2, X,.	Solute molecular weight. Number of solutions(X).
W_a,W_b,...,W_x,.	Solute weight fractions in solutions a, b, ..., X.
C_0,C_1,C_a,C_b,...,C_x,.	Capacity of dielectric cell with air, solvent and solutions a,b,...,X respectively between its plates. The capacity of the leads and other stray capacities are calculated (equal to $(C_0 E_1 - C_1)/(E_1 - 1)$ and subtracted from the capacity reading for each solution before its dielectric constant is calculated.
WE,W_1,Z_a,Z_b,...,Z_x,.	Weight of pyknometer empty, filled with solvent, and filled with the solutions.
N_a,N_b,...,N_x,.	Refractive index of each solution.

The same sequence of solutions must be maintained for each experimental quantity; if a particular result is not available for a solution then a number <0 must be inserted for its corresponding capacity, pyknometer weight or refractive index.

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Summary—An ALGOL computer programme is described for the calculation of an electric dipole moment from measurements made on dilute solutions in a non-polar solvent.

Zusammenfassung—Ein ALGOL-Computerprogramm zur Berechnung eines elektrischen Dipolmoments aus Messungen an verdünnten Lösungen in einem unpolaren Lösungsmittel wird beschrieben.

Résumé—On décrit un programme d'ordinateur ALGOL pour le calcul d'un moment dipolaire électrique à partir de mesures faites sur des solutions diluées dans un solvant non polaire.

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DETERMINATION OF COPPER AND MOLYBDENUM IN THE HARD DENTAL TISSUES OF RATS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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The analysis of teeth for copper and molybdenum was undertaken to investigate the uptake of these two elements by the hard dental tissues of rats. The inorganic matrix of teeth is considered to be apatitic in nature and can be represented by the simple formula $Ca_{10}(PO_4)_6X_2$ where X is most often hydroxyl or fluoride. This matrix behaves as an ion-exchange system, giving rise to the unequal distribution of various trace elements throughout the teeth. Both copper[1] and molybdenum[2] have been determined in erupted human teeth by neutron-activation analysis. However, in the case of molybdenum, difficulties arose because of matrix effects and the small sample weight.

Early determinations of molybdenum by atomic absorption, by David,[3,4] employed a fuel-rich air–acetylene flame. However, significant chemical interference occurred in the presence of calcium and phosphorus. Amos[5] showed that chemical interferences occurred to a lesser degree with a nitrous oxide–acetylene flame and also that the sensitivity was higher. In view of these findings the nitrous oxide–acetylene flame was considered more suitable for this investigation, as high concentrations of calcium and phosphorus were present in the teeth and levels of molybdenum were low.

In a preliminary calibration with aqueous solutions of copper and molybdenum the sensitivities were found to be of the order of 0·15 and 0·5 ppm respectively. However, it was expected that the levels of copper and molybdenum in the aqueous solutions derived from the teeth would be below these. Consequently, liquid–liquid extraction methods, which would simultaneously concentrate the analyte and eliminate some of the interfering elements, were considered. Solvent extraction also has the additional advantage of increasing the sensitivity, if the organic solution is sprayed into the flame.

Malissa and Schoffmann[6] used ammonium pyrrolidine dithiocarbamate (APDC) for complexation and extraction of a number of heavy metals; further additions have been made to this list by Mulford.[7] APDC has been widely used for extracting copper, for example from plants and soils by Allan[8] and from urine by Berge.[9] Brooks[10] simultaneously extracted copper, cobalt, iron, lead, nickel and zinc from sea-water with APDC, and Butler[11] successfully used the reagent for the extraction of molybdenum from plant materials.

EXPERIMENTAL

Apparatus

A Perkin–Elmer model 303 atomic-absorption spectrophotometer was used with a standard air–acetylene burner head (0·0115 × 4 in.) for the copper determination and the flat-topped nitrous oxide–acetylene burner head (0·019 × 2 in.) for the molybdenum. The recorder read-out accessory and a Hitachi recorder were used. Acetylene was used as fuel for both analytes (2·4 l./min for Cu and 5·6 l./min for Mo) and the oxidant was air for copper (14·6 l./min) and nitrous oxide for molybdenum (12·5 l./min). The spectral sources were 'Intensitron' hollow-cathode lamps, the 324·7-nm(Cu) and 313·2-nm(Mo) lines being used.

Procedure

The teeth were dried in a hot-air oven at 105° for 48 hr, then 1 g of tooth sample was digested in 3 ml of concentrated (62%) perchloric acid in a Kjeldahl flask. When digestion was complete, the solution was transferred quantitatively to a 50-ml graduated flask and diluted to volume. A small portion was withdrawn and the pH checked to ensure it was in the desired range 1·0–1·4. Then 1 ml of aqueous 5% w/v APDC solution was added to 40 ml of the sample solution in a separating funnel, followed by 4 ml of methyl isobutyl ketone (MIBK). The mixture was shaken for 3 min and the phases allowed to separate for 4 min. The aqueous phase was discarded and the organic phase aspirated into an air–acetylene flame to analyse for copper and into a fuel-rich nitrous oxide–acetylene flame to analyse for molybdenum.

Suitable copper and molybdenum standards in a matrix corresponding to the levels found in rat's teeth by Mansell[12] were used for the calibration.

RESULTS AND DISCUSSION

Preliminary investigation

Complex formation between APDC and copper or molybdenum occurs under acid conditions, so the extraction into MIBK was tested over a wide range of acidity, varied with perchloric acid, which was used for the dissolution of the teeth. The optimum pH range for copper extraction was 1·2–1·7 and for molybdenum 1·0–1·4. It was found that the copper absorption gradually fell but the molybdenum absorption increased as the volume of APDC solution (1% w/v) used was increased from 1 ml. The optimum volume for molybdenum was 5 ml (or 1 ml of a 5% solution).

Since both copper and molybdenum are readily chelated with APDC and extracted into MIBK, they were extracted simultaneously in the analysis of the teeth. Because the level of molybdenum in teeth is lower than that of copper, the extraction conditions were selected to favour molybdenum (*i.e.*, pH 1·0–1·4; the digestion procedure always gave a final pH of about 1·1 for the 50 ml of sample solution). Simultaneous extraction had the advantage that more sample was available for the single extraction and sample preparation time was greatly reduced. The maximum error that could be caused in the copper result by variation of the pH over the range 1·0–1·4 was about 2·5%.

The APDC/MIBK extraction resulted in enhanced sensitivity for both analytes, the absorption for copper being almost doubled and that for molybdenum increased fourfold.

Extraction studies

Teeth contain 36% calcium and 17% phosphorus (w/w), and the chief trace elements present in rat's teeth were found by Mansell[12] to be 144 ppm iron, 24 ppm zinc, 1·8 ppm manganese, <1·3 ppm cobalt and <0·5 ppm nickel.

Precision, interference, and recovery studies were made with standards containing 7350 ppm calcium, 3480 ppm phosphorus, 3·0 ppm iron, 0·5 ppm zinc, 0·04 ppm manganese, 0·03 ppm cobalt and 0·01 ppm nickel. These concentrations gave a matrix equivalent to 1 g of tooth treated to give 50 ml of solution. In all the studies, 40 ml of sample solution were extracted with 4 ml of MIBK.

An estimate of the precision of the method was obtained from the results for five samples containing 0·2 ppm copper and five containing 0·8 ppm molybdenum. These samples gave a mean absorbance value of 0·164 for copper and 0·121 for molybdenum. The standard deviation was 0·0008 for copper and 0·0012 for molybdenum, which corresponds to coefficients of variation of 0·5 and 1·0% respectively.

Table 1 shows the results of recovery studies.

Table 1. Recovery studies on teeth

Element	Present, *ppm*	Added, *ppm*	Found, *ppm*	Recovery, %
Mo	0·15	0·05	0·196	98·0
	0·15	0·10	0·247	98·8
	0·15	0·15	0·292	97·0
Cu	5·2	1·0	6·18	99·7
	5·2	1·5	6·70	100·0
	5·2	2·0	7·20	100·0

The results of interference studies are shown in Table 2. Ions were considered as not interfering when they produced an error in absorbance of less than twice the coefficient of variation. The copper and molybdenum levels used were chosen in accordance with those found attainable in the teeth of rats fed on diets enriched in copper and molybdenum.

Calcium and phosphorus interfered in both analyses, but the effect was offset by the presence of iron, and of zinc in the case of copper determination. Copper interfered in the molybdenum determination.

When chemical interferences occur the method of standard addition is ideal, but at least three and possibly four sample aliquots are required for satisfactory results. Because of the small sample weight available in this study, it was impossible to obtain three suitable aliquots which had Cu and Mo concentrations above the limit of detection. Teeth from a large number of rats were pooled to give two samples for analysis either by the standard-addition method or by calibration with standards of a matrix equivalent to that of the teeth. The levels found were 6·50 ppm Cu and 0·21 ppm Mo by standard addition and 6·30 ppm Cu and 0·23 ppm Mo by calibration. Both methods were considered satisfactory since the samples were pooled.

Table 2. Interference studies

Concn. in aqueous phase,* *ppm*	Relative absorption, %	
	Copper	Molybdenum
No additions	100	100
Ca (7350), P (3480)	92	94
Fe (3), Ca, P	94	97
Zn (0·5), Fe, Ca, P	97	95
Mn (0·04), Zn, Fe, Ca, P	97	95
Co (0·03), Mn, Zn, Fe, Ca, P	97	95
Ni (0·01), Co, Mn, Zn, Fe, Ca, P	97	95
Mo (0·6), Ni, Co, Mn, Zn, Fe, Ca, P	97	—
Cu (0·12), Ni, Co, Mn, Zn, Fe, Ca, P	—	90

* The concentrations are not repeated in the Table, and are to be understood as referring to all the mixtures.

CONCLUSION

The analysis of the teeth for copper and molybdenum was very rapid and straightforward, owing to the simultaneous extraction with APDC. The precision of the method was acceptable, and the results of the recovery test indicated that the extraction procedure was reliable.

Because of possible chemical interferences it would have been desirable to use the method of standard addition. However, this was not possible on account of the number of sample aliquots required for each determination by this method and the small amount of sample available. Interference effects were readily overcome by the use of standards with a matrix similar to that of the sample.

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Summary—The measurement of uptake of copper and molybdenum from the diet into rat's teeth required the use of an accurate but rapid method of analysis. The simultaneous extraction of copper and molybdenum with APDC from the sample, combined with atomic absorption, proved to be both accurate and reliable. Interference from other elements present in the sample was easily overcome by the use of standards with a matrix equivalent to that of the teeth.

Zusammenfassung—Die Messung der Aufnahme von Kupfer und Molybdän aus dem Futter in die Zähne von Ratten erforderte eine genaue, aber rasche Analysenmethode. Die gleichzeitige Extraktion von Kupfer und Molybdän mit APDC aus der Probe und Atomabsorption erwiesen sich als genau und zuverlässig. Die Störung durch andere in der Probe vorhandene Elemente ließ sich leicht durch die Verwendung von Standards umgehen, die diselbe Matrix besaßen wie die Zähne.

Résumé—La mesure de la fixation dans les dents de rat du cuivre et du molybdène de la ration alimentaire a nécessité l'emploi d'une méthode d'analyse précise mais rapide. L'extraction simultaneé du cuivre et du molybdène de l'échantillon par l'APDC, combinée avec l'absorption atomique, s'est révélée être à la fois précise et sûre. L'interférence d'autres éléments présents dans l'échantillon a été aisément surmontée par l'emploi d'étalons avec une matrice équivalente à celle de la dent.

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SPECTROPHOTOMETRIC DETERMINATION OF ASCORBIC ACID WITH POTASSIUM HEXACYANOFERRATE(III)

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The reaction between hexacyanoferrate(III) and ascorbic acid has been used by several workers for visual, potentiometric, amperometric and photometric titrations of both ascorbic acid and hexacyanoferrate(III).[1-8] In our earlier work[9-11] the same reaction has been used as the basis for spectrophotometric determinations of microquantities of the reactants by using the total catalytic decomposition of the hexacyanoferrate(II) formed in the process. Since acid and alkaline aqueous solutions of hexacyanoferrate(III) show a rather intense absorption maximum in the visible spectral region at 420 nm ($\varepsilon = 1{\cdot}01 \times 10^3$ l. mole^{-1} . cm^{-1}) where the reaction products [hexacyanoferrate(II) and dehydroascorbic acid] do not absorb,[12,13] it is obvious that a determination of ascorbic acid with hexacyanoferrate(III) is feasible by measuring the absorbance of the reaction mixture at 420 nm against a reagent blank or water.

In this paper we present the optimum conditions necessary for the direct spectrophotometric determination of ascorbic acid with hexacyanoferrate(III). This new procedure for the determination of ascorbic acid is accurate, more rapid, simpler and completely different from methods already published where hexacyanoferrate(III) was used as a reagent. Here it is used to determine the quantity of ascorbic acid in some pharmaceutical preparations (tablets and injections).

EXPERIMENTAL

Apparatus

The absorbances were measured with a Unicam SP 600 spectrophotometer, with 1-cm glass cells. A pH-meter with a saturated calomel-glass electrode system was used for the pH measurements, accurate to ±0·05 pH units.

Reagents

All chemicals used were of analytical-reagent grade.

McIlvaine buffer, pH = 5·2, was prepared by mixing 107·2 ml of 0·2*M* disodium hydrogen phosphate and 92·8 ml of 0·1*M* citric acid.

Potassium hexacyanoferrate(III) solution, $5 \times 10^{-3}M$, was prepared from Merck reagent. The solution remains stable for a few weeks if protected from light.

Ascorbic acid solution, approximately $1 \times 10^{-3}M$ (0·0180 g/100 ml), was prepared from the Riedel reagent (99·7%) and standardized against 0·1*M* sodium hydroxide.[14] Only fresh solutions were used for the spectrophotometric measurements, because of their low stability.

The analysed tablets and injections containing ascorbic acid were obtained on the local market. Their solutions were also prepared immediately before use, and 2 ml of the sample solution contained about 200 μg of ascorbic acid.

All glassware was washed with redistilled water and all the solutions and subsequent dilutions were made with redistilled water because of the decomposition of ascorbic acid by traces of metallic impurities.

Procedure

To 2 ml of McIlvaine buffer (pH 5·2) add 1 ml of $5 \times 10^{-3}M$ hexacyanoferrate(III) and 2 ml of sample solution containing about 200 μg of ascorbic acid. Mix the solution, place the sample in the 'check' position and the reagent blank in the 'measure' position of the spectrophotometer and compare at 420 nm. This arrangement gives absorbances which are a direct measure of the hexacyanoferrate(III) reduced by the ascorbic acid. Find the amount of ascorbic acid by reference to a calibration curve or a calibration equation. Measure immediately after mixing the reactants or within a period of 3 hr.

Résumé—La mesure de la fixation dans les dents de rat du cuivre et du molybdène de la ration alimentaire a nécessité l'emploi d'une méthode d'analyse précise mais rapide. L'extraction simultaneé du cuivre et du molybdène de l'échantillon par l'APDC, combinée avec l'absorption atomique, s'est révélée être à la fois précise et sûre. L'interférence d'autres éléments présents dans l'échantillon a été aisément surmontée par l'emploi d'étalons avec une matrice équivalente à celle de la dent.

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Prepare the calibration curve from a series of standard solutions containing between 45 and 360 μg of ascorbic acid in 2 ml and proceed as described above.

RESULTS AND DISCUSSION

The quantitativeness of the reaction and the rate at which ascorbic acid reduces hexacyanoferrate(III) depend on various factors,[15] principally the pH and the kind of buffer. Acetate buffer is not suitable, and the Britton-Robinson buffers can be used only in a very narrow region around pH 6. McIlvaine's buffer proved most suitable, and the reduction rate is satisfactory in the pH range from 4 to 6 (Fig. 1). Below pH 4 the reduction rate is slow and after a certain time the reaction mixtures become green, *i.e.*, Prussian blue is produced.[16] Above pH 6, only an hour after mixing of the reactants there is a considerable reducing effect of dehydroascorbic acid on hexacyanoferrate(III), which other authors have already found.[1,7] It is therefore optimal to work at about pH 5. The reduction is then rapid and even over a longer time interval dehydroascorbic acid has no influence.

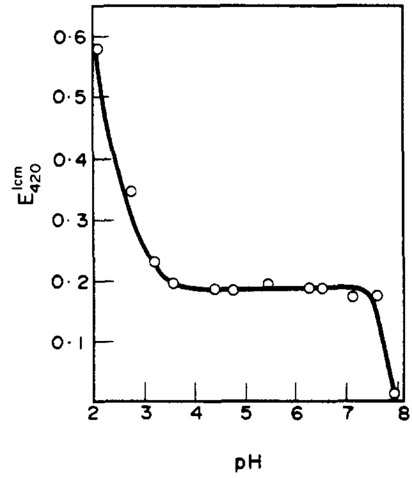

Fig. 1. Dependence of reaction between hexacyanoferrate(III) and ascorbic acid on pH: [hexacyanoferrate(III)] = 1 × $10^{-3}M$; [ascorbic acid] = 0·4 × $10^{-3}M$; measured against water 5 min after mixing.

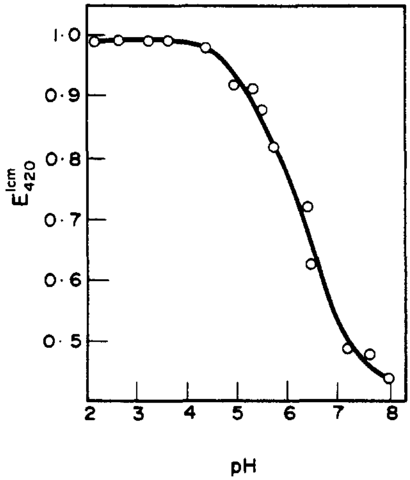

Fig. 2. Dependence of reaction between hexacyanoferrate(III) and uric acid on pH: [hexacyanoferrate(III)] = 1 × $10^{-3}M$; [uric acid] = 0·25 × $10^{-3}M$; measured against water 5 min after mixing.

The possibility of working with potassium hydrogen carbonate instead of a buffer, as recommended by some authors,[6,8] has been examined. The addition of 5–10 mg of potassium hydrogen carbonate is sufficient but the reaction mixtures are less stable and the interferences by foreign substances more pronounced because of the higher pH.

When McIlvaine buffer is used the temperature (18–35°) and time (up to 3 hr) do not influence the reaction. The absorbance can therefore be measured immediately after mixing the reactants or within 3 hr.

The amount of ascorbic acid that can be determined by the suggested method is limited by the concentration of hexacyanoferrate(III), the maximum (360 μg) corresponding to a 20% excess of the reagent. With a hexacyanoferrate(III) concentration of 1 × $10^{-3}M$ in the reaction mixture (absorbance of reagent blank 1·012) the most accurate results are obtained by analysing samples containing 180–270 μg of ascorbic acid (absorbance measured 0·4–0·6).

A 200-fold amount (w/w) of glucose, urea, citric and tartaric acids, a 50-fold excess of creatine and a 2-fold excess of creatinine do not interfere, but very small quantities or uric acid (as sodium urate) give positive errors. At pH >3·5 uric acid itself reduces hexacyanoferrate(III), especially at higher pH values (Fig. 2). In general all agents that reduce hexacyanoferrate(III) or oxidize hexacyanoferrate(II) at pH 5·2 will interfere. So do all substances that absorb at 420 nm.

Ten replicate analyses of a standard ascorbic acid solution over a period of five consecutive days gave a relative standard deviation of ±1·3% at the 225-μg level.

Good reproducibility, accuracy and greater simplicity than that of most procedures used so far, make this technique very satisfactory in laboratory practice. The measurements can also be made on a Pulfrich visual photometer with a blue filter S 42 or S 43. The proposed procedure could also be used for determination of ascorbic acid in all natural products (fruits, juices, plant tissues, *etc.*) containing ascorbic acid, provided they are not appreciably coloured.

Table 1. Ascorbic acid determination in some pharmaceutical preparations

	Ascorbic acid, *g*			
Preparation	Iodimetric method[17]	Proposed method	Average with 95% confidence limit*	Rel. std. devn. %
Vitamin C injections	0·476	0·473	0·509 ± 0·080	6·4
"Pliva" Zagreb	0·505	0·533		
0·500 g/inj.	0·515	0·524		
Vitamin C tablets	0·494	0·505	0·492 ± 0·030	2·4
"Pliva" Zagreb	0·473	0·489		
0·500 g/tabl.	0·496	0·481		

* Calculated by means of Student's *t*.

Table 2. Recovery of ascorbic acid

	Ascorbic acid, *μg*					
Preparation	In sample	Added	Total	Found	Recovery, %	
Vitamin C injections	114	90	204	209	102·5	101·7
"Pliva" Zagreb	114	180	294	297	101·0	
Vitamin C tablets	64	90	154	158	102·6	99·7
"Pliva" Zagreb	64	180	244	239	98·0	
	64	270	334	329	98·5	

The proposed method has been used for the determination of ascorbic acid in some pharmaceutical preparations (tablets and injections) containing ascorbic acid. Table 1 presents the results and comparison with the iodimetric method.[17] Table 2 gives the results of recovery experiments. All results are in good agreement and show that the method is applicable to such determinations.

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Summary—A new, simple and rapid method of determination of ascorbic acid in amounts of 45–360 μg is described. The ascorbic acid is determined spectrophotometrically at 420 nm from the decrease in absorbance it causes in $1 \times 10^{-3}M$ hexacyanoferrate(III) in McIlvaine buffer at pH 5·2. The proposed method is suitable for the determination of ascorbic acid in pharmaceutical preparations and probably natural products.

Zusammenfassung—Eine neue einfache und rasche Methode für Bestimmung der Ascorbinsäure in Mengen von 45 bis 360 μg ist beschrieben. Die Ascorbinsäure wurde spektrophotometrisch bei 420 nm auf Grund der Verminderung der Absorption, welche die Ascorbinsäure in $1 \,.\, 10^{-3}M$ Hexacyanoferrat(III) lösung (McIlvaine Puffer pH 5,2) verursacht, bestimmt. Die vorgeschlagene Methode ist für die Bestimmungen der Ascorbinsäure in pharmazeutischen Präparaten und vielleicht auch in den Naturstoffen geeignet.

Résumé—Une nouvelle et rapide méthode d'analyse de l'acide ascorbique en concentrations de 45–360 μg environ est décrite. L'acide ascorbique est spectrophotometriquement déterminé à 420 nm d'après le décroissement de l'absorbence qu'elle cause en $1 \,.\, 10^{-3}M$ hexacyanoferrat(III) dans un médium acide (McIlvaine tampon pH 5,2). La méthode proposée est convenable pour la détermination de l'acide ascorbique dans les produits pharmaceutiques et probablement dans des produits naturels.

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ANALYTICAL DATA

SPECIES IN THE COBALT(II) CHLORIDE–2-NITROSO-1-NAPHTHOL SYSTEM IN BENZENE–ETHANOL MIXTURES*

(*Received* 14 *December* 1972. *Accepted* 13 *February* 1973)

In earlier work[1] the reaction of cobalt(II) chloride with 2-nitroso-1-naphthol in 96 : 4 v/v benzene–ethanol medium, which is characterized by low donor and dielectric properties, was examined. To investigate the influence of the solvent the study has been extended to mixtures with various benzene–ethanol ratios. The two solvent components have very different dielectric constants (DEC) and donicity (represented approximately by the donor number DN):

	DEC[2]	DN[3]
benzene	2·271	4·9
ethanol	24·339	30·4

Thus increasing ethanol content increases both the donor and dielectric properties.

EXPERIMENTAL

Materials, apparatus and procedures for the spectrophotometry were the same as before.[1] NMR spectra were recorded on a Varian A/60 spectrometer, for hexadeuterobenzene solutions, with tetramethylsilane as an internal reference, at 29°.

RESULTS AND DISCUSSION

The visible-region absorption spectra of cobalt(II) chloride in the solvent mixtures examined are similar to those reported earlier;[1] the apparent molar absorptivity decreases with increasing ethanol concentration (Fig. 1). This may be attributed to increasing co-ordinative disproportionation of $CoCl_2$, as solvent donicity increases,[4] so that the equilibrium (S represents solvent)

$$2\,{}^{tetr}CoCl_2S_2 + 2S \rightleftharpoons {}^{tetr}CoCl_3S^- + {}^{oct}CoClS_5^+ \qquad (1)$$

is shifted towards the right and involves a configurational change. The molar absorptivity of the octahedral species is much lower than that of the tetrahedral species.[5]

The spectrophotometric investigation was performed at 525 nm where the molar absorptivities of the complexes are higher than those of the reagents. The mole-ratio[6] and, where possible, straight-line[7] methods were used. The complexation ratios and concentration quotients at equilibrium are reported in Table 1.

Table 1. Values of the concentration quotients at equilibrium for the cobalt(II) chloride–2-nitroso-1-naphthol system in benzene–ethanol mixtures at 25°C

Ethanol concn., % *v/v*	Dielectric constant*	β_1	β_2	β_3	β_4
100	24·339	—	—	—	$2·3 \times 10^{14}$
75	18·4†	—	—	—	$1·4 \times 10^{14}$
50	11·8†	—	50×10^7	11×10^{11}	—
25	7·5†	—	$7·8 \times 10^7$	$2·0 \times 10^{11}$	—
4	2·5†	$1·2 \times 10^3$‡	$2·7 \times 10^7$‡	—	—

* From ref. 2.
† By graphical evaluation from ref. 2.
‡ From ref. 1.

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* Work supported financially by the Consigno Nazionale dette Ricerche, Rome, Italy.

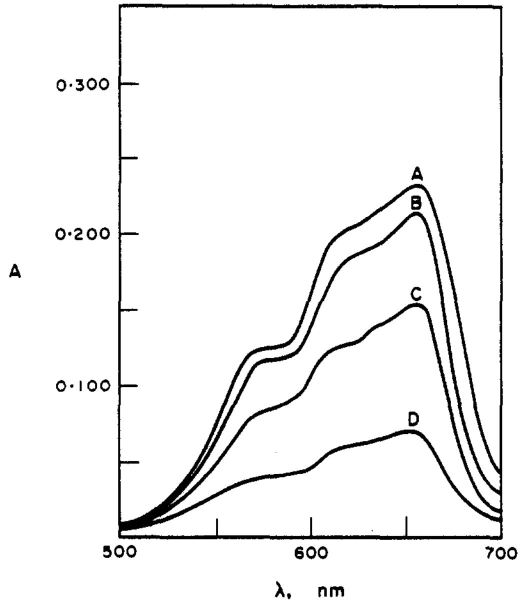
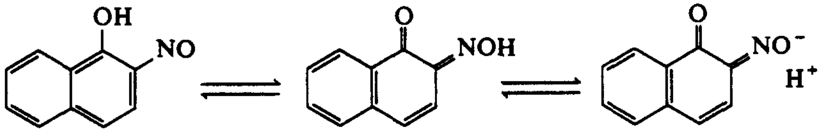


Fig. 1. Absorption spectra of 1·1 × $10^{-3}M$ $CoCl_2$ in benzene–ethanol mixtures (at 25°C) measured *vs.* solvent.

Ethanol concentration % v/v: *A* 25, *B* 50, *C* 75, *D* 100.

The results show: (*i*) that the ratio L/M of the predominant species increases with increasing ethanol concentration, and (*ii*) that all the complexes formed are octahedral.

The first point can be explained in terms of the variation in DEC and DN. When the DEC increases, deprotonation of the ligand is favoured; according to Chatterjee[8] the quinonoid form (**II*a*,*b***) should predominate:



(I) **(II*a*)** **(II*b*)** (2)

The Lewis-base strength of the single donor group (=NO⁻) is raised and may be high enough to prevail over the effect of solvent mixture donicity, even if the latter increases with ethanol concentration. A high donicity of the medium can disfavour the co-ordination of the other donor group of the naphthol so that the ligand acts as if monodentate. The other co-ordinative sites of the cobalt(II) should be occupied by ethanol molecules since the DEC value accounts for cleavage of Co–Cl bonds. On this hypothesis the 4 : 1 species may be ascribed the formula $Co(EtOH)_2(L)_4^{2-}$. To check the validity of this, we made some NMR measurements on the solid obtained from cobalt(II) chloride and 2-nitroso-1-naphthol dissolved in ethanol. The spectra showed the presence of bound ethanol molecules, with resonance peaks at $\delta = 1{\cdot}0$ for the CH_3 protons and at about $\delta = 3{\cdot}2$ for the CH_2 protons.

Reverse considerations apply when the benzene concentration is increased. The low donicity favours non-ionization of the compound and the low DEC opposes dissociation. The 2-nitroso-1-naphthol can act as a bidentate ligand by displacing solvation molecules. The donicity due to the ethanol is decreased owing to the small amount present. The formation of the ML_2 species may occur as follows

$$^{\text{tetr}}CoCl_2S_2 + \underset{\text{bidentate}}{2L} \rightleftharpoons {}^{\text{oct}}CoCl_2(L)_2 + 2S \qquad (3)$$

where S is the particular solvent species co-ordinated to the cobalt(II).

The second point was that the solvent effect does not affect the configurational equilibria. We may suppose that at low DEC values, the ligand displaces the co-ordinated ethanol molecules

$$^{\text{tetr}}CoCl_2(ETOH)_2 + \underset{\text{bidentate}}{2L} \rightleftharpoons {}^{\text{oct}}CoCl_2(L)_2 + 2EtOH \tag{4}$$

At higher DEC values, where ionization of both $CoCl_2$ and L occurs, the ligand groups replace chloride ions because the extent of dissociation of the chloride increases and the donicity of the ethanol increases with ethanol concentration in the mixed solvent.

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Summary—The cobalt(II) chloride–2-nitroso-1-naphthol system in mixtures of benzene and ethanol has been investigated spectrophotometrically. The complexation ratios of the species present have been determined and the values of the respective concentration quotients at equilibrium at 25° have been calculated. These values seem to be dependent to only a small extent on the variation of the mixture composition; the most considerable aspect is the decrease of the complexation ratios with increasing benzene concentration.

Zusammenfassung—Das System Kobalt(II)-Chlorid–2-Nitroso-1-naphthol in Gemischen von Benzol und Äthanol wurde spektrophotometrisch untersucht. Die Komplexbildungsverhältnisse der vorhandenen Spezies wurden ermittelt und die Werte der betreffenden Konzentrationsquotienten im Gleichgewicht bei 25° berechnet. Diese Werte scheinen von der Zusammensetzung der Mischung nur in geringem Maße abzuhängen; der am ehesten ins Gewicht fallende Aspekt ist das Nachlassen der Komplexbildungsverhältnisse mit zunehmender Benzolkonzentration.

Résumé—On a étudié spectrophotométriquement le système chlorure de cobalt (II)-2-nitroso 1-naphtol dans des mélanges de benzène et d'éthanol. On a déterminé les rapports de complexation des espèces présentes et calculé les valeurs des quotients de concentration respectifs à l'équilibre à 25°. Ces valeurs semblent ne dépendre que pour une petite quantité de la variation de la composition du mélange; l'aspect le plus important est la décroissance des rapports de complexation parallèlement à l'accroissement de la concentration en benzène.

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POLAROGRAPHY OF CADMIUM MALATE COMPLEXES

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EXPERIMENTAL

The apparatus and the experimental technique are the same as described earlier.[1] The temperature was maintained at 300 ± 1°K throughout the investigations.

RESULTS AND DISCUSSION

In each case a well-defined reduction wave was obtained. The plots of E *vs.* log $i/(i_d - i)$ were straight lines with slopes of 30 ± 1 mV. The temperature coefficient of $E_{1/2}$ in the range 0·00–0·7M malic acid was found to be 0·9 ± 0·1 mV/deg. These results, coupled with direct proportionality of the diffusion current to the square root of

The second point was that the solvent effect does not affect the configurational equilibria. We may suppose that at low DEC values, the ligand displaces the co-ordinated ethanol molecules

$$^{\mathrm{tetr}}\mathrm{CoCl_2(ETOH)_2} + \underset{\mathrm{bidentate}}{2\mathrm{L}} \rightleftharpoons {}^{\mathrm{oct}}\mathrm{CoCl_2(L)_2} + 2\mathrm{EtOH} \qquad (4)$$

At higher DEC values, where ionization of both $CoCl_2$ and L occurs, the ligand groups replace chloride ions because the extent of dissociation of the chloride increases and the donicity of the ethanol increases with ethanol concentration in the mixed solvent.

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Zusammenfassung—Das System Kobalt(II)-Chlorid–2-Nitroso-1-naphthol in Gemischen von Benzol und Äthanol wurde spektrophotometrisch untersucht. Die Komplexbildungsverhältnisse der vorhandenen Spezies wurden ermittelt und die Werte der betreffenden Konzentrationsquotienten im Gleichgewicht bei 25° berechnet. Diese Werte scheinen von der Zusammensetzung der Mischung nur in geringem Maße abzuhängen; der am ehesten ins Gewicht fallende Aspekt ist das Nachlassen der Komplexbildungsverhältnisse mit zunehmender Benzolkonzentration.

Résumé—On a étudié spectrophotométriquement le système chlorure de cobalt (II)-2-nitroso 1-naphtol dans des mélanges de benzène et d'éthanol. On a déterminé les rapports de complexation des espèces présentes et calculé les valeurs des quotients de concentration respectifs à l'équilibre à 25°. Ces valeurs semblent ne dépendre que pour une petite quantité de la variation de la composition du mélange; l'aspect le plus important est la décroissance des rapports de complexation parallèlement à l'accroissement de la concentration en benzène.

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POLAROGRAPHY OF CADMIUM MALATE COMPLEXES

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EXPERIMENTAL

The apparatus and the experimental technique are the same as described earlier.[1] The temperature was maintained at 300 ± 1°K throughout the investigations.

RESULTS AND DISCUSSION

In each case a well-defined reduction wave was obtained. The plots of E *vs.* log $i/(i_d - i)$ were straight lines with slopes of 30 ± 1 mV. The temperature coefficient of $E_{1/2}$ in the range 0·00–0·7M malic acid was found to be 0·9 ± 0·1 mV/deg. These results, coupled with direct proportionality of the diffusion current to the square root of the effective head of mercury indicated that the two-electron reduction is reversible and entirely diffusion-controlled. The increase in $E_{1/2}$ with pH between the pK_1 and pK_2 values of malic acid suggests the involvement of hydrogen ion in the electrode reduction of the complex in this pH range.

Effect of pH

The effect of pH on the half-wave potential was studied for $6 \times 10^{-4}M$ cadmium/0·1M potassium nitrate at different concentrations of malic acid. In each case two clear breaks at pH 3·5 and 5·8, corresponding to the pK_1 and pK_2 values of malic acid, were obtained. Below pH 3·5 little complexation occurs in the concentration range under investigation. The slopes of the straight lines between pK_1 and pK_2 (Fig. 1) for 0·2 and 0·4M malic acid media are 26 ± 1 mV and 29 ± 1 mV, indicating the participation of a proton in the reduction process. Above pH ~ 5·8 the half-wave potential becomes independent of pH; hence no hydrogen ion is involved in this reduction.

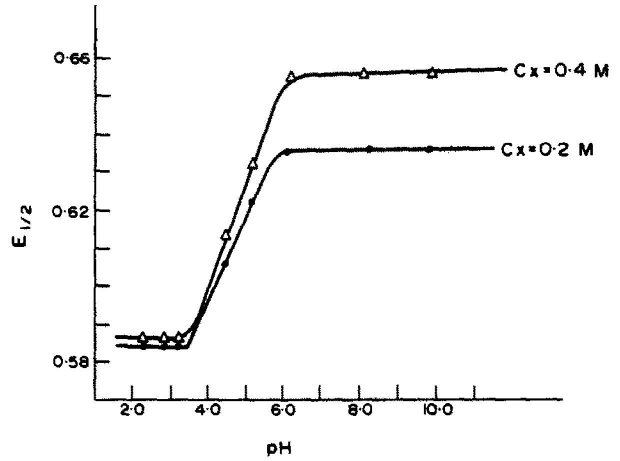

Fig. 1. Plot of $-E_{1/2}$ *vs.* pH.

Effect of ligand concentration

At pH 3·1, a small shift in $E_{1/2}$ with increasing malic acid concentration is observed. As the plot of $-E_{1/2}$ *vs.* log$[H_2A]$ is a straight line, Lingane's method[2] was applied to determine the equilibrium constant for the reaction $Cd^{2+} + H_2A \rightleftharpoons Cd(H_2A)^{2+}$. The value log $K = 0{\cdot}57$ was found.

At pH 8·0 (pH > pK_2) the half-wave potential becomes more negative with increase in ligand concentration. Since the plot of $-E_{1/2}$ *vs.* $-\log[A^{2-}]$ is a curve indicating stepwise complex formation, the method of DeFord and Hume[3] was used to evaluate the stability constants of the complex species so formed.

The stability constants so obtained were log β_1 = 1·9, log β_2 = 2·8, log β_3 = 3·4.

Complex species and electrode reactions

Malic acid is a saturated dicarboxylic acid with pK_1 = 3·30 and pK_2 = 5·12.[4] Therefore three species, H_2A, HA^- and A^{2-} are available to co-ordinate with Cd^{2+}. At pH < pK_1, H_2A predominates and if the reaction is that postulated by Campi,[5] to yield $Cd(H_2A)$ as the complex formed, no protons are involved in the electrode reduction. Campi's value[5] for log K for this complex was 1·34.

At pH > pK_2, where A^{2-} predominates, there will again be no protons involved in the electrode reaction. At intermediate pH values, however, if HA^- is the ligand [*cf.* Campi[5]—log K for Cd(HL) quoted as 2·36] and can be protonated in the electrode reaction, according to $Cd(HA)^+ + 2e + H^+ + Hg \rightleftharpoons Cd(Hg) + H_2A$ then the slope of $-E_{1/2}$ *vs.* pH should be 30 mV as observed. We did not attempt to evaluate log K for Cd(HL).

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Summary—The electrode reduction reaction of cadmium malate complexes at various pH values and ligand concentrations has been studied. At pH $< pK_1$ the complex $Cd(H_2A)$, $\log K = 0{\cdot}57$, exists. At pH $> pK_2$ $Cd(A^{2-})_n$ species exist, $\log \beta_1 = 1{\cdot}9$, $\log \beta_2 = 2{\cdot}8$, $\log \beta_3 = 3{\cdot}4$. At intermediate pH the complex Cd(HA) exists.

Zusammenfassung—Die Elektrodenreduktion von Cadmium-MalatKomplexen wurde bei verschiedenen pH-Werten und Ligandenkonzentrationen untersucht. Bei pH $< pK_1$ liegt der Komplex $Cd(H_2A)$ mit $\log K = 0.57$ vor. Bei pH $> pK_2$ gibt es die Spezies $Cd(A^{2-})_n$-mit $\log \beta_1 = 1{,}9$, $\log \beta_2 = 2{,}8$ und $\log \beta_3 = 3{,}4$. Bei dazwischen liegenden pH-Werten liegt der Komplex Cd(HA) vor.

Résumé—On a étudié la réaction de réduction à l'électrode de complexes de malate de cadmium à différentes valeurs de pH et concentrations de complexes. A pH $< pK_1$ le complexe Cd (H_2A), $\log K = 0{,}57$, existe. A pH $> pK_2$, l'espèce Cd (A^{2-}) existe, $\log \beta_1 = 1{,}9$, $\log \beta_2 = 2{,}8$ et $\log \beta_3 = 3{,}4$. A pH intermédiaire, le complexe Cd(HA) existe.

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AN ION-SELECTIVE ELECTRODE SYSTEM FOR CONTINUOUSLY MONITORING CYANIDE ION, BASED ON A COMPUTERIZED GRAN PLOT TECHNIQUE

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Summary—A procedure for the continuous monitoring of cyanide ion with an ion-selective electrode is described, based on the use of the Gran plot standard-addition technique. The mean concentration of the sample reservoir is measured continuously during a time span of 6 min. The use of a computer programme facilitates calculation of the results. Because the combined weights of several data points are used to calculate the unknown concentration, random errors tend to be eliminated and in addition there is no need for reference calibration curves.

The increasing use of ion-selective electrodes for continuous monitoring has led to a need for a suitably rapid procedure for the interpretation of the measurements. When ion-selective electrodes are used to monitor a flow-stream, provision must be made in the analytical system to divert the sample and insert suitable standards. One major drawback of using ion-selective electrodes in the direct potentiometric mode is that the constant term in the Nernst equation drifts at a rate which depends primarily on the temperature variation in the surroundings. The electrodes, therefore, require restandardization at intervals which depend on the degree of accuracy required. Most continuous monitoring systems so far described have employed the direct potentiometric approach. A computer treatment of potentiometric measurements made with interruptions for standardization has been described for the IBM blood-monitoring system,[2] which measures pH, pO_2, pCO_2, pNa^+ and pK^+. A similar general approach has been used with the Digital Equipment Corporation PDP 8 system.[3]

The method of standard additions provides one approach to the problem of improving the accuracy and precision of direct potentiometric determinations.[4,5] Parameters such as the unknown concentration, the electrode response slope and the standard potential can be evaluated from the e.m.f. values obtained after multiple standard additions, by means of a non-linear least-squares curve-fitting technique with the aid of computers.[6]

Alternatively the unknown concentration can be obtained by the graphical method of Gran.[7] Although the use of this technique in conventional titrimetry has been largely overlooked,[8] it has recently found important applications in potentiometry.[9] Jagner and Årén,[10] for example, have described a computer system which monitors the argentometric titration of sea-water by calculating in real time a Gran extrapolation of the end-point. The present report describes a fully automated approach to the Gran plot procedure, based on the use of a Technicon "AutoAnalyzer." The sample flow is continuously supplied without interruption and is mixed with a series of 3 or 4 standards presented

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sequentially and interspersed with a water-wash. The potential readings obtained from these continuous multiple standard additions are then used to evaluate the concentration of the continuous-flow sample by use of the Gran plot method. The results thus obtained represent the average concentration of the flow-stream during a time-span of 4½ or 6 min and hence the present method is not too far away from the goal of providing analytical information of flow-stream conditions on a continuous real-time basis.

THEORY

The Gran plot standard-addition technique

If a known volume, V ml, of standard solution of concentration C is added to V_0 ml of sample solution of unknown concentration C_0, then the potential of the electrochemical cell consisting of the appropriate indicator electrode and a reference electrode is given by

$$E = E^\circ + S \log\left[\frac{C_0 V_0 + CV}{V_0 + V}\right] + S \log \gamma + E_j \tag{1}$$

where E°, E, and E_j are respectively the standard potential, the equilibrium potential and the junction potential of the electrode system, γ is the activity coefficient, and S is 2·303 RT/nF.

By rearranging equation (1) we obtain,

$$(V_0 + V)10^{E/S} = 10^{(E^\circ + E_j)/S}(C_0 V_0 + CV)\gamma \tag{2}$$

Provided that the ionic strengths of the samples are sufficiently high to be unaffected by the addition of standards, γ and E_j remain constant, and hence if $(V_0 + V)10^{E/S}$ is plotted against V a straight line results which intercepts the volume axis at a point V_E, such that

$$C_0 V_0 = -CV_E \tag{3}$$

This approach forms the basis of the Gran plot standard-addition method used by Liberti and Mascini[9] for the potentiometric determination of fluoride with a fluoride-activity electrode. The procedure is superior to a single-point direct potentiometric measurement or a single standard-addition because the combined weights of several data points are used to calculate the unknown concentration and random errors will tend to be eliminated.

Application of the technique to continuous analysis

Instead of being used as described above, the Gran plot technique can be applied to continuous analysis by using the experimental arrangement shown in Fig. 1. A continuous sample flow is maintained at 2F ml/min and mixed with a continuous buffer flow at F ml/min, and a series of standards is added sequentially at a flow-rate of F ml/min, interspersed with a water-wash. Assuming that there is no significant change in the junction potential and activity coefficient, we have, *cf.* equation (1),

$$E_i = \text{constant} + S \log \frac{2\mathrm{F}C_0 + \mathrm{F}C_i}{4\mathrm{F}}$$

$$= \text{constant} + S \log \frac{2C_0 + C_i}{4} \tag{4}$$

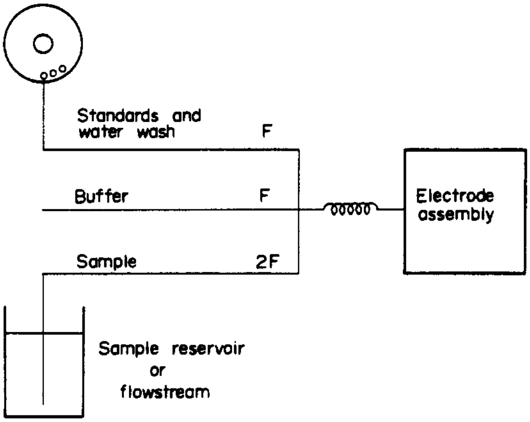

Fig. 1. The basic experimental arrangement for continuous analysis by the Gran plot procedure.

where E_i is the potential of the electrode system when the concentration of the standard-addition stream is C_i, and C_0 is the concentration of the test-sample solution.

Rearranging, we obtain

$$10^{E_i/S} = 10^{\text{constant}} \times \frac{2C_0 + C_i}{4} \tag{5}$$

By plotting $10^{E_i/S}$ *vs.* C_i, a straight line is obtained which intercepts the abscissa at C_A where

$$C_A = -2C_0 \tag{6}$$

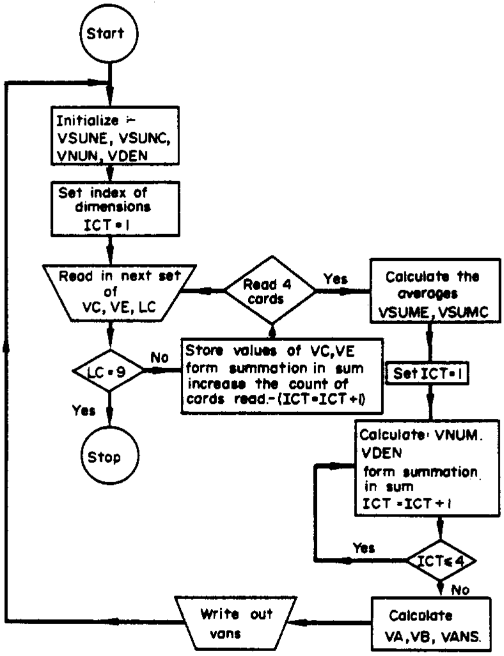

Fig. 2. Flow-chart for the programme AUTOGR.

Data processing and computation

Instead of manual plotting of $10^{E_i/S}$ *vs.* C_i, use can be made of a computer programme (AUTOGR) which has the following functions: (*i*) memorizing the sets of input data VE and VC where VE is the measured cell potential and VC is the concentration of the addition standard; (*ii*) computation of Y, where $Y = 10^{VE/S}$; (*iii*) fitting of a straight line by the linear least-squares method to the sets of values of Y and VC for each sample and locating the intercept of this line on the concentration axis; (*iv*) evaluation and print-out of the unknown concentration from the value of the intercept, according to equation (6). A flow-chart for the computer programme AUTOGR is shown in Fig. 2; the complete listing of the programme and the input format are obtainable from the authors on request.

EXPERIMENTAL

Apparatus

A Corning Digital Electrometer (Model 101, EEL-Corning, Halstead, Essex) was used for potentiometric measurements. The analogue response was displayed on a Servoscribe potentiometric recorder (Smiths Ind., U.K.). The indicator electrode was an Orion cyanide-activity electrode (Model 94-09 E.I.L. Chertsey, Surrey) fitted into a flowthrough cell. A double-junction reference electrode (Orion Model 90-02), with a 10% potassium nitrate solution in the outer compartment was used as the reference.

Standard "Auto Analyzer" modules (Technicon Corporation, Basingstoke, Hants), principally the peristaltic pump II and Sampler II, were used for the manipulation of samples and standards.

Reagents

All chemicals used were of analytical-reagent grade. Stock cyanide solutions were standardized argentometrically by Liebig's method and stored in a polythene bottle.

Procedure

The manifold employed for this method is shown in Fig. 3.

Sample and buffer solutions are supplied continuously at constant flow-rates as indicated, together with four different known standards, presented sequentially and interspersed with a water-wash. The complete 4-standard cycle takes 6 min, each standard being fed in for 60 sec, followed by a 30-sec wash.

RESULTS AND DISCUSSION

Response of the cyanide electrode

The response of the cyanide-activity electrode to cyanide ions as well as its selectivity characteristics under both static and flow conditions were found to be the same as

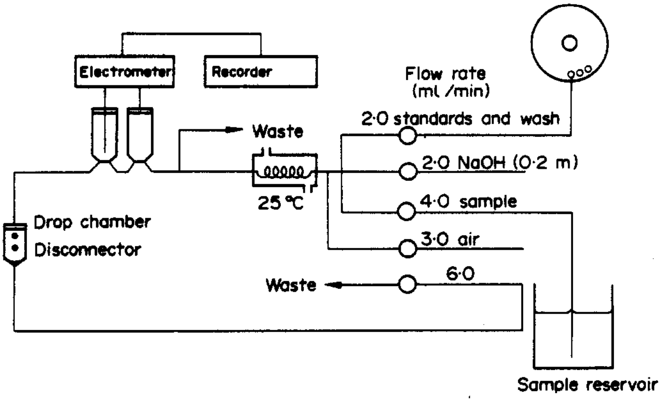

Fig. 3. Flow-diagram for the continuous determination of cyanide by the Gran plot standard-addition method.

Table 1. Analysis of some cyanide samples by the automatic Gran plot standard-addition method

Sample concn., $10^{-3}M$ CN$^-$	Potential readings of sample/standard mixtures, *mV*				Cyanide concn., found, $10^{-3}M$
	S1*	S2*	S3*	S4*	
6·0	−234·5	−240·9	−245·5	−249·9	$5{\cdot}8_7$
5·0	−231·5	−238·1	−243·8	−248·0	$4{\cdot}9_7$
4·0	−228·0	−236·0	−241·7	−246·4	$4{\cdot}0_3$
3·0	−224·0	−233·0	−239·5	−244·7	$2{\cdot}9_5$
2·0	−219·3	−230·0	−237·0	−243·0	$1{\cdot}9_7$
1·0	−213·2	−226·0	−234·5	−240·8	$0{\cdot}9_6$
0·6	−179·5	−185·6	−190·5	−194·5	$0{\cdot}60_8$
0·5	−176·5	−183·4	−188·7	−193·0	$0{\cdot}50_5$
0·4	−172·8	−180·7	−186·6	−191·4	$0{\cdot}39_5$
0·3	−169·0	−178·0	−184·5	−189·5	$0{\cdot}30_0$
0·2	−164·5	−174·9	−184·0	−187·7	$0{\cdot}19_8$
0·1	−158·4	−171·1	179·5	−185·5	$0{\cdot}10_5$

* For the first 6 samples, the cyanide concentrations of the standards were: S1, 0·005*M*; S2, 0·010*M*; S3, 0·015*M*; S4, 0·020*M*.

For the last 6 samples, the same standards were diluted 10-fold.

reported.[11] The linear range of the electrode was from 10^{-2} to $10^{-5}M$ with an average slope of approximately −57 mV per decade change in cyanide concentration. The cyanide standards were prepared with 0·1*M* sodium hydroxide as background electrolyte and to ensure that there was no protonation of cyanide ions.

Analysis of samples containing known concentrations of cyanide

Samples with known cyanide concentrations ranging from 0·006 to 0·001*M* were analysed by the Gran plot standard-addition technique, following the procedure previously described. A series of four standards was used for each sample. The same cyanide samples and standards were then diluted 10-fold and the experiment repeated. The results are summarized in Table 1.

Conclusions

The Gran plot standard-addition technique provides a useful solution to the problem of continuous monitoring with ion-selective electrodes. Because the combined weights of several data points are used to calculate the unknown concentration, random errors tend to be eliminated. As the electrode slope remains virtually constant throughout the course of a single measurement there is no need for other than very occasional recalibration of the electrode. The present system gives the average concentration of the sample reservoir (or flow-stream) during a time-span of 6 min. This could be further shortened by reducing sample hold-up in the flowthrough cell. Hence, the proposed method is not too far away from the goal of providing a continuous real-time monitoring of flow-stream compositions.

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Zusammenfassung—Ein Verfahren zur kontinuierlichen Überwachung der Cyanidkonzentration mit einer ionenselektiven Elektrode wird beschrieben; sie beruht auf dem Gran-Diagramm und der Standard-Zugabe. Die mittlere Konzentration des Probenreservoirs wird in einer Zeitspanne von 6 min kontinuierlich gemessen. Die Verwendung eines Computerprogramms erleichtert die Berechnung der Ergebnisse. Weil die kombinierten Gewichte mehrerer Meßpunkte zur Berechnung der unbekannten Konzentration verwendet werden, fallen die zufälligen Fehler heraus; ferner sind Bezugseichkurven nicht notwendig.

Résumé—On décrit une technique pour le contrôle continu de l'ion cyanure avec une électrode sélective, basée sur l'emploi de la technique d'addition d'étalon de Gran. La concentration moyenne du réservoir d'échantillon est mesurée de manière continue pendant un intervalle de temps de 6 mn. L'emploi d'un programme de calculatrice facilite le calcul des résultats. Parce que les poids d'ensemble de plusieurs points de données sont utilisés pour calculer la concentration inconnue, les erreurs fortuites tendent à être éliminées et, de plus, il n'est pas besoin de courbes d'étallonnage de référence.

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DETERMINATION OF Hg(II) IN ACIDIC MEDIA BY STRIPPING VOLTAMMETRY WITH COLLECTION

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Summary—Stripping voltammetry with collection at a rotating ring–disk electrode having a platinum ring and a glassy-carbon disk was used for the determination of Hg(II) in 1·0*M* H_2SO_4 medium in the range 0·10–4·00 ppM. Satisfactory results were obtained only after a thin film of Au (two monolayer equivalents) was electroplated on the disk electrode. The average relative deviation of the results for determination at the 0·10-ppM level was 7·5%. The limit of detection for the technique is approximately 0·01 ppM.

Recently, we described an electroanalytical technique called stripping voltammetry with collection (SVWC), using a rotating ring–disk electrode (RRDE) for the determination of silver in acidic media at trace levels.[1] The detection limit for SVWC was demonstrated to be significantly lower than that for conventional stripping voltammetry (CSV) at a rotating disk electrode (RDE). In essence, SVWC requires the electro-deposition of the desired species at the disk electrode of an RRDE followed by the voltammetric stripping of the deposit according to the usual procedure for CSV. A fraction of the species stripped from the disk electrode is transported by convection and diffusion to the surface of the ring electrode where it can undergo further electrochemical reaction. The resultant current peak at the ring electrode is integrated and can be quantitatively related to the bulk concentration of the species sought according to equation (1).[1,2]

$$|Q_r| = 0{\cdot}62 nF\pi R_1{}^2\omega^{1/2}D^{2/3}\nu^{-1/6}NC^b T_{\mathrm{dep}} \qquad (1)$$

where

$|Q_r|$ = the absolute value of the integral of the current–time peak for the electrochemical reaction at the ring electrode
n = number of Faradays/mole of electrons transferred
F = the Faraday
R_1 = radius of the disk electrode
ω = angular velocity of the electrode rotation
D = diffusion coefficient of the species sought
ν = kinematic viscosity of the test solution
N = collection efficiency of the RRDE
C^b = bulk concentration of species sought
T_{dep} = time for accumulation of the deposit at the disk electrode before stripping

SVWC is more sensitive than CSV because the reaction at the ring electrode occurs at a constant applied potential, and the charging-current background is theoretically zero.

SVWC has been applied to the determination of silver in 0·1*M* sulphuric acid at the 0·01-ppM level with T_{dep} = 10·0 min and ω = 41·9 rad/sec.[1]

The use of CSV for the determination of Hg(I) or Hg(II) has not been extensively explored. The use of platinum and gold electrodes is not satisfactory because deposited mercury amalgamates the electrode material and rapidly diffuses into the bulk of the electrode. Consequently, multiple stripping peaks are obtained. In the case of platinum, the anodic dissolution of the Hg–Pt compound occurs simultaneously with the absorption of oxygen and/or formation of platinum oxide at the electrode surface. Hence, the current due to stripping of mercury cannot be accurately determined.[3] Various forms of carbon have been tested as electrodes for the determination of Hg(II) by CSV. Emmott[4] described the use of a carbon-paste electrode for the determination of Hg(II) in 1·8*M* lithium sulphate medium. He reported a linear relation between the anodic peak current for the stripping of deposited mercury and $C^b_{\text{Hg(II)}}$ for T_{dep} = 15·0 min, over the range 0·08–2·5 ppm. Perone and Kretlow[5] used a wax-impregnated graphite electrode for the determination of down to 0·8 ppM Hg(II) in 0·1*M* potassium cyanide medium for T_{dep} = 30·0 min. Multiple peaks were observed for intermediate concentrations which could not be satisfactorily explained since no compounds of Hg with C are known. Kabanova and Zalogina[6] determined Hg(II) down to 0·8 ppm in 0·1*M* perchloric acid medium by using a glassy-carbon electrode. Multiple stripping peaks were found for a solution containing 8 ppm Hg(II).

We report here the results of a study using an RRDE having a glassy-carbon disk and a platinum ring, for the determination of Hg(II) in 1·0*M* sulphuric acid medium. Multiple peaks for the stripping of Hg were not obtained when cations which could be electro-deposited simultaneously with Hg(II) were absent from the test solution.

EXPERIMENTAL

Notation

Subscripts *d* and *r* to the symbols for current, *I*, and potential, *E*, designate the corresponding quantities at the disk and ring electrodes. Superscripts *a* and *c* used with E_d designate the anodic and cathodic limits of a cyclic potential scan. The potential of the disk electrode used for the deposition of a metal is $E_{d,\,dep}$. All electrical currents are reported in μA and quantities of electrical charge in μC. All electrode potentials were measured and are reported in volts *vs.* the saturated calomel electrode (SCE).

Instrumentation

The RRDE had a glassy-carbon disk and a platinum ring and was obtained from Pine Instrument Co., Grove City, Pennsylvania. The geometric parameters were R_1 = 0·3787 cm, R_2 = 0·3989 cm, R_3 = 0·4214 cm, α = 0·168, β = 0·211, and N = 0·170. The synchronous rotator, electrochemical cell, and four-electrode potentiostat were described earlier.[1] All areas of peaks on *I–E* curves were measured with a Keuffel and Esser Compensating Planimeter.

Reagents

The supporting electrolyte for all experiments reported here was 1·0*M* sulphuric acid. All solutions were prepared with triply-distilled water that was demineralized after the first distillation and then distilled from alkaline permanganate. Unless specified otherwise all chemicals were Baker Analyzed Reagent Grade. A stock solution of Hg(II) was prepared by dissolving triply distilled mercury in cold, concentrated nitric acid (Mallinckrodt Reagent Grade) followed by dilution with water to give a solution 1·00 × 10^{-3}*M* in Hg(II) and 0·10*M* in nitric acid. The stock solution was stored in an opaque polyethylene bottle. Standard additions of the stock solution to the supporting electrolyte were made with 2·000-ml and 0·2000-ml μm syringes. A stock solution of Au(III) was prepared by dissolving gold in a minimum of *aqua regia* and diluting with water and nitric acid to produce a solution 2·173 × 10^{-3}*M* in Au(III) and 1·0*M* in nitric acid.

Procedures

Electro-deposition of gold. During deaeration of the solution of supporting electrolyte, E_d was scanned cyclically at 5·0 V/min with E_d^c = −0·40 V, E_d^a = 1·10 V, E_r = +0·80 V, and ω = 41·9 rad/sec. Then the scan of E_d was stopped at 1·10 V and an aliquot of the stock solution of Au(III) was added. The solution was allowed to mix. E_d was scanned cathodically to 0·00 V and held for the desired value of T_{dep}. E_r was maintained at +0·80 V because deposition of Au was not needed at the ring electrode. E_d was scanned to 1·10 V, and the electrode was removed from the solution and rinsed with distilled water.

Determination of Hg(II). During deaeration of the solution of supporting electrolyte, E_d was scanned cyclically at 5·0 V/min with $E_d^c = -0{\cdot}40$ V, $E_d^a = 1{\cdot}10$ V (1·00 V when the Au film was absent), $E_r = 0{\cdot}80$ V, and $\omega = 41{\cdot}9$ rad/sec. An aliquot of Hg(II) solution was added, ω was changed to the desired value, and the solution was allowed to mix. The cathodic scan of E_d was stopped at the chosen value of $E_{d,\,dep}$, and deposition of Hg at the disk electrode continued for the desired value of T_{dep}. E_r was switched to the appropriate value for collection of the mercury species approximately 2 min before the expiration of T_{dep}, and I_r was allowed to decay to a steady-state value. At the expiration of T_{dep}, the cyclic scan of E_d was begun in the anodic direction, and the I_r-E_d curves recorded for the anodic half of the first and second cyclic scans. The collection peak for the second scan was considered the blank, *i.e.*, $T_{dep} = 0{\cdot}0$ min.

RESULTS AND DISCUSSION

Glassy-carbon disk electrode with no Au film

It was found that mercury can be electrolytically deposited and stripped at the glassy-carbon disk electrode of the RRDE in 1·0*M* sulphuric acid that is $1{\cdot}00 \times 10^{-5}M$ in Hg(II). The potential of the stripping peak on the I_d–E_d curve was approximately 0·45 V. The species stripped from the disk electrode was redeposited at the platinum ring electrode at $E_r = 0{\cdot}00$ V.[3] Figure 1 is a plot of Q_r as a function of $E_{d,\,dep}$ for $0{\cdot}10 \text{ V} \geq E_{d,\,dep} \geq -0{\cdot}80$ V. The value of $E_{1/2}$ for the deposition process at the glassy-carbon disk electrode is approximately −0·23 V, and it was concluded that the deposition was limited by convective-diffusional mass transport for $E_{d,\,dep} \leq -0{\cdot}50$ V. The standard reduction potential for the Hg^{2+}/Hg couple is 0·61 V *vs.* SCE,[8] and it is obvious that the deposition at a glassy-carbon electrode is very irreversible.

The species produced by the voltammetric stripping of Hg at the glassy-carbon disk electrode could be oxidized or reduced at the ring electrode. Figure 2 is a plot of the integral of the peak on the I_r–E_d curve at $E_d \sim 0{\cdot}4$ V as a function of E_r. The

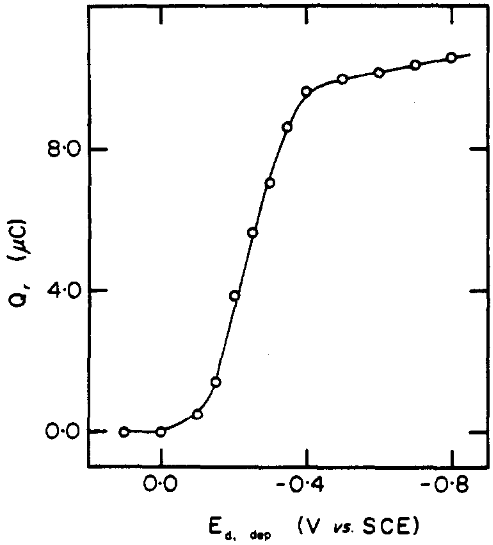

Fig. 1. Q_r–$E_{d,\,dep}$ curve for Hg on glassy-carbon disk electrode. $C^b_{Hg(II)} = 1{\cdot}0 \times 10^{-5}M$, $E_r = 0{\cdot}00$ V *vs.* SCE, $T_{dep} = 1{\cdot}00$ min, $\omega = 41{\cdot}9$ rad/sec, rate of anodic scan of $E_d = 5{\cdot}0$ V/min.

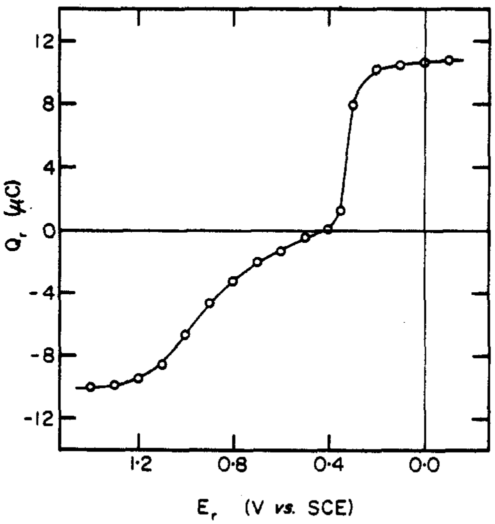

Fig. 2. Q_r–E_r curve for the species of Hg stripped from glassy-carbon disk electrode. $C^b_{Hg(II)} = 1{\cdot}0 \times 10^{-5}M$, $E_{d,\,dep} = -0{\cdot}60$ V *vs.* SCE, $T_{dep} = 1{\cdot}00$ min, $\omega = 41{\cdot}9$ rad/sec, rate of anodic scan of $E_d = 5{\cdot}0$ V/min.

value of $E_{1/2}$ for the cathodic process at the ring electrode is approximately 0·32 V and the $E_{1/2}$ for the anodic process is approximately 0·91 V. The limiting cathodic and anodic values of Q_r are virtually equal in magnitude and it was concluded that >95% of the deposited mercury is stripped at the glassy-carbon disk electrode as Hg(I). Reactions consistent with the data in Figs. 1 and 2 are given by equations (2)–(5).

Deposition at the disk electrode:

$$\mathrm{Hg(II)} + 2\mathrm{e} \longrightarrow \mathrm{Hg} \quad (E_{1/2} = -0{\cdot}23\ \mathrm{V}) \tag{2}$$

Stripping at the disk electrode:

$$\mathrm{Hg} \longrightarrow \mathrm{Hg(I)} + \mathrm{e} \quad (E_{\mathrm{peak}} = 0{\cdot}40\ \mathrm{V}) \tag{3}$$

Ring electrode:

$$\mathrm{Hg(I)} + \mathrm{e} \longrightarrow \mathrm{Hg} \quad (E_{1/2} = 0{\cdot}32\ \mathrm{V}) \tag{4}$$

$$\mathrm{Hg(I)} \longrightarrow \mathrm{Hg(II)} + \mathrm{e} \quad (E_{1/2} = 0{\cdot}91\ \mathrm{V}) \tag{5}$$

The fact that mercury is stripped as Hg(I) which can be oxidized to Hg(II) at the ring electrode makes it possible to use SVWC at this electrode for the determination of Hg(II) in the presence of Ag(I). This is not possible by CSV without the use of complexing agents, because the stripping peaks for mercury and silver have significant overlap. I_d–E_d and I_r–E_d curves for $E_r = 0{\cdot}00$ V and 1·20 V are shown in Fig. 3 for 1·0*M* sulphuric acid that is $1{\cdot}00 \times 10^{-6}M$ in Hg(II) and $3{\cdot}00 \times 10^{-7}M$ in Ag(I). Both Hg(I) and Ag(I) are reduced at the ring electrode at $E_r = 0{\cdot}00$ V, but only Hg(I) is electroactive at the ring electrode at $E_r = 1{\cdot}20$ V. The value of Q_r for $E_r = 1{\cdot}20$ V can be used for the determination of Hg(II), and the difference of the absolute values of Q_r at $E_r = 0{\cdot}00$ V and 1·20 V can be used for the determination of Ag(I).

A linear plot of Q_r *vs.* T_{dep} with zero intercept is expected on the basis of equation (1), and was obtained for $C^b_{\mathrm{Hg(II)}} \geq 1{\cdot}00 \times 10^{-5}M$ with $0{\cdot}0\ \mathrm{min} < T_{\mathrm{dep}} \leq 20{\cdot}0$ min and

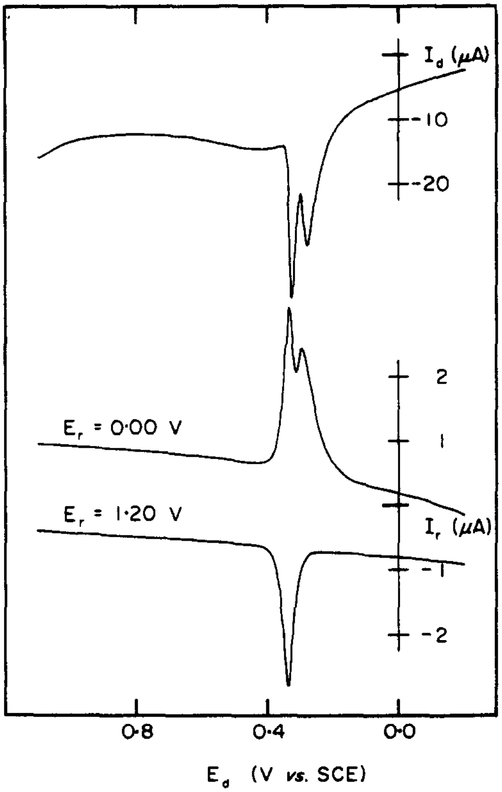

Fig. 3. I_d–E_d and I_r–E_d curves for SVWC at RRDE in mixture of Hg(II) and Ag(I). $C^b_{Hg(II)} = 1\cdot0 \times 10^{-6}M$, $C^b_{Ag(I)} = 3\cdot0 \times 10^{-7}M$, $E_{d,\,dep} = -0\cdot60$ V, $T_{dep} = 2\cdot00$ min, $\omega = 94\cdot3$ rad/sec, anodic scan rate of $E_d = 5\cdot0$ V/min.

$E_{d.\,dep} = -0\cdot50$ V. The plot was not linear, however, for $C^b_{Hg(II)} \leqslant 1\cdot00 \times 10^{-5}M$ as illustrated by the curve in Fig. 4 for $1\cdot00 \times 10^{-6}M$ Hg(II). Apparently, the electroreduction of Hg(II) on a glassy-carbon disk electrode at $E_d = -0\cdot50$ V is limited by convective-diffusional processes only after a finite amount of mercury has been deposited. For $C^b_{Hg(II)} \geq 1\cdot00 \times 10^{-5}M$, the time required for the development of the requisite amount of deposit was much less than all values of T_{dep}, and no curvature in the plot of Q_r vs. T_{dep} was observed. Attempts to deposit mercury at $E_{d,\,dep} < -0\cdot50$ V were not successful owing to the interference by bubbles of hydrogen formed at the electrode surface.

The values of Q_r, obtained from day to day, for $E_{d,\,dep} = -0\cdot50$ V and $C^b_{Hg(II)} = 1\cdot00 \times 10^{-6}M$, varied dramatically. Because indeterminate amounts of Cu(II) and other cations are present in all reagents, SVWC was performed in $1\cdot0M$ sulphuric acid medium that was $1\cdot00 \times 10^{-6}M$ in Hg(II) and $1\cdot00 \times 10^{-6}M$ in Cu(II). An anodic peak on the I_d–E_d curve for the stripping of the deposit of copper was observed at approximately 0·0 V. A plot of Q_r vs. T_{dep} for the redeposition of Hg(I) stripped from the disk electrode at $E_d \sim 0\cdot4$ V is shown in Fig. 4. The dramatic increase in values of Q_r due to the presence of Cu(II) was concluded to be due to a greater reversibility for electrodeposition of Hg(II) at a film of copper in comparison with that at a bare glassy-carbon electrode. It is expected that the same effect would result from the presence on the

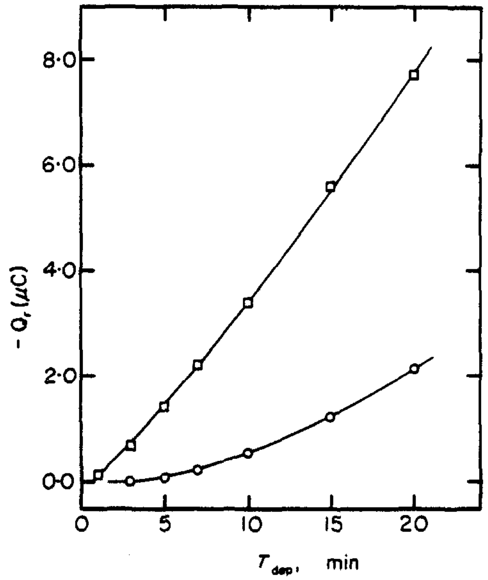

Fig. 4. Q_r–T_{dep} curves for Hg on glassy-carbon disk electrode. $E_{d,dep} = -0{\cdot}50$ V *vs.* SCE, $E_r = +1{\cdot}20$ V, $\omega = 41{\cdot}9$ rad/sec, rate of anodic scan of $E_d = 5{\cdot}0$ V/min, Curves: ○—$C^b_{Hg(II)} = 1{\cdot}0 \times 10^{-6}M$; □—$C^b_{Hg(II)} = 1{\cdot}0 \times 10^{-6}M$, $C^b_{Cu(II)} = 1{\cdot}0 \times 10^{-6}M$.

glassy-carbon disk electrode of a film of any metal which forms an amalgam. It was concluded that the day-to-day variation of Q_r noted above for $C^b_{Hg(II)} = 1{\cdot}00 \times 10^{-6}M$ was due to fluctuations of the level of trace metal ions in the supporting electrolyte.

Use of gold film for SVWC

If analytical advantage is to be taken of the increased reversibility for electro-deposition of mercury at a metal-film electrode, it is desirable that the film be semi-permanent and that its preparation does not involve doping of the test solution. The use of a copper film is not satisfactory because copper is stripped at potentials more cathodic than those for stripping of mercury. The use of a platinum film was concluded to be unsatisfactory because the electrolytic dissolution of the Hg–Pt compound occurs simultaneously with the formation of platinum oxide.[3] Johnson, Napp and Bruckenstein[8] found that a small quantity of an unidentified, soluble electroactive species is produced at a platinum disk electrode simultaneously with the anodic formation of platinum oxide. That species reacts at the ring electrode at the potentials used for collection of ionic mercury, and the ring current resulting from only the mercury cannot be quantitatively determined. Furthermore, a portion of the platinum film would be removed as soluble Pt(II) during electrochemical reduction of the platinum oxide on the cathodic scan of E_d. After several cyclic scans, the platinum film would have to be renewed.[8]

A thin film of gold electroplated on the glassy-carbon disk of the RRDE, according to the procedure described earlier, was found to produce the desired results. The electrolytic dissolution of the Hg–Au compound was found to occur on the anodic scan of E_d at values less than those for formation of gold oxide. For $E_d^a \leq 1{\cdot}15$ V, it was found that all the mercury was stripped from the gold film, no oxide was formed, and no gold was lost on repeated cyclic scans of E_d. The gold film was indefinitely stable.

Electrodeposition of gold at the glassy-carbon disk electrode at $E_{d,\,\mathrm{dep}}$ = 0·00 V was shown to occur by a process limited by convective-diffusional mass transport. A plot of $I_{d,\,\mathrm{lim}}$ *vs.* $\omega^{1/2}$ was linear as predicted by the Levich equation.[2] The diffusion coefficient of Au(III) in 1·0*M* sulphuric acid was calculated to be 1·00 × 10^{-5} cm^2/sec. The quantity of gold electroplated at the disk electrode was calculated from the integral of the electrical current predicted by the Levich equation, over the period T_{dep}. The equivalent number of monolayers of gold deposited was calculated, assuming that the packing density for bulk gold applies to the gold film.

I_r–E_d curves are shown in Fig. 5, which were obtained at the RRDE with the equivalent of 2 monolayers of gold on the glassy-carbon disk electrode. The curves were obtained with E_r = 0·00 V, E_d^a = 1·10 V and E_d^c varied for successive cyclic scans from −0·20 V to 0·60 V by 0·20-V increments. The concentration of Hg(II) was sufficiently large for a substantial amount of Hg to be deposited at $E_d^c \leq$ 0·20 V even if the scan was not halted at E_d^c. For $E_d^c \leq$ 0·20 V, a stripping peak for bulk mercury was obtained during the anodic scan of E_d at 0·34 V. The cathodic ring current observed for values of $E_d >$ 0·4 V was concluded to correspond to reduction of the ionic mercury produced by electrolytic dissolution of the Hg–Au compound. The I_r–E_d curve shown in Fig. 5 for the cathodic scan of E_d exhibits the effects of shielding of the flux of Hg(II) from the bulk solution at the ring electrode for values of $E_d <$ 0·8 V. These results are consistent with the conclusions that mercury is deposited at the gold film at underpotential for 0·4 V < E_d < 0·6 V, with the resultant formation of an Hg–Au compound, and that bulk mercury is deposited for $E_d <$ 0·3 V after the intermetallic compound is formed. Bruckenstein *et al.*[9–14] have discussed deposition at underpotential.

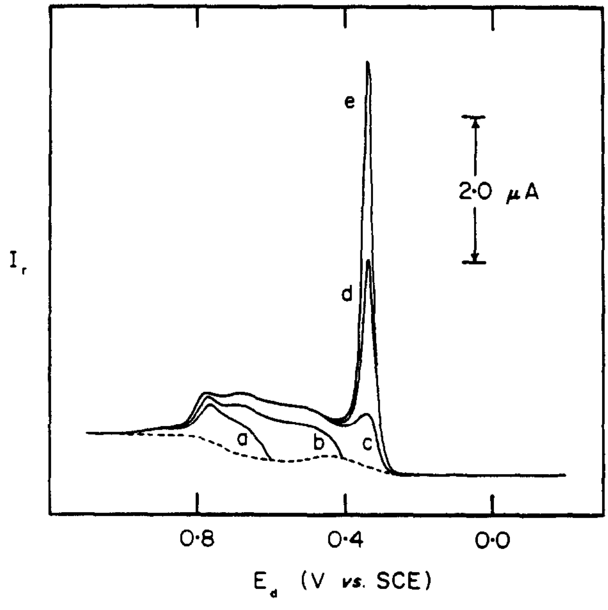

Fig. 5. I_r–E_d curves for SVWC of Hg at RRDE with Au film. $C^b_{\mathrm{Hg(II)}}$ = 5·0 × 10^{-6}*M*, E_r = 0·00 V *vs.* SCE, ω = 262 rad/sec, rate of anodic scan of E_d = 2·0 V, Curves: (*a*) E_d^c = 0·60 V, (*b*) E_d^c = 0·40 V, (*c*) E_d^c = 0·20 V, (*d*) E_d^c = 0·00 V, and (*e*) E_d^c = −0·20 V.

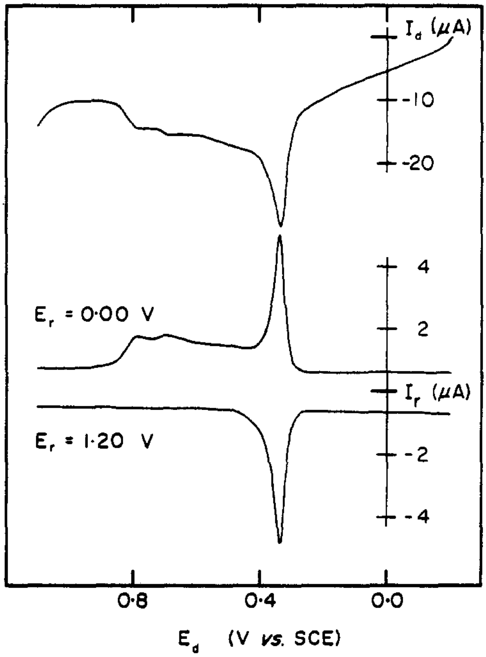

Fig. 6. I_d–E_d and I_r–E_d curves for SVWC of Hg at RRDE with Au film. $C^b_{Hg(II)} = 1·0 \times 10^{-6}M$, $E_{d,\,dep} = -0·20$ V *vs.* SCE, $T_{dep} = 2·0$ min, $\omega = 262$ rad/sec, rate of anodic scan of $E_d = 5·0$ V/min.

The I_d–E_d curve obtained on the anodic scan of E_d for $C^b_{Hg(II)} = 1·0 \times 10^{-6}M$ and the corresponding I_r–E_d curves for $E_r = 0·00$ V and 1·20 V are shown in Fig. 6. Collection peaks on the I_r–E_d curves occurred simultaneously with the appearance of the stripping peak for bulk mercury at $E_d = 0·34$ V for $E_r = 0·00$ V and +1·20 V. This observation is consistent with the conclusion that bulk mercury at the disk electrode is stripped as Hg(I). A collection wave for $E_d > 0·4$ was obtained only for $E_r = 0·00$ V and it was concluded that Hg(II) is the only soluble product of the electrolytic dissolution of the Hg–Au compound.

Multiple stripping peaks for a single element are not desirable in the quantitative application of stripping voltammetry, and it was hoped that the use of the single peak at $E_d = 0·8$ V would be adequate for the determination of Hg(II) by SVWC at an RRDE. Bulk mercury is not formed at the gold film until the formation of the Hg–Au compound is complete. Hence, the appearance of a single peak can be assured by the precise control of ω, T_{dep}, or the quantity of sample taken.

To determine the optimum thickness of the gold film, the I_r–E_d curves from SVWC for $C^b_{Hg(II)} = 1·0 \times 10^{-6}M$ were compared for varying quantities of gold deposited at the disk electrode. The curves are shown in Fig. 7. In the total absence of gold, no collection peak was obtained. For a quantity of gold equivalent to 0·1 monolayer, a small collection peak was obtained for the stripping of bulk mercury, and a collection wave was obtained for the dissolution of the Hg–Au compound. Apparently the quantity of mercury deposited was more than sufficient to amalgamate the small quantity of gold present and bulk mercury was also formed. As the quantity of gold was increased to the equivalent of 2 monolayers, the collection peak corresponding to the stripping of bulk mercury disappeared

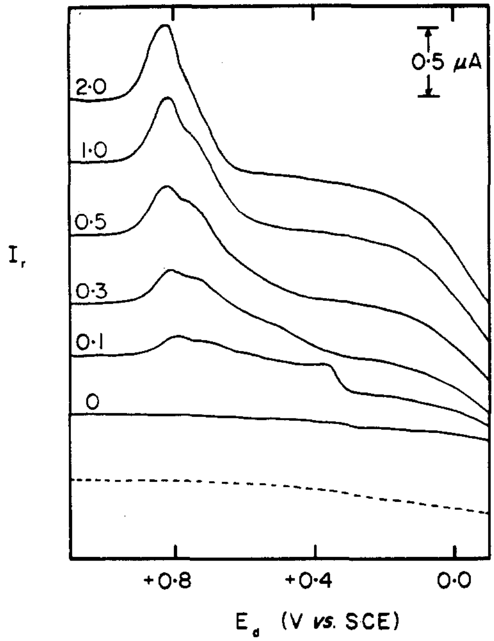

Fig. 7. I_r–E_d curves for SVWC of Hg at RRDE with Au film of variable thickness. $C^b_{\mathrm{Hg(II)}} = 1{\cdot}0 \times 10^{-6}M$, $E_{d,\,\mathrm{dep}} = -0{\cdot}20$ V *vs.* SCE, $E_r = 0{\cdot}00$ V, $\omega = 41{\cdot}8$ rad/sec, rate of anodic scan of $E_d = 5{\cdot}0$ V/min, ——— curves for varying thickness of Au film (monolayer equivalents of Au indicated in figure), ----- curve for Au film of 2·0 monolayer equivalents and $C^b_{\mathrm{Hg(II)}} = 0{\cdot}0M$.

and the collection wave for the dissolution of the amalgam developed into a well-defined peak. The values of Q_r for 1 and 2 monolayers were the same. A gold film equivalent to 2 monolayers was used for all remaining studies. The I_r–E_d curve is also shown for 2 monolayer equivalents of gold in the absence of mercury. No collection peaks were obtained.

Values of Q_r for the single collection peak obtained on the I_r–E_d curve at $E_d \sim 0{\cdot}8$ V are shown in Fig. 8 as a function of $E_{d,\,\mathrm{dep}}$. For the values $T_{\mathrm{dep}} = 2{\cdot}0$ min and $C^b_{\mathrm{Hg(II)}} = 5{\cdot}0 \times 10^{-8}M$, no bulk mercury was deposited. The curve in Fig. 8 is, in essence, an I–E curve for the electrolytic formation of the Hg–Au compound. The $E_{1/2}$ for the process is approximately 0·52 V, which is consistent with the conclusion that the Hg–Au compound is formed by the deposition of mercury at underpotential. The rate of deposition for the values of parameters used for Fig. 8 is limited by convective-diffusional processes for $E_{d,\,\mathrm{dep}} \leq 0{\cdot}3$ V.

It is predicted, on the basis of equation (1), that Q_r for the collection peak at $E_d \sim 0{\cdot}8$ V should be a linear function of $\omega^{1/2}$ and T_{dep} so long as the limiting amount of the Hg–Au compound has not formed, *i.e.*, for small values of Q_r. This was verified for $Q_r < 1{\cdot}6$ μC, using the gold film of 2 monolayer equivalents. The limiting value of Q_r was approximately 2 μC. On the basis of $Q_r = 2$ μC, the stoichiometry of the Hg–Au compound was calculated to be Hg : Au = 1 : 33. A possible explanation for the lack of a simple stoichiometry would result if the gold deposit existed in patches rather than a uniform film. Repeated measurements of the limiting value of Q_r on several gold films gave results virtually identical with that reported here.

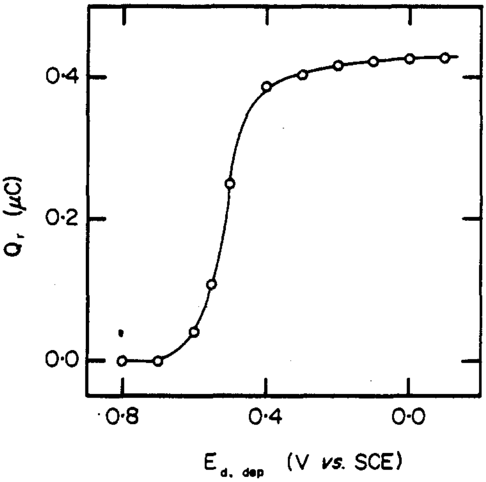

Fig. 8. Q_r–$E_{d,\,dep}$ curve for Hg on glassy-carbon disk electrode with Au film. $C^b_{Hg(II)} = 5{\cdot}0 \times 10^{-8}M$, 2 monolayer equivalents of Au, $E_r = 0{\cdot}00$ V *vs.* SCE, $T_{dep} = 2{\cdot}00$ min, $\omega = 41{\cdot}9$ rad/sec, rate of anodic scan of $E_d = 5{\cdot}0$ V/min.

A calibration curve relating log Q_r for the collection peak at $E_d \sim 0{\cdot}8$ V to log $C^b_{Hg(II)}$ for $5{\cdot}00 \times 10^{-10}M \leq C^b_{Hg(II)} \leq 2{\cdot}00 \times 10^{-8}M$ (0·10–4·00 ppM) was linear. The values of $C^b_{Hg(II)}$ were obtained by the technique of standard additions. Values of Q_r were corrected for the blank measured for zero concentration of mercury. The average relative deviation at $5 \times 10^{-10}M$ Hg(II) was 7·5%. For that determination, only 28 pg of mercury were deposited and stripped at the gold-film disk electrode. On the basis of the results obtained in this study, it was concluded that the detection limit for the determination of Hg(II) in 1·0*M* sulphuric acid medium by SVWC is approximately 0·01 ppM.

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Zusammenfassung—Zur Bestimmung von Hg(II) in 1,0 M H_2SO_4 im Konzentrationsbereich 0,10–4,00 ppM wurde die inverse Voltametrie verwendet. Dabei kam eine rotierende Ring-Scheibenelektrode mit einem Platinring und einer Scheibe aus glasigem Kohlenstoff zum Einsatz. Zufriedenstellende Ergebnisse wurden erst erhalten, nachdem ein dünner Au-Film (entsprechened zwei Monoschichten) elektrolytisch auf der Scheibenelektrode abgeschieden worden war. Bei 0,10 ppM betrug die mittlere relative Abweichung der Ergebnisse 7,5%. Die Nachweisgrenze liegt bei dieser Arbeitsweise bei etwa 0,01 ppM.

Résumé—On a utilisé la voltammétrie de dissolution avec collection sur une électrode rotative anneau-disque ayant un anneau de platine et un disque de carbone vitreux pour le dosage de Hg (II) en milieu H_2SO_4 1,0*M* dans le domaine 0,10–4,00 ppM. Des résultats satisfaisants ont été obtenus seulement après qu'une mince pellicule d'Au (deux équivalents de couche monomoléculaire) ait été déposée électrolytiquement sur l'électrode-disque. L'écart relatif moyen des résultats pour le dosage au niveau de 0,10 ppM a été de 7,5%. La limite de détection pour la technique est approximativement de 0,01 ppM.

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SYSTEMS THEORY IN ANALYSIS—I*

DEFINITIONS AND INTERPRETATIONS IN THE BASIC TERMS OF SYSTEMS THEORY

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Summary—The twelve basic terms of systems theory—system, element, relation, function, structure, organization, feedback, Black Box, model, input–output analysis, trial-and-error method, simulation—are given general definitions and are also interpreted in terms of chemical analysis. The distinction between a generally acceptable brief and precise definition and an interpretation peculiar to one particular specialized field avoids, in the case of universally used terms, a biased view and conception. Simple systems are deliberately chosen and the terms used are clarified by means of diagrams. A system-oriented approach is outlined, with feedback-coupled stages (defining the problems, setting the limits, designing the model, simulation) which has proved useful in practical systems analysis and in systems design. The working group will report, in subsequent publications, on specific analytical systems which are of considerable importance in automation. Those with special interests in these fields are warmly invited to communicate their critical opinions, suggestions, and examples of interpretations based on these definitions.

1. INTRODUCTION

The modern developments in science and technology are characterized just as much as the modern findings in economics and sociology by certain aspects of the use of cybernetics and information theory. As a result new ways of thinking and working have been developed and applied which are largely independent of specific disciplines. Systems theory, with its two main divisions of systems analysis and systems design, is of the utmost significance for both thought and application in these new categories. Both well-established and new terms are used in the field of systems theory, and together create a basis of common understanding between experts in various disciplines, such as the analytical chemist and the computer specialist, or between the physical chemist and the biologist. A unique interpretation must be associated with each term. The necessary

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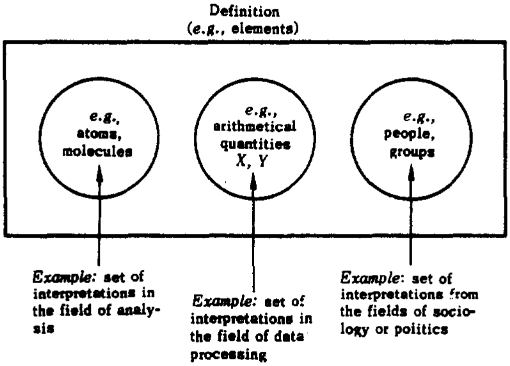


Fig. 1. Definitions and interpretations of terms.

explanations of these terms are all too often biased by the one-sided views and conceptions of the specialist concerned. The lack of many such adequate explanations can be avoided if two levels of explanation are distinguished—*definition* and *interpretation.*

The definition should describe a term briefly and precisely in a way which can be generally accepted and at the same time be independent of any particular concept. The interpretation, on the other hand, should elucidate the specific concept in terms of one particular discipline or field of application. It enlarges on the definition by use of specific examples. Only in the case of uniquely applied specialized terms will the definition and the interpretation coincide. Interpretations are subdivisions of a universal quantity—the definition—as illustrated in Fig. 1.

2. DEFINITION OF THE BASIC TERMS

Table 1 presents a compilation of the basic terms of systems theory, considered to be acceptable by all of the study group. In composing this set, both the terminology of cybernetics[1] and the opinions of experts in a wide variety of disciplines were taken into consideration.

Table 1. Basic terms of systems theory—Definitions

System	demarcated arrangement of a set of elements and a set of relationships between these elements
Element	*given or chosen relevant components* of a specific system
Relationship	*given or chosen relevant coupling* of the elements of a specific system
Function	*behaviour patterns and effects* of a system
Structure	known relationships between the elements of a system which lead to specific functions
Organisation	Break-down of a system into subsystems with relevant relationships between them. Subsystems can also have the appearance of elements
Feedback	Function by means of a closed sequence of relationships
Black Box	system with structure unknown at the time, but with given magnitudes of input and output.
Model	system which represents in part, functions and/or structures of a real or an abstract original system.
Input–output analysis	method of elucidation of functions of a system based on investigation of the relationships between the input and output
Trial-and-error method	method of stepwise elucidation of functional relationships in a system making use of established facts
Simulation	copying of a specific function of a system by means of a functional model

A necessary condition for a coherent complex of terms to be self-consistent and non-contradictory is that terms and their attendent definitions can be meaningfully substituted in all definitions which use terms already defined. From this aspect, only *element*, *relationship*, and *function*, with the italicised parts of their definitions, are basic terms which are formed from well-defined conceptual terms of everyday speech, namely "component, combination, behavioural property, effect." In a second group of definitions only the basic terms are considered relevant. They are:

System	(element, relationship)
Structure	(relationship, function)
Feedback	(function, relationship).

In all other definitions, terms from the second group are also included:

Organization	(system, relationship, sub-system = element)
Black Box	(system, structure, function)
Model	(system, function, structure)
Input–Output Analysis	(system, function, relationship)
Trial-and-Error Method	(function, system)
Simulation	(function, system, model).

The additional important terms "arrangement, break down, sequence, explanation, relationship, understanding, reproduction" belong to everyday speech and have their usual meanings. Only the terms "set" and "magnitude" are mathematical expressions which require an additional interpretation.

3. INTERPRETATION OF THE BASIC TERMS

3.1 *System, element, relationship*

System. The demarcation and existence of at least two elements between which there must be at least one relationship is fundamental to the term *system*. The arrangement demarcated can be real or imaginary. From this aspect we can speak of conceptual and material systems. The demarcation of the system is either given or is chosen by the analyst or the designer in terms of expediency. By means of a system some specific aspect of the conceptual or material world is isolated and characterized by a single designation. Typical examples of conceptual systems are the Periodic Table, chemical equilibria, mathematical formulae, arithmetical number systems, and an encyclopedia of organic compounds. Examples of material systems are television sets, washing machines, motor vehicles, measuring instruments, and analytical apparatus and instruments. In an intermediate position come sociological and political groupings, so that the family, working group, political party, village, town, state, enterprise may be considered to be both conceptual and material systems.

Element. The adjective "relevant" states expressly that only components absolutely essential to the understanding of the demarcation, the behaviour and the effects, should be termed elements in systems theory. The actual elements are either given, or chosen according to the purpose and limits of the approach to the system.

A system can contain a large number of like or unlike elements. These form a set—in the mathematical sense—called, after Cantor, a compilation of certain well-differentiated objects from perception and thought. In principle, like elements can be combined as a part or subdivision (of a system) and be specifically designated. As an example, take the analytical system "aqueous solution of two acids HA and HB": we can differentiate the following sub-divisions of systems-theory elements.

Molecules: H_2O, HA, HB
Ions: H^+, OH^-, A^-, B^-.

Systems with a number of unlike elements are termed *complicated* in systems theory. However, a simple enumeration of the type and number of the elements is certainly not adequate as a description of a system. In each case there must also be mentioned the state in which an element is found or which it adopts. Such a description is achieved through quantification of states which may be either constant or variable.

The necessary demarcation of the relevant elements of a specific system includes, after the definition, the assignment of symbols, magnitudes and dimensions. Thus, in the example above, for the element HA we may have:

Defining: HA = acetic acid solution
Symbolizing: acetic acid = CH_3COOH (or HOAc)
Quantifying: concentration factor C (*e.g.*, 1 or 10^{-5})
Dimensioning: concentration units, mole/litre (molarity).

Relationship. The connection (between elements) can be material, energetic or informational, but is often a combination of these. Information can be transmitted, transformed and stored only in material or energetic forms. What has been stated concerning relevance in connection with elements also applies to relationships. Moreover the relevant relationships of a system form a part and possibly a subdivision, which is either given, or chosen according to expediency. The immediate effect of a relationship is a change of state of a single element or of a subdivision of elements, and with that it ends. The demarcation of the relationships according to their nature and number is generally much more difficult than for the elements. Systems with numerous different relationships are termed, in systems theory, *complex*. In analytical systems, for example, "dissociation" presents a number of relevant relationships in an equilibrium system. A chemical equilibrium is defined by means of a dissociation equation such as

$$HA \rightleftharpoons H^+ + A^-$$

and is symbolized by the special relationship character $\rightleftharpoons$. The relationship character + symbolizes simultaneous presence of the two elements.

Figure 2 summarizes the relationships and their meanings in a schematic form. The effect of relationships is particularly striking in chemical buffer systems where the magnitudes (in number and dimension) of the states, such as concentrations and activities, of the relevant elements are interrelated strictly according to the equilibrium constants.

3.2 *Function, structure, organization, feedback*

Function. Every system exists in either a conceptual or a material environment. The behavioural patterns towards the environment or the effects on the environment are collectively termed function. Thought-systems fulfil a function of winning knowledge,

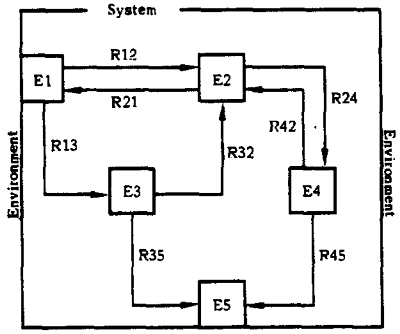


Fig. 2. Schematic diagram of a system with 5 elements E and 8 relationships R.

conveying information, or regulating behaviour. In material systems the function can, moreover, be interpreted as directed towards a specific objective. Systems are connected with the environment through peripheral elements which we can differentiate as either input or output elements. Input relationships lead from the environment to the input elements; output relationships go from the output elements to the environment.

The states of the input elements effected by the input relationships are characterized by the corresponding input quantities. It is of considerable significance for the practical use of a system that only the functions themselves need be known, *i.e.*, only the working instructions for connecting input and output are necessary for us tò be able to operate the system. Knowledge of the other system elements and relationships is in no way necessary. This at first apparently astonishing state of affairs is taken for granted in such systems as television sets, washing machines, wrist-watches, auto-analysers, and in connection with tables of mathematical functions.

All relevant effects of the environment on à system are collectively termed the *input* of the system. The states of the output elements are controlled only by the system elements. The output quantities thus resulting determine the effect of the output relationship on the environment; collectively, the *output* of the system. The external connection of input and output makes possible a description of the function of the system.

The analytical system "acid HA dissolved in water" possesses the function of the specific effect of the H^+ ion. This function can be described unambiguously in the form of an input–output table or an input–output curve relating as input, the quantity of acid HA added to a given amount of water, to the measured value of the pH (as output) without knowledge of the mechanism of the process.

Structure. We can only speak of a knowledge of the structure of a system when all the relevant relationships within the system, which lead to the respective functions, are known. Naturally this inevitably demands a complete knowledge of the nature, number, and dimensions of the possible magnitudes of the states of the necessary elements. It must be emphasized that a specific function can be fulfilled by a number of structures. Thus television receivers, which have the same function, may be constructed quite differently. The term structure has apparently always been understood and used in chemistry in the same sense as its definition in systems theory. Organic elemental analysis, for example, yields the nature and number of atoms of the chemical elements present—which are here identical with the elements of systems theory—but certainly does not tell us the "chemical" structure which only becomes known when the relevant relationships such as the arrangement and nature of the bonds between the elements have been discovered.

Organization. In consideration of a complicated or even of a complex system, the only successful approach to an understanding and comprehension of, in particular, the function of the system, lies in breaking down the multiplicity of elements and relationships present into suitably chosen subdivisions.

The new modular systems obtained by appropriate subdivision of the system possess all the characteristics of an independent system such as input and output and fulfil a specific function. The term subsystem should simply express the fact that an arrangement into a larger system is being considered. An important aim of organization is the deliberate reduction of the number of relationships assumed or originally present. The subsystems are therefore so chosen as to make possible the minimum number of relevant connections between them. It may be necessary when first attempting to give an overall or function-oriented description of a large system to interpret the subsystems as elements. In terms of structure in a system, one speaks of coarse structure when dealing with known relationships between subsystems, and of fine structure for relationships within the subsystems themselves.

Organization plays an important practical role both in systems analysis and in systems design. Proper organization in the design of real everyday systems of considerable complexity leads to the principle of structural modules. When a particular function of the system is not working, the fault may be sought by testing the subfunctions of the individual modules, which are equivalent to subsystems, and be very quickly corrected. Business, municipal and educational concerns are examples of organizations in which the important elements people, working tools, and capital must be linked both in aims and information, in the form of subsystems such as departments, working groups and institutes.

Feedback. Feedback is always present when the last element of a series (i.e. a subsystem) is connected to the first by some relationship which directly affects the state of the latter element. By means of this effect there is realized a specific function which is aimed at minimizing variations between output quantities. When it is aimed at minimizing differences between a given quantity and that actually occurring, the feedback is said to be *controlling*. Let us take again as a chemical example the process occurring in a buffer system. The desired value here is a certain pH value. Within the capacity of the buffer the effect of addition of acid or alkali on the pH is controlled by feedback, from the law of mass-action.

On the other hand should the feedback result in a continuous approach to an initially unknown limiting value then one speaks of *iteration*. In such a case an acceptably small deviation is chosen, and the feedback process is terminated when the actual deviation becomes less than this. Typical examples of iterative feedback are loops and jumps in computer programmes. In the calculation of the water–gas equilibrium in the system carbon–hydrogen–oxygen, the equilibrium pressures of the upwards of 25 possible components can only be arrived at by iterative procedures. Feedback in thought processes is called *deduction*. Deductions are of considerable importance not only in mathematical reasoning, but also in the investigation and testing of individual functions of systems.

Figure 3 shows a pictorial representation of the relationships between the basic terms discussed in section 3.2

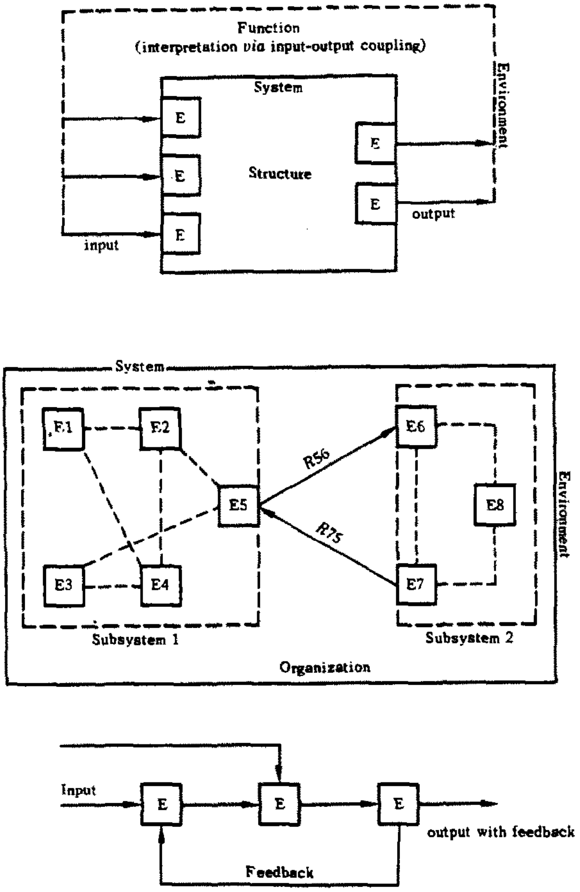


Fig. 3. Interpretation of function, structure, organization and feedback.

3.3 *Black Box, model*

Black Box. The term Black Box is a perceptual designation for systems having a structure that is largely unknown (or is not necessarily known). According to the definition, input and output quantities may be determined or may be given. These quantities contain information about the possible states of the peripheral elements of the system concerned. When a sufficiently large number of these states is known, input, output, and hence also the functions, can be described. Conversely a specific function can be given and interpreted through the resultant states of the peripheral elements.

Basically two groups of Black Boxes can be distinguished. To the first belong systems with *completely* unknown structure. These are the favoured topics of scientific *research*, and are to be explained or investigated for particular, known or desired functions of causal structures. As a further step the *development* of the discovery of the optimum structure may serve for the realization of a particular function through modification of an already investigated basic structure.

To the second group belong systems with structures that are simply not known to the layman or the person using them. Such structures are well understood by experts

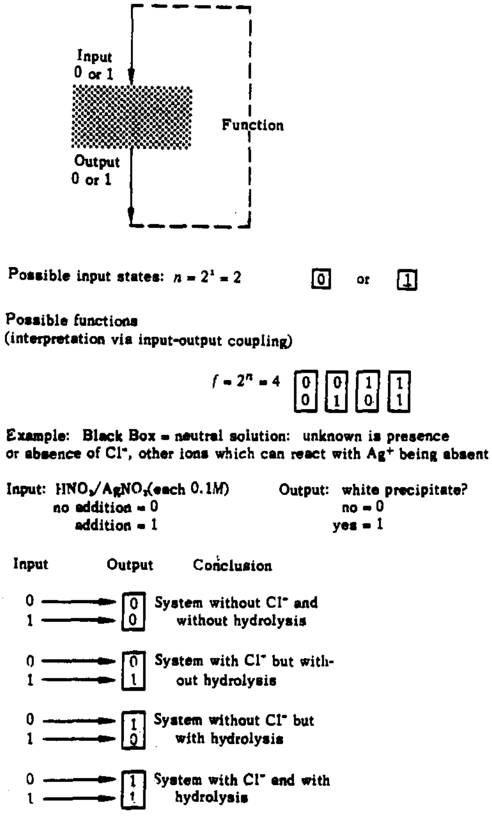


Fig. 4. Simplest Black Box.

and are described in detail in text-books, patent literature and other sources. In principle the layman would have the possibility of informing himself about the structure. People learn at school, and through training and experience, to know and understand the structures of many such systems which are initially Black Boxes to them. We might say the system then becomes a "White Box" for them. On the other hand, many pieces of equipment in modern technology must be accepted as Black Boxes because an individual's capacity to learn is limited by his mental ability and the time available.

In cases where one is only concerned with utilizing a particular function, the Black Boxes of the second group become an expedient aid to the solution of numerous problems. Figure 4 shows the simplest Black Box possible, in the form of a system with one input and one output, which can therefore realize only two states of the peripheral elements at any given time.

Model. Models are illustrations of specific structures or simply descriptions of specific functions of conceptual or material systems. They are useful for gaining knowledge, conveying information, or for regulating behaviour and at the same time for simulating properties of interest of structures and functions of an original system by means of simplified analogue representations. For this reason models may or may not be suitable for a given purpose. Some functions of electromagnetic wave systems can be represented only by a wave model, others by a particle model. The wave model is suitable for explaining diffraction, whereas atomic absorption and emission are better described by a

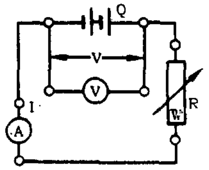
Model		Demarcation of the elements	
Structure	Function	Element	State
Circuit diagram 	Ohm's law $I = \frac{V}{R} [A]$	Current source 	————
		Ammeter 	Ampere, I in [A]
		Voltmeter 	Volt, V in [V]
		Resistance 	Ohm, R in [Ω]
Chemical equation $HA \rightleftharpoons H^+ + A^-$	Law of mass action $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\alpha^2}{(1-\alpha)} \cdot C_A$ (mole/l.)	Acid Molecule HA	$[HA] = (1-\alpha) \cdot C_A$ (mole/l.)
		Hydrogen ion H^+	$[H^+] = \alpha \cdot C_A$ (mole/l.)
		Acid anion A^-	$[A^-] = \alpha \cdot C_A$ (mole/l.)
		where α = dissociation degree of (dimensionless) C_A = acid concentration (mole/l.)	

Fig. 5. Simple structural and functional models.

model based on radiation particles. Of considerable importance in model building are analogies between elements and relationships in the original system on the one hand, and in the model on the other. In this way an analogous original system may be useful as a model for another system. A typical example is Bohr's very much simplified atomic model which represents a copy of the planetary systems with the analogies sun = atomic nucleus, planets = electrons, and gravitational field = electrical force, all coming into play. Models can only partly describe an original system. Thus working drawings represent only the complete structural model of a machine, and subfunctions and total functions of the machine must be separately described by means of a mathematical model.

Figure 5 gives two examples of simple structural and functional models.

3.4 *Input–output analysis, trial-and-error method, simulation*

Input–output analysis. Input–output analysis is a systems analysis technique which aims at explaining the functions of systems, generally treated as Black Boxes, on the basis of information on the states of the input and output elements. Should insufficient data be available, the input signals are varied between fixed limits while the output signals are recorded. An important part of input–output analysis is an external feedback between output and input and in particular a deduction concerning cause and effect. These deductions aid in the formulation of suitable input–output relationships and also the continuous improvement of a model function for the system being studied.

The relationship between input and output can be either unequivocal or probability-controlled. Unequivocal input–output relationships are those where the probability P for the occurrence of a particular input is virtually 100%. One can say that the output resulting from a given input is entirely predictable. Probability-controlled input–output relationships are characterized by the fact that one and the same input may give rise to different outputs, which are predictable with a probability $P < 100\%$. In the latter case not only input–output analysis but also control of the system become very much more difficult.

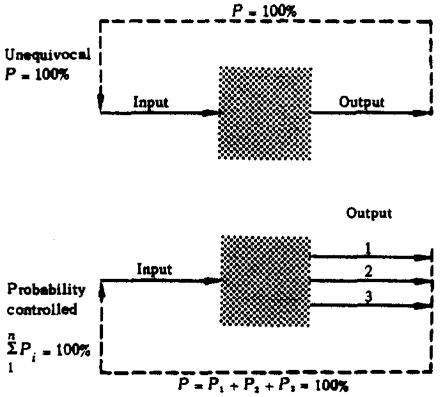


Fig. 6. Unequivocal and probability-controlled relationships.

The nuclear disintegration of a small number of atoms considered with respect to time (as input) and occurrence of disintegration (as output) is a typical probability-controlled process. Only when a sufficiently large number of atoms is considered will the effect of probability become negligibly small and a similar number of disintegrations occur in a similar interval of time, being predictable from a knowledge of the half-life and the disintegration equation.

Naturally, as far as possible it is sought to avoid statistical influences in systems in common use—they are to be considered as faults in a system or as interfering with the reliability. Such interferences can be very much reduced through feedback—in other words by suitable control mechanisms—in which case one speaks of automation. Another approach lies in a clever choice and demarcation of the permitted magnitudes of the states. Examples are the careful laying down and maintenance of working conditions such as working range, amount of reagents, temperature, volume, and other relevant parameters used in analytical investigations so that the probability effect as seen in the form of errors or loss of control is decidedly reduced.

In Fig. 6 the concepts of unequivocal and probability-controlled relationships are shown schematically.

An important practical use of input–output analysis is the *testing* and *control* of everyday systems for faultless behaviour. In this way analytical procedures or apparatus may be checked fairly easily for adherence to certain analytical functions by insertion of test signals (as input) and critical examination of the resulting measurements (as output). When such tests or controls are limited in this way to one or only a few known functions, input–output analysis can prove a useful and valuable aid in this special application, even for complex systems.

A comprehensive variation of the input signals to a Black Box system with an initially unknown function is in practice only feasible for relatively simple systems. In such cases the possible functions can be predicted and input–output analysis used to decide which of the possible functions is in fact realized. In this connection Fig. 7 shows a simple example in which a model with the same function as that of the system being studied is shown in addition to that system and all possible functions are explored in turn, whether meaningful or not. Bowman[2] has already shown that even in a system with only eight input elements and one output element, with states equal to 0 or 1, this

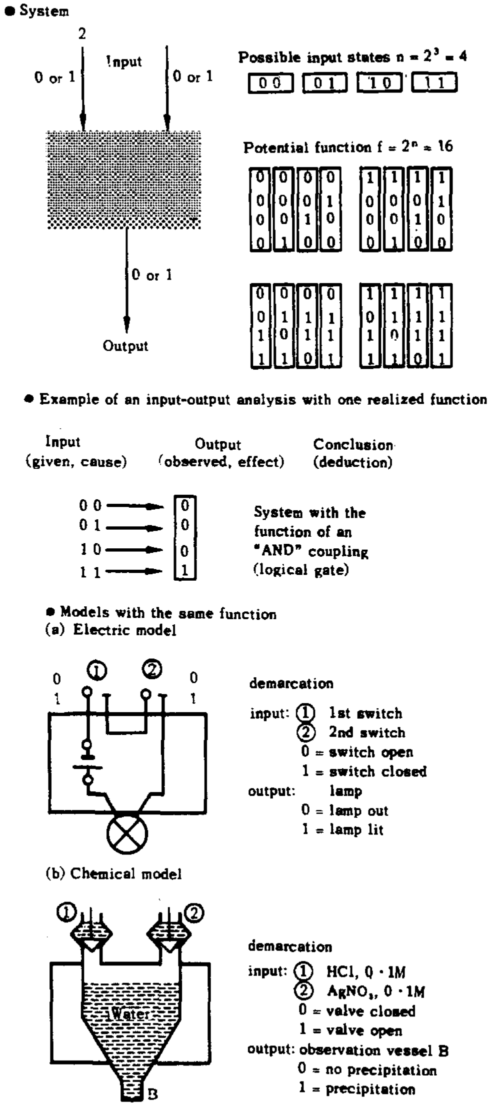


Fig. 7. Simple input–output analysis.

perfectionist way of going about things is quite useless. In this case there are $n = 2^8 = 256$ different inputs possible, and the astronomical number of $f = 2^n = 1{\cdot}2 \times 10^{77}$ possible functions. Thus pure input–output analysis is very rapidly ruled out as a means of ascertaining the unknown functions of a system.

The trial-and-error method. In contrast to the schematic and solely external-recording technique of input–output analysis, this is an active method aimed at explaining how the functions arise from the system; it is the basis of learning processes and research ability. The essential features of the trial-and-error method are that the ideas and the treatment should be purposive and should be assessed for their success. With regard to a specific goal, such as the solution of a given problem, one attempts at first a logical break-down of a large Black Box into a number of smaller Black Boxes which are connected to each other by as few relevant and unequivocal subfunctions as possible. This stepwise progressive logical dismantling is equivalent to a search for and finding of functionally essential sub-systems, in other words the investigation of an organization decisive for the functions of the complete system. As the name of the method suggests, pertinent considerations, and experiments if necessary, are explored and the results criticised and classified according to whether they are successful. In connection with the trial-and-error method, one may speak of "learning by results," "systematic testing," and "heuristic procedures."

Typical of the successful application of the trial-and-error method is the way in which Mendeleeff discovered the periodic system of the elements in 1868. He first wrote out on small cards the atomic weight, other properties, and compounds, of the 65 elements known at that time—we could now say that he collected and demarcated the states of the elements of the system. For months on end the cards were pushed around on the wall of the laboratory until some order—an organization—became apparent through functional similarities.

The stroke of genius lay in the acceptance of "holes," and the astonishingly accurate prediction of the properties of three then unknown elements, gallium, scandium, and germanium, which were found soon afterwards, in 1875, 1879, and 1886, respectively, not without the help of his predictions. Today we know not only of the subsystems alkali metals, alkaline earth metals, chalcogenides, noble gases and halogens, *etc.* but also of numerous other relationships in the form of electron configurations, physical dimensions and combining properties. The development of a new analytical research technique is at least in its early stages typified by trial-and-error in order to establish the best apparatus and operating conditions. The usefulness and reliability of individual modules and procedural steps may be tested more systematically as subsystems within the concept of an investigational system, by input–output analysis.

Figure 8 shows in a simple example the success of such a break down by trial-and-error as applied to Bowman's Black Box, whereby the number of possible functions is reduced from $1{\cdot}2 \times 10^{77}$ to only 784.

Simulation. The functions of an original system can be copied only to a limited extent even by a suitably designed model. In this respect corresponding function-models, also termed *simulators*, can be real (material) or abstract. Essential functions of the original system "aeroplane" are imitated during the training of pilots by flight simulators. Material simulators can be designed for motor vehicles, space conditions, learning processes, and many other things. Particularly valuable, however, are the abstract simulations of functions by mathematical models, such as, for example, the Monte Carlo method for optimizing quantitative chemical processes. In this manner functions of both simple and of complicated or even complex original systems may be not only simulated, but also predicted so as to help obtain some information, plan some activity, or make some decisions. Mathematical simulation, particularly when carried out on electronic computers, is often less time-consuming, less troublesome, and also much safer than actually carrying out experiments or spending months observing the real original system.

The simulation of coupled chemically reacting systems with 30 or more components in the liquid or gas phase, by use of a computer programme, has become of great practical significance; thousands of equilibrium states may be calculated as functions of concentrations, pressures, and temperatures in a matter of minutes. Here is a very simple example of the simulation of a chemical reaction.

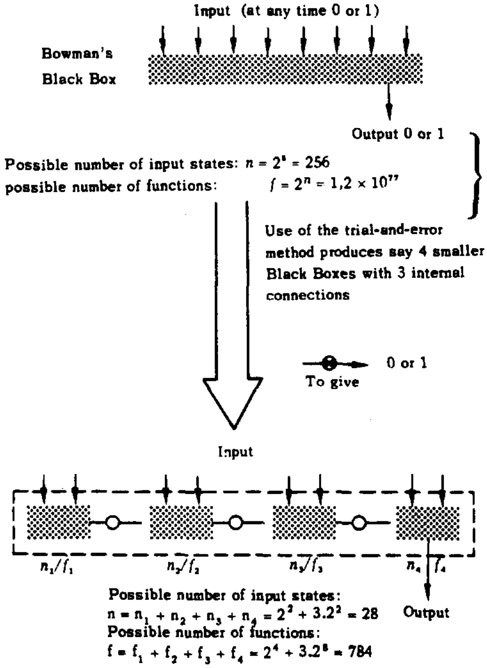


Fig. 8. Example of logical break-down of a Black Box into simpler units.

The chemical equation

$$HA \rightleftharpoons H^+ + A^-$$

is the abstract model of the dissociation of a weak acid. The function of the system may be described by the equation

$$K = C \cdot \frac{\alpha^2}{(1 - \alpha)}$$

derived from the law of mass action

$$K = [H^+] \cdot [A^-]/[HA]$$

where α is the degree of dissociation and C the total acid concentration. When $\alpha \ll 1$, the approximation $\alpha = \sqrt{K/C}$ is valid. One can now simulate, *i.e.*, calculate, values of α (as output) for given values of C (as input) using the simplified equation describing the dissociation properties of the original system "aqueous HA." The equation $\alpha = \sqrt{K/C}$ is the corresponding model function—or simulator—for the problem.

4. SYSTEM-ORIENTED WORKING METHODS

In the practice of systems analysis or systems design, the necessary thought and action are generally characterized by the four stages

Problem definition	Problemstellung
Demarcation	Abgrenzung
Model design	Modellerstellung
Simulation	Simulation

which are easily remembered, at least in German, by the initials PAMS. Figure 9 gives a general outline of the procedure.

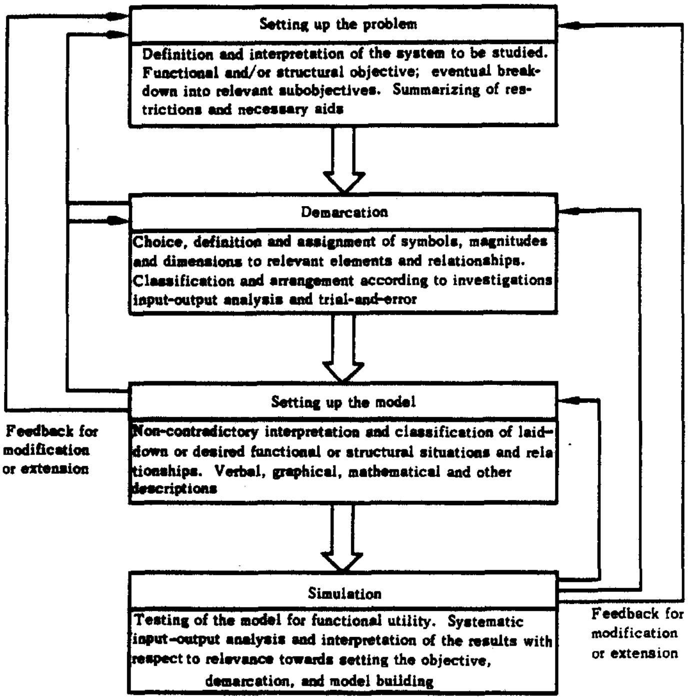


Fig. 9. The systems-oriented working technique PAMS.

The definition of each problem covers a particular system which must be recognized, demarcated, and designated. It appears at first very much as a Black Box, and the apparent problem lies in elucidation or construction of the functions or, more comprehensively, of the structures. The solution sought is to be described in terms of a single objective, which in the case of larger systems may be broken down into a sequence of subobjectives if need be. From this point on, the available aids and restrictions should be considered, and compiled in tabular form. By aids may be understood personnel, apparatus or machines, and other materials, and by restrictions, time, cost, and investment capital. Of course, for a difficult problem, only a crude correlation could be expected at a first attempt, and this must be further refined or modified in the successive stages through use of feedback from new knowledge.

Careful demarcation of elements and relationships relevant to the system and its objectives is a decisive factor for the rapid and successful solution to the problem. In this connection given limits of states must be considered, or such limits must be logically chosen. Since the problem at first assumes the nature of a Black Box, one is necessarily restricted in the initial approach to demarcating peripheral elements which have to be defined, and assigned symbols, magnitudes, and dimensions. Consider as an example of correct demarcation with high information content the input element HCl in an analytical problem. The addition of reagent, corresponding to input relationship, is unequivocally demarcated by

$$\boxed{20\ \text{mmole HCl (in 10·0 ml, aqueous, } 20 \pm 2°\text{C)}}$$

and is described in such a way as to be quantitatively reproducible. The nature of the system element is defined and symbolized by HCl. The state of this element is given magnitude and dimensions by "20 mmole." The information quoted in brackets provides an additional demarcation which can be left out of the preceding general stipulation.

Likewise the statement

addition of HCl

allows one to drop any demarcation which may make unavoidable an undesired probability-controlled relationship in the corresponding analytical system. Especially in the design of an analytical research system, a large number of other elements and relationships in addition to the reagents must be considered and demarcated. One may mention here equipment and techniques used for controlling the magnitude of the physical states. With such extensive systems a classification of the elements and treatment is inconvenient as a first step towards a definitive organization, in which case the methods of trial-and-error and input–output analysis are of most use for the demarcation investigation.

The results of such investigations should be summarized in tabular or graphical form, and continuously added to and refined. At this stage aspects may arise which necessitate a reconsideration and perhaps a modification of the original problem.

In the third stage a model is conceived, making use of the demarcation results and further information from the literature, specialist knowledge, and experience. This model retains without contradiction the already known facts and relationships and offers a functional or even a structural solution to the problem. The first model concepts are usually still of a very hypothetical nature or are limited to a part of the problem. Often the tedious work of setting up the model for the whole system can be very much simplified by the introduction and functional coupling of a prefabricated model as a subsystem. The first model concept must in any case be tested for its usefulness in the sense of achieving its aim, and if necessary be modified in the fourth stage, the simulation. In the case of extensive systems one must at this stage also seek the organization—that is a linking up into function-oriented subsystems. In setting up an analytical problem, the verbal and visual description of the experimental arrangement, of the sequence of the procedure, and of the final calculation can be interpreted as a model appropriate to the problem. Here, taking and preparing the sample, separation or masking of foreign substances, as well as the actual method of determination, can be considered as subsystems. In an even more general sense the division may be into planning, execution, and computation. Arithmetical models play an important role in most cases of computation. The practical application of GLC, X-ray crystallography, and the very powerful tool of mass spectrometry is scarcely possible without the use of suitable arithmetical models for the computation of the large number of data produced. Furthermore, there are some problems where the creation of an arithmetical model is really the nucleus of the problem. An example is the calculation of simultaneous equilibria in chemically reacting systems in solution or in the gas phase, with a large number of reacting species.

Prefabricated arithmetical models in the form of computer programmes for general use are turning out to be an indispensible aid to the solution of problems which would otherwise remain unsolved because of the demands on time, cost, and personnel. Another type of prefabricated model includes standardized systems, in which the limits of the states of the system elements and the relationships are extensively defined in the form of procedure and calculation instructions. In this way analytical quantitites can be interpreted as subsystems with definitions of the working range, sample size and content.[3] These subsystems can make the planning of procedures and the comparison of results much easier.

In the last stage, the simulation, the functional utility of the model conceived in the third stage may be tested in terms of achieving its goal, but specific final states of the original system are also often predicted with the help of functional models. Through simulation, new knowledge and experience should be gained which allow continuous refinement of the model or prediction of a state and behaviour of the original system under certain given conditions. Furthermore, the results of simulation can be successful in extending the demarcation or even the problem itself. The functional models employed for the simulation are either realistic or appear as conceptual models or as abstract arithmetical models in which these types are often combined. Such a conceptual model is the double-helix model of DNA used for the simulation of genetic processes. Realistic models include model railways or point- and signal-control desks used to simulate railway traffic, or experimental layouts for the simulation of heavy-current electrical engineering.

The process of simulation is characterized by the methods of input–output analysis, whereas aspects of trial-and-error methods are usually adopted for improving the model by feedback from the results. The more difficult a problem is, the more often, as a rule, must the PAMS sequence be repeated either in part or in full, with constantly renewed feedback until a satisfactory solution is arrived at. Figure 9 gives a survey of the system-oriented working method PAMS.

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Zusammenfassung—Die zwölf Grundbegriffe der Systemtheorie—System, Element, Relation, Funktion, Struktur, Organisation, Rückkopplung, Black Box, Modell, Input–Output-Analyse, Trial-and-Error-Methode, Simulation—werden allgemein definiert und in Bezug auf die chemische Analyse interpretiert. Die Unterscheidung zwischen einer allgemein akzeptablen kurzen und genauen Definition und einer für ein spezielles Gebiet eigentümlichen Interpretation vermeidet im Falle universell verwendeter Begriffe einseitige Ansichten und Vorstellungen. Es werden mit Bedacht einfashe Systeme ausgewählt und die verwendeten Begriffe an Diagrammen klargemacht. Ein systemorientierter Weg mit rückgekoppelten Stufen PAMS (Problemstellung, Abgrenzung, Modell-Erstellung, Simulation) wird skizziert, der sich in der praktischen Systemanalyse und im Systementwurf bewährt hat. Die Arbeitsgruppe wird in späteren Publikationen über spezielle analytische Systeme berichten, die bei der Automation von erheblicher Bedeutung sind. Forscher mit besonderen Interessen auf diesen Gebieten werden herzlich eingeladen, ihre auf diesen Definitionen beruhenden kritischen Meinungen, Vorschläge und Interpretationsbeispiele mitzuteilen.

Résumé—On donne des définitions générales aux douze termes basiques de la théorie des systèmes—système, élément, relation, fonction, structure, organisation, contre-réaction, boîte noire, modèle, analyse des entrées et des sorties, méthode par approximations successives, simulation—et on les interprête aussi sous l'angle de l'analyse chimique. La distinction entre une définition brève et précise généralement acceptable et une interprétation propre à un domaine spécialisé particulier évite, dans le cas de termes universellement utilisés, une vue et une conception polarisées. Des systèmes simples sont délibérément choisis et les termes utilisés sont clarifiés au moyen de diagrammes. On indique une voie orientée vers les systèmes, avec stades couplés de

contre-réaction (définissant le problème, fixant les limites, concevant le modèle, simulation) qui s'est révélée utile dans l'analyse de systèmes pratiques et dans la conception de systèmes. Le groupe de travail traitera, dans des publications ultérieures, de systèmes analytiques spécifiques qui sont d'une importance considerable en automation. Ceux qui ont un intérêt particulier dans ces domaines sont chaudement invités à communiquer leurs opinions critiques, suggestions et exemples d'interprétations basées sur ces définitions.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR CHANGE

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Summary—The rates of colour change reactions of metallochromic indicators such as XO, PAN, PAC and TAC at the equivalence point were measured in the chelatometric titration of copper, nickel, zinc or cobalt. Hexamine buffer has strong disturbing effects on the rate of colour change of the copper or nickel XO chelate. The effects of various auxiliary complex-forming agents were also examined. Bathophenanthroline, 2,2'-bipyridyl, 8-hydroxyquinoline, TPTZ, ethylenediamine, iminodiacetic acid, acetylacetone, 1,10-phenanthroline and glycine improve the colour change of the XO and PAN chelates of copper. Some titration methods for copper or nickel with XO or PAN as indicator are proposed.

In a chelatometric titration, the colour change of the indicator near the equivalence point is governed by the rate of the substitution reaction between the metal indicator chelate and the titrant, as well as by the equilibrium involved. Few papers have been published on the rate of the colour-change reaction.[1-3] Since Xylenol Orange (XO) forms an inert complex with copper or nickel, it cannot be used as an indicator in direct titration of these metal ions. Přibil[1] found that in the titration of copper with XO as indicator the colour change is remarkably improved by addition of a small amount of 1,10-phenanthroline. Berndt and Šára[2] found that acetate does the same and that copper can be titrated at about 70° in acetate buffer solution. However, the role of such auxiliary complex-forming agents is not yet fully elucidated.

An extensive study has been made of the effects of various auxiliary complex-forming agents on the rates of colour change reactions of metal indicators. From the results some titration methods for copper or nickel are proposed.

EXPERIMENTAL

Reagents

PAN [1-(2-pyridylazo)-2-naphthol] was purified by vacuum sublimation. XO was used as supplied. PAC [2-(2-pyridylazo)-4-methylphenol][4] and TAC [2-(2-thiazolylazo)-4-methylphenol][5] were synthesized by the procedures described previously. The 1,10-phenanthroline solution was prepared with redistilled water and a small quantity of hydrochloric acid. The solutions of copper nitrate and nickel nitrate were prepared from copper metal (99·999% purity) and reagent-grade nickel nitrate respectively.

Procedure

A solution (100 ml) containing metal ion ($5 \times 10^{-4}M$), indicator ($2{\cdot}5 - 5 \times 10^{-6}M$), EDTA ($4{\cdot}75 \times 10^{-4}M$), buffer solution and an auxiliary complex-forming agent was placed in a silica cell with light-path of 5·0 cm. Then 0·5 ml of $6 \times 10^{-3}M$ EDTA (*i.e.*, a 1% excess) was rapidly added by syringe with stirring. The transmittance of the solution at a suitable wavelength was recorded as a function of the reaction time. All experiments were done at 25 ± 2°.

RESULTS AND DISCUSSION

Copper

The buffers used in chelatometric titrations sometimes show complex-forming tendencies with the metal ions to be titrated. MES [2-(*N*-morpholino)ethanesulphonic acid] buffer[6] complexes copper only negligibly. The rates of colour change reactions of various copper-indicator chelates with EDTA were measured at various pH values. The results are shown in Table 1. Since the optimum pH range[7,8] for titration of copper with XO or PAN as indicator is between 5 and 6, hexamine and acetate buffers were also examined.

The effects of various auxiliary complex-forming agents are shown in Table 2. Small amount of 2,2′-bipyridyl, 8-hydroxyquinoline, bathophenanthroline, 1,10-phenanthroline and 2,4,6-Tris(2-pyridyl)-5-triazine (TPTZ) improve the rate of the colour-change reaction of XO remarkably, and also that of PAN. Ethylenediamine, iminodiacetic acid, acetylacetone and glycine also improve matters with both indicators, but are effective only in high concentrations. α-Picoline and pyridine make the reactions slower.

The absorption spectra of the copper–XO and copper–PAN chelates have λ_{max} at 575 and 550 nm respectively. On addition of 1,10-phenanthroline, the λ_{max} values shift to 580 and 540 nm respectively. These shifts are due to formation of mixed-ligand complexes and also occur near the equivalence point of a copper–EDTA titration with XO or PAN as indicator. Hence formation of a mixed-ligand complex may be the decisive factor in improvement of the rate of colour change.

Přibil[1] considered that the increase in the rate of colour change of the metal–indicator complex MI by an auxiliary complex-forming agent was due to a rapid substitution reaction near the equivalence point

$$MI + X = MX + I \tag{1}$$

followed by a rapid substitution reaction with titrant Y

$$MX + Y = MY + X \tag{2}$$

Table 1. The half-life of the colour change reactions in the titration of copper*

		$t_{1/2}$, *sec*			
Buffer	pH	XO	PAN	TAN	TAR
0·05*M* MES	3·5		5		
	4·5	8	8	2	2
	5·5	12	14	2	2
	6·0	28	14	2	2
	6·5		18		
0·1*M* acetate	4·2		8		
	5·1	12	23		
	5·5	18	29		
	5·9	25	40	2	2
0·1*M* hexamine	5·5		14		
	6·0	300	14	2	2
0·1*M* triethanolamine	6·0	18	14		

* If the concentration of free EDTA is about the same as that of the metal-indicator complex initially present and the reaction is second order, the rate of reaction can be expressed as $-d[A]/dt = k[A]^2$ where [A] is the concentration of either species. If $[A]_0$ is the initial concentration of indicator then $t_{1/2} = 1/k[A]_0$.

Table 2. Effects of auxiliary complex-forming agents on indicators for the titration of copper (pH 6, in MES buffer)

	$t_{1/2}$, *sec*	
Auxiliary complex-forming agent	XO	PAN
$10^{-6}M$ 1,10-phenanthroline	2	2
$10^{-6}M$ 2,2'-bipyridyl	2	2
$10^{-6}M$ bathophenanthroline	3	2
$10^{-6}M$ 8-hydroxyquinoline	3	3
$10^{-5}M$ TPTZ	3	6
$10^{-6}M$ DDC*	23	6
$2 \times 10^{-2}M$ α-picoline	174	21
$2 \times 10^{-2}M$ pyridine	157	45
$10^{-3}M$ ethylenediamine	2	8
$10^{-3}M$ iminodiacetic acid	2	2
$10^{-3}M$ acetylacetone	7	6
$10^{-2}M$ glycine	2	8

* Sodium diethyldithiocarbamate.

The X liberated in reaction (2) immediately reacts with more MI according to (1). However, from the conditional stability constants[7,8] of the copper chelates at pH 6 ($K_{\mathrm{Cu(PAN)'}} = 10^{10\cdot 1}$, $K_{\mathrm{Cu(XO)'}} = 10^{8\cdot 1}$, $K_{\mathrm{Cu(phen)'}} = 10^{9\cdot 0}$) it might be difficult to substitute X for I. We therefore propose that a mixed ligand complex is formed

$$\mathrm{MI + X = MIX} \tag{3}$$

and that it is this which undergoes the rapid substitution reaction with EDTA

$$\mathrm{MIX + Y = MY + I + X} \tag{4}$$

followed by repetition of reaction (3). The copper–PAN complex has a stable planar structure.[9] When 1,10-phenanthroline is added, the structure of the copper–PAN chelate may change to a distorted octahedron.[10] This is the reason why the mixed-ligand complex is labile.

Nickel

With the exception of 1,10-phenanthroline and 2,2'-bipyridyl, none of the auxiliary complexing agents had an improving effect (Table 3), and even with these two the rate is not improved sufficiently for practical use.

Other metals

The colour change of the Zn–XO complex in hexamine, acetate or MES buffer solution was fast, the half-life being 2 sec.

The colour change of the Co–XO complex is slow as in the case of copper, and again 1,10-phenanthroline improves the rate (Table 3).

Titrations

When 1-(2-thiazolylazo)-2-naphthol (TAN) or 4-(2-thiazolylazo)resorcinol (TAR) is used as indicator, the colour change at the equivalence point is very sharp in the titration of copper.[11] The half-lives of these colour change reactions are 2 sec (Table 1).

Table 3. The half-life of colour change reactions for nickel and cobalt

Buffers and auxiliary complex-forming agents*	$t_{1/2}$, sec							
	Nickel						Cobalt	
	XO	(pH)	PAC	(pH)	TAC	(pH)	XO	(pH)
0·05*M* MES	86	(4)	7000	(5)	26	(6)	14	(5)
	560	(5)					39	(6)
0·1*M* acetate	112	(4)	7000	(5)	20	(6)	28	(5)
	980	(5)						
0·1*M* hexamine	1600	(5)			25	(6)	21	(5)
							40	(6)
$5 \times 10^{-6}M$ 1,10-phenanthroline	70	(5)	380	(5)	10	(6)	6	(6)
	9	(5)†						
$10^{-6}M$ bathophenanthroline	770	(5)			25	(6)		
$10^{-6}M$ 8-hydroxyquinoline	770	(5)			14	(6)		
$10^{-6}M$ 2,2′-bipyridyl	270	(5)			14	(6)		
$10^{-5}M$ TPTZ					21	(6)		
$5 \times 10^{-4}M$ iminodiacetic acid	3000	(5)			17	(6)		
$10^{-3}M$ ethylenediamine	2000	(5)						
$10^{-2}M$ glycine	600	(5)						

* Auxiliary complex-forming agents were added to 0·05*M* MES buffer solutions.
† At 50°.

For a sharp colour change at the equivalence point, then, the half-life for the indicator reaction under the titration conditions should be less than about 10 sec.

It was found that a sufficiently rapid colour change can be obtained by the addition of 1,10-phenanthroline, 8-hydroxyquinoline, 2,2′-bipyridyl, bathophenanthroline, TPTZ, ethylenediamine, iminodiacetic acid or glycine in the titration of copper with XO or PAN as indicator. However, the indicator colour change occurs before the equivalence point if the concentration of auxiliary complex-forming agent is high. The effects of auxiliary complex-forming agent on the colour change near the equivalence point were examined by photometric titration at constant speed. Concentrations from 10^{-6} to $10^{-5}M$ of 1,10-phenanthroline, 2,2′-bipyridyl, bathophenanthroline, 8-hydroxyquinoline, and TPTZ are enough to yield a sharp colour change at room temperature, but ethylenediamine, iminodiacetic acid and glycine must be present in concentrations of $10^{-3}M$.

When the concentration of 1,10-phenanthroline is high, the colour change of PAN occurs slightly after the equivalence point, because the formation constant of the mixed-ligand complex[12] ($K_{\mathrm{Cu(PAN)(phen)}} = 10^{21 \cdot 2}$) is higher than that of the copper-PAN chelate[7] ($K_{\mathrm{Cu(PAN)}} = 10^{15 \cdot 6}$). However, in the visual titration, a sharp colour change can be obtained.

In the titration of nickel, with XO as indicator, if a small amount of 1,10-phenanthroline is added and the solution is heated to >50°, a very sharp colour change is obtained. Since the colour contrast between XO and its nickel chelate at pH 5–6 is large, XO is recommended as a good indicator for nickel. With TAC as indicator the presence of 1,10-phenanthroline permits the titration of nickel at room temperature.

The buffer solutions used in chelatometric titrations must obviously be chosen with due regard to their effect on the rate of indicator colour change.

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Zusammenfassung—Die Farbänderungsreaktionen von Metallfarbindikatoren wie XO, PAN, PAC und TAC am Äquivalenzpunkt wurden bei der chelatometrischen Titration von Kupfer, Nickel, Zink oder Kobalt verfolgt. Hexamin-Puffer stört die Farbänderung des Kupfer- oder Nickel-XO-Chelats stark. Der Einfluß verschiedener Hilfs-Komplexbildner wurde ebenfalls untersucht. Bathophenanthrolin, 2,2′-Bipyridyl, 8-Hydroxychinolin, TPTZ, Äthylendiamin, Iminodiessigsäure, Acetylaceton, 1,10-Phenanthrolin und Glycin verbessern den Farbumschlag der XO- und PAN-Chelate von Kupfer. Einige Titrationsmethoden für Kupfer oder Nickel mit XO oder PAN als Indikator werden vorgeschlagen.

Résumé—On a mesuré les vitesses des réactions de changement de coloration d'indicateurs métallochromes tels que XO, PAN, PAC et TAC au point d'équivalence dans le titrage chélatométrique du cuivre, du nickel, du zinc ou du cobalt. Le tampon à l'hexamine a de fortes influences perturbatrices sur la vitesse du changement de coloration du chélate XO du cuivre ou du nickel. On a aussi examiné les influences de divers agents auxiliaires générateurs de complexes. Les bathophénanthroline, 2,2′-dipyridyle, 8-hydroxyquinoléine, TPTZ, éthylènediamine, acide iminodiacétique, acétylacétone, 1,10-phénanthroline et glycine améliorent le changement de coloration des chélates XO et PAN du cuivre. On propose quelques méthodes de titrage pour le cuivre ou le nickel avec XO ou PAN comme indicateur.

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ANALYSIS OF PRECISION OF ACTIVATION-ANALYSIS METHODS*

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Summary—The precision of an activation-analysis method prescribes the estimation of the precision of a single analytical result. The adequacy of these estimates to account for the observed variation between duplicate results from the analysis of different samples and materials, is tested by the statistic T, which is shown to be approximated by a χ^2 distribution. Application of this test to the results of determinations of manganese in human serum by a method of established precision, led to the detection of airborne pollution of the serum during the sampling process. The subsequent improvement in sampling conditions was shown to give not only increased precision, but also improved accuracy of the results.

The *precision* of an analytical method is one of its most important performance characteristics, expressing its ability to reproduce results within a predictable range, when applied correctly to a material of known composition. In spite of its importance, no generally accepted definition of the concept is available.

The precision of an *analytical result* is usually expressed in terms of its standard deviation σ, and may also be defined as the absolute weight of the result, ω, given by

$$\omega = \frac{1}{\sigma^2} \tag{1}$$

The precision of the best mean, μ, of n independent results, becomes

$$\omega_\mu = \sum^n \omega_i \tag{2}$$

and the average precision of these results is

$$\bar{\omega} = \frac{\sum^n \omega_i}{n} \tag{3}$$

The precision of an *analytical method* is here defined as a set of quantitative instructions for the estimation of the precision of a single analytical result. This definition is in line with the definitions of performance characteristics and analytical methods proposed by Wilson.[1]

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Estimation of precision

The precision of a single analytical result represents the overall effect of a number of independent, random errors, associated with different stages of the analysis

$$\sigma^2 = \sigma_a{}^2 + \sigma_b{}^2 + \cdots + \sigma_n{}^2 \tag{4}$$

The individual contributions are determined by the actual experimental conditions under which a particular result is obtained, and will depend on the type and quantity of material analysed, as well as on the result itself. In a rigidly standardized procedure for routine analysis within a limited range of concentrations, the precision of the analytical method may be expressed simply as a constant absolute or relative standard deviation.

In activation analysis the useful range of an analytical method may cover many orders of magnitude, and different components of the total variance will dominate at different levels. In addition, the statistics of the counting process introduce a variance component into equation (4), which may well be different even for identical samples. The precision of an activation analysis method must therefore specify the estimation of individual variance components, and the precision of a single result is estimated as the overall effect of counting statistics, and of relative and absolute random errors.

The adequacy of the estimated analytical precision is tested by the repeated analysis of homogeneous samples, representative of materials and concentrations for which the method is claimed suitable. However, the statistical analysis of such data cannot be made with conventional analysis of variance, which assumes the same precision for all data, nor with weighted analysis of variance, which requires all standard deviations to have known ratios. The analysis of precision of activation-analysis results therefore requires a somewhat different approach.

MATHEMATICAL CONSIDERATIONS

The mathematical development corroborates the analogy between errors of which the contribution to the precision is *estimated a posteriori* by means of instructions included in the precision of the analytical method, and errors making a contribution which is *known a priori.*

Estimated precision

Let a number, M, of different materials be subjected to repeated analysis, and let the total number of analytical results be N, where $N \geq 2M$. Let the mth material be analysed I_m times, and let y_{im} represent the ith result. Thus we have

$$m = 1, \ldots, M$$

$$i = 1, \ldots, I_m \qquad \text{for material } m$$

and

$$\sum_1^M I_m = N$$

With an estimated precision of the results $\hat{\omega}_{im}$ given by

$$\hat{\omega}_{im} = \frac{1}{s_{im}{}^2} = w_{im} \tag{5}$$

their mean value is estimated by

$$\hat{\mu}_m = \frac{\sum_{I}^{I_m} w_{im} y_{im}}{\sum_{I}^{I_m} w_{im}} \tag{6}$$

in strict analogy with the case of known precision.

For all materials together the residual sum of squares, T is given by

$$T = \sum_{m}^{M} \sum_{I}^{I_m} w_{im}(y_{im} - \hat{\mu}_m)^2 \tag{7}$$

which can be shown to approximate asymptotically to the χ^2-distribution with

$$\sum_{m}^{M} (I_m - 1) = N - M \text{ degrees of freedom,}$$

valid in the case of known precision.

This, however, does not mean that such an approximation is justified for the analysis of precision of a limited number of actual analytical results.

Duplicate analysis

If each material is analysed only twice, equation (7) is reduced to

$$T = \sum_{1}^{M} \frac{(y_{1m} - y_{2m})^2}{s_{1m}^2 + s_{2m}^2} \tag{8}$$

Provided $(y_{1m} - y_{2m})$ has a normal distribution with zero mean and variance $(\sigma_{1m}^2 + \sigma_{2m}^2)$, and $(s_{1m}^2 + s_{2m}^2)$ is a central estimate of $(\sigma_{1m}^2 + \sigma_{2m}^2)$, the individual terms in the expression

$$T = \sum_{1}^{M} \frac{(y_{1m} - y_{2m})^2/(\sigma_{1m}^2 + \sigma_{2m}^2)}{(s_{1m}^2 + s_{2m}^2)/(\sigma_{1m}^2 + \sigma_{2m}^2)} \tag{9}$$

will have a χ^2-distribution with 1 degree of freedom in the numerator, whereas the estimate of the denominator is unity.

If the relative standard error of the estimated precision is sufficiently small, then the values of T have a χ^2-distribution with M degrees of freedom; if in addition $(s_{1m}^2 + s_{2m}^2)$ is independent of $(y_{1m} - y_{2m})$, the degree of approximation is directly expressed by the deviations from unity of the denominator in equation (9).

Under such conditions the statistic T in equation (8) is suitable for testing the adequacy of the estimated precision to account for the observed variability of duplicate results.

Poisson statistics

Estimates of precision based on the Poisson distribution are of paramount importance for analytical results based on the measurement of radioactivity.

Let the analytical results be calculated as

$$y_{im} = K_{im} \times P_{im} \quad \text{and} \quad s_{im}^2 = K_{im}^2 \times P_{im}$$

where the factor K converts the recorded number of counts, P, into the final result.

The individual terms in equation (8) now become

$$S_m = \frac{(y_{1m} - y_{2m})^2}{s_{1m}{}^2 + s_{2m}{}^2} = \frac{(P_{1m} - \kappa_m P_{2m})^2}{P_{1m} + \kappa_m{}^2 P_{2m}}, \tag{10}$$

where $\kappa_m = K_{2m}/K_{1m}$.

For $\kappa = 1$ all conditions specified in the preceding section are fulfilled.[2]

For κ in the neighbourhood of 1 the correlation between the terms $(P_{1m} + \kappa_m{}^2 P_{2m})$ and $(P_{1m} - \kappa_m P_{2m})$ is small, so that deviations from the χ^2-distribution are caused only by deviations from unity of the denominator in equation (9).

Application of the χ^2 distribution to test the adequacy of estimates of precision based on Poisson distributions by means of equation (8) is therefore justified.

APPLICATIONS IN ACTIVATION ANALYSIS

In the precision of an activation-analysis method contributions from the counting process to the precision of the analytical result should be estimated on the basis of a Poisson distribution, rather than a binomial distribution.[3] In addition, the number of counts recorded in an actual analysis will always be large enough to justify an approximation to the normal distribution.

The situation where a duplicate analysis is based on a single counting of the comparison standard is therefore accurately depicted in the preceding section with $\kappa_m \neq 1$ representing the decay correction.

For the analysis of precision of the analytical method, however, each sample should be activated separately along with its own comparison standard, so that all sources of variation are allowed to influence the results. In this case κ_m becomes a variable, but in return its value will be close to $\kappa_m = 1$, and its precision will usually be much higher than that of the analytical result. The χ^2-distribution of equation (10) is therefore retained with good approximation.

The analysis of precision of activation-analysis results may thus safely be performed by assuming a χ^2 distribution for the values of T from equation (8).

$$T = \sum_1^M \frac{(y_{1m} - y_{2m})^2}{\hat{\sigma}_{1m}{}^2 + \hat{\sigma}_{2m}{}^2} \tag{11}$$

and in analogy with equation (4)

$$\hat{\sigma}^2 = s_a{}^2 + s_r{}^2 + s_c{}^2 \tag{12}$$

represents the combined effect of all absolute and relative, random errors, as well as counting statistics (variances $s_a{}^2$, $s_r{}^2$ and $s_c{}^2$ respectively).

The preferred experimental design is to analyse in duplicate, which also gives the most efficient coverage of range and materials. If more than two results are available for the same material, randomly selected, independent pairs may be included in the calculation of T to increase the number of degrees of freedom.

If the materials analysed are known to be homogeneous, high values of T indicate lack of control of some significant parameter, and improvements in the analytical procedure should be introduced. Low values of T indicate lack of independence of different contributions to the precision, or failure of the experimental design to encompass all expected sources of variation.

Determination of manganese in human serum

A neutron-activation analysis method for the determination of low concentrations of manganese has been developed by Damsgaard.[4] The method employs radiochemical separation by solvent extraction of 1 mg of added manganese carrier, and the chemical yield is determined by ^{54}Mn tracer.

In this case counting statistics include a contribution from the yield measurement, and the only remaining known source of random error is the variation of the ratio of the neutron-flux densities, to which sample and comparison standard are exposed during irradiation. The contribution of this effect to the precision of results has been measured previously and can be expressed as a relative standard deviation of 3·5 %. The corresponding variance is added to the counting statistics according to (12), which now represents the estimated precision of a particular result.

The adequacy of these estimates was tested by analysis of Bowen's kale and dried animal blood from IAEA. These materials are expected to be homogeneous, and their manganese concentrations differ by 2 orders of magnitude; they are thus eminently suitable for testing the precision of the analytical method.

A total of 10 single determinations, equivalent to 5 duplicates, was made on these two materials, and the resulting value of T according to (11) is given in Table 1, and does not indicate the presence of unknown sources of variation.

The method was next applied to the analysis of duplicate samples of human serum, taken by the staff of a large Copenhagen hospital with great care to avoid contact with materials likely to contaminate the samples with traces of manganese.

A total of 11 duplicate samples was analysed, and the resulting value of T given in Table 1 clearly reveals the presence of unknown sources of variation.

The precision of the analytical method being well established, it was concluded that duplicate samples of the same serum were not identical, but caused an additional, estimated standard error of 0·34 ppM. The corresponding decrease of precision leaves no possibility of detecting differences between individual samples of serum, as shown in the first column in Table 2.

Considerable improvements in the sampling procedure were therefore required, and a detailed study[5] of the individual steps indicated that contamination might be caused by airborne particulate matter—usually referred to as dust. Another set of samples was

Table 1. Experimental tests of estimated precision of manganese determinations

Material	Kale	Blood	Serum
Manganese level	15 *ppm*	0·15 *ppm*	0·5 *ppM*†
M	1	1	11
N	4	6	22
Degrees of freedom*	5		11
T	2·73		285
$P(\chi^2 > T)$	0·75		$< 10^{-10}$

* Number of independent pairs = duplicates.

† ppM = parts per milliard.

Table 2. Tests of improvement of sampling conditions for serum

Sampling conditions	Original	Improved	
Standard error, ppM	$s_a = 0{\cdot}34$	$s_a = 0{\cdot}34$	$s_a = 0{\cdot}04$
Variation between	Samples	Duplicates	Samples
M	1	11	1
N	11	22	11
Degrees of freedom	10	11	10
Test parameter	$F^* = 1{\cdot}02$	$T = 0{\cdot}29$	$F^* = 10{\cdot}43$
Probability	0·50	$<10^{-5}$	$< 0{\cdot}001$

* Estimated population variance multiplied by average estimated precision of a single determination with 11 degrees of freedom.

therefore obtained by the same technique as previously, but under more secluded conditions, and by keeping the samples covered essentially all the time. A total of 11 duplicate samples was again analysed, and the value of T was calculated on the assumption that no improvement had been achieved, so that the estimated sampling error was 0·34 ppM.

The resulting value of T given in Table 2 clearly shows that a highly significant reduction of variation between duplicate samples was in fact observed as a consequence of shielding the samples from atmospheric pollution. The residual variation between duplicate samples corresponded to a standard deviation of 0·04 ppM, and the precision of a single determination is now entirely satisfactory for the detection of differences between samples of serum, as shown in the last column of Table 2.

Precision and accuracy

The detection of airborne contamination of serum samples by the analysis of precision also has implications for the accuracy of the results. The reduction of *variation* between duplicates brought about by improvements in sampling conditions does not necessarily mean that the *level* of contamination has been reduced to insignificance.

In the present instance, however, this seems to be the case with a high degree of certainty, because the mean concentrations are not significantly influenced by the improved sampling conditions, as shown in Table 3.

The quantities of dust present in different samples of serum can reasonably be expected to have a Poisson distribution, which means that their variance ratios equal the ratios of the means.

Table 3. Mean and standard error for alternative sampling conditions

Sampling conditions	Sample mean *ng/ml*	Standard error (*ng/ml*) of Mean	Standard error (*ng/ml*) of Sampling
Original	0·62	0·10	0·34
Improved	0·54	0·05	0·04

Here, a variance ratio of 75 corresponds to a difference of 0·08 ± 0·12 ng/ml between the means, and the level of contamination for the improved sampling conditions is estimated at well below 0·005 ng/ml, which is completely negligible.

DISCUSSION

The sensitivity for the detection of unknown errors by the analysis of precision far exceeds that obtained with mere comparison of means, as brought out by the insignificance of the difference between mean values in Table 3. In addition, the materials analysed need not have known concentrations, so long as their homogeneity can be trusted.

The type of errors detected may be random, as well as non-random, and may have a bearing also on the accuracy of the results. On the other hand, a constant bias will usually escape detection, but proof of its existence requires knowledge of the analytical precision.

The localization of errors is performed by stepwise application of the method to establish the stage of the entire procedure where uncontrolled variation appears. The origin of the errors, however, must be left to the imagination of the analyst. Once the probable origin has been decided, the source of error may be eliminated; alternatively its effect may be measured separately, as was the case with the effect of a slightly different neutron flux-density between sample and comparison standard in the present example.

With proper control of the analytical procedure, unknown errors must be referred to the sampling procedure—or to actual heterogeneity of the material. Contamination by contact with equipment used in the sampling process may be estimated by neutron activation of the equipment and subsequent analysis of an inactive sample.[6]

The effect of airborne pollution of the sample (observed in the present example) can hardly be eliminated entirely, but at the same time no direct experimental measurement of its influence suggests itself. The variance contribution from this source therefore had to be estimated from the same results as used in the analysis of precision.

The problems involved in such estimation have recently been studied by Currie,[7] who showed that the determination of a small residual error with good precision requires a very large number of experimental results.

In the present example the residual error was greater than the known errors, while at the same time it was insignificant compared with the variation between samples. The current value of 0·04 ppM may thus be included in the precision of the entire analytical procedure as an acceptable estimate of the standard error of sampling.

CONCLUSION

Verification of the estimated precision of analytical results is an important part of the quality control of analytical work, and may be performed by the analysis of precision with a χ^2 test. Knowledge of precision is also necessary for judgement of the accuracy of the analytical method.

The great range covered by activation-analysis methods makes the analysis of precision particularly appropriate, and at the same time the techniques employed are not very susceptible to human interference, hence the results are less subject to unforeseeable sources of error. Conditions for reliable estimates of precision in activation analysis are therefore very favourable.

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Zusammenfassung—Die Genauigkeit einer aktivierungsanalytischen Methode schreibt die Abschätzung der Genauigkeit eines einzelnen Analysenergebnisses vor. Inwieweit diese Abschätzung die beobachtete Variation zwischen Doppelergebnissen der Analyse verschiedener Proben und Materialien wiedergibt, wird durch das statistische T geprüft, das, wie gezeigt wird, sich durch eine X^2-Verteilung annähern läßt. Die Anwendung dieses Tests auf die Ergebnisse von Manganbestimmungen in menschlichem Serum mit einer Methode von wohl bekannter Genauigkeit führte zu der Entdeckung, daß das Serum während der Probenahme aus der Luft verunreinigt wurde. Die daraufhin vorgenommenen Verbesserungen bei der Probenahme ergaben nicht nur eine höhere Genauigkeit, sondern auch eine bessere Richtigkeit der Ergebnisse.

Résumé—La précision d'une méthode d'analyse par activation prescrit l'estimation de la précision d'un seul résultat analytique. La valeur de ces estimations pour rendre compte de la variation observée entre des résultats répétés de l'analyse de différents échantillons et produits, est appréciée par la statistique T, qui est reconnue être calculée de manière approchée par une distribution χ^2. L'application de cette méthode d'appréciation aux résultats de dosages de manganèse dans le sérum humain par une méthode de précision établie, a conduit à la détection d'une pollution par l'air du sérum pendant le processus d'échantillonnage. On a montré que le perfectionnement des conditions d'échantillonnage donne non seulement une précision accrue, mais aussi une fidélité améliorée des résultats.

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DETERMINATION OF OXYGEN AND SILICON IN ROCKS BY 14-MeV NEUTRON-ACTIVATION ANALYSIS AND ITS PRECISION

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Summary—Oxygen and silicon have been determined in the six new U.S. Geological Survey standard rocks and two standard refractory materials by 14-MeV neutron-activation analysis, followed by both single and multichannel analyser counting of the induced ^{16}N (4·5–8 MeV gamma radiation) and ^{28}Al activities (1·78 MeV photopeak). Owing to the long analysing time per pulse, dead-time corrections are necessary in multichannel analyser counting. Four methods were investigated in this work: counting in the live-time mode without additional correction, short counting corrected by an external live-time scaler, the method of Bartošek, and the method of Schonfeld. Each measurement was controlled by a simultaneous measurement with a single-channel analyser. Silica ignited at 1000° was used as a reference. Correction was made for the interfering elements, F, P, Al, Fe and Mg, using literature data. Attention was paid to neutron, gamma and beta attenuation. For oxygen the mean coefficient of variation for a single determination with a single-channel analyser was 1·7%, for silicon 1·1%. The mean results for single-channel counting were compared with literature values.

Oxygen and silicon are the most abundant elements in the earth's crust.[1] The classical gravimetric determination of silicon is precise but time-consuming. No simple chemical method for the determination of oxygen in rocks exists. Normally the elemental composition of rocks is expressed in terms of oxides. This can, however, give rise to faulty results, especially when elements are present in different oxidation states. Therefore a direct determination of oxygen can provide valuable information. Oxygen and silicon can easily be determined with 14-MeV neutrons. The following reactions are commonly used: $^{28}Si(n, p)^{28}Al$ and $^{16}O(n, p)^{16}N$. Both reactions give rise to short lived radionuclides ($t_{1/2}$: 2·24 min and 7·13 sec respectively). Measuring the counts accumulated in the region 4·5–8 MeV for oxygen and under the 1·78-MeV photopeak for silicon with a single-channel analyser is the simplest and most commonly used method. Since several other major elements (Al, Fe) in rocks can be determined simultaneously with a multichannel analyser, it is convenient to use the same instrument for the determination of oxygen and silicon. Several authors have made use of a multichannel analyser, especially for the silicon determination, as appears from a recent annotated bibliography.[2] With a multichannel analyser, serious dead-time problems arise, owing to the relatively long analysing time per pulse, compared with a single-channel analyser. This can give rise to errors, especially when dealing with short-lived radionuclides.

Several solutions have been proposed to overcome the difficulties associated with multichannel analyser counting of short-lived species.[3–10] Four methods were used in this

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Table 1. Nuclear reactions on oxygen and silicon and interference reactions

Element	Reaction	Isotopic abundance, %	Cross-section *mb*	Half-life	γ-energy, *MeV* and (abundance, %)
O	$^{16}O(n, p)^{16}N$	99·759	35·1	7·13 sec	6·13(68); 7·12(5)
	$^{16}O(n, 2n)^{15}O$	99·759	0·5	122 sec	0·511(100)
	$^{17}O(n, p)^{17}N$	0·0374	112	4·14 sec	0·87; 2·19
	$^{18}O(n, \alpha)^{15}C$	0·2039	11	2·3 sec	5·3
Si	$^{28}Si(n, p)^{28}Al$	92·21	250(400)	2·24 min	1·78(100)
	$^{29}Si(n, p)^{29}Al$	4·70	100(35)	6·52 min	1·28(85); 2·43(15)
	$^{30}Si(n, \alpha)^{27}Mg$	3·09	45(125)	9·5 min	0·18(0·7); 0·84(70); 1·01(30)
F	$^{19}F(n, \alpha)^{16}N$	100	57	7·13 sec	6·13(68); 7·12(5)
B	$^{11}B(n, p)^{11}Be$	80·39	3·3	13·7 sec	6·81(4·4); 7·99(1·7)
P	$^{31}P(n, \alpha)^{28}Al$	100	140	2·24 min	1·78(100)
Al	$^{27}Al(n, \alpha)^{24}Na$	100	120	15·00 hr	1·37(47); 2·75(52)
	$^{27}Al(n, \gamma)^{28}Al$	100	0·53	2·24 min	1·78(100)
Fe	$^{56}Fe(n, p)^{56}Mn$	91·66	115	2·582 hr	1·81(29)
Mg	$^{24}Mg(n, p)^{24}Na$	78·70	200	15·00 hr	1·37(47); 2·75(52)

work: counting in the live-time mode without additional correction, short counting corrected by an external live-time scaler,[3] the method of Bartošek,[9] and the method of Schonfeld.[10] These methods have already been discussed and compared in detail elsewhere.[11]

Nuclear data

Activation with 14-MeV neutrons is rapid and essentially non-destructive. For the direct analysis of oxygen in bulk samples, it is probably the only reliable method available. Neutrons of *ca.* 14 MeV are produced *via* the $^{3}H(d, n)^{4}He$ reaction. Irradiation of oxygen and silicon with these fast neutrons gives rise to several reactions, which are summarized in Table 1. The most important interfering reactions in the determination of oxygen and silicon are also given. The most commonly used nuclide for oxygen determination is ^{16}N, which gives highly energetic gamma-rays that can be counted without interference above 4·5 MeV. For silicon the prominent 1·78-MeV photopeak of 2·24-min ^{28}Al is commonly used. In analysis of rocks and soils the 1·78-MeV photopeak often contains contributions from iron and magnesium; nuclear interference from aluminium and phosphorus must also be taken into account.

EXPERIMENTAL

Apparatus

The neutron generator was a SAMES Type J accelerator (150 kV, 2·5 mA) with a 100 MHz–60 W radiofrequency ion-source. The 14-MeV neutrons were produced by the $^{3}H(d, n)^{4}He$ reaction from a 90-Ci rotating water-cooled tritium target (Nukem Type RTE-1). To ensure stable conditions the beam was kept at 600 μA and the accelerating potential at 150 kV. Focusing provided a beam variable from 10 to 30 mm dia. The neutron production was controlled by means of a pneumatically operated removable tantalum screen. The pneumatic transfer system consisted of a pair of aluminium tubes with rectangular cross-section (26·5 × 9·5 mm). The entire activation and counting process was controlled automatically. The neutron generator, transfer system and counting equipment have been described in detail elsewhere.[12,13]

Irradiated samples were counted with a 7·6 × 7·6 cm NaI(Tl) detector (resolution *ca.* 8%), coupled to an NE-5281 preamplifier and an NE-4603 amplifier. The double delay-line differentiated output of the amplifier was fed to an NE-4602 single-channel analyser and to the converter of an Intertechnique SA 40B 400-channel analyser. Each measurement with the multichannel analyser was controlled by a simultaneous measurement with the single-channel analyser. Since the output of a neutron generator is not constant, neutron monitoring was required to normalize the induced activities. This was performed by means of a low-geometry BF_3 counter, placed behind the concrete shielding wall, 5 m away from the tritium target.

The NaI(Tl) detector had to be shielded to lower the background, at least for silicon analysis. For oxygen determinations a 2·7 g/cm^2 aluminium absorber was used when analysing rocks with a density different from that of the standard.

Preparation of samples and standards

The six new U.S.G.S. standard rocks[14] G-2 (granite), GSP-1 (granodiorite), AGV-1 (andesite), PCC-1 (peridotite), DTS-1 (dunite) and BCR-1 (basalt) were analysed. In addition two refractory standards 1·68 and 1·69 (Groupement des Utilisateurs de Matériaux Réfractaires, Brussels) were also included. Each sample was dried at 110° for at least 30 hr. The sample holders were cylindrical polyethylene boxes (5 mm internal thickness, 12·7 mm dia, 0·63 cm^3 volume) carefully selected for equal dimensions. The weight of each sample was kept constant (1·1 g) by pressing the powders into the boxes. Owing to the higher density of DTS-1 and PCC-1, 1·3 g of these samples was needed to fill the boxes completely. Two sample holders were packed from each of the eight standard materials available and sealed. These sample holders were placed in polyethylene cylindrical transfer "rabbits" (9 mm thickness, 26 mm diameter) fitting the pneumatic system as shown in Fig. 1.

Oxygen and silicon standards were prepared from silica of different origins:

I Quarz feinkörnig, E. Merck (Darmstadt).
II Anidride silicica, Carlo Erba (Milano).
III Quartz tube, Quartz & Silice (Paris).

The silica was ground to pass through a 150-mesh sieve, rehomogenized by tumbling for 2 hr, and ignited at 1000°. Standard type I has the same density as the rock samples, when packed in the polyethylene sample holders, hence it is most suitable for rock analysis. To obtain information about the composition of silica, the other silica samples were analysed for Si and O, using I as a standard.

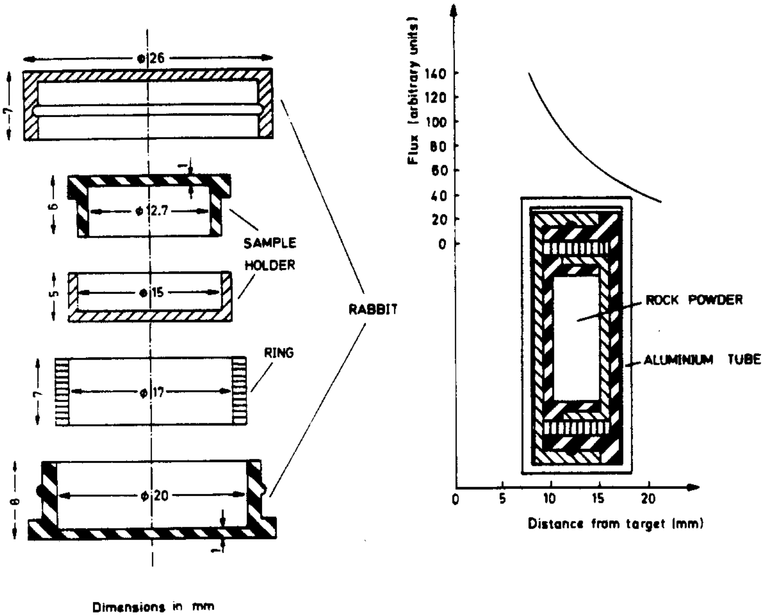

Fig. 1. High-pressure polyethylene sample container and rabbit for 14-MeV neutron-activation analysis of rocks.
Left: exploded view.
Right: irradiation position of the sample in pneumatic tube of rectangular section; also shown is the local axial flux gradient.

Table 2. Determination of oxygen and silicon in silica and silicon (using I as a standard)

Type	Oxygen, %	Silicon, %	Sum of O and Si, %
I SiO_2 (Merck)	(30) $53{\cdot}2_5 \pm 0{\cdot}9_5$	(30) $46{\cdot}7_5 \pm 0{\cdot}3_4$	$100{\cdot}0_0 \pm 1{\cdot}0_1$
II SiO_2 (Carlo Erba)	(30) $54{\cdot}1_8 \pm 1{\cdot}3_2$	(26) $46{\cdot}6_7 \pm 0{\cdot}3_2$	$100{\cdot}8_5 \pm 1{\cdot}3_6$
III SiO_2 (Quartz & Silice)	(20) $53{\cdot}0_9 \pm 1{\cdot}0_9$	(19) $46{\cdot}7_9 \pm 0{\cdot}4_1$	$99{\cdot}8_8 \pm 1{\cdot}1_6$
IV Si (Metallurgie Hoboken)	—	(8) $99{\cdot}5_8 \pm 0{\cdot}9_6$	$99{\cdot}5_8 \pm 0{\cdot}9_6$

Numbers of analyses are given in brackets; errors are given as absolute standard deviation on a single measurement.

Moreover, standard I was used to determine the Si content of a semiconductor-grade silicon disk (Metallurgie Hoboken). For types I and II, three different samples were taken, for type III, two samples; only one silicon disk was available. The results, obtained with the single-channel analyser, are shown in Table 2.

The results were corrected for neutron and gamma ray attenuation due to the difference in density between the samples. For the determination of oxygen, 1 cm of aluminium was placed between the irradiated samples and the detector to shield against the high-energy ^{16}N beta-particles. It appears from Table 2 that, after ignition at 1000°, the different types of silica can be considered to be stoichiometric.

Fifteen type I standards were prepared. This permits the irradiation of another standard after every 3–5 samples. In the same way samples of Fe_2O_3, Al_2O_3 and MgO were made for determining the corresponding interference. Since the oxygen content of the irradiation boxes was not negligible, a blank correction was performed by irradiating and counting empty sample holders in "rabbits" in the same way as the samples and standards. For silicon this correction corresponds to a background subtraction. To check the reproducibility of the packing, the oxygen content of four soil samples (designated DC) was determined with a single-channel analyser. The results, normalized to sample 1, are shown in Table 3.

Procedure

The analysis cycles are given in Table 4. It can be seen that for the development of multichannel analyser dead-time corrections, simultaneous countings were performed with single-channel and multichannel analysers. For actual analyses, it is sufficient to use either one or the other. For the method of Schonfeld,[10] an external live-time scaler was started, simultaneously with the multichannel analyser, for a measurement of the live time during 6 sec clock time. The result was printed with a Teletype in the next 5 sec, after which the live-time scaler was started again for 6 sec. This cycle was interrupted by the stopping of the multichannel analyser. The punched data were fed to a computer (DEC PDP-9) and the true ^{28}Al counting rate at the beginning of the measurement was calculated by numerical integration.

Interferences

Silicon determination. Fast-neutron irradiated iron produces ^{56}Mn, a gamma-emitter with a peak at 1·81 MeV. With a NaI(Tl) detector, the 1·78-MeV peak of ^{28}Al cannot be distinguished from the 1·81-MeV gamma-peak of ^{56}Mn. Owing to the half-life of ^{56}Mn (2·582 hr) this interference becomes perceptible after successive irradiations of the same sample. Moreover a part of the Compton continuum of ^{24}Na formed by the $^{27}Al(n, \alpha)^{24}Na$ and the $^{24}Mg(n, p)^{24}Na$ reactions, contributes to the total number of counts, when summing up the ^{28}Al 1·78-MeV photopeak. Aluminium may interfere through the $^{27}Al(n, \gamma)^{28}Al$ reaction and phosphorus through the $^{31}P(n, \alpha)^{28}Al$ reaction. Known quantities of Fe_2O_3, Al_2O_3 and MgO were

Table 3. Reproducibility of packing

Sample	Weight, relative to DC 1 = 100%	Normalized ^{16}N activity relative to DC 1 = 100%
DC 1	100·00	(9) 100·00
DC 2	96·93	(9) $96{\cdot}1_4 \pm 1{\cdot}5_1$
DC 3	97·85	(9) $98{\cdot}3_2 \pm 1{\cdot}4_0$
DC 4	99·01	(8) $98{\cdot}8_8 \pm 0{\cdot}8_9$

Number of analyses between brackets; errors as absolute standard deviation on a single determination.

Table 4. Analysis cycles

MCA dead-time correction	Irradiation time, *sec*	Waiting time after the end of irradiation, *sec*	Start counting	Waiting time after the end of irradiation, *sec*	Start counting
No correction*	5	3	SCA 1 MCA 1 for 18 sec in the LT mode		
Short counting time	10	6	SCA 1 MCA 1§ for 3 sec in the CT mode	82	SCA 2 MCA 2§ for 24 sec in the CT mode
Bartošek's method	5	3	SCA 1 MCA 1† for 24 sec in the CT mode	79	SCA 2 MCA 2† for 204 sec in the CT mode
Schonfeld's method	10	6	SCA 1	82	SCA 2 MCA 2 for 204 sec in the CT mode

SCA 1: single-channel analyser (above 4·5 MeV) for 16 sec.
MCA 1: multichannel analyser (0 → 10 MeV).
SCA 2: single-channel analyser (1·78-MeV photopeak) for 200 sec.
MCA 2: multichannel analyser (0 → 3 MeV).
LT: live time.
CT: clock time.

* Only oxygen was determined.

§ During the counting on the multichannel analyser, the external live-time scalar indicated the total live time of the measurement.

† During the measurements the dead-time of the multichannel analyser was automatically kept constant at 50%, as described by Bartošek.[9]

irradiated along with the samples and standards under the same conditions. It was found experimentally that 100% Fe produces an apparent silicon content of 0·92%, 100% Al corresponds to 0·43% Si and 100% Mg to 0·37% Si. The correction factor for phosphorus was taken from the literature.[15] (100% P_2O_5 produces an amount of ^{28}Al equivalent to 21% Si).

Oxygen determination. Fluorine produces ^{16}N *via* the ^{19}F(n, α)^{16}N reaction. The correction factor for this reaction was also taken from the literature[16] (100% F equivalent to 41·5% oxygen). The low boron content of the samples studied, the low cross-section of ^{11}B and the low branching-ratio of the high-energy gamma-radiation make the interference from the ^{11}B(n, p)^{11}Be reaction negligible,[17] provided that the high-energy beta-particles are excluded.

Corrections for the presence of interfering elements were made, based on chemical analysis data compiled by Flanagan.[14]

Neutron, gamma-ray and beta-ray attenuation

Owing to the similar composition of the rock samples studied, neutron, gamma-ray and beta-ray attenuation is no problem as long as weight and density are equal. This is not the case for PCC-1 and DTS-1. For samples heavier than the standard, neutron, gamma and beta attenuation results in a negative systematic error. Nargolwalla *et al.*[18,19] studied the effect of neutron and gamma-ray attenuation in detail. Neutron and gamma attenuation can be expressed as a simple exponential absorption law of the general form:

$$f = f_0 \exp(-\varepsilon d)$$

The total correction factor results in

$$C_x/C_s = \exp[-(\Delta\Sigma + \Delta\mu)d]$$

where

C_x = correction factor for the sample.
C_s = correction factor for the standard.
$\Delta\Sigma$ = difference in total removal cross-section between sample and standard.
$\Delta\mu$ = difference in total linear attenuation coefficient between sample and standard.
d = effective sample thickness.

Table 5. Determination of oxygen (%) in rocks, with a single-channel analyser (using standard type I)

Sample	With additional Al absorber ($2{\cdot}7$ g/cm^2)	Without additional absorber
G-2	$48{\cdot}0_0 \pm 0{\cdot}6_8$	$47{\cdot}8_3 \pm 1.4_9$
DTS-1	$43{\cdot}8_8 \pm 0{\cdot}6_3$	$43{\cdot}4_7 \pm 1{\cdot}1_6$
PCC-1	$46{\cdot}7_5 \pm 0{\cdot}7_6$	$46{\cdot}1_7 \pm 1{\cdot}0_1$

25 Analyses per sample: errors given as absolute standard deviation on a single measurement.

Experimentally[20] it was found that the effective sample thickness for neutrons and gamma-rays is approximately the same. From the known composition of samples and standards, the neutron and gamma attenuation correction factor can be calculated if d is determined, d depending on the neutron-flux distribution in the sample. The d-value used in the calculations was determined from the neutron-flux measurements of Van Grieken *et al.*[21] The correction for neutron and gamma-ray attenuation was taken into account only for the samples PCC-1 and DTS-1, yielding the following results.

For oxygen PCC-1 $46{\cdot}7_5$ (uncorrected) $46{\cdot}9_0$ (corrected),
DTS-1 $43{\cdot}8_8$ (uncorrected) $44{\cdot}1_1$ (corrected).
For silicon PCC-1 $19{\cdot}8_9$ (uncorrected) $20{\cdot}0_1$ (corrected),
DTS-1 $18{\cdot}9_7$ (uncorrected) $19{\cdot}1_2$ (corrected).

In the discussion above it was assumed that only the gamma radiation was counted and that the beta radiation was kept from the detector by means of a suitable absorber. If this is not the case, additional errors are possible owing to the varying degrees of self-absorption in samples of different densities.[22,23] The effect is most likely to occur with oxygen analyses, because of the high energy beta-particles of ^{16}N. In order to estimate the importance of this effect, the following experiment was carried out. Samples PCC-1, DTS-1 and G-2 were analysed for oxygen, using standard type I, once with an additional $2{\cdot}7$ g/cm^2 aluminium absorber, and once with only 2 mm of polyethylene and the $1{\cdot}5$ mm of aluminium of the pneumatic tube between sample and detector can (window *ca.* 200 mg/cm^2 aluminium). The results are shown in Table 5.

It can be seen that the effect under the present experimental conditions is negligible for rock powders having the same apparent density as the standard (quartz sand), such as G-2. Failure to insert a suitable absorber can, however, give rise to significant errors for rocks having a different density, such as DTS-1 and PCC-1. No additional absorber has been used for the counting of ^{28}Al (maximum beta energy: $2{\cdot}85$ MeV), since most of the beta-particles are stopped in the rabbit, the pneumatic tube, the detector can and the reflector.

Calculation of results

For oxygen the total number of ^{16}N pulses between $4{\cdot}5$ and 8 MeV was taken into account. The results were corrected for the interfering reaction ^{19}F(n, α)^{16}N, using the F content given by Flanagan.[14]

For silicon, the total number of counts under the ^{28}Al $1{\cdot}78$-MeV photopeak was summed. The underlying Compton continuum from nuclides emitting high-energy gamma-rays must be taken into account. Correction for Fe, Al and Mg contributions to the $1{\cdot}78$-MeV peak was carried out *via* appropriate standards, taking the Fe, Al, Mg contents listed by Flanagan.[14] A correction was also performed for the interfering reaction ^{31}P(n, α)^{28}Al.

After a blank correction, the integrated peak area was normalized to the same neutron flux and corrected for dead-time in the case of multichannel analyser counting, using the methods described elsewhere.[11] The mean of the normalized and corrected activities of the SiO_2 standards was used for the calculation of the oxygen and silicon content in the samples.

RESULTS AND DISCUSSION

The results for oxygen and silicon obtained with single-channel counting are given in Tables 6 and 7. The results for oxygen and silicon obtained with the multichannel analyser by using various dead-time correction methods are given in Tables 8 and 9. Two samples from the same rock or refractory material were prepared and irradiated

Table 6. Determination of oxygen with single channel analyser in U.S.G.S. standard rocks and refractory standards

Sample	Simultaneously with the measurement in live time mode	Simultaneously with Bartošek's method	Simultaneously with short counting time	Simultaneously with Schonfeld's method	Grand mean	Correction for F	Corrected grand mean
G-2	(16) $48{\cdot}0_5 \pm 0{\cdot}5_7$	(10) $48{\cdot}2_0 \pm 0{\cdot}3_2$	(12) $48{\cdot}1_5 \pm 0{\cdot}4_0$	(14) $47{\cdot}7_4 \pm 0{\cdot}3_0$	(52) $48{\cdot}0_0 \pm 0{\cdot}1_8$	0·06	$47{\cdot}9_4$
GSP-1	(15) $47{\cdot}5_6 \pm 0{\cdot}6_4$	(9) $47{\cdot}7_4 \pm 0{\cdot}9_2$	(12) $47{\cdot}5_8 \pm 0{\cdot}1_4$	(14) $47{\cdot}9_4 \pm 1{\cdot}0_2$	(50) $47{\cdot}5_9 \pm 0{\cdot}1_3$	0·16	$47{\cdot}4_3$
AGV-1	(15) $47{\cdot}1_4 \pm 0{\cdot}5_3$	(10) $47{\cdot}8_1 \pm 0{\cdot}2_0$	(12) $47{\cdot}1_7 \pm 0{\cdot}2_1$	(14) $47{\cdot}2_3 \pm 0{\cdot}3_6$	(51) $47{\cdot}4_6 \pm 0{\cdot}1_3$	0·02	$47{\cdot}4_4$
PCC-1	(12) $46{\cdot}9_3 \pm 0{\cdot}5_7$	(10) $46{\cdot}6_8 \pm 0{\cdot}5_8$	(12) $46{\cdot}7_3 \pm 0{\cdot}1_9$	(14) $46{\cdot}7_5 \pm 0{\cdot}6_2$	(48) $46{\cdot}7_5 \pm 0{\cdot}1_7$	—	$46{\cdot}7_5$*
DTS-1	(12) $43{\cdot}9_7 \pm 0{\cdot}3_7$	(10) $43{\cdot}9_5 \pm 0{\cdot}8_7$	(12) $43{\cdot}9_4 \pm 0{\cdot}4_4$	(14) $43{\cdot}4_2 \pm 0{\cdot}6_9$	(48) $43{\cdot}8_8 \pm 0{\cdot}2_5$	—	$43{\cdot}8_8$*
BCR-1	(13) $44{\cdot}5_8 \pm 0{\cdot}2_5$	(10) $45{\cdot}2_8 \pm 0{\cdot}5_1$	(12) $45{\cdot}0_9 \pm 0{\cdot}2_1$	(14) $45{\cdot}8_1 \pm 0{\cdot}5_6$	(49) $44{\cdot}9_7 \pm 0{\cdot}1_5$	0·02	$44{\cdot}9_5$
1·68	(16) $49{\cdot}8_2 \pm 0{\cdot}7_1$	(10) $49{\cdot}4_6 \pm 0{\cdot}4_5$	(12) $49{\cdot}4_9 \pm 0{\cdot}6_3$	(14) $49{\cdot}4_4 \pm 0{\cdot}8_3$	(52) $49{\cdot}5_3 \pm 0{\cdot}3_0$	—	$49{\cdot}5_3$
1·69	(15) $48{\cdot}4_8 \pm 0{\cdot}6_7$	(10) $48{\cdot}2_8 \pm 0{\cdot}6_4$	(12) $48{\cdot}2_8 \pm 0{\cdot}2_5$	(14) $48{\cdot}7_4 \pm 0{\cdot}8_4$	(51) $48{\cdot}3_3 \pm 0{\cdot}2_1$	—	$48{\cdot}3_3$

* Neutron and gamma attenuation not taken into account (see Table 10); detector shielded for ^{16}N beta particles
Between brackets: number of analyses.

Table 7. Determination of silicon with single channel analyser in U.S.G.S. standard rocks and refractory standards

Sample	Simultaneously with Bartošek's method	Simultaneously with short counting time	Simultaneously with Schonfeld's method	Grand mean	Corrections P	Fe	Al	Mg	Corrected grand mean
G-2	(8) $32{\cdot}7_2 \pm 0{\cdot}3_2$	(12) $32{\cdot}5_7 \pm 0{\cdot}2_1$	(14) $32{\cdot}3_7 \pm 0{\cdot}1_8$	(34) $32{\cdot}4_9 \pm 0{\cdot}1_3$	0·03	0·02	0·03	—	$32{\cdot}4_1$
GSP-1	(8) $31{\cdot}9_3 \pm 0{\cdot}2_9$	(12) $31{\cdot}8_5 \pm 0{\cdot}1_9$	(14) $31{\cdot}8_5 \pm 0{\cdot}2_4$	(34) $31{\cdot}8_7 \pm 0{\cdot}1_3$	0·06	0·03	0·03	—	$31{\cdot}7_5$
AGV-1	(8) $27{\cdot}7_9 \pm 0{\cdot}1_7$	(12) $27{\cdot}9_5 \pm 0{\cdot}1_3$	(14) $28{\cdot}0_7 \pm 0{\cdot}1_0$	(34) $27{\cdot}9_9 \pm 0{\cdot}0_7$	0·10	0·04	0·04	—	$27{\cdot}8_1$
PCC-1	(8) $19{\cdot}9_8 \pm 0{\cdot}1_4$	(12) $20{\cdot}0_1 \pm 0{\cdot}1_0$	(14) $20{\cdot}0_9 \pm 0{\cdot}0_9$	(34) $20{\cdot}0_4 \pm 0{\cdot}0_6$	—	0·05	—	0·10	$19{\cdot}8_9$*
DTS-1	(8) $19{\cdot}0_9 \pm 0{\cdot}1_5$	(12) $19{\cdot}1_4 \pm 0{\cdot}2_1$	(14) $19{\cdot}2_1 \pm 0{\cdot}1_6$	(34) $19{\cdot}1_4 \pm 0{\cdot}1_0$	—	0·06	—	0·11	$18{\cdot}9_7$*
BCR-1	(8) $25{\cdot}2_2 \pm 0{\cdot}1_7$	(12) $25{\cdot}5_6 \pm 0{\cdot}0_9$	(14) $25{\cdot}7_6 \pm 0{\cdot}2_2$	(34) $25{\cdot}5_2 \pm 0{\cdot}0_8$	0·08	0·09	0·03	—	$25{\cdot}3_2$
1·68	(8) $26{\cdot}1_0 \pm 0{\cdot}1_0$	(12) $25{\cdot}8_1 \pm 0{\cdot}1_3$	(14) $25{\cdot}8_6 \pm 0{\cdot}1_7$	(34) $25{\cdot}9_7 \pm 0{\cdot}0_7$	0·03	0·01	0·09	—	$25{\cdot}8_4$
1·69	(8) $17{\cdot}2_5 \pm 0{\cdot}1_9$	(12) $17{\cdot}2_4 \pm 0{\cdot}0_9$	(14) $17{\cdot}2_9 \pm 0{\cdot}1_3$	(34) $17{\cdot}2_6 \pm 0{\cdot}0_7$	—	—	0·14	—	$17{\cdot}1_2$

* Neutron and gamma attenuation not taken into account (see Table 11); Between brackets: number of analyses.

Table 8. Determination of oxygen with multichannel analyser in U.S.G.S. standard rocks and refractory standards

Sample	Measurement in live time mode	Bartošek's method	Short counting time
G-2	(16) $48{\cdot}4_6 \pm 0{\cdot}6_8$	(10) $47{\cdot}7_7 \pm 0{\cdot}3_0$	(12) $47{\cdot}9_8 \pm 0{\cdot}7_6$
GSP-1	(15) $48{\cdot}1_9 \pm 0{\cdot}6_3$	(9) $47{\cdot}4_9 \pm 0{\cdot}8_8$	(11) $47{\cdot}3_7 \pm 0{\cdot}4_4$
AGV-1	(14) $47{\cdot}3_3 \pm 0{\cdot}5_4$	(10) $47{\cdot}5_3 \pm 0{\cdot}4_4$	(12) $47{\cdot}0_1 \pm 0{\cdot}6_7$
PCC-1	(12) $46{\cdot}4_7 \pm 0{\cdot}4_8$	(10) $46{\cdot}3_4 \pm 0{\cdot}5_6$	(12) $47{\cdot}1_1 \pm 0{\cdot}4_9$
DTS-1	(12) $43{\cdot}9_5 \pm 0{\cdot}3_9$	(10) $43{\cdot}6_4 \pm 0{\cdot}8_4$	(12) $43{\cdot}9_9 \pm 0{\cdot}5_9$
BCR-1	(13) $45{\cdot}0_6 \pm 0{\cdot}4_0$	(10) $45{\cdot}0_9 \pm 0{\cdot}5_9$	(12) $45{\cdot}5_2 \pm 0{\cdot}5_7$
1·68	(16) $49{\cdot}8_4 \pm 0{\cdot}6_5$	(9) $49{\cdot}0_0 \pm 0{\cdot}5_9$	(12) $49{\cdot}1_0 \pm 0{\cdot}7_0$
1·69	(15) $48{\cdot}7_1 \pm 0{\cdot}5_3$	(10) $48{\cdot}1_0 \pm 0{\cdot}8_2$	(12) $48{\cdot}3_3 \pm 0{\cdot}9_2$

Between brackets: number of analyses.

Neutron and gamma attenuation not taken into account; detector shielded for ^{16}N beta particles.

Table 9. Determination of silicon with multichannel analyser in U.S.G.S. standard rocks and refractory standards

Sample	Bartošek's method	Short counting time	Schonfeld's method
G-2	(10) $32{\cdot}5_2 \pm 0{\cdot}2_2$	(12) $32{\cdot}4_2 \pm 0{\cdot}2_4$	(14) $32{\cdot}2_7 \pm 0{\cdot}2_2$
GSP-1	(10) $31{\cdot}6_2 \pm 0{\cdot}3_1$	(12) $31{\cdot}7_1 \pm 0{\cdot}1_8$	(14) $31{\cdot}8_0 \pm 0{\cdot}2_6$
AGV-1	(10) $27{\cdot}7_2 \pm 0{\cdot}1_8$	(12) $27{\cdot}8_5 \pm 0{\cdot}2_2$	(14) $27{\cdot}9_5 \pm 0{\cdot}1_2$
PCC-1	(10) $19{\cdot}7_1 \pm 0{\cdot}1_9$	(12) $19{\cdot}8_2 \pm 0{\cdot}1_6$	(14) $19{\cdot}9_6 \pm 0{\cdot}1_0$
DTS-1	(10) $18{\cdot}9_8 \pm 0{\cdot}0_9$	(12) $19{\cdot}2_7 \pm 0{\cdot}1_1$	(14) $19{\cdot}2_2 \pm 0{\cdot}1_1$
BCR-1	(10) $25{\cdot}4_3 \pm 0{\cdot}2_2$	(12) $25{\cdot}3_8 \pm 0{\cdot}2_1$	(14) $25{\cdot}6_7 \pm 0{\cdot}2_7$
1·68	(9) $25{\cdot}6_3 \pm 0{\cdot}2_1$	(12) $25{\cdot}7_7 \pm 0{\cdot}1_8$	(14) $25{\cdot}7_6 \pm 0{\cdot}1_5$
1·69	(10) $17{\cdot}1_3 \pm 0{\cdot}1_3$	(12) $17{\cdot}2_7 \pm 0{\cdot}1_0$	(14) $17{\cdot}2_5 \pm 0{\cdot}1_1$

Between brackets: number of analyses.
Neutron and gamma attenuation not taken into account.

4–8 times. This yielded two results with corresponding coefficients of variation. The results given are the weighted means of these two results, according to the equation

$$\mu = \frac{\sum_i x_i/s_i^2}{\sum_i 1/s_i^2}$$

the variance of the weighted mean being given by

$$s_\mu^2 = \frac{1}{\sum_i 1/s_i^2}$$

The grand mean and the coefficient of variation for the determinations with a single-channel analyser were calculated according to the equations above, from the total number of results available for a set of two different samples from the same rock or refractory material, *i.e.*, 6 for silicon and 8 for oxygen.

For oxygen the mean relative deviation for a single determination from the original replicate analysis with a single-channel analyser is 1·7%, which is higher than that derived from counting statistics (1·4%). For silicon analyses with the single-channel analyser the coefficient of variation is about 1·1%, which is also higher than counting statistics (0·8%). From this the additional instrumental error could be estimated to be 0·7–1·0%. For a different set-up Van Grieken *et al.*[24] found 1·4–1·7%. The lower error may be due to the fact that the rock powders are irradiated about 2 mm farther away from the tritium target, so that the flux gradient is less steep.

The results with the multichannel analyser have been discussed in detail elsewhere.[11] It appears that the precision with the various multichannel analyser methods is practically the same as with the single-channel analyser, except for the oxygen determinations done by using a short multichannel analyser counting time (worse counting statistics).

Small systematic deviations occur, when comparing the various dead-time correction methods with the corresponding single-channel analyser results, but these deviations are insignificant. The method of Bartošek *et al.*[9] seems to have the advantages of simplicity and general applicability. It is valid for all kinds of mixtures of short-lived radionuclides and no calculation is needed. Owing to the imposed dead-time (50%) the measurement suffers from counting losses. In a newer version, a modification allows a wide range of imposed dead-times.

Table 10. Comparison of oxygen results for the U.S.G.S. standard rocks and refractory standards

Reference Sample	14	14 †	26	16	29	27	25	This work (SCA)
G-2	$48{\cdot}4_1$	$48{\cdot}3_1$		$48{\cdot}0_9$	49·0		$48{\cdot}1_0$	$47{\cdot}9_4$
GSP-1	$47{\cdot}8_3$	$47{\cdot}7_1$		$47{\cdot}3_8$	48·2		$47{\cdot}6_6$	$47{\cdot}4_3$
AGV-1	$47{\cdot}2_9$	$46{\cdot}3_8$		$46{\cdot}9_0$	47·2	47·8	$46{\cdot}8_0$	$47{\cdot}4_4$
PCC-1	$47{\cdot}0_3$	$46{\cdot}6_2$		$46{\cdot}0_5$	45·0		$46{\cdot}5_4$	$46{\cdot}9_0$*
DTS-1	$44{\cdot}3_1$	$44{\cdot}2_6$		$43{\cdot}4_3$	41·4		$44{\cdot}1_4$	$44{\cdot}1_1$*
BCR-1	$45{\cdot}5_5$	$44{\cdot}8_1$		$44{\cdot}5_4$	44·7	45·8	$44{\cdot}9_1$	$44{\cdot}9_5$
1·68			$49{\cdot}3_8$					$49{\cdot}5_3$
1·69			$48{\cdot}7_9$					$48{\cdot}3_3$

* Corrected for neutron and gamma attenuation.

† The calculated values of Flanagan, corrected for the loss of water released at 110°.

Table 11. Comparison of silicon results for the U.S.G.S. standard rocks and refractory standards

Reference Sample	14	14 †	26	15	28	29	27	This work (SCA)
G-2	$32{\cdot}3_5$	$32{\cdot}3_9$		$32{\cdot}5_2$	$33{\cdot}3_1$	31·7		$32{\cdot}4_1$
GSP-1	$31{\cdot}4_5$	$31{\cdot}4_9$		$31{\cdot}5_6$	$32{\cdot}6_5$	31·9		$31{\cdot}7_5$
AGV-1	$27{\cdot}5_8$.	$27{\cdot}8_7$		$27{\cdot}8_5$	$28{\cdot}8_0$	27·6	$27{\cdot}7_7$	$27{\cdot}8_1$
PCC-1	$19{\cdot}5_7$	$19{\cdot}6_6$		$19{\cdot}6_2$	$20{\cdot}1_8$	18·5		$20{\cdot}0_1$*
DTS-1	$18{\cdot}9_1$	$18{\cdot}9_2$		$18{\cdot}9_0$	$19{\cdot}8_5$	19·3		$19{\cdot}1_2$*
BCR-1	$25{\cdot}4_7$	$25{\cdot}6_8$		$25{\cdot}4_3$	$26{\cdot}5_9$	25·0	$25{\cdot}6_8$	$25{\cdot}3_2$
1·68			$25{\cdot}7_3$					$25{\cdot}8_4$
1·69			$17{\cdot}1_4$					$17{\cdot}1_2$

* Corrected for neutron and gamma attenuation.

† The calculated values of Flanagan, corrected for the loss of water released at 110°. The data of column 2 were multiplied by a factor given by the ratio: total percentage/total percentage after drying.

The results obtained in this work with the single-channel analyser are compared with literature values in Tables 10 and 11. In general the results for oxygen (Table 10) agree quite well with those of Volborth *et al.*[16] and Bibby,[25] except for AGV-1. As can be seen from Table 6, the result for AGV-1, obtained with the single-channel analyser and Bartošek's method, is rather high and contributes heavily to the weighted mean. If this result is omitted the grand mean for AGV-1 becomes $47{\cdot}1_8\%$, and corrected for fluorine $47{\cdot}1_6\%$. The oxygen values reported here are 0·1–0·6% lower than the values calculated from Flanagan,[14] and after correction for water loss at 110° the mean difference is zero. When considering the rock samples with an insignificant water loss and equal density compared to the SiO_2 standards, *e.g.*, G-2 and GSP-1, the agreement between Volborth *et al.*,[16] Bibby[25] and this work is clear. For the refractory materials 1·68 and 1·69, the water loss at 1050° is only 0·19% and 0·15% respectively. The reported results agree with the oxygen content calculated from the certificate values. It should be noted that the samples of Volborth *et al.*[16] and Morgan *et al.*[27] were not dried. Moreover, in view of the difficulties resulting from the possible variation of the amount of adsorbed water

(88·81% O) in fine rock powders analysed under different atmospheric conditions, it is probable that these reported results could not be expected to be more accurate than $\pm 0{\cdot}2_0\%$ O on an interlaboratory basis.[16]

For the silicon determinations (Table 11) with the single-channel analyser the reported results agree well with the data of Vincent *et al.*[15] and the calculated values (minus H_2O^-) from Flanagan. A neutron and gamma-ray attenuation correction had, however, to be applied to PCC-1 and DTS-1, because of their difference in density from that of the standard. This correction increases the silicon values for PCC-1 and DTS-1 by $0{\cdot}1_2$ and $0{\cdot}1_5\%$, respectively. The silicon results reported here for the U.S.G.S. standard rocks are slightly higher than those from Flanagan, except for BCR-1. The influence of drying at 110° is pronounced for the standard rock BCR-1 ($25{\cdot}4_7\%$ Si $\rightarrow 25{\cdot}6_8\%$ Si). Systematic errors in classical chemical schemes may lead to low silicon results.[30] The silicon results for the refractory materials are in good agreement with the certificate.

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Zusammenfassung—In den sechs neuen Standardgesteinen vom U.S. Geological Survey und in zwei feuerfesten Standardmaterialien wurden Sauerstoff und Silicium durch 14 MeV-Neutronenaktivierungsanalyse bestimmt. Die induzierten ^{16}N-(4,5–8 MeV-Gammastrahlung) und ^{28}Al-Aktivitäten (1,78 MeV-Photopeak) wurden mit Hilfe eines Ein- und Vielkanalanalysators gezählt. Durch die lange Analysenzeit pro Impuls sind beim Zählen mit dem Vielkanalanalysator Totzeitkorrekturen notwendig. In dieser Arbeit wurden vier Methoden untersucht: Zählzeit in Aktivzeit ohne weitere Korrektur, Kurzzählung mit Korrektur mittels einen externen Aktivzeitzähler, die Methode von Bartošek und die Methode von Schonfeld, Jede Messung wurde durch eine gleichzeitige Messung mit einem Einkanalanalysator kontrolliert. Bei 1000° geglühtes Siliciumdioxid wurde als Bezugssubstanz angewandt. Für die störenden Elemente F, P, Al, Fe und Mg wurde mit Hilfe von Literaturdaten korrigiert. Die Abschwächung von Neutronen, Gamma und Betastrahlen wurde beachtet. Für Sauerstoff betrug der mittlere Variationskoeffizient einer Einzelbestimmung mit einem Einkanalanalysator 1,7 %, für Silicium 1,1 %. Die Mittelwerte der Einkanal-Zählungen wurden mit Literaturwerten verglichen.

Résumé—On a dosé l'oxygène et le silicium dans six nouveaux étalons de roche du U.S. Geological Survey et dans deux étalons de matériaux refractaires par analyse par activation aux neutrons de 14 MeV. Les comptages des activités de ^{16}N (radiation gamma de 4,5 à 8 MeV) et de ^{28}Al (photopic de 1,78 MeV) furent effectués à l'aide d'un analyseur monocanal ou d'un sélecteur multicanal. Le temps d'analyse par impulsion étant long, il est nécessaire d'appliquer une correction dans le cas du sélecteur multicanal. Quatre méthodes furent étudiées dans le présent travail: comptage dans le mode temps actif; comptage court en temps réel avec mesure externe du temps actif; comptage corrigé par la méthode de Bartošek et par la méthode de Schonfeld. Chaque méthode fut controlée par un comptage simultané à l'aide de l'analyseur monocanal. La silice calcinée à 1000°C fut utilisée comme standard. A partir des données de la littérature une correction fut appliquée pour les interférences dûes aux éléments F, P, Al, Fe et Mg ainsi que pour l'atténuation des neutrons, des gamma's et des bêta's. Pour l'analyseur monocanal le coefficient moyen de variation était de 1,7 % pour l'oxygène et de 1,1 % pour le silicium. Les valeurs moyennes dans le cas du monocanal furent comparées à celles de la littérature.

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QUANTITATIVE PHOSPHORESCENCE STUDY OF INTERACTIONS OF CYTOSINE AND CYTIDINE AND ITS NUCLEOTIDES IN FROZEN AQUEOUS SOLUTION*

EVIDENCE FOR ANOMALOUS HEAVY-ATOM EFFECT

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Summary—Phosphorescence *vs.* pH titration curves of cytosine, cytidine, cytidine-5′-monophosphate (CMP), -diphosphate (CDP) and -triphosphate (CTP) were obtained in methanol/water 10/90 v/v and in various aqueous sodium halide solutions frozen at 77°K. As shown by the shape of the titration curve, molecular aggregates or "puddles" of cytosine and cytidine were shown to occur only in relatively concentrated frozen solution ($10^{-3}M$), these aggregates being dissociated in dilute frozen solutions ($\leq 10^{-4}M$) or in $\sim 1M$ sodium chloride. No molecular aggregation could be found even in concentrated solutions of CMP, CDP, and CTP. Lower concentrations of sodium bromide or iodide ($10^{-1}M$) were demonstrated to give "reversed" sigmoidal phosphorescence titration curves in the case of cytidine, due to an *anomalously large heavy-atom enhancement factor* in acidic solution, ranging between 30 and 50.

Aggregation of nucleic acid–bases and derivatives has been shown to occur in frozen aqueous solution[1–3] and has received in the past few years a renewed interest.[4–10] The existence of such molecular aggregates is supported by studies on sections of frozen aqueous matrix of thymine,[1] by low-temperature fluorescence and phosphorescence measurements of purine bases,[6,10] thymine and 1,3-dimethylthymine[6,8] nucleotides and dinucleotides,[4,5,7,10b] as well as by ESR studies.[4,8] Intermolecular interactions in these aggregates generally result in a red-shift in the fluorescence spectra[7,8,10b] and in a decrease of both fluorescence and phosphorescence quantum yields,[4,6,7,10b] although an increase in phosphorescence intensity and phosphorescence/fluorescence ratio with aggregate concentration has been demonstrated in the case of thymine and its derivatives.[8] In this last case, the mechanism resulting in this increase of intersystem-crossing at high aggregate concentration has not yet been elucidated.[8,11] The influence of low melting point organic solvents or of electrolytes on the formation of aggregates is still a matter of discussion. Indeed, while it has been theorized by Wang[1,2] that as the solution freezes, "puddles" of solute molecules together with some organic solvent or electrolyte are formed, several authors have claimed that aggregates are completely or partially dissociated by the addition of sodium chloride,[4,7,10] ethanol, ethylene glycol, propylene

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glycol[6,7,11] or glucose and sodium acetate.[10b] In the case of purine derivatives[12] and other organic compounds,[13,14] we have observed an increase of the phosphorescence intensity by several orders of magnitude upon introducing a few per cent of methanol or sodium halide into pure frozen aqueous matrix, an effect which could also be attributed to the dispersion of molecular aggregates present in pure frozen aqueous solution, although we have proposed a physical matrix effect as a more probable interpretation.[14] Because of their significant influence upon the luminescence properties of nucleic acid bases and derivatives, pH effects also have to be considered in the study of molecular aggregates. Recently, it has been shown by Montenay-Garestier and Helene[9] that fluorescence and phosphorescence titration curves of cytidine in pure frozen aqueous solution at 77°K exhibit a luminescence intensity maximum at a pH value close to the ground-state pK value. This anomalous behaviour, compared to the classical sigmoidal shape of luminescence titration curves of cytidine in a water–propylene glycol glass, would indicate the formation of aggregates and the existence of charge-transfer interactions between cytidine and its cation.[9] However, surprisingly, addition of sodium chloride or ethanol did not change the peak shape of the luminescence titration curve, which would signify the persistence of aggregation in these predominately aqueous frozen solutions. That these findings are also significant in the photochemistry and the photobiology of nucleic acids has been recently demonstrated by the occurrence of a photoreaction of cytidine in the frozen state, yielding charge-transfer complexes similar to those found in the pH-luminescence studies.[15]

In order to re-examine more thoroughly the different factors involved in the aggregation, "puddle" formation or dispersion of nucleic acid bases and derivatives in frozen solutions, we have undertaken the present study of the effect of pH, and of sodium halide, methanol and solute concentrations upon the phosphorescence of isolated bases of nucleic acid, their mononucleosides and mononucleotides. In the present paper, we are more specifically concerned with the investigation of these effects upon the phosphorescence spectra and phosphorescence intensity of cytosine and cytidine and its mononucleotides. Because of their low phosphorescence quantum yield, cytosine and cytidine were considered previously as very weak phosphors, especially in acidic and neutral frozen solutions.[16,17] In basic solution, the low-temperature fluorescence and phosphorescence intensities were approximately equal because of increase of intersystem-crossing from the π, π^* singlet to triplet states in the anionic form.[17] However, we have also shown in this paper that phosphorescence intensity of cytosine and cytidine can be considerably increased in acidic media upon addition of minimum quantities of sodium bromide or iodide to frozen water–methanol matrices.

EXPERIMENTAL

Apparatus

Phosphorescence excitation and emission spectra at 77°K were obtained on an Aminco-Bowman spectrophotofluorometer (SPF) equipped with an Aminco-Keirs phosphoroscope attachment and an Aminco Ratio Photometer (American Instrument Co., Silver Spring, Md.). The 150-W xenon arc lamp was powered by an Aminco xenon-lamp power-supply (Model 422-818). The RCA-1P28 multiplier phototube (American Instrument Co.) was powered by the Aminco Ratio Photometer. Phosphorescence spectra were taken on the Ratio Photometer in the ratio mode and recorded on a Moseley Autograph Recorder (Moseley Co., Pasadena, Calif.). Phosphorescence intensities were measured by using the normal mode of the Ratio Photometer with a low-noise nanoammeter.[18]

A rotating capillary tube, approximately 0·9 mm bore and 2 mm wall thickness, made from T21 Suprasil quartz capillary tubing (Amersil Inc., Hillside, N.J.) was used as the sample cell in the same conditions as previously described.[12–14]

Materials

Cytosine, cytidine, cytidine-5′-monophosphate (CMP) sodium dihydrate, cytidine-5′-diphosphate (CDP) sodium dihydrate and cytidine-5′-triphosphate (CTP) sodium dihydrate were purchased from Nutritional Biochemical Co. (Cleveland, Ohio) and used without further purification.

Solvents used were spectral quality methanol and demineralized water.

Method

Stock solutions of cytosine and cytidine and derivatives (concentrations 5×10^{-4}–$10^{-3}M$) were prepared in water or methanol/water 10/90 v/v, with or without various additions of sodium chloride, bromide or iodide. More dilute solutions were obtained by successive dilution with the appropriate solvent (with or without sodium halide). The pH of the stock and diluted solutions was adjusted with microquantities of concentrated hydrochloric acid, as needed. Phosphorescence signal *vs.* pH measurements were performed by adding microvolumes of 0·1*M* aqueous sodium hydroxide to acidic stock or diluted solutions of the compound, measuring room-temperature pH values and immediately taking the phosphorescence signal intensity from the nanoammeter output of the Aminco-Bowman SPF. The pH-meter was previously calibrated against buffer solutions (pH 4·00, 7·00 and 10·00). For all pH values, phosphorescence measurements were taken at 77°K in duplicate or triplicate. Reproducibility of the phosphorescence signals was found to be within 5% for all the solutions used.

A slit arrangement of 3,3,3,3 (in mm, corresponding to 17-nm excitation and emission spectral half-bandpass) was used for all phosphorescence measurements.

RESULTS AND DISCUSSION

Effect of pH on phosphorescence intensity and spectral characteristics

Phosphorescence excitation and emission maxima wavelengths of cytosine, cytodine and its nucleotides are given in Table 1. Excitation spectra are corrected for xenon arc-lamp response and lamp intensity fluctuations with the ratio photometer. Emission

Table 1. Phosphorescence spectral characteristics of cytosine and cytidine and nucleotides in aqueous neutral, acidic and basic solutions[a] at 77°K

	Peak wavelength[b], *nm*					
	Acidic solution[d]		Neutral solution[e]		Basic solution[f]	
Compound (salt)[c]	Excitation maximum	Emission maximum	Excitation maximum	Emission maximum	Excitation maximum	Emission maximum
Cytosine	339	418	311[h]	396[h]	299	396
Cytidine	295	415	290[g]	420[g]	287	412
Cytidine (NaCl: 0·1*M*)	299	419	292[g]	420[g]	290	420
Cytidine (NaBr: 0·1*M*)	289	424	281[h]	420[h]	282	420
Cytidine (NaI: 0·1*M*)	295	424	291[h]	420[h]	292	420
CMP	294	414	288	410	285	410
CDP	294	416	285	412	285	411
CTP	294	420	288	420	284	410

[a] Concentrations approximately 10^{-5}–$10^{-4}M$ according to the compounds. All spectra obtained with the ratio photometer, for methanol/water 10/90 media.

[b] Peak wavelength error ±3 nm.

[c] Nature and concentration of the added salt.

[d] pH ≃ 2·3.

[e] pH ≃ 7·0, unless otherwise noted.

[f] pH ≃ 10·5.

[g] pH = 4·0.

[h] pH = 5·5.

spectra are characterized by broad and structureless bands. Excitation and emission peak wavelengths agree reasonably well with the available literature data for cytidine and its nucleotides,[9,11,16,17] although small differences could be attributed to instrumental factors or solvent effects. We observed small shifts of the phosphorescence emission maximum wavelengths upon varying the pH, but we did not obtain the red-shift of the phosphorescence maximum at pH 4·1 noted in the case of cytidine by Montenay, Garestier and Helene[9] (see Table 1 and Fig. 5). There was also a significant shift towards longer wavelengths (900–2000 cm^{-1} according to the nature of the nucleotide or nucleoside) of the excitation maximum upon acidification of the solution, in agreement with a similar red-shift observed in the room-temperature absorption spectra of cytidine.[17] In the case of cytosine, however, an unexpected and important red-shift (about 3200 cm^{-1}) of the excitation maximum and a change in the shape of the excitation spectrum took place upon acidification.

Phosphorescence intensity *vs.* pH curves in methanol/water 10/90 v/v at 77°K are shown for cytosine and cytidine and its nucleotides in Figs. 1–3. In the case of cytosine and cytidine, the curves for phosphorescence *vs.* pH exhibit a different behaviour according to the concentration used. At a concentration of $10^{-3}M$, the phosphorescence titration

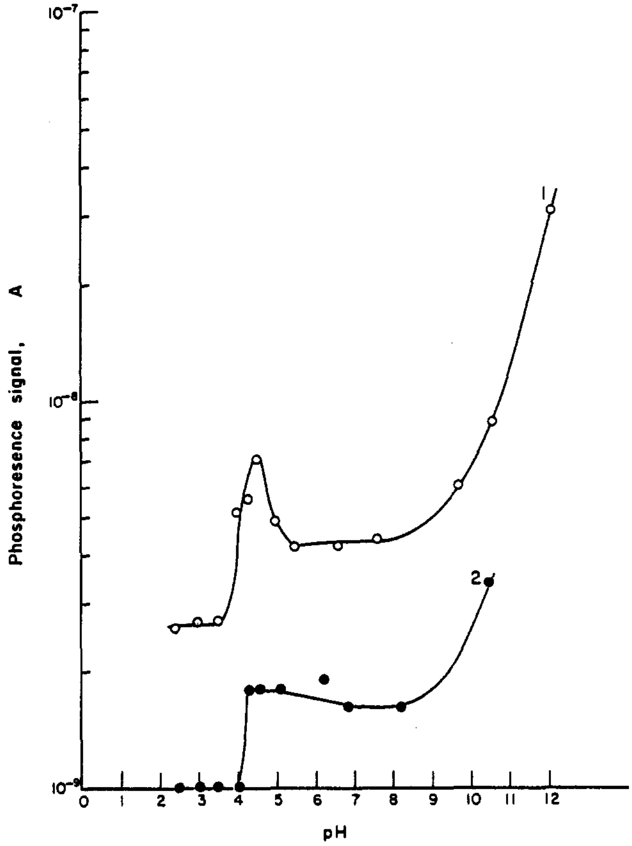

Fig. 1. Phosphorescence signal (in A) of cytosine ($4 \times 10^{-4}M$, curve 1; $9 \times 10^{-5}M$, curve 2) as function of pH in methanol/water 10/90 v/v at 77°K. Intensity measured at emission maximum wavelength.

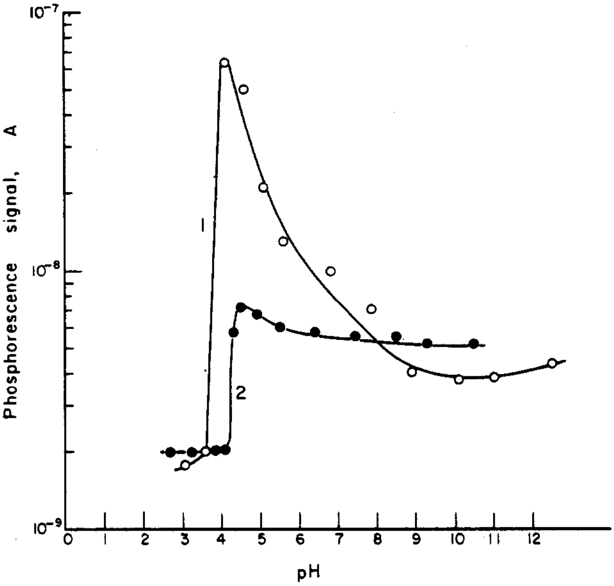

Fig. 2. Phosphorescence signal (in A) of cytidine ($10^{-3}M$, curve 1; $10^{-4}M$, curve 2) as function of pH in methanol/water 10/90 v/v at 77°K. Intensity measured at emission maximum wavelength.

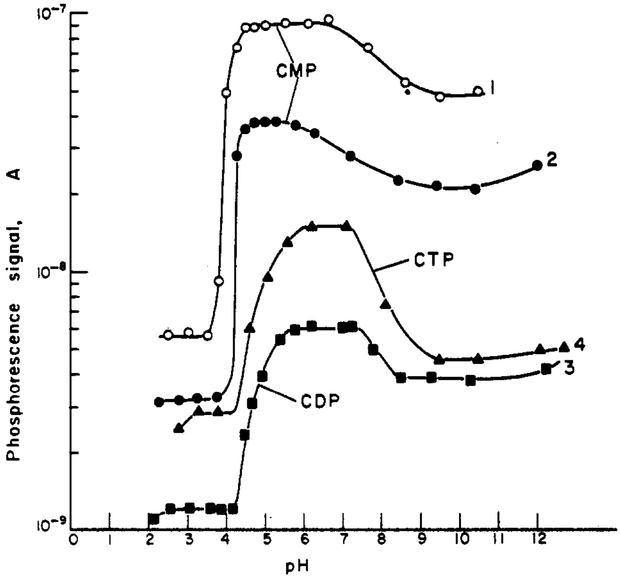

Fig. 3. Phosphorescence signal (in A) of CMP ($10^{-3}M$, curve 1; $10^{-4}M$, curve 2), CDP ($10^{-5}M$, curve 3) and CTP ($5 \times 10^{-5}M$, curve 4) as function of pH in methanol/water 10/90 v/v at 77°K. Intensity measured at the emission maximum wavelength of each compound.

curves are characterized by a large increase of phosphorescence signal (about 3- and 36-fold increase, respectively, for cytosine and cytidine), followed by a smaller decrease, as the solution becomes less acidic. This phenomenon results in a peak in the vicinity of the ground-state pK_a of cytosine ($pK_a = 4{\cdot}45$)[18] and of cytidine ($pK_a = 4{\cdot}22$)[18] (see Figs. 1 and 2). At pH values larger than about 9, the phosphorescence signal of cytidine stays approximately constant, while a large phosphorescence increase is noted for cytosine in the pH region 10–12, because of the formation of the more phosphorescent anionic species. At concentrations of $10^{-4}M$ or lower, the anomalous peak observed close to the ground-state pK_a value disappears completely in the case of cytosine and is largely reduced in the case of cytidine; furthermore, smaller increases in phosphorescence intensity are noted at the pK_a value (3·7-fold increase with $10^{-4}M$ but 36-fold increase with $10^{-3}M$ cytidine). The formation of aggregates and of a charge-transfer complex between cytidine and its cation has been proposed to explain the anomalous peak in the luminescence titration curves of cytidine in frozen aqueous solution.[9] In the present study, we confirm these results, but we found also that this phosphorescence intensity maximum is dependent on the concentration of cytosine or cytidine present in the frozen matrix. This phenomenon suggests that "puddles" of cytosine or cytidine molecules and cations together with methanol molecules are only formed at relatively high solute concentration (5×10^{-4}–$10^{-3}M$) in methanol/water snowed matrices, therefore permitting the occurrence of charge-transfer interactions between neutral molecule and cation in equal concentrations at a pH value close to the ground-state pK_a. In contrast, at lower concentrations ($\leq 10^{-4}M$), "puddles" would be partially or completely dispersed, resulting in the increase of intermolecular distances between cytidine or cytosine neutral molecules and cations and in the impossibility of charge-transfer interactions, as demonstrated by the disappearance of the peak in the phosphorescence titration curves at concentrations $\leq 10^{-4}M$.

In the case of cytidine mono-, di- and triphosphate, phosphorescence intensity *vs.* pH curves exhibit a similar behaviour with 5- to 16-fold increases in phosphorescence signal at a pH value close to the ground-state pK_a of the particular compound, followed by a plateau region occurring over about 2 pH units, then by decrease in phosphorescence intensity by a factor of 1·6–3·1 in the pH region 7–9 (see Fig. 3). The classical sigmoidal shape of these titration curves indicates that, in contrast to cytosine and cytidine, no aggregates of cytidine mono-, di- or triphosphate are formed in frozen methanol/water solution, even at concentrations as high as $10^{-3}M$ (see curve 1 in Fig. 3). This may be due to the size of the voluminous phosphate groups or to electronic repulsion between these groups, which would increase the distance between cytidine phosphate and its cation and therefore would prevent the formation of any charge-transfer complex. In agreement with our results, it has been found recently by Kleinwachter[10b] that CMP exhibits relatively weak aggregation in pure ice matrix and that complete disaggregation occurs in sodium acetate–glucose matrix. The decrease observed in the pH 7–9 region for all the cytidine phosphates might be due to the ionization of the phosphate groups.

Halide effect studies

We have also investigated the effect of sodium chloride, bromide and iodide on the phosphorescence spectral characteristics and phosphorescence intensity of cytidine as a function of pH. Phosphorescence excitation and emission maxima are not seriously shifted upon addition of sodium halides (Table 1). As in methanol/water mixtures, a red-shift of the excitation maximum is observed upon acidification of the three halide solutions of cytidine (see Fig. 6).

With 0·1M sodium chloride in methanol/water 10/90 v/v or in pure aqueous frozen solutions, phosphorescence titration curves of cytidine ($10^{-3}M$) exhibit a peak at pH 3·7–4·1 close to the ground-state pK_a of cytidine (Fig. 4, curves 1 and 2), while at lower concentrations of cytidine ($10^{-4}M$) or in about 1·7M sodium chloride medium, the phosphorescence intensity maximum disappears completely, resulting in a sigmoidal phosphorescence titration curve (Fig. 4, curves 3 and 4). This change of behaviour as a function of sodium chloride or cytidine concentration strongly suggests that the molecular aggregates or "puddles" are completely dissociated in frozen matrices upon addition of various concentrations of sodium chloride ranging between 0·1M for diluted cytidine solutions ($\leq 10^{-4}M$) and 1·7M for more concentrated nucleoside solutions ($10^{-3}M$). The present evidence of non-aggregation in dilute aqueous sodium chloride solutions supports our previous interpretation that the contribution of molecular aggregates to the variation of phosphorescence signal with solvent composition is of little importance in frozen dilute aqueous solutions, compared to physical matrix effects.[14]

The effect of sodium bromide and sodium iodide on the phosphorescence titration curves is completely different. Indeed, in 0·1M sodium bromide or iodide methanol–water solutions, a decrease of the phosphorescence signal of cytidine by a factor of 2·3–7·9 occurs as the pH is increased in the region 4–6. A plateau region is then observed from pH 7 to 12 (see Fig. 5). This dramatic change in the variation of phosphorescence intensity with pH results in "reversed" sigmoidal curves which are close mirror images of the corresponding curves with sodium chloride.

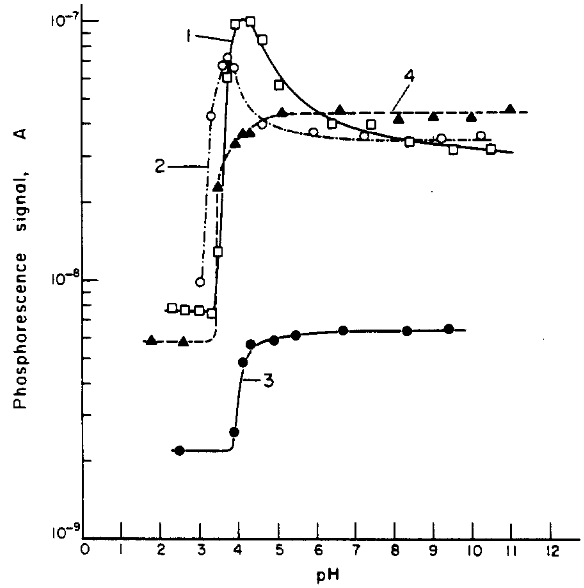

Fig. 4. Effect of sodium chloride on the phosphorescence titration curve of cytidine. Curves 1, 2 and 4 were obtained with $10^{-3}M$ cytidine and curve 3 with $10^{-4}M$ cytidine.
Curve 1, in 0·1M NaCl in methanol/water 10/90 v/v solution.
Curve 2, in 0·1M NaCl.
Curve 3, in 0·1M NaCl in methanol/water 10/90 v/v solution.
Curve 4, in 1·7M NaCl.

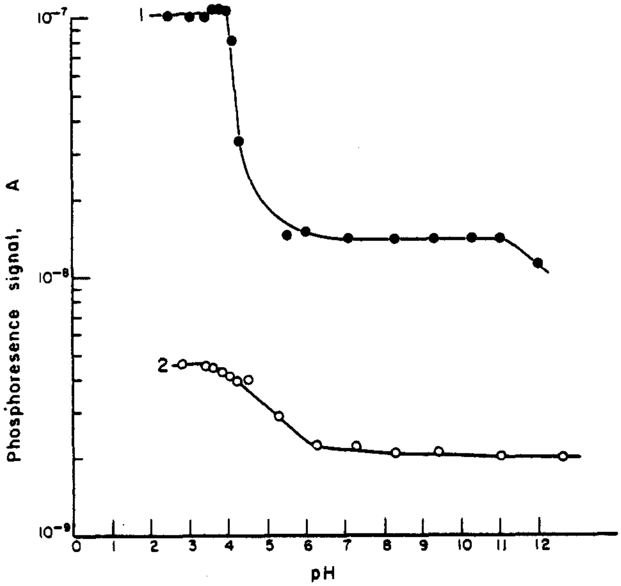

Fig. 5. Effect of sodium bromide and iodide on the phosphorescence titration curve of cytidine. Curve 1, $7 \cdot 5 \times 10^{-5} M$ cytidine in $0 \cdot 1 M$ NaBr in methanol/water 10/90 v/v solution. Curve 2, $3 \cdot 9 \times 10^{-6} M$ cytidine in $0 \cdot 1 M$ NaI in methanol/water 10/90 v/v solution.

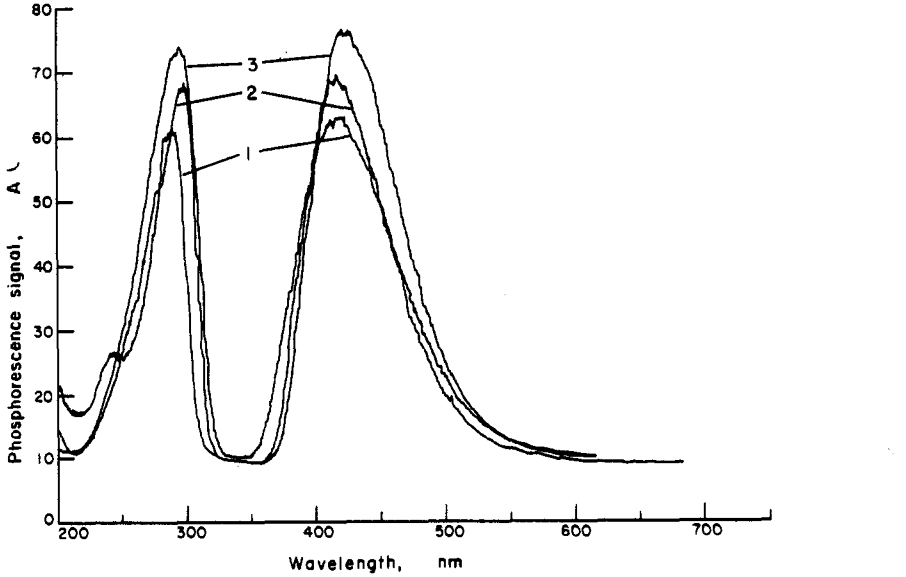

Fig. 6. Effect of pH on the phosphorescence excitation and emission spectra of cytodine in $0 \cdot 1 M$ NaCl in methanol/water 10/90 v/v at 77°K.

Curve 1, pH: 10·4.
Curve 2, pH: 2·4.
Curve 3, pH: 4·0.

Table 2. Heavy-atom effect on phosphorescence intensity of cytidine in frozen matrix at 77°K

Sample matrix[a]	Enhancement factor[b] I_p^{NaX}/I_p pH 10	pH 2·5	Detection[c] limit, M
Methanol/water 10/90 v/v ($0{\cdot}01M$ NaOH)	—	—	10^{-5}
$0{\cdot}1M$ NaCl	1·2	1·1	4×10^{-6}[d]
$0{\cdot}1M$ NaBr	2·7	50.	1×10^{-7}[e]
$0{\cdot}1M$ NaI	4·8	31.	8×10^{-7}[e]

[a] Methanol/water v/v 10/90 as solvent, except otherwise noted.

[b] Enhancement factor calculated from the ratio of the phosphorescence intensity (at maximum wavelength) in methanol–water–sodium halide solutions (I_p^{NaX}) and in methanol-water (I_p), with equal concentrations of cytidine ($10^{-4}M$).

[c] Detection limit is defined as the concentration giving a phosphorescence signal (located on the linear part of the analytical curve) that is twice the background noise.

[d] In water solution, pH 3·7.

[e] In pH 2·5 solution.

Heavy-atom effect

In fact, the anomalous reversed shape of the phosphorescence titration curves of cytidine with sodium bromide or iodide results from large enhancements of the phosphorescence signal in the acidic region where the signal was at a minimum value with sodium chloride as well as with methanol/water solutions. It is well known that the introduction of a heavy atom (such as iodine and bromine) into a matrix enhances the phosphorescence signal, owing to the increase of the spin–orbit coupling of excited singlet and triplet states. This results in the increase of the rate constant of intersystem-crossing from the excited singlet to the excited triplet state.[19] We have recently attributed the enhancement of the phosphorescence signal in aqueous sodium bromide and iodide solutions to this type of external heavy-atom effect.[14,20] In the case of cytidine, the heavy-atom enhancement factors determined in the alkaline region of the phosphorescence titration curves ranged between 2·7 and 4·8, values which might be reasonably expected from our previous assumptions that a compound with a low phosphorescence quantum efficiency (such as cytidine) should exhibit a relatively high heavy-atom effect.[20] However, anomalously high values of enhancement factors, ranging between 30 and 50, are obtained in acidic sodium bromide or iodide solutions of cytidine* (see Table 2). This strongly indicates that powerful interactions are present between cytidine cations—the predominant species at pH 2·5—and iodide or bromide ions, increasing manyfold the rate of intersystem-crossing between the excited singlet and triplet states. These interactions might be due to charge-transfer complexes in which iodide or bromide ions would act as electron donor and

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* An enhancement factor of 60 is also obtained for acidic sodium bromide solutions of cytosine.

cytidine cations as electron acceptor. Comparable weak complexes have been postulated between a phosphorescent aromatic molecule and an heavy-atom perturber, such as alkyl halides[19] or alkali metal halides.[21] As a consequence of the large heavy-atom enhancement factors observed in acidic solution, the limit of detection of cytidine is increased by one or two orders of magnitude in acidic sodium iodide or bromide solution (Table 2), as determined from the linear log-log plot of cytidine concentration *vs.* phosphorescence signal. Such findings are also of interest for the analytical bioassay of cytidine and related nucleotides.

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Zusammenfassung—Titrationskurven der Phosphoreszenz in Abhängigkeit vom pH-Wert von Cytosin, Cytidin, Cytidin-5′-monophosphat (CMP), -diphosphat (CDP) und-triphosphat (CTP) wurden in Methanol-Wasser 10:90 (v/v) und in verschiedenen eingefrorenen wäßrigen Natriumhalogenidlösungen bei 77°K aufgenommen. Wie die Form der Titrationskurven zeigt, kommen Molekülaggregate oder "Puddel" von Cytosin und Cytidin nur in ziemlich konzentrierter eingefrorener Lösung vor ($10^{-3}M$); in verdünnten eingefrorenen Lösungen ($< 10^{-4}M$) oder in $\sim 1M$ Natriumchlorid sind diese Aggregate dissoziiert. Selbst in konzentrierten Lösungen von CMP, CDP oder CTP konnte keine Molekülaggregation gefunden werden. Niedrigere Konzentrationen von Natriumbromid oder-jodid ($10^{-1}M$) ergaben im Fall des Cytidins "umgekehrte" sigmoide Phosphoreszenz-Titrationskurven. Diese rühren von einem anomal großen Schweratom-Verstärkungsfaktor in saurer Lösung, der zwischen 30 und 50 beträgt.

Résumé—On a obtenu les courbes de titrage phosphorescence-pH des cytosine, cytidine, cytidine 5′-monophosphate (CMP), -diphosphate (CDP) et -triphosphate (CTP) en méthanol/eau 10/90 v/v et dans diverses solutions aqueuses congelées d'halogénure de sodium à 77° K. Comme il apparaît par l'allure des courbes de titrage, on a montré que des agrégats ou "flaques" de cytosine et cytidine ne se manifestent qu'en solution congelée relativement concentrée (10^{-3} M), ces agrégats étant dissociés en solutions congelées diluées ($< 10^{-4}$ M) ou en chlorure de sodium

$\sim 1M$. On n'a pas pu trouver d'association moléculaire même en solutions concentrées de CMP, CDP et CTP. On a démontré que des concentrations plus faibles de bromure ou d'iodure de sodium (10^{-1} M) donnent des courbes de titrage par phosphorescence sigmoïdales "inversées" dans le cas de la cytidine, ayant pour cause *un facteur d'exaltation par atome lourd anormalement grand* en solution acide, se situant entre 30 et 50.

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AROMATIC SULPHONATE ION-SELECTIVE ELECTRODE MEMBRANE WITH CRYSTAL VIOLET AS ION-EXCHANGE SITE

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Summary—Four triphenylmethane derivatives (cations) and a high molecular-weight quaternary ammonium ion were used as the ion-exchange site in the liquid membranes of electrodes responsive to aromatic sulphonate ions, such as benzenesulphonate and α-naphthalenesulphonate. The nitrobenzene or 1,2-dichloroethane membrane containing the Crystal Violet-aromatic sulphonate pair had good sensitivity, showing an approximately Nernstian response down to $10^{-4}M$ sulphonate. The potential of the Crystal Violet membrane was independent of pH variation from 2·5 to 12. Chloride and sulphate ions in the aqueous sample solution did not affect the electrode potential. 1,3,6-Naphthalenetrisulphonate exerted essentially no influence on the potential of the α-naphthalenesulphonate electrode. The interference of the nitrate ion was relatively large. The conductivity and association of the solute species in the membrane were estimated.

Various kinds of ion-selective electrodes with liquid membranes have been developed in the past several years. Of the ion-selective electrodes for aromatic sulphonates, Coetzee and Freiser[1] reported the *p*-toluenesulphonate ion-selective electrode having a 1-decanol membrane containing methyltricaprylammonium ion (Aliquat 336S) as ion-exchange site, as well as many other anion-sensitive electrodes using ion-association extraction systems, and showed that the membrane electrode had linear Nernstian response from 10^{-1} to $10^{-3}M$ *p*-toluenesulphonate and was useful down to $10^{-4}M$. Bonner and Lunney[2] measured the activity of the same sulphonate species by using a concentration cell with a liquid membrane containing dialkyldimethylammonium chloride (Humuko Kemamine Q-1902-C). In a previous communication,[3] the Crystal Violet cation was reported to be an effective ion-exchange site in the membrane of an electrode responsive to aromatic sulphonates such as benzenesulphonate. This paper presents details of the analytical performance of the sulphonate ion-sensitive electrodes using Crystal Violet as well as analogous triphenylmethane derivatives as ion-exchange site in the membrane. The distribution of the exchanger between the membrane and an aqueous phase, and ionic conductances and the association of the solute ions in the membrane have been measured in relation to the performance of the electrode.

EXPERIMENTAL

Chemicals and membrane solutions

Four triphenylmethane dyes, *i.e.*, Crystal Violet (CV), Methyl Violet (MV), Malachite Green (MG) and Fuchsine Basic (F) were obtained as chloride salts from Kishida Kagaku Co. Sodium aromatic sulphonates were obtained from Wako Pure Chemicals Co. and Tokyo Kasei Kogyo Co. An aromatic sulphonate salt of Crystal Violet was precipitated by mixing concentrated aqueous solutions of the sodium sulphonate and of Crystal Violet. The precipitate was washed with demineralized water and dried in vacuum. Elemental analysis of the precipitate showed that it had a chemical composition essentially identical to the calculated one. The sulphonate salts of the other dyes and the iodide salt of Crystal Violet were prepared in similar manner. The organic solution of the sulphonate was prepared by dissolving a known amount of the precipitate in solvents such as nitrobenzene (NB), 1,2-dichloroethane (DCE), chloroform *etc.* The organic solution of dodecyloctylmethylbenzylammonium sulphonate (DOMBA-S) was prepared by the extraction method from the aqueous solution. DOMBA was supplied in chloride form by Kao Soap Co. and used as received. All other chemicals used were of reagent or analytical grade.

Electrode

The performance of the sulphonate ion-sensitive electrode was estimated by measurement of the electromotive force (e.m.f.) of the following cell.

SCE|Solution I (reference)|Organic liquid membrane|Solution II (sample)|SCE.

The cell assembly is the same as that described elsewhere.[4] The lower part of a glass U-tube was filled with 10 ml of the organic solution containing an ion-exchange site such as Crystal Violet, by which the reference and sample solutions (10 ml of each) were separated. The reference and sample solutions were connected to the saturated calomel electrodes through an agar bridge saturated with potassium chloride. Solutions I and II are aqueous solutions of the same sulphonate as that in the membrane. The concentration of the reference solution was 0·1*M* for sodium benzenesulphonate (BS) and toluenesulphonate (TS) and 0·01*M* for α-naphthalenesulphonate (NS). The effect of diverse ions on the electrode response to a primary sulphonate ion was examined by adding the ions to solution II. An alternative estimation of selectivity was performed with the "mixed solution method,"[5] a procedure which assesses the selectivity coefficient from the measurement of e.m.f. for sample solutions containing a fixed amount of interferent and varying amounts of the primary sulphonate ion. In this case an Orion liquid-membrane electrode barrel (92 type) equipped with a Millipore filter solvinert membrane (pore size 0·25 μm) was used. The e.m.f. (membrane potential) was measured with a Takeda-Riken electrometer No. TR-8651. The membrane potential was stable over the concentration range of Nernstian response.

Conductivity

Conductances of organic membrane solutions were measured at 25° by means of a conductivity cell with a cell constant 0·221 cm^{-1}, and a Yanagimoto Conductivity Meter Model MY-7. For these measurements, the organic membrane solvent was purified by distillation.

Distribution of the membrane solute between organic and aqueous phases

The equilibrium distribution of the membrane solute was estimated by the spectrophotometric determination of the solute concentration in the equilibrated aqueous phase, after 10 min shaking of the organic solution with an equal volume of water. The absorbance at 592, 570, 609 and 542 nm was measured for the determination of Crystal Violet, Methyl Violet, Malachite Green and Fuchsine Basic, respectively.

RESULTS AND DISCUSSION

Selection of ion-exchange site species and solvent

No elution of the ion-exchanger from the electrode membrane to the adjacent aqueous solution is desirable if a highly sensitive electrode is to be obtained. The elution of the ion-exchanger depends on the solvent species used, the combination of ion-exchange site and counter-ion chosen, and the adjacent aqueous solution.

Table 1 shows that among analogous dyes, Crystal Violet and Methyl Violet salts have high distribution ratios, as expected from their relatively hydrophobic functional groups, this being consistent with the behaviour of the potential of the dye-containing membrane electrodes, as shown in Fig. 1, in which the potentials of these two membranes give a linear response over a wider range of the logarithm of the molar concentration of benzenesulphonate. At higher concentrations (0·01–1*M*), the potentials are independent of the dye species in the membrane.

Table 2 gives the distribution of the Crystal Violet–benzenesulphonate ion-pair between organic solvent and water. Nitrobenzene and 1,2-dichloroethane are better as the membrane solvent, because of the high distribution ratios as well as their high dielectric constants, which give high conductance to the membrane.

Table 1. Distribution of benzenesulphonate salt of triphenylmethane dye between 1,2-dichloroethane and water at 25°C

Triphenylmethane dye	$D = C_0/C_w$*
Crystal Violet	$1{\cdot}8 \times 10^2$
Methyl Violet	$1{\cdot}2 \times 10^2$
Malachite Green	41
Fuchsine Basic	$9{\cdot}6 \times 10^{-2}$

* D is distribution ratio; C_0 and C_w are concentrations of dye in organic and aqueous phases, respectively.

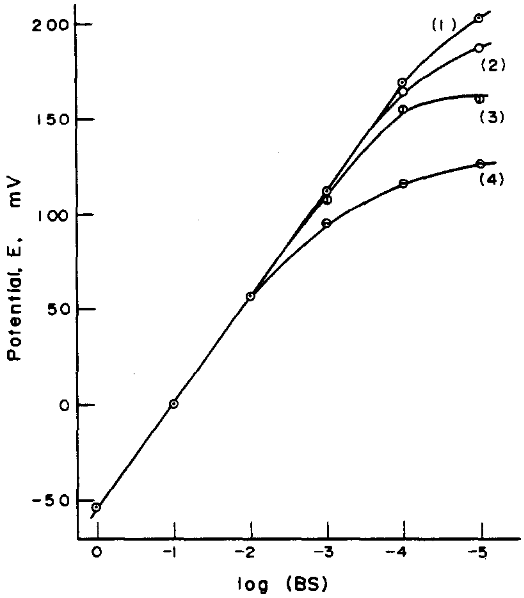

Fig. 1. Membrane potential of the benzenesulphonate (BS) electrode with a 1,2-dichloroethane membrane containing the dye cation as ion-exchange site, at 25°C. Dye: (1) CV, (2) MV, (3) MG, (4) F.

Table 2. Distribution of benzenesulphonate salt of crystal violet between organic solvent and water at 25°C

Solvent	D
Nitrobenzene	$2{\cdot}2 \times 10^3$
1,2-Dichloroethane	$1{\cdot}8 \times 10^2$
Chloroform	$1{\cdot}0 \times 10^2$
Monochlorobenzene	2·0
Carbon tetrachloride	1·8
Benzene	0·6

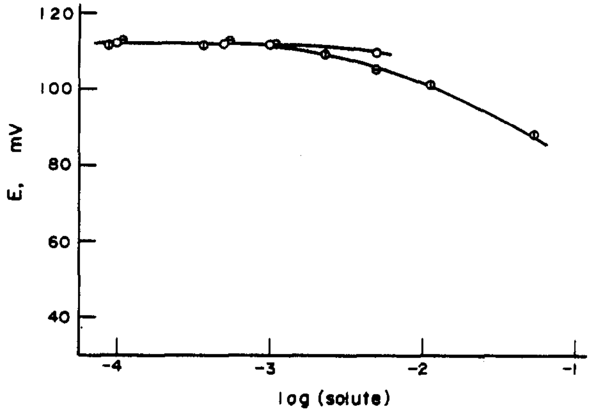

Fig. 2. Membrane potential *vs.* membrane solute concentration at 20°C.
—○—: CV-BS in NB, —⊖—: CV-BS in DCE, —◐—: DOMBA-BS in DCE.
Molar concentration ratio of Soln. I to Soln. II: 100.

The concentration of ion-exchanger in the membrane may also affect the membrane potential. As shown in Fig. 2, if the concentration of the membrane solute is kept in the range 1×10^{-4}–$1 \times 10^{-3}M$, the electrode has a constant and stable potential. At concentrations of membrane solute below $10^{-4}M$, the potential is unstable, whereas at concentration higher than the stable range the potential tends to decrease, probably because of elution of membrane solute into the adjacent aqueous solutions. In the work described here the concentration of the membrane solute was $5 \times 10^{-4}M$, except for the case noted.

Crystal Violet membrane electrode

From the results mentioned above, a 1,2-dichloroethane or nitrobenzene solution containing Crystal Violet is expected to give a good electrode membrane. The potential-concentration relationships of the electrodes with Crystal Violet membranes responsive to benzenesulphonate, toluenesulphonate and α-naphthalenesulphonate ions are shown in Fig. 3. Each electrode had an approximately Nernstian slope (56 mV/log C, where C is the molar concentration of the sulphonate ion) down to $10^{-4}M$ and was useful to $10^{-5}M$. The figure also shows the response of the electrode with the quaternary ammonium salt liquid membrane, which deviates from Nernstian linearity even at $10^{-4}M$.

The pH-effect on the potentials of the benzenesulphonate- and α-naphthalenesulphonate-sensitive electrodes was examined by measuring the e.m.f. of the cell in the sample solution with varying acidity, which was changed by adding an appropriate amount of hydrochloric acid and/or sodium hydroxide solution. The variation of pH from 2·5 to 12 yielded no change of the membrane potentials of either electrode, though small potential drops were observed below around pH 2, probably arising from conversion of Crystal Violet into its acidic form and the change of the liquid junction potential between the sample solution and an agar–potassium chloride bridge.

Interference of diverse ions

The effect of diverse ions on the benzenesulphonate electrode is shown in Fig. 4. Less interference was observed with the α-naphthalenesulphonate electrode. The effect

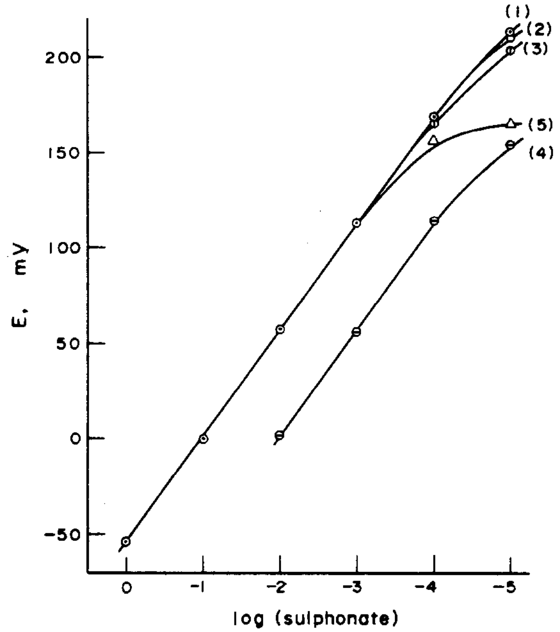

Fig. 3. Membrane potentials of the sulphonate electrodes with the Crystal Violet membranes at 20°C.
Membrane: (1) CV-toluenesulphonate in DCE, (2) CV-BS in NB, (3) CV-BS in DCE, (4) CV-NS in DCE, (5) DOMBA-BS in DCE.

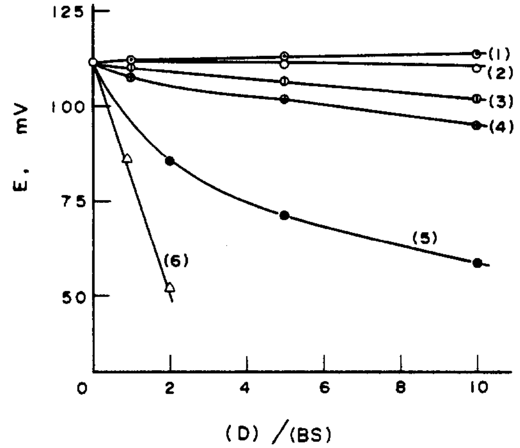

Fig. 4. Effect of diverse ions (D) on the membrane potential of the benzenesulphonate (BS) electrode at 20°C.
Membrane: CV-BS in DCE.
Soln. I: 0·1*M* BS, Soln. II; 0·001*M* BS + diverse ion (D).
Diverse ions: (1) Cl^-, SO_4^{2-}, 1,3,6-naphthalenetrisulphonate, (2) phenol-4-sulphonate, (3) benzoate, (4) benzene-*m*-disulphonate, (5) NO_3^-, (6) NS.

of interferents is usually expressed by a selectivity coefficient $K_{i,j}$ in the following equation.

$$E_M = \text{Const.} + 2{\cdot}303RT/Z_iF \,.\, \log(a_i + K_{i,j} \,.\, a_j^{z_i/z_j})$$

where E_M is the membrane potential and z_i, z_j and a_i, a_j are the charges and activities of the primary sulphonate ion i and interferent j in the sample solution,

Table 3. Selectivity coefficients $K_{i,j}$

Benzenesulphonate electrode			α-Naphthalenesulphonate electrode		
Interferent, j	C_j, M	$K_{BS,j}$	Interferent, j	C_j, M	$K_{NS,j}$
Cl^-	0·5	0·003	Cl^-	0·5	0·0004
NO_3^-	0·005	0·76	NO_3^-	0·005	0·03
phenol-4-sulphonate	0·005	0·016	benzenesulphonate	0·005	0·07
benzene-*m*-disulphonate	0·005	0·005	1,5-naphthalenedisulphonate	0·005	0·0007
benzoate	0·005	0·04	1,3,6-naphthalenetrisulphonate	0·1	0·00006
α-naphthalenesulphonate	0·00025	16	4-hydroxy-2-naphthalenesulphonate	0·005	0·025
1,3,6-naphthalenetrisulphonate	0·005	0·0008	2,3-dihydroxynaphthalene-6-sulphonate	0·005	0·00045

respectively. In estimation of the selectivity coefficient, the molar concentrations were used instead of the activities. The observed $K_{i,j}$ values for several anions are summarized in Table 3. Nitrate interferes with the Nernstian behaviour of the benzenesulphonate and α-naphthalenesulphonate electrodes, though chloride gives no significant interference. Sulphate also does not interfere, even in large excess. Substitution of an additional hydrophilic functional group, *i.e.*, sulphonate or hydroxyl group, in the interfering species, decreases its interference. 1,3,6-naphthalenetrisulphonate has little or no effect on the potentials of the benzenesulphonate or α-naphthalenesulphonate electrodes, whereas α-naphthalenesulphonate changes the potential of the benzenesulphonate electrode considerably.

Conductivity of the electrode membrane

The conductivity of Crystal Violet salts in nitrobenzene and 1,2-dichloroethane are shown in Fig. 5. The concentration-dependence of the molar conductance of each salt shows that the sulphonate salt in nitrobenzene is nearly completely dissociated over a wide concentration range, but is moderately associated in 1,2-dichloroethane.

The limiting molar conductance of the solute and the association constant were estimated by the Shedlovsky method,[6] using the conductance data. The results are listed in Table 4. The limiting conductivities of Crystal Violet cation and sulphonate ion in nitrobenzene were based on the reported limiting conductivity value of the iodide ion.[7] The association between the Crystal Violet cation and its counter-anion is negligibly small in nitrobenzene and is not so large even in 1,2-dichloroethane. In the latter solvent, about 20% of the Crystal Violet salt is in ion-association complexes at $5 \times 10^{-4}M$ concentration, which corresponds to the membrane concentration. The mobility of benzenesulphonate is not so different from that of naphthalenesulphonate. Eisenman and his co-authors showed that the selectivity coefficient is governed by the square of the ratio of the distribution ratio (between membrane solvent and water, at infinite dilution) of the salts of the interferent and the primary anion with a common cation, if the membrane solute is completely dissociated and the mobilities of two competitive anions are equal.[8] The distribution ratio of the α-naphthalenesulphonate salt of Crystal Violet between 1,2-dichloroethane and water was observed to be $1·0 \times 10^3$ at 25°. Comparing

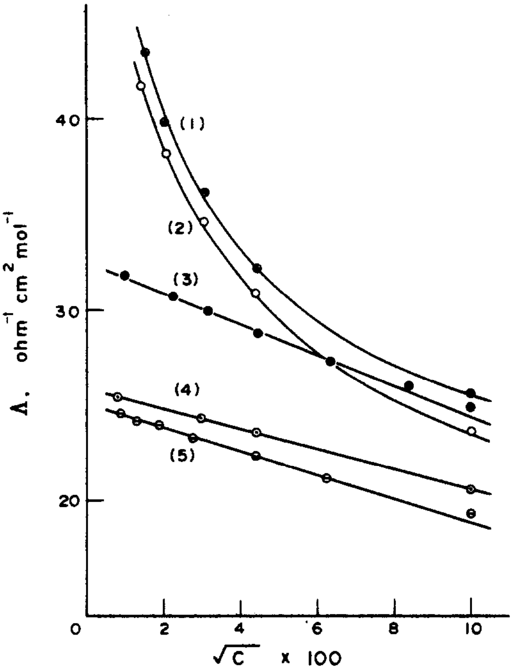

Fig. 5. Conductivities of the 1,2-dichloroethane and nitrobenzene membranes at 25°C. 1,2-dichloroethane membrane: (1) CV–BS, (2) CV–NS. Nitrobenzene membrane: (3) CV–I^-, (4) CV–BS, (5) CV–NS.

Table 4. Conductivity and association constant of the Crystal Violet salt in nitrobenzene and 1,2-dichloroethane at 25°C

Anion	Limiting molar conductivity and association constant					
	In nitrobenzene				In 1,2-dichloroethane	
	Λ_0*	λ_+*	λ_-*	K†	Λ_0	K
I^-	32·5	12·1	20·4‡	22		
benzenesulphonate	26·1	12·1	14·0	~2	56·2	$1·5 \times 10^3$
α-naphthalenesulphonate	25·0	12·1	12·9	~7	54·1	$1·4 \times 10^3$

* λ_+ and λ_- are the limiting molar conductivities of cation and anion, respectively, in units of ohm^{-1}cm^{2}mole^{-1} ($\Lambda_0 = \lambda_+ + \lambda_-$)

† K is the association constant of CV with the respective anion.

‡ From reference 7.

this distribution ratio and that of the corresponding benzenesulphonate salt in Table 2 with the observed selectivity coefficient between benzenesulphonate and α-naphthalenesulphonate ions supports the Eisenman theory, though only qualitatively.

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Zusammenfassung—Vier Triphenylmethan-Derivate (Kationen) und ein quartäres Ammoniumion mit hohem Molekulargewicht wurden als Ionenaustauschzentren in den flüssigen Membranen von Elektroden verwendet, die auf aromatische Sulfonationen wie Benzolsulfonat und α-Naphthalinsulfonat ansprechen. Die Membran aus Nitrobenzol order 1,2-Dichloräthan mit dem Paar Kristallviolett-aromatisches Sulfonat wies eine gute Empfindlichkeit auf; das ungefähr Nernst'sche Verhalten reichte bis hinunter zu $10^{-4}M$ Sulfonat. Das Potential der Kristallviolett-Membran war von pH-Änderungen zwischen 2,5 und 12 unabhängig. Chlorid- und Sulfationen in der wäßrigen Probenlösung änderten das Elektrodenpotential nicht. 1,3,6-Naphthalintrisulfonat war praktisch ohne Einfluß auf das Potential der α-Naphthalinsulfonat-Elektrode. Die Storung durch das Nitration war relativ groß. Leitfähigkeit und Assoziation der getlösten Spezies in der Membran wurden abgeschätzt.

Résumé—On a utilisé quatre dérivés du triphénylméthane (cations) et un ion ammonium quaternaire de haut poids moléculaire comme siège d'échange d'ions dans les membranes liquides d'électrodes sensibles aux ions sulfonates aromatiques, tels que le benzènesulfonate et l'α-naphtalène sulfonate. La membrane de nitrobenzène ou de 1,2-dichloréthane contenant la paire Crystal Violet-sulfonate aromatique a une bonne sensibilité, montrant une réponse approximativement Nernstienne jusqu'à une concentration aussi faible que 10^{-4} M de sulfonate. Le potentiel de la membrane de Crystal Violet est indépendant de la variation de pH de 2,5 à 12. Les ions chlorure et sulfate dans la solution aqueuse d'échantillon n'affectent pas le potentiel d'électrode. Le 1,3,6-naphtalène trisulfonate n'exerce essentiellement pas d'influence sur le potentiel de l'électrode à l'α-naphtalène sulfonate. L'interférence de l'ion nitrate est relativement grande. On a estimé la conductivité et l'association de l'espèce dissoute dans la membrane.

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THERMOMETRIC TITRATION IN INVESTIGATION OF THE FORMATION OF POLYANIONS OF MOLYBDENUM(VI), TUNGSTEN(VI), VANADIUM(V), AND CHROMIUM(VI)—I

COMPARISON OF THERMOMETRIC AND POTENTIOMETRIC TITRATION CURVES

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Summary—A new twin-cell thermometric titrator has been devised and used for thermometric titration of solutions of sodium molybdate, sodium tungstate, sodium orthovanadate, ammonium metavanadate, and potassium chromate with perchloric acid. The thermometric titration curves were compared with corresponding pH-titration curves for elucidation of the reactions occurring in the titrations. Thermometric titrimetric methods have been developed for the determination of tungsten, vanadium and chromium.

We have been interested in the formation of polyanions, in the course of mineral acid titration of a neutral solution containing a salt of an oxyanion such as molybdate, tungstate, orthovanadate, metavanadate, and chromate. A number of investigators have approached this problem with the aid of various physical and chemical methods. For example, the polymerization of molybdate has been investigated by potentiometric and conductometric titration,[1] cryoscopic titration,[2] polarography and amperometry,[3] Raman spectroscopy and ultracentrifugation,[4] and ultraviolet spectrophotometry,[5] and isopolymolybdate anions such as $Mo_4O_{13}^{2-}$, $Mo_6O_{21}^{6-}$, $Mo_7O_{24}^{6-}$, and $Mo_8O_{26}^{4-}$ have been reported as the polymerization products in the course of acidification. Jahr and Fuchs[6] have reviewed the methods applicable for the study of the formation of polyoxyanions containing molybdenum, tungsten and vanadium respectively, and also listed the polymerization products. However, their review did not include thermometric titrations, and it may be said that this method has never been applied sufficiently to investigations of the formation of polyoxyanions.

Though thermometric titration is widely used for investigation of complexation reactions, the results have to be confirmed by other methods such as potentiometric or conductometric titration.[7] Precise thermometric titrations have been used alone to determine simultaneously free energy changes (ΔG) and enthalpy changes (ΔH), by Christensen *et al.*,[8-11] who interpreted the titration curves with aid of a computer.

Recently, however, Cabani and Gianni[12] showed that these simultaneous determination techniques seem to be limited in application to only simple reactions. The lack of reliability of the method may be due to the difficulty of obtaining a sufficiently accurate titration curve, since in the classical thermometric titrator the heat of dilution and the change of heat capacity during the titration had serious effects on the titration curve. Now, with a thermometer of new type, the thermometric titration method can be used alone not only for determination of the end-point in titrations but also for elucidation of complicated processes in a reaction.

We used the new titrator to obtain thermometric titration curves for sodium molybdate, tungstate and orthovanadate, ammonium metavanadate and potassium chromate with perchloric acid. The pH–titration curves for the same systems were also determined, and the reaction processes deduced from results obtained by both methods. Tungstate, vanadate, and chromate were found to give thermometric titration curves with inflections at a fixed mole ratio between the salts and the acid, and therefore can be determined by titration with a standard acid solution.

A thermometric titrator having two titration vessels and two burettes was first devised by Tyson *et al.*[13] In their apparatus the temperature-sensing device consisted of four thermistors connected in parallel. We have tried to make such a device, but failed to prepare two identical sets of four thermistors having the same resistance–temperature response. Hence, only two thermistors of the same resistance–temperature response were chosen and used in our apparatus. Tyson *et al.*[13] used polyethylene cups as titration vessels, in which significant losses of heat could not be prevented during the titration. They recommended the rapid injection of titrant into the vessel, *e.g.*, within 10 sec, to obtain a titration curve of good shape. We used a Dewar flask as the titration vessel to avoid heat loss, and the titration could be achieved adiabatically even at a reduced rate of titration for relatively slow reactions.

EXPERIMENTAL

Apparatus

Thermometric titrator. The apparatus was similar to a thermometric titrator TMT-1A supplied commerically by TOA Electronic Co. Ltd., Tokyo, except for the titration system. The titration system was improved by substituting two syringe-type automatic injection burettes for the original burette. The essential features of the apparatus are shown in Fig. 1. The titration vessels were 50-ml Dewar flasks. The titration rate was 0·2 ml/min.

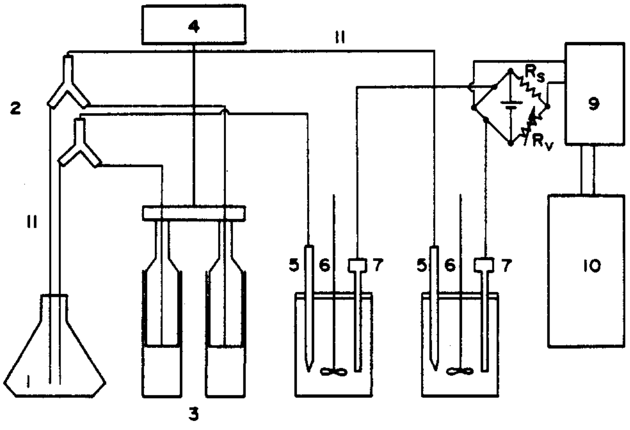

Fig. 1. Thermometric titration apparatus.
1 Titrant vessel; 2 three-way taps; 3 injection syringe burettes; 4 synchronous burette motor; 5 burette tips; 6 stirrer; 7 thermistor (R at 25°C = 20 kΩ, $B = 2800 \pm 10$ K, time-constant = 0·3 sec); 8 adiabatic titration vessels (Dewar); 9 amplifier; 10 recorder; $R_s = 20$ kΩ; R_v = variable resistor; 11 Teflon tube.

Potentiometric titration. A Metrohm Potentiograph E336 and glass electrode were used.

Reagents

Perchloric acid. Reagent grade perchloric acid (70%) was diluted with water to an appropriate concentration, and standardized with sodium carbonate solution as usual.

Sodium molybdate solution, 0·5*M*. Standardized with 8-hydroxyquinoline.[14]

Sodium tungstate solution, 0·5*M*. Standardized as for the molybdate.

Sodium vanadate solution, 1·0*M*. Standardized volumetrically.[15]

Ammonium vanadate solution, 0·1*M*. Standardized as for the tungstate.

Potassium chromate solution, 1·0*M*. Standardized as for tungstate.

All salts used were Wako Chemicals' extra pure grade. Samples from two separate batches were used for the sodium tungstate, metavanadate and chromate, potassium tungstate and chromate, and ammonium metavanadate. Samples from three separate batches of sodium orthovanadate were used. The tungstates were checked gravimetrically as tungstic oxide,[16] and the vanadates and the chromates volumetrically by the method of Kolthoff and Sandell.[15]

Procedure

The two titration vessels were charged, one with 10–30 ml of sample solution and the other with an equal volume of reference solution, the solutions having been brought to thermal equilibrium with the surroundings. All titrations were carried out at room temperature (25 ± 0·5°). The titrant concentration was 90–100 times that of the titrand, so that the reaction was complete on addition of about 0·1–0·3 ml, and thus the volume change and consequent heat capacity change were kept to a minimum. The cover with its attached thermistors, stirrers, and burette tips was fitted, and when the thermistor-bridge recorder gave a steady trace the synchronous burette motor was started to perform the titration. A suitable bridge sensitivity was chosen by trial and error. The trace was 10–30 cm long for each titration, so the titration volumes could be measured to three significant figures.

The pH-titrations were carried out by successive addition of 0·05-ml portions of perchloric acid to 100 ml of salt solution.

To obtain precise titration curves at high molar ratios of the added acid to salt, the acidified salt solutions were titrated thermometrically and potentiometrically with perchloric acid.

RESULTS AND DISCUSSION

Throughout this paper the inflection point of the titration curve is called the *Z*-value, *i.e.*, the molar ratio of added perchloric acid to neutral salt taken initially. Both thermometric and potentiometric titrations were performed, for comparison purposes.

Acidification of sodium molybdate solutions

The pH-titration curves were identical with those reported by others;[1] the *Z*-value fell between 1·2 and 1·5 for titration of 0·2–0·04*M* sodium molybdate and this value agrees with that found by other researchers.[1,17]

The thermometric titration curves are shown in Fig. 2. Three distinct break-points can be observed on the titration curve of 0·2*M* sodium molybate (Fig. 2*A*), but only one on the pH-titration curve. The inflections have *Z*-values of 1·14, 1·43 and 2·00, respectively. For 0·04*M* molybdate solution, three inflections could still be observed (Fig. 2*B*), but the form of the curve and the *Z*-values differed from those in Fig. 2*A*. The *Z*-values were 1·25, 1·40 and 3·6, respectively. The corresponding pH titration curve had only one *Z*-value, at 1·5, and that was quite obscure. For molybdate solution in lower concentration ($5 \times 10^{-3}M$) only one inflection point was observed on the thermometric curve (Fig. 2*C*), and the *Z*-value was 1·50. The pH-titration curve had no inflection at all.

These results show thermometric titration to be superior to pH-titration. The variation of the *Z*-values with initial concentration of molybdate will give much information about the polymerization of molybdate and the chemical species appearing during the acidification. The process of the acidification of molybdate can be interpreted as follows from the three inflections of the thermometric titration and from the results of other

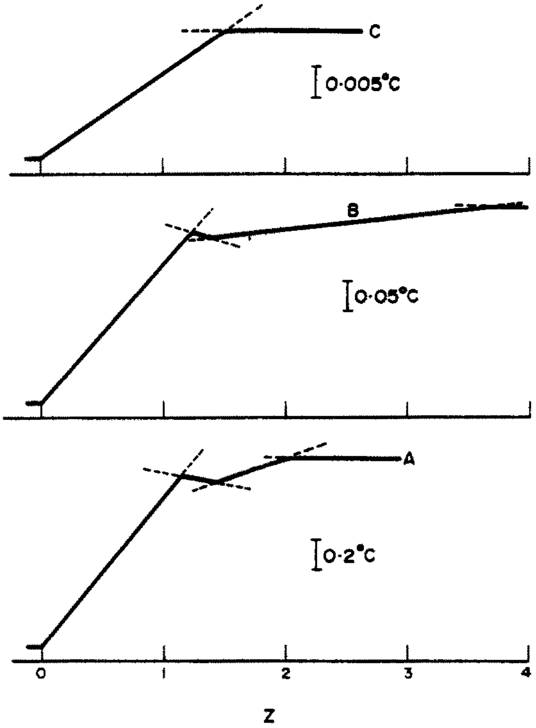

Fig. 2. Thermometric titrations of sodium molybdate with perchloric acid. $[Na_2MoO_4]$: A 0·2250*M*; B 0·0428*M*; C 0·00535*M*. The ordinate is relative heat change during the titration.

investigators.[1–5] From Fig. 2, it can be seen that the first inflection is shifted to higher *Z*-values with decreasing initial concentration of molybdate. When the initial sodium molybdate solution is about 0·2*M* the first product is the heptamolybdate:

$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$; calculated *Z*-value 8/7 = 1·143 (observed = 1·14)

From 0·04*M* molybdate, both heptamolybdate and octamolybdate can be formed so as to exist simultaneously. From 0·005*M* molybdate, the octamolybdate is the first product formed:

$8MoO_4^{2-} + 12H^+ = Mo_8O_{26}^{4-} + 6H_2O$; calculated *Z*-value 12/8 = 1·50 (observed = 1·50)

The second inflection is given by

$Mo_7O_{24}^{6-} + 2H^+ = H_2Mo_7O_{24}^{4-}$; calculated *Z*-value 10/7 = 1·43 (observed 1·43)

and the third by

$8H_2Mo_7O_{24}^{4-} + 32H^+ = 7H_4Mo_8O_{26} + 10H_2O$; calculated *Z*-value 112/56 = 2·00. (observed 2·00)

In Fig. 2B, the *Z*-value of the second inflection is lower than the calculated value. This seems to indicate, as mentioned above, that part of the heptamolybdate was converted directly into octamolybdate, without intermediate protonation.

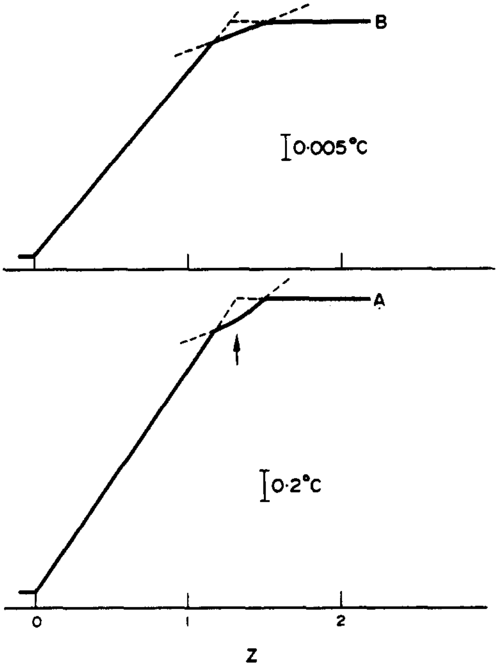

Fig. 3. Thermometric titrations of sodium tungstate with perchloric acid. [Na_2WO_4]: A 0·2030*M*; B 0·00502*M*.

Acidification of sodium tungstate solutions

The pH-titration curves for 0·005–0·5*M* sodium tungstate all have a single *Z*-value of 1·2, but the inflection point becomes difficult or impossible to observe as the tungstate concentration of the starting solution decreases. For sodium tungstate concentrations >0·01*M* a light yellow precipitate formed during the titration. Thermometric titration curves are shown in Fig. 3. Three inflections were observed for 0·2*M* sodium tungstate, the second of which was attributed to the heat of precipitation, and only two were observed for 0·005*M* sodium tungstate. The *Z*-values of the two inflections were 1·17 and 1·50. The polymerization can be elucidated as described below and the fixed *Z*-value in thermometric titrations can be applied for the determination of tungstate. Typical results are shown in Table 1.

Table 1. Comparison of results for tungsten determination. (Each value is the average of 50 determinations)

		Tungsten, %		
			Thermometric	
Compound	Sample No.	Gravimetric[17]	1st inflection	2nd inflection
Sodium tungstate	1	55·5 (0·43)*	55·7 (0·15)*	55·4 (0·62)*
	2	55·6 (0·30)	55·7 (0·16)	55·4 (0·68)
Potassium tungstate	1	50·7 (0·65)	50·6 (0·14)	50·5 (0·48)
	2	50·6 (0·50)	50·6 (0·17)	50·5 (0·59)

* Coefficient of variation = $100[\Sigma(x_i - \bar{x})^2/n]^{1/2}/\bar{x}$ %.

From the thermometric titration curves and results obtained by other methods[18–20] we can postulate the first inflection as corresponding to

$$6WO_4^{2-} + 7H^+ = HW_6O_{21}^{5-} + 3H_2O\text{; calculated } Z\text{-value } 7/6 = 1{\cdot}167 \text{ (observed } 1{\cdot}17)$$

and the second as

$$HW_6O_{21}^{5-} + 2H^+ = H_3W_6O_{21}^{3-}\text{; calculated } Z\text{-value } 9/6 = 1{\cdot}500 \text{ (observed } 1{\cdot}50).$$

Acidification of sodium orthovanadate solutions

The pH-titration curves had one inflection at a Z-value of 1·0 irrespective of the initial concentration of vanadate initially taken. A second inflection was observed for 0·2 and 0·08M vanadate but not 0·02M vanadate.

Thermometric titration curves are shown in Fig. 4. Three inflections with Z-values 1·00, 1·50 and 3·0 were found for 0·2M vanadate but only one at Z-value 1·00 for the 0·02M solution. The Z-value of the first inflection point of both the types of titration curve corresponds to protonation of the vanadate ion:[21,22]

$$VO_4^{3-} + H^+ = HVO_4^{2-} \text{ calculated } Z\text{-value } 1{\cdot}00 \text{ (observed } 1{\cdot}00).$$

The second inflections of both titration curves are dependent on the concentration of vanadate and the reaction is as follows.[21,22]

$$2HVO_4^{2-} + H^+ = HV_2O_7^{3-} + H_2O\text{; calculated } Z\text{-value } 3/2 = 1{\cdot}50 \text{ (observed } 1{\cdot}50).$$

The third inflection could correspond to:

$$5HV_2O_7^{3-} + 15H^+ = H_6V_{10}O_{28}\text{; calculated } Z\text{-value } 30/10 = 3{\cdot}00 \text{ (observed } 3{\cdot}0).$$

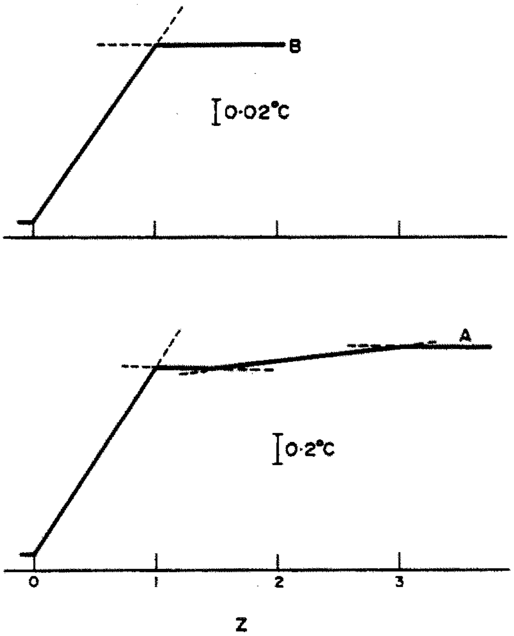

Fig. 4. Thermometric titrations of sodium orthovanadate with perchloric acid. [Na_3VO_4]: A 0·2466M; B 0·0247M.

Howarth *et al.*,[22] on the basis of their NMR observations, concluded that the dimerization was acid-catalysed, and rapid for 0·125*M* vanadate. In our work the dimerization was rapid for 0·2*M* vanadate but seemed to occur scarcely at all in 0·02*M* vanadate since the second inflection which indicates the initiation of the formation of $H_6V_{10}O_{28}$ could not be observed at all for the 0·02*M* solution.

Acidification of ammonium metavanadate solution

The $V_4O_{12}^{4-}$ ion is said to be already present in the test solution.[23–25] The pH-titration curves give a single inflection point at a *Z*-value of 0·4 for all concentrations of ammonium metavanadate.

Thermometric titration curves are shown in Fig. 5 and have three inflections at *Z*-values of 0·40, 1·00 and 2·00, the third being less clear-cut. The thermometric titration curve for 0·02*M* ammonium vanadate has only one inflection at a *Z*-value of 0·4. The first inflection seems to be independent of the concentration of vanadate, but the others not.

Vanadium in 0·005–0·5*M* orthovanadate and in 0·01–0·1*M* metavanadate can be determined by thermometric titration since the *Z*-values of the first inflections are independent of the initial vanadate concentration. Table 2 shows typical results.

From the thermometric titration curves and the results of other investigators[21,23] the course of acidification of metavanadate appears to be

$$5V_4O_{12}^{4-} + 8H^+ = 2V_{10}O_{28}^{6-} + 4H_2O\text{; calculated } Z\text{-value; } 8/20 = 0{\cdot}400 \text{ (observed } 0{\cdot}400)$$

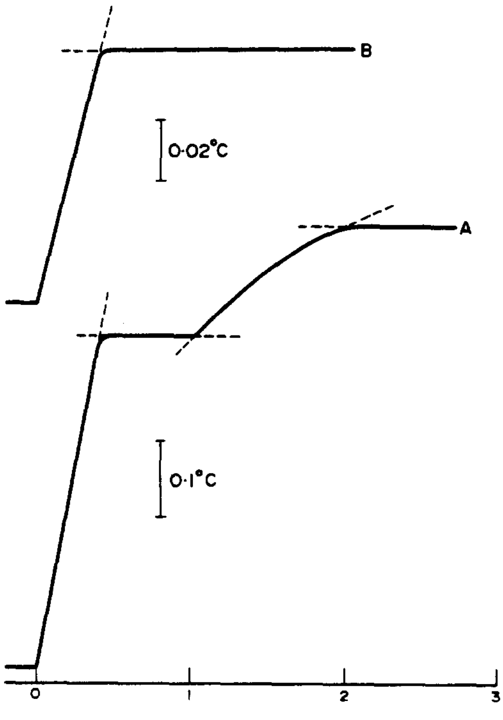

Fig. 5. Thermometric titrations of ammonium metavanadate with perchloric acid. $[NH_4VO_3]$: A 0·1000*M*; B 0·0200*M*.

Table 2. Comparison of results for vanadium determination. (Each value is the average of 50 determinations)

Compound	Sample No.	Vanadium, %	
		Volumetric[12]	Thermometric
Sodium orthovanadate	1	23·7 (2·9)*	24·6 (1·7)*
	2	24·2 (2·5)	25·1 (1·0)
	3	24·0 (2·7)	24·6 (1·3)
Ammonium metavanadate	1	43·1 (0·88)	43·5 (0·24)
	2	42·4 (0·80)	43·2 (0·35)
Sodium metavanadate	1	41·2 (1·1)	41·7 (0·31)
	2	40·4 (1·1)	41·4 (0·45)

* Coefficient of variation.

followed by

$$V_{10}O_{28}^{6-} + 6H^+ = H_6V_{10}O_{28}\text{; calculated } Z\text{-value } 20/20 = 1{\cdot}00 \text{ (observed } 1{\cdot}00)$$

and

$$H_6V_{10}O_{28} + 10H^+ = 10VO_2^+ + 8H_2O\text{; calculated } Z\text{-value } 40/20 = 2{\cdot}00 \text{ (observed } 2{\cdot}0)$$

This last step may go in two stages: $H_6V_{10}O_{28} = 5V_2O_5 + 3H_2O$ followed by $V_2O_5 + 2H^+ = 2VO_2^+ + H_2O$. The formation of V_2O_5 is independent of the hydrogen ion concentration but dependent on that of vanadate.[21] Therefore its formation would be rapid in 0·1*M* solution, but slow in 0·01*M* solution; the second and the third inflections would consequently not be observed for the more dilute solution.

Acidification of potassium chromate solutions

The pH-titration curves all have a single inflection at a *Z*-value of 1.0. The thermometric titration curve for 0·5*M* potassium chromate, shown in Fig. 6, has an inflection at a *Z*-value of 1·00, and slight breaks at *Z*-values of about 0·1 and 0·25. The

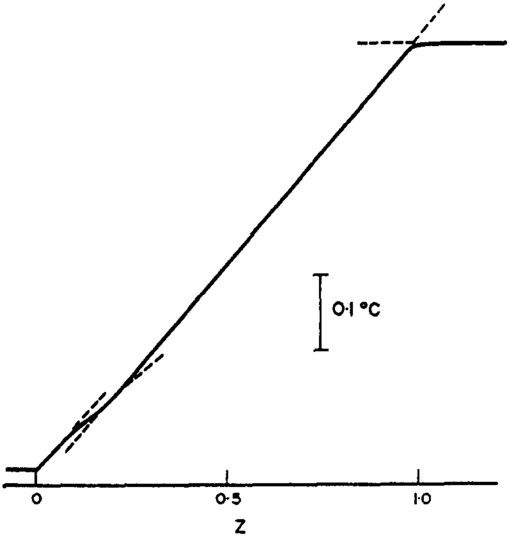

Fig. 6. Thermometric titration of 0·5136*M* potassium chromate with perchloric acid.

Table 3. Comparison of results for chromium determination. (Each value is the average of 50 determinations)

Compound	Sample No.	Chromium, %	
		Volumetric[12]	Thermometric
Potassium chromate	1	26·7 (1·0)*	26.7 (0·10)*
	2	26·7 (1·0)	26·7 (0·11)
Sodium chromate	1	31·8 (1·0)	32·0 (0·32)
	2	31·6 (1·3)	31·7 (0·30)

* Coefficient of variation.

curves for other chromate concentrations are similar in form. As the Z-value for chromate titration is always 1·00, chromate can be determined by thermometric titration. Results are shown in Table 3. The thermometric titration confirms the condensation of chromate to form dichromate.

The pH-change in the pH-titration is based on ΔG, but the temperature change in the thermometric titration depends on ΔH. From $\Delta G = \Delta H - T\Delta S$, comparison of the two titration curves gives some idea of whether the reaction mechanism is mainly influenced by ΔH or ΔS. For example, in the acidification of tungstate the process before the first inflection seems to have large ΔH and ΔS, whereas the process between the first and the second inflections has large ΔH but rather small ΔS.

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Zusammenfassung—Ein neues Gerät mit Zwillingszelle zur thermometrischen Titration wurde konstruiert und zur thermometrischen Titration von Lösungen von Natriummolybdat, Natriumwolframat, Natriumorthovanadat, Ammoniummetavanadat und Kaliumchromat mit Überchlorsäure verwendet. Die thermometrischen Titrationskurven wurden mit entsprechenden pH-Titrationskurven verglichen, µm die bei den Titrationen ablaufenden Reaktionen aufzuklären. Thermometrische Titrationsmethoden zur Bestimmung von Wolfram, Vanadium und Chrom wurden entwickelt.

Résumé—On a conçu un nouvel appareil de titrage thermométrique à cellules jumelées et l'a utilisé pour le titrage thermométrique de solutions de molybdate de sodium, tungstate de sodium, orthovanadate de sodium, métavanadate d'ammonium et chromate de potassium par l'acide perchlorique. On a comparé les courbes de titrage thermométrique avec les courbes de titrage pH correspondantes pour élucider les réactions se produisant dans les titrages. On a développé des méthodes titrimétriques thermométriques pour le dosage de tungstène, vanadium et chrome.

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SEPARATION OF MOLYBDENUM FROM INTERFERING ELEMENTS BY EXTRACTION AS PHOSPHOMOLYBDENUM BLUE

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Summary—A simple method is described for the separation of molybdenum from titanium, zirconium, chromium, manganese, iron, cobalt, nickel, uranium and aluminium in a wide variety of samples in <30 min. Phosphomolybdenum blue is produced by boiling for 2 min a molybdate solution containing phosphate to give Mo/P = 20–37 (w/w) with hydrazine sulphate in 0·1*N* sulphuric acid. The volume and acidity are adjusted to give a molybdenum concentration of 0·6–5 my/ml in 0·4–0·5*N* sulphuric acid. The phosphomolybdenum blue is 99·5% extracted with methyl isobutyl ketone in a single extraction. The residual molybdenum and hydrazine in the aqueous phase are oxidized with a few drops of liquid bromine and the molybdenum is quantitatively extracted with the same solvent from 1*N* sulphuric acid as its reddish brown thiosulphato complex. The molybdenum is stripped by ammonia–hydrogen peroxide solution. The back-extract is heated to boiling and filtered to remove the insoluble hydroxides of traces of accompanying elements. The thiosulphate in the filtrate is destroyed by boiling for 4–5 min with excess of hydrogen peroxide in slightly ammoniacal medium. The molybdenum is determined finally by cerimetry or other standard methods.

"Molybdenum blue" is the basis of several procedures for the estimation of μg amounts of phosphorus, germanium, silicon, arsenic and molybdenum.[1–5] It has, however, not been studied for the separation of molybdenum by solvent extraction, although it is sufficiently stable to atmospheric oxygen[6] and extractable by oxygenated organic solvents.[5,7,8] Such a study is considered of interest as very few elements form molybdenum blues.

EXPERIMENTAL

Reagents and solutions

Molybdenum solution. Sodium molybdate dihydrate was dissolved in water to give a molybdenum concentration of 20 mg/ml and aliquots were suitably diluted to give 100 and 10 μg/ml concentrations.

Sodium phosphate solution. Disodium hydrogen phosphate dihydrate (2·874 g) was dissolved in water and made up to 250 ml to give 2 mg of phosphorus/ml.

Sodium thiosulphate solution, 40% w/v.

Sulphuric acid, 1, 4 and 25*N*.

Methyl isobutyl ketone. The fraction boiling at 114–116° was used.

Hydrazine sulphate.

Solutions of other elements. Prepared by dissolving the sodium or potassium salts in water or dilute sulphuric acid to give 10 or 20 mg/ml concentrations of the ions.

Samples. Synthetic samples were made by dissolving suitable amounts of generally available salts in dilute sulphuric acid so as to give the compositions given in Table 6, where the first four samples represent Hastelloy A, Nimonic 80, ferromolybdenum and molybdenum silicide respectively, and the others were composed to test the scope of the method.

Ferromolybdenum. Finely powdered sample (0·1 g) was heated with 10 ml of sulphuric acid (1 + 10) and 3 ml of concentrated nitric acid, till fumes of sulphur trioxide evolved. The residue was dissolved by warming with 10 ml of water, neutralized with 10*M* sodium hydroxide and adjusted to 0·1*N* in sulphuric acid for analysis by the procedure.

Separation procedure

Extraction of phosphomolybdenum blue. To a solution containing molybdate (Mo 0·6–5 mg/ml) and other ions in a 50-ml beaker, a suitable amount of sodium phosphate solution was added to give Mo/P = 20–37 (w/w) and the mixture adjusted to be 0·1*N* in sulphuric acid and 15 ml in volume. Hydrazine sulphate [1 mg/mg of reducible ions but 5 mg/mg of Cr(VI)] was added and the solution was boiled for 2–3 min with frequent stirring to avoid crust formation. The solution was cooled to room temperature and transferred to a 150-ml separatory funnel along with the rinse water. After adjustment to be 0·4*N* in sulphuric acid and 20 ml in volume, the solution was shaken for 2 min with an equal volume of methyl isobutyl ketone (MIBK). On settling, the aqueous phase was drawn off into a 100-ml beaker.

Any titanium (or zirconium) present in the sample was completely precipitated by careful addition of phosphate before adjustment of the Mo/P ratio. Phosphomolybdenum blue was produced and extracted as above, without removal of the precipitate.

Extraction of residual molybdenum as thiosulphato complex. The little unextracted molybdenum and excess of hydrazine sulphate in the aqueous phase were oxidized with a few drops of liquid bromine (added by micropipette). Excess was boiled off and the solution was cooled and transferred to another separatory funnel containing 25 ml of MIBK and enough 25*N* sulphuric acid to give 1*N* sulphuric acid concentration in a final volume of 25 ml of aqueous solution. The volume was made up to 23·5 ml with cold water and 1·5 ml of 40% sodium thiosulphate solution were added and the whole immediately shaken for 5 min. The aqueous phase, along with any precipitate at the phase interface, was drawn off into another separatory funnel already containing the same volume of solvent and thiosulphate solution as before and shaken immediately for 5 min. The aqueous phase was drawn off, leaving any reddish-brown precipitate in the funnel. The precipitate was washed in the funnel by shaking with two 1-ml portions of water. The aqueous phases were rejected.

For each 100 mg of iron(III), when present, an additional 2 ml of thiosulphate solution were added to reduce it to iron(II).

Back-extraction of molybdenum. All the MIBK phases along with any reddish-brown precipitate, were transferred to a 250-ml separatory funnel and the molybdenum was quantitatively stripped by 2 min of vigorous shaking, first with an equal volume of just ammoniacal hydrogen peroxide solution containing 5 ml of 6% hydrogen peroxide, and then with half this volume of water made just alkaline with 2*M* sodium hydroxide (ammonia causes emulsions) and containing 5 ml of 6% hydrogen peroxide. The back-extracts were heated to boiling for 4–5 min with excess of hydrogen peroxide and any precipitate was filtered off. The clear filtrate and washings were acidified with hydrochloric acid, excess of hydrogen peroxide was boiled off and any molybdenum blue formed was oxidized with bromine water. After the excess of bromine had been boiled off, the solution was taken for determination of molybdenum.

Determination of the elements. Molybdenum in amounts <5 mg was determined colorimetrically,[9] and in amounts >5 mg either by the oxinate method[10] or titrimetrically by cerimetry.[11] Other elements were determined by appropriate gravimetric methods.[12] Very low extraction of elements was confirmed by very sensitive tests.[12,13]

RESULTS AND DISCUSSION

Production and extraction of phosphomolybdenum blue

Of the reagents[14,15] used for reduction of phosphomolybdate, hydrazine sulphate is found most suitable as it requires low acidity, and can easily be destroyed if necessary. In the absence of phosphate, hydrazine reduces molybdate quantitatively to isopolymolybdenum blue at $\leq 0{\cdot}3N$ acidity on heating, but stable emulsions are formed on shaking with oxygenated organic solvents, with little extraction. These difficulties are overcome by adding phosphate before reduction to give Mo/P (w/w) = 20–37. Reducing in $\leq 0{\cdot}1N$ sulphuric acid medium and extracting with MIBK from 0·4–0·5*N* sulphuric acid (Mo $\geq$ 0·6 mg/ml), gives almost quantitative ($\geq 99\%$) extraction. Reduction or extraction at higher acidities (Table 1) or lower concentration of molybdenum (Table 2) or with a different solvent (Table 3) or Mo/P ratio outside the given range (Table 4) decreases the extraction. Changing the medium to hydrochloric acid is not advantageous. At Mo concentrations ≤ 5 μg/ml, no blue colour is formed. Traces of silicate introduced in the reagents will behave similarly to phosphate.

Table 1. Effect of acidity on phosphomolybdenum blue formation and extraction
(Mo = 4·9 mg/ml; Mo/P = 37)

Production		Extraction		
			$\%E_{Mo}$	
$[H_2SO_4]$, N	$\%E_{Mo}$ from 0·6N H_2SO_4	Acidity, N	H_2SO_4 medium	HCl medium
0·02	99·4	0·2	97·4	99·6
0·04	99·1	0·4	99·5	99·3
0·10	99·0	0·5	99·5	—
0·20	96·4	0·6	99·0	99·3
0·60	83·8			

Table 2. Dependence of molybdenum extraction on Mo concentration
(Mo/P = 30; 24 mg of $Na_2S_2O_3 \cdot 5H_2O$ per ml; extraction from 1N H_2SO_4)

Mo *mg/ml*	$\%E_{Mo}$*	Mo *mg/ml*	$\%E_{Mo}$†
4·90	99·5	0·004	97·2
2·45	99·5	0·008	97·0
1·22	99·5	0·020	97·0
0·61	99·5	0·040	97·0
0·30	89·8	0·080	94·9
0·15	83·7	0·20	91·6
0·05	63·3	0·40	79·5
0·005	45·0§		

* As phosphomolybdenum blue.
† As thiosulphato complex.
§ Blue not visible.

Table 3. Extraction by some oxygenated solvents
(Mo = 5·1 mg/ml; Mo/P = 30)

Solvent	Mo extraction, %
Methyl isobutyl ketone	99·5
TBP–benzene (1 : 1)	98·1
Isopentyl alcohol	80·1
Isopentyl acetate	37·1
*Ether	10·0

* Peroxide-free and pre-equilibrated with blank solution.

Table 4. Effect of Mo/P ratio
(4·9 mg Mo/ml aqueous phase)

Mo : P w/w	Mo extraction, %
0·5*	—
1·0†	—
10	98·6
20	99·5
30	99·5
37	99·5
50	91·8
60	83·6
80†	—
100†	—

* No blue but an unextractable reddish-brown colour.
† Emulsifies on shaking with the solvent.

The ions of manganese, copper, vanadium, chromium and iron cause a lowering of the degree of extraction by up to 8%, in that order (Table 5). The extraction is almost completely suppressed by large amounts of arsenate, phosphate and complexing agents.

Most elements are extracted either not at all or only in traces[16] under the conditions of the method. Titanium, niobium, antimony, bismuth, cerium, zirconium, strontium, barium and lead are precipitated as hydrolytic products, phosphates or sulphates and are not extracted. Vanadium is not extracted when present alone, but in presence of molybdate and phosphate forms phosphovanadomolybdate which is co-extracted. Tungsten(VI) is about 55% extracted because of the phosphate present. The extraction of phosphorus alone is only 6%, while that of molybdenum is 99·5%. As the Mo/P ratio and the molybdenum concentration in the raffinate are thus unfavourably altered, a supplementary method is necessary for recovering the residual molybdenum (0·5%).

Extraction of residual molybdenum as thiosulphato complex

As none of the solvent extraction methods[17,18] was found suitable, the reaction with thiosulphate used by Falciola[19] for the detection of molybdenum, has been investigated for the purpose. The same solvent as for phosphomolybdenum blue extraction is used to facilitate back-extraction of the total molybdenum. A reddish-brown precipitate appears at the phase interface, if there is delay in shaking with the solvent after addition of thiosulphate. It decreases if the solvent and thiosulphate are added in that order and shaken immediately. Equilibrium is reached in 5 min with extraction of $\geq 97{\cdot}0\%$ Mo from 1*N* sulphuric acid containing 24 mg of $Na_2S_2O_3 \cdot 5H_2O$ per ml and $<0{\cdot}2$ mg of Mo/ml (Table 2). Higher concentrations of reagents and molybdenum increase the reddish-brown precipitate. Lower concentrations of the reagents decrease, and of molybdenum increase, the extraction. In near-saturation concentrations, sodium chloride enhances the extraction by about 12% but sodium sulphate lowers it by 30%, at 0·8 mg of Mo/ml. Ti(IV), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Al(III), U(VI), Sb(III) and Bi(V) are extracted either in traces or not at all. Sn(II) is 16·5% extracted. Cu(II) forms a brown precipitate and partly gets into the solvent, giving 7·5% extraction.

Table 5. Effect of some ions on phosphomolybdenum blue formation and extraction with MIBK (Mo = 4·9 mg/ml; Mo/P = 30)

Salt added*	Mo extraction, (%)	Salt added*	Mo extraction, (%)
None	99·5	Sodium vanadate (0·38)	96·1
Sodium chloride (5)	99·5	Disodium salt of EDTA (1)†	92·8
Sodium silicate (0·1)	99·9	Chromium sulphate (1)	91·6
Cobalt sulphate (1)	99·7	Ferric alum (1·5)	91·6
Nickel sulphate (1·5)	99·5	Sodium arsenate (1·2)	6·6
Calcium sulphate (0·1)	99·3	Sodium oxalate (1)†	2·6
Aluminium sulphate (0·8)	99·3	Potassium bifluoride (3)†	1·6
Sodium sulphate (5·1)	98·7	Sodium tartrate (5)†	0·1
Manganese sulphate (2·2)	97·7	Sodium acetate (5)†	0·03
Copper sulphate (2·5)	97·3	Sodium citrate (5)†	0·02

* Numbers in brackets give the amount in g per 20 ml of aqueous phase before production of the blue colour.

† Added after production of the blue colour.

Table 6. Analysis of samples by the proposed method

Sample composition		
Matrix*	Mo added, *mg*	Mo found,† *mg*
Fe (50) Ni (150)	59·7	59·7
Fe (6) Ni (50) Cr (100) Co (50) Al (12) Ti (12)	29·8$_5$	29·9
Fe (34) Cu (0·25) Al (0·1) Si (1·5) C (0·1)	69·6$_5$	69·6
Fe (4) Si (34) S (0·04) Cu (0·42) Al (0·37)	60·0	60·0
Co (15) Ni (20) Mn (10) Fe (30)	79·6	79·6
U (90) Co (40) Al (20) Cr (15)	99·5	99·5
Cr (50) U (25) Fe (10) Co (20) Ni (15) Mn (25) Al (10)	19·9	19·9
U (40) Fe (50) Co (45) Ni (55) Mn (60) Al (35)	49·7$_5$	49·8
Ferromolybdenum	58·9‡	58·8

* Numbers in brackets are mg of element.
† Average of triplicate analyses, differing by ±0·02.
‡ By oxinate method.[10]

Back-extraction and determination of molybdenum

The thiosulphate in the back-extracts is oxidized[20] by boiling the ammoniacal solution with excess of hydrogen peroxide for 4–5 min. Any hydroxide precipitate due to traces of other extracted elements (Fe, Cu, Bi *etc*) is filtered off without any loss of molybdenum by adsorption.[21]

Thus, the method separates molybdenum from Fe(III), Co(II), Ni(II), Cr(VI), Mn(II), U(VI), Ti(IV), Zr(IV) and Al(III). Its applicability is shown by the satisfactory analysis of a wide variety of synthetic samples and ferromolybdenum which would take several hours for analysis by existing procedures (Table 6). The separation of most of the common reducible elements makes it possible to use the redox titrimetric method for determination of molybdenum, facilitating rapid routine determination. The cerimetric method using hydrazine sulphate reduction of Mo(VI) to Mo(V)[11] is found very convenient for the purpose. The procedure takes about 30 min for a single separation and determination, requiring very ordinary reagents.

Acknowledgements—The authors wish to express their sincere thanks to Prof. S. M. Mukherji, Head of the Chemistry Department, for facilities and the junior author is highly grateful to the authorities of Kurukshetra University for a research scholarship.

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Zusammenfassung—Eine einfache Methode zur Abtrennung von Molybdän von Titan, Zirkonium, Chrom, Mangan, Eisen, Kobalt, Nikkel, Uran und Aluminium in 30 min in vielen verschiedenen Proben wird beschrieben. Man erzeugt Phosphomolybdänblau, indem man eine Molybdatlösung, die Phosphat im Gewichtsverhältnis Mo/P = 20–37 enthält, 2 min mit Hydrazinsulfat in 0·1 N Schwefelsäure kocht. Volumen und Acidität werden auf eine Molybdänkonzentration von 0·6–5 mg/ml in 0·4–0·5 N Schwefelsäure eingestellt. Das Phosphomolybdänblau wird in einem einzigen Extraktionsgang mit Methylisobutylketon zu 99·5% extrahiert. Das in der wäßrigen Phase verbliebene restliche Molybdän und Hydrazin wird mit ein paar Tropfen flüssigem Brom oxidiert und das Molybdän mit dem selben Lösungsmittel aus 1 N Schwefelsäure als rötlichbrauner Thiosulfatokomplex quantitativ extrahiert. Das Molybdän wird in Ammoniak-Wasserstoffperoxidlösung zurückextrahiert. Der Rückextrakt wird zum Sieden erhitzt und filtriert, um die unlöslichen Hydroxide von Spuren der Begleitelemente zu entfernen. Das Thiosulfat im Filtrat wird durch 4–5-minütiges Kochen mit überschüssigem Wasserstoffperoxid in schwach ammoniakalischem Medium zerstört. Das Molybdän wird schließlich durch Cerimetrie oder andere gängige Methoden bestimmt.

Résumé—On décrit une méthode simple pour la séparation du molybdène des titane, zirconium, chrome, manganèse, fer, cobalt, nickel, uranium et aluminium dans une large variété d'échantillons en 30 mn. Le bleu de phosphomolybdène est produit par ébullition pendant 2 mn d'une solution de molybdate contenant du phosphate pour donner Mo/P = 20–37 (p/p) avec du sulfate d'hydrazine en acide sulfurique 0,1*N*. On ajuste le volume et l'acidité pour donner une concentration en molybdène de 0,6–5 mg/ml en acide sulfurique 0,4–0,5*N*. Le bleu de phosphomolybdène est extrait à 99,5% par la méthylisobutyl cétone en une seule extraction. Le molybdène résiduaire et l'hydrazine dans la phase aqueuse sont oxydés avec quelques gouttes de brome liquide et le molybdène est extrait quantitativement avec le même solvant à partir d'acide sulfurique 1*N* sous forme de son complexe thiosulfate brun-rougeâtre. Le molybdène est extrait par une solution d'ammoniaqueperoxyde d'hydrogène. L'extrait en retour est chauffé à ébullition et filtré pour éliminer les hydroxydes insolubles de traces d'éléments accompagnateurs. On détruit le thiosulfate dans le filtrat par ébullition de 4–5 mn avec un excès de peroxyde d'hydrogène en milieu légèrement ammoniacal. Le molybdène est finalement dosé par cérimétrie ou par d'autres méthodes habituelles.

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SHORT COMMUNICATIONS

DETERMINATION OF CALCIUM OXIDE IN CALCINED PHOSPHATE ORES

(*Received* 15 *February* 1973, *Accepted* 21 *February* 1973)

Widely-varying quantities of calcium carbonate are frequently found in commercial deposits of phosphate rock, and beneficiation of the latter often includes a calcination step. Other minerals occurring with tricalcium phosphate are the fluoride, sulphate, and silicates of calcium; carbonates and silicates of magnesium are also usually present. In the mining and extractive metallurgy of phosphate ores, it would be useful to have a direct, rapid measure of the amount of calcium oxide derived from the thermal decomposition of calcium carbonate.

Quicklime or hydrated lime in the form of aqueous solutions or suspensions is used extensively in industry for pH control or as a source of calcium ions. The production of quicklime from limestone, particularly for mining and metallurgical use in remote regions, is often carried out in small and inefficient units, and the quality of the final product can be very variable. A simple but effective differentiation of calcium oxide from unburned limestone, long used in the field of extractive metallurgy, is based on the fact that calcium oxide forms with a sucrose solution a water-soluble saccharate which can be readily titrated with standard oxalic acid solution, whereas calcium in the form of carbonate and silicate does not react with sucrose.[1] It occurred to us that this procedure might be applied to the determination of calcium oxide in calcined phosphate rock which also contained the carbonate, fluoride, sulphate and silicates of calcium, and the carbonate and oxide of magnesium.

To test this possibility, a known quantity of calcium carbonate, with and without the addition of tricalcium phosphate, calcium fluoride, calcium sulphate and magnesium oxide was calcined at 1000° for 1 hr in a platinum crucible. The ignited material was transferred to a 500-ml volumetric flask, and 30 g of sucrose and about 300 ml of water were added. The flask was thoroughly shaken until the sugar had dissolved, the solution

Table 1. Effect of various constituents of phosphate rock on the determination of calcium oxide by the sucrose–oxalic acid method

Added	0·1*N* Oxalic acid for titration of aliquot *ml*	CaO found in sample *g*
(*a*)		
0·5000 g of CaO derived from calcination of 0·8924 g of $CaCO_3$	17·45	
	17·45	0·5000
(*b*)		
(*a*) above, plus 0·5 g each of $Ca_3(PO_4)_2$, CaF_2, $CaSO_4 . 2H_2O$	17·49	
and MgO	17·51	0·5014
(*c*)		
(*b*) above, plus addition after calcination, but before titration, of 0·5 g of $CaCO_3$ and 0·5 g of $MgCO_3$	17·55	
	17·53	0·5026

was made up to 500 ml, and allowed to stand for 1 hr with occasional shaking. Part of the solution was filtered, and a 50-ml aliquot of the filtrate was titrated with 0·1*N* oxalic acid, with phenolphthalein as indicator.

A quantity of calcium carbonate and of magnesium carbonate was also added to the mixtures above, after ignition of the latter but before the titration with oxalic acid. All reagents were of analytical grade. The added amounts of the carbonate, oxide, phosphate, fluoride, and sulphate of calcium, and of the carbonate and oxide of magnesium, were considerably in excess of those normally encountered in phosphate ores which require calcination.

Typical results are illustrated in Table 1. It is evident that relatively large quantities of the carbonate, phosphate, fluoride and sulphate of calcium, and of the carbonate and oxide of magnesium, have no significant effect on the determination of calcium oxide by this procedure. The results are quite satisfactory for routine work in beneficiation investigations.

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R. S. YOUNG

REFERENCE

1. R. S. Young, *Chemical Analysis in Extractive Metallurgy*, p. 83. Griffin, London, 1971.

Summary—It has been shown that an existing procedure to differentiate calcium oxide from the carbonate and silicate of calcium can be used in the presence of the phosphate, fluoride and sulphate of calcium, and of the carbonate and oxide of magnesium. It is based on the reaction in aqueous solution of calcium oxide with sucrose to form calcium saccharate, and subsequent titration with oxalic acid solution. The method has application for a direct chemical determination of calcium oxide in phosphate rock where calcination of accompanying carbonate is necessary in beneficiation processes.

Zusammenfassung—Eine bestehende Vorschrift, Calciumoxid von Calciumcarbonat und -silicat zu unterscheiden, kann auch in Gegenwart von Calciumphosphat, -fluorid und -sulfat sowie von Magnesiumcarbonat und -oxid verwendet werden. Sie beruht auf der Reaktion von Calciumoxid mit Rohrzucker in wäßriger Lösung zu Calciumsaccharat und nachfolgender Titration mit Oxalsäurelösung. Die Methode kann zur direkten chemischen Bestimmung von Calciumoxid in Phosphatgestein dienen, wo eine Röstung des begleitenden Carbonats in Aufbereitungsprozessen notwendig ist.

Résumé—On a montré qu'une technique existant pour différencier l'oxyde de calcium du carbonate et du silicate de calcium peut être utilisée en la présence de phosphate, fluorure et sulfate de calcium, et de carbonate et d'oxyde de magnésium. Elle est basée sur la réaction en solution aqueuse de l'oxyde de calcium avec, le saccharose pour former du saccharate de calcium, et sur le titrage subséquent par une solution d'acide oxalique. La méthode a son application dans un dosage chimique direct de l'oxyde de calcium dans une roche au phosphate où la calcination du carbonate qui l'accompagne est nécessaire dans les opérations de concentration.

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APPLICATION OF THE FISSION-TRACK TECHNIQUE TO THE DETERMINATION OF URANIUM IN NATURAL WATERS

(*Received* 4 *September* 1972. *Revised* 12 *October* 1972. *Accepted* 7 *March* 1973)

In a previous paper,[1] the applicability of the fission-track technique to the analysis of natural waters was stated in brief, but the details were not described. Here, the recommended procedure is given.

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Before the application of the technique to natural waters, the uranium should be collected into a 2 ml of 8*M* hydrochloric acid. Natural waters low in minerals are evaporated to dryness in a platinum dish, and the residue is dissolved in 2 ml of 8*M* hydrochloric acid after treatment with hydrofluoric and perchloric acids to remove silica. The uranium of samples high in minerals, however, should be separated before the dissolution in hydrochloric acid, because part of the minerals may be dissolved or may interfere with the absorption of the uranium by the resins used in the next step of the procedure.

Because of the determination limit and the uranium content of natural waters, 100 ml of water sample are necessary.

EXPERIMENTAL

Procedure

To 100 ml of solution containing 10 ng of uranium, 200 ml of conc. hydrochloric acid were added. The solution was run through a Dowex 1-X8 column at a flow-rate of <0·5 ml/min. The absorbed uranium was eluted with 10 column-volumes of 0·1*M* hydrochloric acid. The eluate was evaporated to dryness, and the residue was dissolved in 2 ml of 8*M* hydrochloric acid. The uranium in this solution was determined by the fission-track technique.[1] The results for various column volumes are shown in Fig. 1. A column volume of 4 ml seems to be the minimum for quantitative recovery, and a 6-ml column was used for all subsequent work.

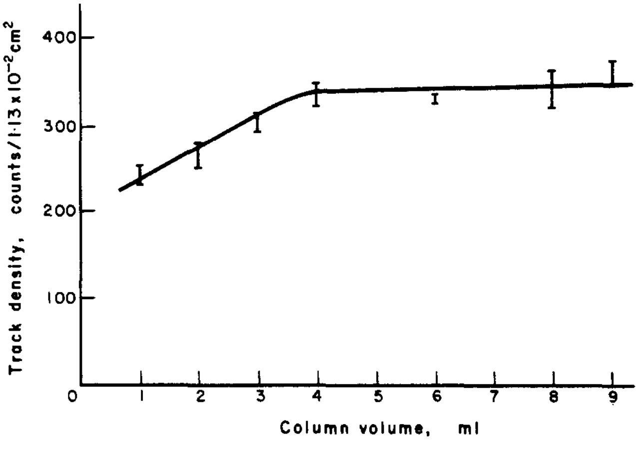

Fig. 1. Recovery of uranium by anion-exchange: 300 ml of 8*M* hydrochloric acid containing 10 ng of uranium are added to the column of Dowex 1-X8. The errors shown are the 95% confidence limits.

Interference of iron

To 2-ml portions of 8*M* hydrochloric acid containing 10 ng of uranium, 10, 50, 100 and 500 μg and 1, 5, 10, 50 and 100 mg of iron(III) were added; 100 mg of pulverized dry Dowex 1-X8 were added to each of these solutions, and the mixture was left for 12 hr with occasional stirring. The resin was filtered off and irradiated along with mica as described in the previous paper.[1] The track density on the mica was plotted against the amount of iron added, as in Fig. 2. The gradual increase of the track density with the amount of iron was probably caused by the trace amount of uranium impurity in the iron added. The result shows that iron up to 10 mg in the sample for analysis does not interfere.

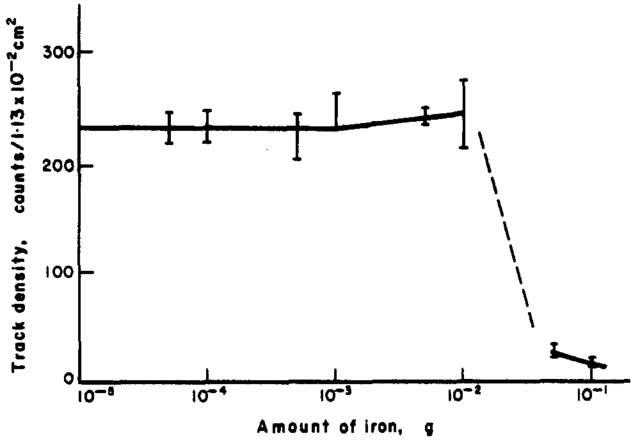

Fig. 2. Interference of iron in the recovery of uranium: 10 ng of uranium were absorbed on 100 mg of pulverized Dowex 1-X8 in 2 ml of 8*M* hydrochloric acid. The errors shown are the 95% confidence limits.

RESULTS

The procedure given was applied to the determination of the uranium content of the river waters in Fukuoka City. The waters were collected on 14 January 1972 at Naka River and Muromi River which flow through the granitic region. The result is shown in Table 1. The high content of N3 and M3 seems to be induced by contamination with sea-water. To avoid laboratory contamination, most of the processes were carried out in a nitrogen-purged dry-box.

Table 1. Uranium content of river waters in Fukuoka City

Sample		Distance from the mouth of the rivers, *km*	Uranium content, *ng/l.*
Naka River	N 1	20	22 ± 7
	N 2	8	23 ± 6
	N 3	0·5	210 ± 40
Muromi River	M 1	11	16 ± 6
	M 2	4	20 ± 10
	M 3	0·5	490 ± 50

The errors shown are the 95% confidence limits.

DISCUSSION

In these fission-track experiments, the samples were irradiated for 20 min with a neutron flux of 3×10^{13} $n.cm^{-2}.sec^{-1}$ in a pneumatic tube of the KUR reactor of the Research Reactor Institute at Kyoto University. This was the upper limit of length of irradiation, because the resin is damaged by heat, and this irradiation condition restricted the determination limit, which could be improved by increasing the total neutron flux through use of a longer irradiation at a lower flux, or of a high flux with sufficient cooling. Thus, the ultimate determination limit depends on the uranium content of the muscovite which gives the blank tracks.

Acknowledgement—The authors wish to thank Mr. S. Osaki, Drs. Iwata and Y. Kiso and the staff of Kyoto University for the irradiation facilities.

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REFERENCE

1. H. Matsuda, Y. Tsutsui, S. Nakano and S. Umemoto, *Talanta*, 1972, **19**, 851.

Summary—A procedure for the determination of the uranium content of natural waters is presented. To 100 ml of natural waters, 200 ml of conc. hydrochloric acid are added and this solution is passed through a 6-ml column of Dowex 1-X8. The uranium is eluted with 60 ml of 0·1*M* hydrochloric acid, and the eluate is evaporated to dryness. The residue is subjected to the fission-track technique described previously. The uranium content of the river waters in Fukuoka City was determined.

Zusammenfassung—Ein Verfahren zur Bestimmung des Urangehaltes natürlicher Wässer wird angegeben. Zu 100 ml des natürlichen Wassers werden 200 ml konz. Salzsäure hinzugefügt und diese Lösung durch eine 6 ml-Säule Dowex 1-X8 gegeben. Das Uran wird mit 60 ml 0,1 M Salzsäure eluiert und das Eluat zur Trockne eingedampft. Der Rückstand wird dem früher beschriebenen Spaltspurverfahren unterworfen. Es wurde der Urangehalt der Flußwässer in der Stadt Fukuoka bestimmt.

Résumé—On présente une technique pour le dosage de la teneur en uranium des eaux naturelles. A 100 ml d'eaux naturelles, on ajoute 200 ml d'acide chlorhydrique concentré, et cette solution est passée sur une colonne de 6 ml de Dowex 1-X8. L'uranium est élué par 60 ml d'acide chlorhydrique 0,1 *M* et l'éluat est évaporé à sec. Le résidu est soumis à la technique de trajectoire de fission décrite antérieurement. On a déterminé la teneur en uranium des eaux de rivière dans la ville de Fukuoka.

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DETERMINATION OF COPPER IN AMMONIUM FLUORIDE SOLUTIONS BY EXTRACTION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY

(*Received* 19 *January* 1973. *Accepted* 26 *February* 1973)

Chemicals (such as hydrochloric, nitric and hydrofluoric acids and ammonium fluoride) used to process semiconductors are known to contain traces of various elements, as shown by the "maximum limits of impurities" quoted by various suppliers. These impurities can be adsorbed to various extents on semiconductor surfaces.[1] Many of them (*e.g.*, Na, Ga, Mn and Fe) do not give much trouble in the manufacturing process, because they can be desorbed from the semiconductor surface by extensive rinsing with demineralized water. Elements such as Au, Ag, Cu, As, Hg, which are commonly present in chemicals, are deposited on silicon surfaces by an electrochemical displacement process and cannot be completely removed by rinsing with demineralized water. This effect can influence the electrical properties and the reliability of electronic components, especially those having an MOS structure (field effect devices). Therefore, quality control analysis of the applied chemicals for these elements is necessary.

The expected Cu concentration in such chemicals is about $10^{-7}\%$ or 10^{-9} g of Cu/g of sample.[2] Because the sample volume should be restricted to 100 ml at most, any method proposed must guarantee a determination of 10^{-7} g of copper and should be simple and rapid. Atomic-absorption spectroscopy (AAS) and preconcentration of the copper seemed to us to be suitable. Copper in the acids commonly used in semiconductor manufacture can be concentrated by volatilization of the reagents in "Teflon" cups. Tests with ^{64}Cu show that no losses of copper occur. However, evaporation of 40% ammonium fluoride solution cannot be easily accomplished, so extraction was chosen for the enrichment. As extraction procedures in the μg range are not always quantitative, the copper was co-extracted as the diethyldithiocarbamate complex into chloroform with Pd(II) as carrier.

EXPERIMENTAL

Instrumentation

A Perkin–Elmer Model 403 atomic-absorption spectrometer was used, with a recorder read-out and a deuterium comparator for background suppression. The gas flow-rates were 4·2 l./min for acetylene and

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Instrumentation

A Perkin–Elmer Model 403 atomic-absorption spectrometer was used, with a recorder read-out and a deuterium comparator for background suppression. The gas flow-rates were 4·2 l./min for acetylene and

17·2 l./min for the air. The sample aspiration rate was 7 ml/min. For maximum sensitivity the 3247·5Å line was used.

Reagents

All reagents were Merck "*pro analysi*" or "Suprapur" quality. The "standard" ammonium fluoride solution was B & A 40% w/v solution, Electronic Grade, Code 2754, Series No. D244 from Allied Chemicals, Morristown, New Jersey. The palladium chloride carrier solution contained 50–60 μg of Pd(II) per ml. The 0·2 w/v sodium diethyldithiocarbamate solution (NaDDC) was freshly prepared for every extraction, as the decomposition rate is fairly high.[3]

Procedure

Transfer 50 ml of the ammonium fluoride solution into a quartz separatory funnel. Add 1 ml of conc ammonia solution, 1 ml of carrier solution containing 50–60 μg of Pd(II) and 5 ml of the NaDDC solution and shake thoroughly. After 10 min extract with 10 ml of chloroform. Repeat the extraction without addition of ammonia. Transfer the combined extracts into a quartz test tube and evaporate the solvent. Dissolve the residue with 10 drops of conc nitric acid and dilute with 2 ml of water. Evaporate this solution to dryness and dissolve the residue with 2 drops of conc hydrochloric acid and 1 drop of conc nitric acid and transfer with water into a 1-ml volumetric flask for measurement by AAS. Run a blank test on the reagents.

RESULTS AND DISCUSSION

The yield of the separation step was determined by adding 0·5 μg of ^{64}Cu (count-rate 3360 cpm) to each of two 50-ml samples of 40% ammonium fluoride solution and performing the separation as described above. The ^{64}Cu activity in the chloroform phase was measured by means of its 0·51-MeV radiation. The extraction yields were 96·1 and 99·3%. With a single extraction a yield of only 70–80% was achieved. Because only 1 ml of solution was available for aspiration in the AAS, we used a recorder instead of the digital read-out, to obtain a better mean value. Experiments with solutions of copper and palladium in nitric acid medium and in aqueous solutions showed neither a matrix effect from the nitric acid nor an interelement effect from the palladium. Also, traces of sulphuric acid, which is formed by the oxidation of the thiocarbamate, do not interfere. So the copper could be determined by comparing the recorder read-out with a calibration curve prepared under similar conditions.

However, to avoid serious erratic results, which can be caused by contamination, incomplete reaction or unknown interelement effects when other impurities are present at higher concentrations, we prefer the standard addition method. The amount of copper added as standard has to be similar in magnitude to the quantity of copper in the sample solution.

To determine the reproducibility of the method the "standard" B & A ammonium fluoride solution was analysed twice by the method described. The ammonium fluoride solution had a copper concentration of $4{\cdot}4 \pm 0{\cdot}2 \times 10^{-7}$%, determined by analysis of 500-ml samples, the copper being preconcentrated by co-precipitation with HgS. Table 1 shows the results.

Table 1.

Method	No. 1 Recorder response, *mm*	No. 1 Cu, *μg*	No. 2 Recorder response, *mm*	No. 2 Cu, *μg*
Calibration curve (*a*) 0·2 μg Cu	77	0·2	77	0·2
(*b*) 50 ml NH_4F soln.	101	0·26	96	0·25
(*c*) blank	20	0·05	23	0·06
(*b*)–(*c*)	81	0·21	73	0·19
$Cu = 0{\cdot}2 \times (b - c)/a$	0·21 μg Cu/50 ml $4{\cdot}2 \times 10^{-7}$% w/v		0·19 μg Cu/50 ml $3{\cdot}8 \times 10^{-7}$% w/v	
Standard addition (*d*) 50 ml NH_4F soln. + 0·2 μg Cu	186		187	
$Cu = 0{\cdot}2 \times [d - (a + c)]/a$	0·23 μg Cu/50 ml $4{\cdot}6 \times 10^{-7}$% w/v		0·22 μg Cu/50 ml $4{\cdot}4 \times 10^{-7}$% w/v	

The results from the calibration-curve method and measurement of (*a*), (*b*) and (*c*) agree well with those obtained by using standard addition [with the additional measurement of (*d*)]. This shows that no contamination or unknown interelement effect is present. The mean value of $4{\cdot}5 \times 10^{-7}\%$ copper is in good agreement with the value of $4{\cdot}4 \pm 0{\cdot}2 \times 10^{-7}$ but two orders of magnitude lower than the maximum limits quoted by the suppliers ($5 \times 10^{-5}\%$). The time needed to perform the analysis is 2 hr, which is acceptable for quality control analysis.

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Summary—Extraction with sodium diethyldithiocarbamate, followed by mineralization and atomic-absorption spectroscopy is used to determine down to $10^{-7}\%$ Cu in 40% ammonium fluoride solution used in the manufacture of semiconductors.

Zusammenfassung—Zur Bestimmung von Cu in Konzentrationen bis herunter zu $10^{-7}\%$ in bei der Herstellung von Halbleitern verwendeter 40%. Ammoniumfluoridlösung wird die Extraktion mit Natriumdiäthyldithiocarbamat mit nachfolgender Mineralisation und Atomabsorptionsspektroskopie verwendet.

Résumé—On utilise l'extraction au diéthyldithiocarbamate de sodium, suivie par la minéralisation et la spectroscopie d'absorption atomique pour doser jusqu'à $10^{-7}\%$ de Cu dans la solution à 40% de fluorure d'ammonium utilisée dans la fabrication de semi-conducteurs.

Talanta, Vol. 20, pp. 897–902. Pergamon Press, 1973. Printed in Great Britain

EMISSIONSSPEKTROGRAPHISCHE BESTIMMUNG VON GERMANIUM UND ZINN IN GALLIUMARSENID

(*Eingegangen am* 13. *November* 1972. *Angenommen am* 16. *März* 1973)

In der Literatur findet man nur wenige Angaben über die Bestimmung von Germanium und Zinn in Galliumarsenid.[1–3] Systematische Untersuchungen wurden bisher nicht ausgeführt. Das Ziel dieser Arbeit war, durch systematische Untersuchungen des Verdampfungsprozesses, durch Optimierung der Anregungs- und Arbeitsbedingungen bei einem möglichst geringen Substanzverbrauch ohne Anreicherungsverfahren eine niedrige Nachweisgrenze und eine hohe Empfindlichkeit zu erzielen.

EXPERIMENTELLER TEIL

Probenvorbereitung

Nach Karpel und Rubinstein[4] ist es möglich, Standardproben durch Mischung von Galliumarsenid mit Metalloxiden herzustellen. Voraussetzung ist eine Korngröße von weniger als 50 μm, damit die Reduktion zum Metall schnell erfolgen kann. Eine Mischung mit Spektralkohlepulver beschleunigt diesen Prozeß. Bei unseren Untersuchungen ergab sich ein optimales Galliumarsenid–Kohlepulver-Gewichtsverhältnis von 1 : 3. Entsprechende Standardproben wurden durch Mischung von Germaniumdioxid, Zinndioxid, Galliumarsenid und Spektralkohlepulver hergestellt und in einer Kugelmühle KM 1 der Firma Janetzki KG homogenisiert und zerkleinert.

Elektrodenformen

Bei der Wahl der Elektrodenformen war vor allem zu berücksichtigen, daß die Elektroden nur eine kleine Probenmenge von *ca.* 15 mg Galliumarsenid–Kohle-Gemisch 1 : 3 aufnehmen sollten und daß bei Verwendung

The results from the calibration-curve method and measurement of (*a*), (*b*) and (*c*) agree well with those obtained by using standard addition [with the additional measurement of (*d*)]. This shows that no contamination or unknown interelement effect is present. The mean value of $4{\cdot}5 \times 10^{-7}\%$ copper is in good agreement with the value of $4{\cdot}4 \pm 0{\cdot}2 \times 10^{-7}$ but two orders of magnitude lower than the maximum limits quoted by the suppliers ($5 \times 10^{-5}\%$). The time needed to perform the analysis is 2 hr, which is acceptable for quality control analysis.

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Als Gegenelektrode wurde ein abgestumpfter Kegel benutzt, dessen Durchmesser an der Spitze 2 mm betrug. (Abb. 1).

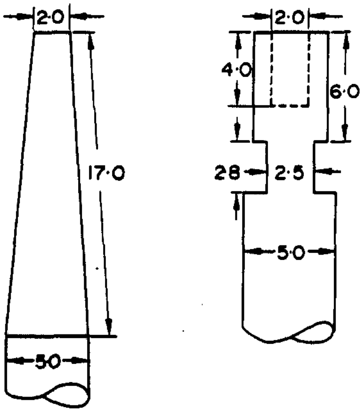

Abb. 1. Gegen- und Probenelektrode (Dimensionen in mm).

Untersuchung des Verdampfungsprozesses

Zur Ermittlung der günstigsten Anregungsbedingungen wurde mittels Fahrspektren (Abb. 2) der Verdampfungsprozeß bei unterschiedlichen Stromstärken eines Gleichstrombogens untersucht. Die Aufnahmen der Spektren erfolgten mit einem Zeitrhythmus von 13 Sekunden. Es wurde kontinuierlich der Spannungsabfall des Bogens aufgezeichnet.

Die Gleichmäßigkeit der Brennspannung gibt Auskunft über die Stabilität des Gleichstrombogens. Mit zunehmender Stromstärke von 6 bis 15 A ist eine zunehmende Stabilität erkennbar. Weiterhin ist zu entnehmen, daß die Brennspannung bei allen Stromstärken am Anfang stetig zunimmt, danach eine gewisse Zeit konstant ist und nach dem totalen Abbrand den für den reinen Kohlebogen charakteristischen unruhigen Verlauf besitzt. Dieser Spannungsverlauf entspricht der Matrixverdampfung. Galliumarsenid besitzt einen Schmelzpunkt[5] von 1238° bei dem der Arsendampfdruck 0,9 at beträgt. Der Siedepunkt[6] des Galliums wird erst bei 2337° erreicht. Aus den Verdampfungskurven geht hervor, daß das Arsen ein Verdampfungsmaximum im ersten Drittel der Reaktion besitzt. Auch die Verdampfung des Galliums beginnt bereits am Anfang sehr stark. Dies ist jedoch nur am Verlauf der Brennspannung erkennbar, da die Funktion $\bar{Y} = f(t)$ im gestrichelten Kurventeil infolge der starken Selbstabsorption viel zu niedrige $\bar{Y}$-Werte aufweist. Die mit fortschreitender Verdampfung abnehmende Arsen- and Galliumatomkonzentration und -ionenkonzentration im Plasma führen zu einer Zunahme der Brennspannung. Das geringfügige Maximum der Intensität der Galliumlinien am Ende des Abbrandes, besonders bei niedrigen Stromstärken führen wir auf eine Diffusion des flüssigen Galliums während des Abbrandes in die kälteren kompakten Zonen der Elektrode zurück. Bei fortschreitendem Abbrand werden auch diese Zonen stark erhitzt und das in ihnen vorhandene Gallium verdampft.

Der Intensitätsverlauf der Linien des Germaniums und des Zinns zeigt eine Verdampfung, die der Galliumverdampfung entspricht, wenn man die Selbstabsorption der Galliumlinien in der Anfangsphase berücksichtigt.

Da die Siedepunkte des Germaniums und des Zinns bei 2830° bzw. bei 2270° liegen, war dieses Verhalten zu erwarten. Auch hier führen wir das Maximum am Ende der Verdampfung bei niedrigen Stromstärken und damit langen Abbrandzeiten auf eine Diffusion des flüssigen Materials in die kälteren Elektrodenzonen zurück, die durch die lange Abbrandzeit begünstigt wird. Diese Ansicht wird auch durch die Gleichzeitigkeit des Auftretens des Maximums und des Kohlebogens (nach der Brennspannung) unterstützt. Wir wählten den mit 12 A betriebenen Bogen aus, da er einen sehr gleichmäßigen Brennspannungsverlauf besaß und eine relativ kurze Abbrandzeit aufwies. Eine weitere Beschleunigung des Verdampfungs prozesses wirkt sich nicht positiv aus.

Auswahl der Analysen- und Referenzlinien

Zur Auswertung der Spektren wurden die in Tabelle 1 angegebenen Analysen-und Referenzlinien miteinander kombiniert.[7] Für die Analysenlinien wurde grundsätzlich eine Untergrundkorrektur vorgenommen, während die Berechnung der Y-Werte der Referenzlinien jeweils mit und ohne Untergrundkorrektur erfolgte.

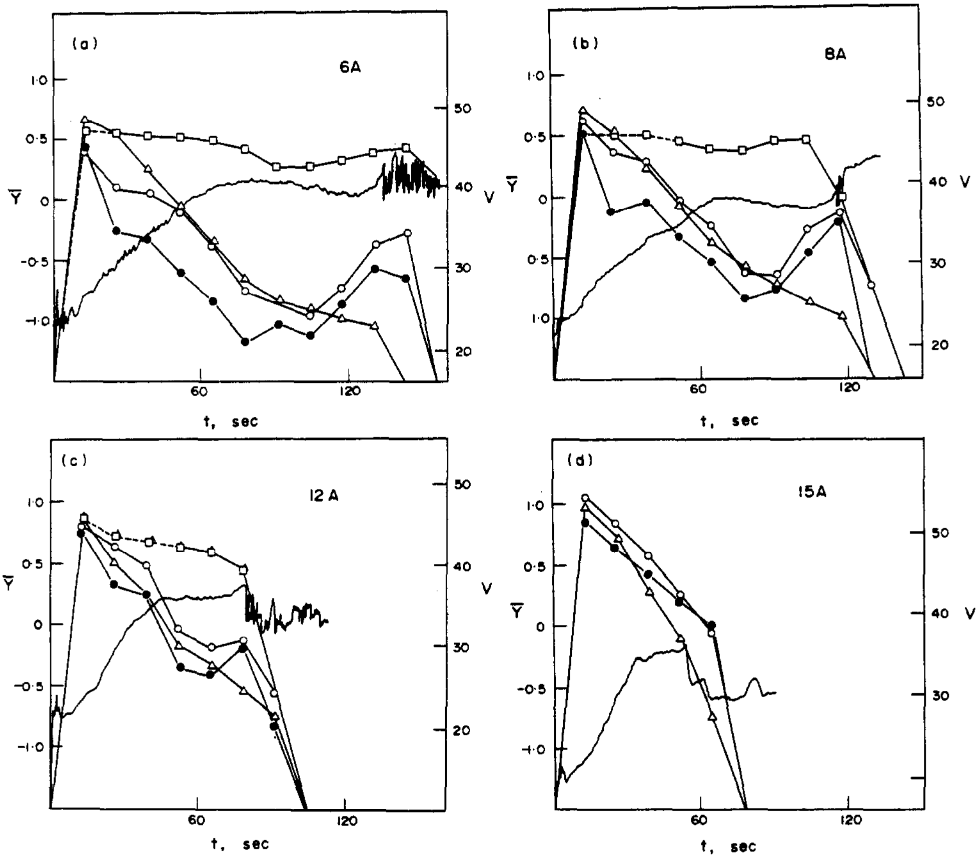

Abb. 2. Fahrspektren von Ge, Sn, As, Ga und Brennspannungsverlauf bei 6, 8, 12 und 15 A.

○———○ Ge △———△ As

●———● Sn □———□ Ga

------ Störung durch Selbstabsorption

Da alle Galliumlinien starke Selbstabsorption zeigen, mußte als innerer Standard Arsen benutzt werden, obwohl das Arsen wegen seines besonders im letzten Drittel abweichenden Verdampfungsverhaltens ebenfalls kein idealer innerer Standard ist. Ein zusätzlicher innerer Standard hätte einmal die Analysenzeit verlängert, zum anderen das Einschleppen von Verunreinigungen begünstigt.

Außer Arsenlinien der 3. Ordnung wurden auch Linien der 4. Ordnung verwendet. Als günstigste Linienkombination ergaben sich für die analytische Bestimmung die ersten drei Linienpaare der Tabelle 1.

Tabelle 1. Analysen- und Referenzlinien

Wellenlänge	Anregungspotential, *eV*	Wellenlänge	Anregungspotential, *eV*
Ge I 3039,06	4,96	As I 3075,32	6,29
Sn I 3175,02	4,33	As I 3119,60	6,29
Sn I 3262,33	4,87	As I 2437,23	—
		As I 2381,18	–

(As I 2437 und As I 2381 sind Linien aus der 4. Ordnung).

Geräte

Für die Aufnahmen wurde ein 2-m Plangitterspektrograph PGS2 des VEB Carl Zeiss Jena in Ebert-Aufstellung benutzt. Als Anregungsgerät wurde der Universalbogenimpulsgenerator UBI 1 des VEB TPW Thalheim verwendet.

Folgende Bedingungen wurden eingehalten:

Gitter: 651 Strich/mm, Blaze-Wellenlänge 10200 Å
Dispersion: 2,34 Å/mm für 3. Ordnung
1,76 Å/mm für 4. Ordnung
Wellenlängen (Plattenmitte): 3. Ordnung 3150 Å
4. Ordnung 2363 Å
Aufnahmebereich: 3. Ordnung 2870–3431 Å
4. Ordnung 2152–2575 Å
Abbildung: Zwischenabbildung
Blenden: Rechteckblende an der Zwischenabbildung
Höhe 8,7 mm
Filter: UG 5(2) Ordnungsfilter

Für die Galliumaufnahmen wurde ein Vorzerleger zur Ordnungsisolierung verwendet, so daß die 4. Ordnung mit einem Spektralbereich von 2467–2883 Å aufgenommen wurde.

Spaltbreite: 20 μm
Elektroden: Qualität TO VEB EKL, Form siehe Abb. 1
Elektrodenabstand: 3 mm, kontinuierlich von Hand nachgeregelt
Anregung: Gleichstromdauerbogen 12 A, Treibspannung 300 V
Belichtungszeit: 102 sec
Photoplatten: Orwo WU 3 spektralblau extrahart
Entwicklung: MH 28 : H_2O = 1 : 4, 19°C, 4 min mechanische Schaukelentwicklung
Fixierbad: Schnellfixiersalz Orwo A 304, 200 g/l., 6 min.

Arbeitsvorschrift

Ca. 5 mg Galliumarsenid werden mit der dreifachen Gewichtsmenge Kohlepulver EK-O vermischt und in der Kugelmühle homogenisiert. Mit diesem Gemisch werden die Trägerelektroden gestopft. Bei sorgfältiger Stopfung enthält die Trägerelektrode 4,8 ± 0,1 mg Galliumarsenid. Die Elektroden wurden unter den oben angegebenen Bedingungen angeregt.

Für die Verfahrenseichung wurden die Elemente Germanium und Zinn in Form ihrer Dioxide in Konzentrationen zwischen 5 und 200 ppm (entspricht 24–960 ng Zinn und Germanium bezogen auf 4,8 mg Galliumarsenid) zugemischt. Für die Eichung wurden 7 Spektren pro Konzentrationswert aufgenommen.

ERGEBNISSE UND DISKUSSION

Die Auswertung der Meßwerte erfolgte mit Hilfe eines Rechenprogramm am Kleinrechner C 8205 des VEB Zentronik. Die Schwärzung der Linien der Photoplatte wurden in der *P*-Transformation gemessen. Die erhaltenen *P*-Werte wurden in *Y*-Werte ($Y = \log I$, I = Lichtintensität) umgerechnet und die Differenzen der *Y*-Werte der Analysen- und Referenzlinien wurden einer linearen Regression unterworfen. Die Fehlerrechnung erfolgte nach Doerffel.[8] Die Ergebnisse sind in Tabelle 2 dargestellt. Die Untergrundkorrektur der Arsenlinien zeigte keinen merklichen Einfluß auf die Geradengleichungen, die errechneten Fehler und die Nachweisgrenze (siehe Tabelle 3).

Tabelle 2. Eichgeraden für Germanium und Zinn (mit Untergrundkorrektur für Analysen- und Referenzlinien)

Linienpaar	Eichgerade	Korrelations-koeffizient	Relative Standard-abweichung, %
$\frac{\text{Ge 3039}}{\text{As 3075}}$	$\Delta Y = 0{,}998 \log c - 2{,}243$	0,997	+11 −10
$\frac{\text{Sn 3175}}{\text{As 3119}}$	$\Delta Y = 1{,}194 \log c - 2{,}962$	0,994	+17 −15
$\frac{\text{Sn 3262}}{\text{As 2437}}$	$\Delta Y = 1{,}075 \log c - 2{,}405$	0,995	+15 −13

Die Berechnung der Nachweisgrenzen erfolgte nach Matherny[9] für Y_N-Werte solcher analytischer Funktionen, die aus korrigierten Y-Werten beider Linien entstanden nach Gleichung (1), und für analytische Funktionen, die aus korrigierten Y-Werten der Analysenlinien und nichtkorrigierten Y-Werten der Referenzlinien entstanden sind, nach Gleichung (2).

Tabelle 3. Nachweisgrenzen für Germanium und Zinn in Galliumarsenid

Linienpaar	$\frac{\text{Ge 3039}}{\text{As 3075}}$		$\frac{\text{Sn 3175}}{\text{As 3119}}$		$\frac{\text{Sn 3262}}{\text{As 2437}}$	
	ng	*ppm**	*ng*	*ppm**	*ng*	*ppm**
mit Untergrundkorrektur für As	14,9	3,1	40,0	7,7	51,8	10,8
ohne Untergrundkorrektur für As	13,0	2,7	30,2	6,3	44,2	9,2

Der Untergrund der Germanium- und Zinnlinien wurde korrigiert.

* Bezogen auf Galliumarsenid.

Tabelle 4. Uberprüfung der Bestimmungsmethode an Originalproben von Galliumarsenid

Element	gefundene Konzentration *ppm*, bezogen auf GaAs	gemittelte Konzentration *ppm*, bezogen auf GaAs	Standardabweichung, *ppm*	Variationskoeffizient, %.
Zinn	11,0 13,4 13,8 10,3 13,7	12,4	± 1,32	± 10,7
Germanium	16,1 18,3 18,0 16,0 17,5	17,2	± 1,07	±6,2

$$\Delta Y_N = \log 3\left[\sqrt{\frac{1}{p-1}\sum_1^p\left(\frac{I_{x,U,i}}{I_{r,i}} - \frac{1}{p}\sum_1^p\frac{I_{x,U,i}}{I_{r,i}}\right)^2}\right] \qquad (1)$$

$$\Delta Y_N = \log 3\left[\sqrt{\frac{1}{p-1}\sum_1^p\left(\frac{I_{x,U,i}}{I_{r,1+U,i}} - \frac{1}{p}\sum_1^p\frac{I_{x,U,i}}{I_{r,1+U,i}}\right)^2}\right] \qquad (2)$$

p = Anzahl der Meßwerte
$I_{x,U,i}$ = Intensität des Untergrundes an der Stelle der Analysenlinie
$I_{r,i}$ = Intensität der Referenzlinie nach Untergrundkorrektur
$I_{r,1+U,i}$ = Intensität der Referenzlinie ohne Untergrundkorrektur

Die Ergebnisse der Berechnungen sind in Tabelle 3 zusammengefaßt.

Tabelle 5. Überprüfung der Bestimmungsmethode an Originalproben durch zusätzliche Germaniumdioxid- und Zinndioxiddotierung

Element	Grundgehalt des GaAs, ppm	Dotierung, ppm	gefundene Gesamtkonzentration, ppm	Dotierung gefunden, ppm	Abweichung %
Zinn	6,2	25,0	32,8	26,6	+6,7
			31,9	25,7	+2,9
			32,0	25,9	+3,5
			29,8	23,7	−5,3
			33,5	27,3	+9,3
Germanium	8,6	25,0	34,3	25,7	+3,5
			32,8	24,2	−2,8
			35,6	27,0	+8,4
			32,5	23,9	−3,9
			33,4	24,8	−0,5

Die Überprüfung des Bestimmungsverfahrens erfolgte durch seine Anwendung auf Germanium- und Zinndotierte Galliumarsenidkristalle. Der Gehalt an Germanium und Zinn wurde für diese Proben bestimmt (Tabelle 4). Ein Teil der gepulverten Substanz wurde mit einer synthetischen Probenmischung der Konzentration von 50 ppm Germanium und Zinn im Verhältnis 1 : 1 gemischt und mit Kohle auf 1 : 3 verdünnt. Das Ergebnis ist in Tabelle 5 dargestellt.

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Zusammenfassung—Es wird eine direkte emissionsspektrographische Methode zur Bestimmung von Germanium und Zinn in Galliumarsenid ausgearbeitet. Sie besitzt eine Nachweisgrenze von 3,1 ppm für Germanium und 7,7 ppm für Zinn bei einem Einsatz von 5 mg Galliumarsenid. Die relative Standardabweichung beträgt für Germanium 11% und für Zinn 16%. Der Verdampfungsprozeß wird untersucht und diskutiert.

Summary—An emission spectrographic determination of germanium and tin in gallium arsenide is described. For a sample of 5 mg the limit of detection is 3·1 ppm germanium and 7·7 ppm tin. The relative standard deviations are 11% for germanium and 16% for tin. The evaporation of the elements during the excitation is discussed.

Résumé—On décrit un dosage spectrographique d'émission du germanium et de l'étain dans l'arséniure de gallium. Pour un échantillon de 5 mg la limite de détection est de 3,1 p.p.m. de germanium et 7,7 p.p.m. d'étain. Les écarts types relatifs sont de 11% pour le germanium et 16% pour l'étain. On discute de l'évaporation des éléments pendant l'excitation.

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DETERMINATION OF HYDROGEN PEROXIDE BY THALLIUM(III) IN THE PRESENCE OF IRON(II)

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Estimation of hydrogen peroxide by permanganate[1] and cerium(IV)[2] in acid solutions is well known. McCurdy and Bell used sodium hypochlorite[3] for the determination in alkaline medium. Though cerium(IV) solutions are quite stable,[4] permanganate[5] and hypochlorite[6] are not. The reaction of thallium(III) and hydrogen peroxide is slow. The high catalytic activity of iron(II) was discovered accidentally during attempts to follow the kinetics of the Tl(III)–H_2O_2 reaction by estimating the peroxide cerimetrically. Thallic perchlorate can therefore be used as a standard for the determination of hydrogen peroxide in the presence of traces of iron(II). Thallic perchlorate is quite stable and its concentration does not change even after 6 months.

EXPERIMENTAL

Reagents

Thallic perchlorate solution was prepared by dissolving thallic oxide in 60% perchloric acid. The undissolved material was filtered off on a sintered-glass crucible. This solution was standardized iodometrically, with starch as the indicator.[7,8]

Hydrogen peroxide solution was prepared by diluting the 20-vol material and standardized by addition of excess of ceric perchlorate and back-titration with iron(II).

Table 1. Determination of H_2O_2 with Tl(III) in the presence of Fe(II)

[Fe(II)], $10^{-5}M$	[$HClO_4$], M	[Tl(III)], $10^{-3}M$	[H_2O_2], taken, $10^{-3}M$	[H_2O_2] found, $10^{-3}M$	Error, %
5·0	0·5	2·00	1·00	1·00	—
5·0	0·5	3·00	2·00	2·00	—
5·0	0·5	8·00	3·00	3·01	0·3
5·0	0·5	7·00	3·00	3·00	—
5·0	0·5	6·00	4·00	4·02	0·5
5·0	0·5	7·00	5·00	5·05	1·0
0·5	0·5	7·00	2·00	2·01	0·5
0·5	0·5	3·00	2·00	2·00	—
0·5	0·5	5·00	4·00	4·02	0·5
0·5	0·5	7·00	6·00	6·02	0·3
5·0	0·5	5·00	4·00	4·02	0·5
5·0	1·0	5·00	4·00	4·01	0·3
5·0	2·0	5·00	4·00	4·02	0·5
5·0	3·0	5·00	4·00	4·01	0·3
5·0	4·0	5·00	4·00	4·0	—
8·5	1·0	4·00	2·00	2·01	0·5
8·5	1·0	8·00	2·00	2·00	—
8·5	1·0	10·0	2·00	2·00	—
8·5	1·0	8·00	4·00	4·01	0·3
8·5	1·0	10·0	8·00	8·02	0·3
0·7	1·0	1·00	0·50	0·50	—
0·7	1·0	1·00	0·55	0·55	—
0·7	1·0	1·00	0·60	0·60	—
0·7	1·0	1·50	0·65	0·65	—
0·7	1·0	1·50	0·70	0·70	—
0·7	1·0	2·00	0·60	0·60	—
0·7	1·0	2·00	0·100	0·101	1·0

Procedure

Equal volumes (10 ml) of thallium(III) and hydrogen peroxide solutions of the concentrations shown in Table 1 were mixed. The concentration of perchloric acid shown in the table is approximate and refers to the mixture. Ferrous sulphate was then added. The reaction between thallium(III) and peroxide occurred immediately. The excess of thallium(III) was determined iodometrically,[8] and hence the amount of peroxide was calculated.

DISCUSSION

The results are in accordance with the equation

$$\mathrm{Tl(III)} + H_2O_2 \longrightarrow \mathrm{Tl(I)} + 2H^+ + O_2 \tag{1}$$

It is obvious that very small concentrations of iron(II) are effective in the catalysis and that variation of the perchloric acid concentration from 0·5 to 4 *M* has no effect. The results for the presence of sulphuric acid, sodium sulphate, sodium nitrate, magnesium sulphate and copper sulphate are not shown, but these species were without effect. Large errors were found if chloride was present.

The iron(II) acts catalytically only if it is added to a mixture of Tl(III) and hydrogen peroxide or hydrogen peroxide is added to a mixture of Tl(III) and Fe(II). If Fe(II) and the peroxide are mixed first and then Tl(III) added, no determination of the peroxide can be made. Iron(III) has no catalytic activity.

The reaction between Tl(III) and peroxide is slow and Fe(II) catalyses it, possibly *via*

$$\mathrm{Tl(III)} + \mathrm{Fe(II)} \rightleftharpoons \mathrm{Tl(II)} + \mathrm{Fe(III)} \tag{2}$$

$$\mathrm{Tl(II)} + H_2O_2 \longrightarrow \mathrm{Tl(I)} + 2H^+ + O_2^- \tag{3}$$

$$\mathrm{Tl(III)} + O_2^- \longrightarrow \mathrm{Tl(II)} + O_2 \tag{4}$$

and thus a cycle of steps (3) and (4) continues till one of the reactants is used up. Oxide anion is postulated as formed in step (3), but some other form could be involved. At any rate some reactive radical ion is formed. If Fe(II) is mixed with peroxide first, the Haber-Weiss mechanism will operate for catalytic disproportionation of the peroxide.[9–11]

A reaction between Tl(II) and Fe(II) is also possible in competition with (3), but it appears to be considerably slower than (3). Similarly catalytic decomposition[13,14] of hydrogen peroxide in the presence of Fe(III) is also possible, but again this is very slow in comparison to the rates of steps (3) and (4). These processes are insignificant in the present investigation because no variation in the stoichiometry of the reaction between Tl(III) and peroxide in the presence of Fe(II) was found.

Chloride inhibits the reaction. It therefore appears that reactions (3) and (4) take place by formation of intermediate complexes of Tl(II) and H_2O_2, and Tl(III) and O_2^- respectively. In the presence of chloride strong chloro-complexes[15,16] are formed and thus the co-ordination sites of the Tl(III) are blocked, inhibiting the formation of the intermediate complexes.

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Summary—A method for estimating hydrogen peroxide by oxidation with excess of thallium(III) in the presence of iron(II) and iodometric determination of excess of thallium(III) is described. Nitrate, sulphate, manganese(II) and copper(II) have no effect. Chloride interferes.

Zusammenfassung—Ein Verfahren zur Bestimmung von Wasserstoffperoxid durch Oxidation mit überschüssigem Thallium(III) in Gegenwart von Eisen(II) und jodometrische Bestimmung des überschüssigen Thallium(III) wird beschrieben. Nitrat, Sulfat, Mangan(II) und Kupfer(II) haben keinen Einfluß, Chlorid stört.

Résumé—On décrit une méthode pour l'estimation du peroxyde d'hydrogène par oxydation avec un excès de thallium(III) en la présence de Fe(II) et dosage iodométrique de l'excès de thallium(III). Les nitrate, sulfate, manganèse(II) et cuivre (II) n'ont pas d'influence. Le chlorure interfère.

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DETERMINATION OF LITHIUM STEARATE IN SEBACATE-BASED LUBRICANTS BY ATOMIC ABSORPTION

(*Received* 16 *January* 1973. *Accepted* 16 *March* 1973)

Sebacate-based lubricants are becoming increasingly important because of their high- and low-temperature properties. A typical sebacate-based lubricant contains 8% lithium stearate, 89% di(2-ethylhexyl) sebacate, 1·5% barium petroleum sulphonate, 1% di-isopropyl phosphite, and 0·5% 2,6-di-t-butyl-*p*-cresol.[1]

Apparently no method has appeared for the determination of lithium stearate [$LiOOC(CH_2)_{16}CH_3$] in sebacate-based lubricants. Lithium stearate has been determined in petroleum-based lubricants by treatment with sulphuric acid and ignition to lithium sulphate.[2] Lithium, sodium and calcium have been determined in petroleum-based lubricants by homogenizing with butyl alcohol, shaking with dilute hydrochloric acid, allowing to stand for 1 hr or preferably overnight, and analysing for lithium, sodium and calcium in the aqueous layer by atomic absorption.[3] For reasons that were not clear, this method gave low results in this laboratory when applied to sebacate-based lubricants.

It was thought at first that the lithium stearate could be determined gravimetrically by treatment of the lubricant with a mixture of sulphuric and nitric acids, evaporation to fumes of sulphuric acid, filtration to remove the barium sulphate, evaporation of the filtrate to dryness, ignition to lithium sulphate, and correction for the phosphate from di-isopropyl phosphite. However, erratic results were obtained by this procedure, since a valid correction factor (deduction for lithium phosphate) could not be established. The reason for the erratic results was that lithium phosphate on ignition produces compounds of rather indefinite composition such as $Li_6H_2P_2O_9$.[4]

Attention was therefore turned to the determination of the lithium by atomic absorption after destroying the organic matter in the lubricant by treatment with a mixture of nitric and perchloric acids or a mixture of nitric and sulphuric acids and evaporation to fumes. However, low results for lithium were obtained at times because of the precipitation of lithium phosphate or metaphosphate (both of which are of limited solubility[5]).

In the method finally adopted, the sample was treated with water and hydrochloric acid and an extraction was performed with ethyl ether to remove the di-isopropyl phosphite, stearic acid, and sebacate. The aqueous solution was then treated with a mixture of nitric and perchloric acids and evaporated to fumes of perchloric acid, and the atomic-absorption measurements were then performed.

EXPERIMENTAL

Reagent

Standard lithium solution (1 ml = 0·3 mg of Li). Weigh 1·5973 g of lithium carbonate into a covered 250-ml beaker, add 20 ml of hydrochloric acid (1 + 1) in small portions, boil for a few minutes, cool, and dilute to 1 litre in a volumetric flask.

Summary—A method for estimating hydrogen peroxide by oxidation with excess of thallium(III) in the presence of iron(II) and iodometric determination of excess of thallium(III) is described. Nitrate, sulphate, manganese(II) and copper(II) have no effect. Chloride interferes.

Zusammenfassung—Ein Verfahren zur Bestimmung von Wasserstoffperoxid durch Oxidation mit überschüssigem Thallium(III) in Gegenwart von Eisen(II) und jodometrische Bestimmung des überschüssigen Thallium(III) wird beschrieben. Nitrat, Sulfat, Mangan(II) und Kupfer(II) haben keinen Einfluß, Chlorid stört.

Résumé—On décrit une méthode pour l'estimation du peroxyde d'hydrogène par oxydation avec un excès de thallium(III) en la présence de Fe(II) et dosage iodométrique de l'excès de thallium(III). Les nitrate, sulfate, manganèse(II) et cuivre (II) n'ont pas d'influence. Le chlorure interfère.

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In the method finally adopted, the sample was treated with water and hydrochloric acid and an extraction was performed with ethyl ether to remove the di-isopropyl phosphite, stearic acid, and sebacate. The aqueous solution was then treated with a mixture of nitric and perchloric acids and evaporated to fumes of perchloric acid, and the atomic-absorption measurements were then performed.

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Preparation of calibration curve

Transfer 2·0, 5·0, 7·5, and 10·0 ml of standard lithium solution into 500-ml volumetric flasks and dilute to the mark with water. Perform the atomic-absorption measurements, using the settings recommended for the instrument. (The following settings were used on the Perkin–Elmer Model 303 Atomic Absorption Spectrophotometer: wavelength, 355·8 nm; scale, 1; meter response, 1; range, visual; slit, 4; gain, 1; filter, in; acetylene flow, 9; air flow, 9). Check the calibration curve each time samples are run.

Procedure

Transfer a 1-g sample to a 250-ml beaker. Add 150 ml of water, 10 ml of hydrochloric acid, and 70 ml of ethyl ether. Stir with a stirring rod, wash into a 500-ml separatory funnel with water, and then rinse the beaker with 10 ml of ethyl ether. Shake the separatory funnel for about 1 min and allow the layers to settle. Transfer the aqueous layer to a 400-ml beaker. Add 10 ml of water to the ether layer in the separatory funnel, shake, and add the aqueous layer to the first aqueous extract. Add 20 ml of nitric acid and 5 ml of perchloric acid to the 400-ml beaker and boil down to about 2–3 ml. Allow to cool and dilute to 500 ml in a volumetric flask. Perform the atomic-absorption measurements as described under preparation of calibration curve. Read off the number of mg of lithium from the calibration curve.

$$\text{Lithium stearate} = \frac{4{\cdot}19 \times \text{mg of Li}}{\text{g of sample}}\ \%$$

RESULTS

The results obtained for lithium stearate in ten samples of sebacate-base lubricants are shown in Table 1. The precision is satisfactory.

Table 1. Results for lithium stearate in sebacate-based lubricants

Sample	Results, %				Sample	Results, %			
1	7·99	7·98	7·80	7·80	6	7·84	7·72	7·78	7·63
2	3·85	3·60	3·73	3·67	7	4·93	4·70	4·93	4·60
3	7·62	7·55	7·62	7·30	8	8·71	8·81	8·46	8·76
4	7·16	7·26	6·98	7·16	9	5·95	6·00	5·98	5·75
5	6·99	6·83	6·92	6·98	10	6·70	6·76	6·61	6·81

The recovery obtained for lithium stearate added to Sample 2 (3·71% lithium stearate) is shown in Table 2. The recoveries were satisfactory (93–106%).

Table 2. Recovery of lithium stearate added to a sebacate-based lubricant[a]

Lithium stearate added, *g*	Total lithium stearate found, *g*	Lithium stearate recovered, *g*
0·0210	0·0567	0·0196
0·0305	0·0670	0·0299
0·0395	0·0789	0·0418
0·0512	0·0901	0·0530

[a] This lubricant contains 3·71% lithium stearate (Sample 2 of Table 1).

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Summary—An accurate method is proposed for the determination of lithium stearate in sebacate-based lubricants. The sample is treated with dilute hydrochloric acid and an extraction is performed with ethyl ether to remove di-isopropyl phosphite which would otherwise interfere by causing the subsequent precipitation of lithium phosphate or lithium metaphosphate. The aqueous extract is then evaporated to fuming with perchloric acid and the lithium is determined by atomic absorption.

Zusammenfassung—Eine genaue Methode zur Bestimmung von Lithiumstearat in Schmiermitteln auf Sebacat-Grundlage wird vorgeschlagen. Die Probe wird mit verdünnter Salzsäure behandelt; es wird mit Diäthyläther extrahiert, um Diisopropylphosphit zu entfernen, das sonst durch die Ausfällung von Lithiumphosphat oder Lithiummetaphosphat stören würde. Der wäßrige Extrakt wird dann bis zum Rauchen mit Überchlorsäure abgedampft und das Lithium durch Atomabsorption bestimmt.

Résumé—On propose une méthode précise pour le dosage du stéarate de lithium dans les lubrifiants à base de sébacate. L'échantillon est traité par l'acide chlorhydrique dilué et l'on effectue une extraction à l'éther éthylique pour éliminer le phosphite de diisopropyle, qui autrement interfèrerait en causant la précipitation subséquente du phosphate de lithium ou du métaphosphate de lithium. L'extrait aqueux est alors évaporé jusqu'à apparition de fumées avec l'acide perchlorique et le lithium est dosé par absorption atomique.

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HYDRAZINE SULPHATE AS REAGENT FOR TITRIMETRIC DETERMINATION OF VANADIUM(V) AND CHROMIUM(VI)

(*Received* 19 *October* 1972. *Revised* 11 *January* 1973. *Accepted March* 1973)

Hydrazine sulphate, $N_2H_4 \cdot H_2SO_4$, has been proposed[1] as a standard in alkalimetry and also for the standardization of solutions of iodine,[2] iodine monochloride,[3] and bromine[4,5] by direct titration, and for many other indirect determinations. Berka, Vulterin and Zýka[6] stated that "the direct potentiometric titration of chromate and vanadate yields unprecise results." Deshmukh and Bapat[7] claim satisfactory results if the hydrazine solution is added in excess and the surplus back-titrated with bromate. Drăgulescu and Mitrănescu[8] reported a direct potentiometric titration of vanadium(V) with hydrazine sulphate in 0·5–4*N* sulphuric acid medium in the presence of osmium tetroxide as catalyst, but the error was rather high, about 1·3%. Singh and Singh[9] used iodine monochloride as catalyst and pre-oxidant in the direct titration and obtained satisfactory results. In this communication we report the conditions developed by us for the accurate direct titrimetric determination of vanadium(V) and chromium(VI), using barium diphenylaminesulphonate as indicator and osmium tetroxide as catalyst.

EXPERIMENTAL

Reagents

Sodium metavanadate solution, 0·2*M*. Prepared from ammonium metavanadate and standardized with iron(II) sulphate solution (itself standardized with dichromate).

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EXPERIMENTAL

Reagents

Sodium metavanadate solution, 0·2*M*. Prepared from ammonium metavanadate and standardized with iron(II) sulphate solution (itself standardized with dichromate).

Hydrazine sulphate solution, 0·05*M*. Prepared from analytical grade $N_2H_4 \cdot H_2SO_4$. The weight purity of the salt agreed with the assay by Kolthoff's bromate method.[10]

Osmium tetroxide solution, 0·2%.

Vanadium(IV) solution, 0·1*N*. Prepared from sodium metavanadate solution by reduction with sulphur dioxide at 70° in sulphuric acid medium and standardized with cerium(IV) sulphate.[11]

Titration of vanadium(V) and chromium(V)

A study of indicator reactions showed that the oxidation of diphenylaminesulphonic acid by vanadium(V) is rather slow in 1·0*N* sulphuric acid but becomes very rapid when 2 ml of syrupy phosphoric acid are added per 50 ml of titration mixture. Under these conditions the reduction of the oxidized indicator is slow but is found to be catalysed by the addition of 0·05 ml of 0·2% osmium tetroxide solution in dilute sulphuric acid. From these observations a procedure has been developed for the visual titration of vanadium(V) with hydrazine sulphate. Diphenylamine and diphenylbenzidine do not function satisfactorily as indicators in this titration. It was found that under the given conditions titrations of chromium(VI) are not reproducible; however, if the chromium(VI) is reacted to give an equivalent amount of vanadium(V) by addition of an excess of vanadium(IV), titrations are satisfactory and accurate.

Procedure

Take 2·5–10 ml of vanadium(V) solution and add enough 4*N* sulphuric acid to give an acidity of 1*N* on dilution to 50 ml. Add 0·5 ml of osmium tetroxide solution, 3 ml of syrupy phosphoric acid and 0·2 ml of 0·2% aqueous solution of barium diphenylaminesulphonate. Dilute to 50 ml and titrate with the hydrazine sulphate solution rapidly at first and slowly towards the end, waiting 10 sec between drops. Subtract 0·02 ml for the indicator correction.

For chromium(VI) add a slight excess of vanadium(IV) and titrate the resultant vanadium(V) as above. Too much excess of vanadium(IV) should be avoided as it retards the oxidation of the indicator.

Interferences

Iron(III), manganese(II), chromium(III), copper(II), molybdenum(VI) and tungsten(VI) do not interfere in the vanadium titration but chromium(VI) does. Nitrate interferes because of its slow reaction with the vanadium(IV) formed.

RESULTS AND DISCUSSION

Representative results for the determination of vanadium(V) and chromium(VI) are given in Table 1.

Table 1. Titrimetric determination of vanadium(V) and chromium(VI)

Vanadium(V), *mmole*				Chromium(VI), *mmole*			
Taken	Found	% Error	Mean deviation	Taken	Found	% Error	Mean deviation
0·0645	0·0647	0·3	+0·107	0·0528	0·0527	0·2	−0·122
0·1652	0·1657	0·3	+0·100	0·1110	0·1113	0·3	−0·041
0·2752	0·2754	0·1	−0·130	0·1513	0·1518	0·3	+0·02
0·3515	0·3513	0·1	−0·146	0·2222	0·2213	0·4	+0·09
0·6606	0·6588	0·3	−0·070	0·3306	0·3294	0·4	+0·05
			*S.D. = 0·13				*S.D. = 0·08

* S.D. = Standard Deviation

Among the earliest to study the oxidation of hydrazine by vanadate in acid medium were Hofmann and Kuspert[12] who stated that the reaction is,

$$4\,VO_3^- + N_2H_5^+ + 11\,H^+ \longrightarrow 4\,VO^{2+} + 8\,H_2O + N_2 \qquad (1)$$

Browne and Shetterly,[13] however, stated that the reaction follows simultaneously and to varying extents a second path:

$$VO_3^- + N_2H_5^+ + 11\,H^+ \longrightarrow NH_4^+ + VO^{2+} + \tfrac{1}{2}N_2 + 2H_2O \qquad (2)$$

This was confirmed by Bray and Cuy[14] who dismissed vanadate as unsuitable for the determination of hydrazine. The non-stoichiometry of the reaction was recently emphasized by Higginson, Sutton and Wright.[15] It is explained in terms of one-electron acceptors [equation(2)] and two-electron acceptors [equation (1)] giving different reaction mechanisms. If both paths are followed to different extents under varying conditions, it will be obvious that the stoichiometry varies. Our experiments show that vanadium(V) reacts with hydrazine accurately according to equation (1) in the presence of osmium tetroxide as catalyst. Even in the absence of the catalyst, vanadium(V) acts mostly as a two-electron acceptor. This behaviour is apparently strange, because the reduction product is vanadium(IV) and not vanadium(III). Higginson, Sutton and Wright suggested a reaction mechanism that would explain this anomaly.

$$\mathrm{V(V)} + \mathrm{N_2H_4} \longrightarrow \mathrm{V(III)} + \mathrm{N_2H_2} \tag{3}$$

$$\mathrm{V(V)} + \mathrm{N_2H_2} \longrightarrow \mathrm{V(III)} + \mathrm{N_2} \tag{4}$$

$$\mathrm{V(V)} + \mathrm{V(III)} \longrightarrow 2\mathrm{V(IV)} \tag{5}$$

The alternative sequence

$$\begin{array}{lllll} \mathrm{V(V)} + \mathrm{N_2H_4} & \longrightarrow & \mathrm{V(IV)N_2H_3} & \longrightarrow & \mathrm{V(III)N_2H_2} \\ & \longrightarrow & \mathrm{V(III)} + \mathrm{N_2H_2} & & \end{array} \tag{6}$$

they rule out on grounds of stability of N_2H_2 being higher than that of N_2H_3 and of the low redox potential (0·36 V) of vanadium(IV) and consider that such a reaction would be much slower than the two-electron sequence. However, the reaction,

$$\mathrm{V(V)} + \mathrm{N_2H_4} \longrightarrow \mathrm{V(IV)} + \mathrm{N_2H_3} \tag{7}$$

would disturb the stoichiometry. We believe that osmium tetroxide forms a complex with N_2H_3 and oxidizes the latter to N_2H_2 before it can dimerize to N_4H_6 and give ammonia.

$$2\mathrm{N_2H_3} \longrightarrow \mathrm{N_4H_6} \longrightarrow \mathrm{N_2} + 2\mathrm{NH_3} \tag{8}$$

The N_2H_2 undergoes oxidation by V(V) to N_2 according to equation (4). The exact role of Os(VIII) is not clear. We consider that it is reduced to a transient species Os(VII) by N_2H_3 and that the Os(VII) is reoxidized to Os(VIII) by vanadium(V). If Os(V) or Os(IV) are formed as intermediates, they can be oxidized only to Os(VI) and not to Os(VIII) by vanadium(V) as observed by Syrokomskii[16] and this would involve a correction for the osmium tetroxide used, which was not the case in our titrations. Csyani[17] assumed the formation of Os(V) for the catalysis of oxidation by chlorates. Thus osmium tetroxide not only accelerates the reaction but also makes it follow a single stoichiometric path.

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Summary—Conditions have been developed for the direct titration of vanadium(V) and chromium(VI) with hydrazine sulphate, barium diphenylaminesulphonate being used as indicator and osmium tetroxide as catalyst.

Zusammenfassung—Die Bedingungen zur direkten Titration von Vanadium(V) und Chrom(VI) mit Hydrazinsulfat wurden entwickelt. Bariumdiphenylaminsulfonat wird als Indikator und Osmiumtetroxid als Katalysator verwendet.

Résumé—On a élaboré les conditions de titrage direct du vanadium (V) et du chrome (VI) par le sulfate d'hydrazine, le diphénylaminosulfonate de baryum étant utilisé comme indicateur et le tétroxyde d'osmium comme catalyseur.

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DESORPTION OF SMALL QUANTITIES OF CHLORAURATE IONS RETAINED ON ANION-EXCHANGERS, IN THE SEPARATION OF GOLD FROM BASE METALS

(*Received* 29 *December* 1972. *Accepted* 1 *March* 1973)

Strongly basic anion-exchangers display a high selectivity towards chloraurate ions, which offers a possibility for increasing their concentration and separating the gold from the associated base metals. Nevertheless, the removal of the ions retained on the resin is troublesome and complicates the subsequent determination of gold.[1–4] Attempts have been made to elute the cyanide complexes of gold from anion-exchangers with a hydrochloric acid solution of thiourea.[5,6] These investigations are, however, rather technological in their approach. Davankov *et al.*,[7] have collected chloraurate ions on the anion-exchangers N-O and TN. Their attempts to elute the gold with acid solutions of thiourea, or dilute solutions of hydrochloric acid in acetone or ethanol, proved unsuccessful. Burstall *et al.*,[8] examined the enrichment of gold from ores by sorption of its cyanide complexes on anion-exchangers. They eluted the gold quantitatively with a mixture of hydrochloric and nitric acids and acetone. Their paper does not present results for microgram quantities. Fritz *et al.*,[9] separated μg amounts of gold from base metals with a polyacrylic resin and obtained good results in the elution of gold with a mixture of hydrochloric acid and acetone.

The present paper deals with the possibility of eluting microgram quantities of gold from Dowex 1 with thiourea. It was established that the desorption proceeds practically to completion at 50° with a 0·3*M* solution of thiourea in 0·1*M* hydrochloric acid. The eluate volume may be decreased by reversing the direction of flow through the column. The elution conditions established are applicable in the separation of gold from copper, nickel and iron and for determination of gold in anodic copper.

EXPERIMENTAL

Reagents

Anion-exchange resin. Dowex 1X8, 50–100 mesh, chloride form.

Standard gold(III) solution. Prepared from $AuCl_3$, *p.a.*, by dissolution in 1*M* hydrochloric acid and standardized gravimetrically by reduction with hydroquinone.[10] This solution was diluted with 1*M* hydrochloric acid to concentrations of 5 and 10 μg/ml.

Standard solutions of nickel, copper(II) and iron(III). Prepared by dissolving the reagent grade chlorides in 1*M* hydrochloric acid.

Thiourea solutions, 0·1 and 0·3M. In 0·1*M* hydrochloric acid.

Sodium chloride solution, 4%.

Sodium fluoride solution, 1%.

p-*Dimethylaminobenzylidenerhodanine solution, 0·05%.* In absolute alcohol.

All reagents were analytically pure.

Ion-exchange columns

A column 35 mm long and 8 mm dia, fitted with a thermostatic jacket, was used. A reversible column[11] of the same dimensions (Fig. 1) was also used, fitted with funnel *A* (with ground-glass joint) for

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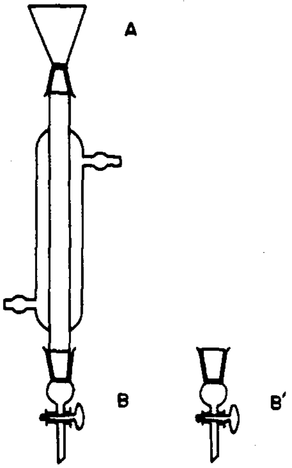

Fig. 1. Reversible column.

introduction of the solutions, and the stop-cock assembly *B* for the outflow. When the column is to be run in reverse, *A* is replaced by a second stop-cock assembly *B′*, the column is inverted, and *B* is replaced by *A*. To avoid disturbance of the resin when the column is inverted, the filling should be secured in place with some glass-wool.

Preliminary work

After sorption of a definite amount of gold, the column was washed with 0·5*M* hydrochloric acid, then eluent was passed through at a rate of 0·5 ml/min, 10-ml fractions being collected and analysed for gold after destruction of the thiourea complex. It was established from experiments with different concentrations of thiourea at room temperature and on heating, that gold is practically completely desorbed with 70 ml of 0·3*M* thiourea at 50° (Fig. 2).

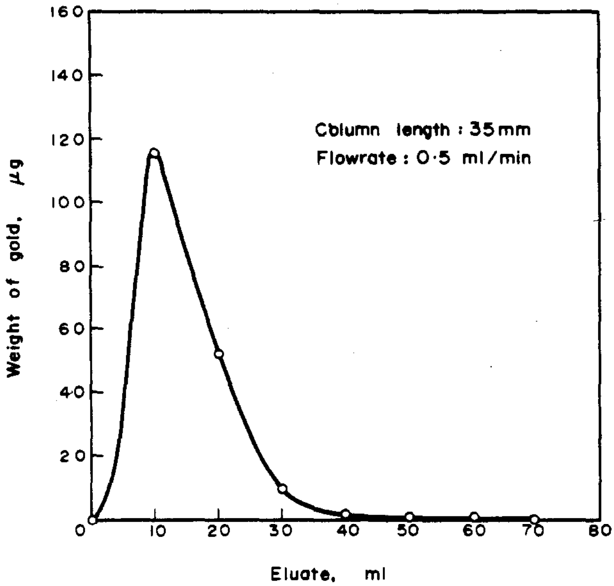

Fig. 2. Elution of gold with 0·3*M* thiourea in 0·1*M* hydrochloric acid.

The use of the reversible column was investigated by sorbing the gold, washing and inverting the column, and eluting at the same rate as before. For complete elution of the gold only 20 ml of 0·3*M* thiourea were needed.

To check that elution of the gold was complete, we passed through the column samples each containing 100 µg of gold, which after washing was eluted with 70 ml (or for reverse-flow 20 ml) of thiourea solution under the conditions indicated above, and we then determined the gold in aliquots of eluate. The results showed that desorption of the gold was practically complete.

Procedure for separating gold from nickel, copper and iron

The sample is taken in a 50-ml beaker, 0·5 ml of 4% sodium chloride solution is added, the mixture is evaporated to dryness over an infrared heater, then the dry residue is dissolved in 10 ml of 0·5*M* hydrochloric acid and the solution passed through the column at a rate of 0·5 ml/min. The column is washed with 0·5*M* hydrochloric acid till a test for the transition-metal ions in the effluent is negative. The gold is eluted at 50° with 70 ml of 0·3*M* thiourea in 0·1*M* hydrochloric acid (20 ml for reverse-flow). The eluate is collected in a 100-ml (or 25-ml) graduated flask and is diluted to the mark. An aliquot of this solution is then transferred to a porcelain crucible, evaporated to dryness, placed in a cold electric oven and heated gradually until ashing is complete. A tiny residue of elemental gold is obtained, which is dissolved in *aqua regia* with slight heating, evaporated to a moist residue, then dissolved in several drops of concentrated hydrochloric acid. Sodium chloride solution (4%, 0·5 ml) is added, and the solution again evaporated to dryness. The residue is dissolved in 1·5 ml of 2*M* hydrochloric acid and the gold determined photometrically with *p*-dimethylaminobenzylidenerhodanine.[12]

If the samples contain iron, 1 ml of aqueous chlorine solution is added before the preliminary evaporation, to suppress reduction of the gold.

Determination of gold in anodic copper

A 0·5 g sample is dissolved in 6 ml of nitric acid (1 + 1), then 2 ml of concentrated hydrochloric acid and 0·5 ml of 4% sodium chloride solution are added and the mixture is evaporated to dryness. The residue

Table 1. Separation of gold from nickel, copper and iron

Foreign ion,	Added, *mg*	Au, *µg*		Std. devn., *µg*
		taken	found	
Ni(II)	5·0	100	99	2
	5·0	100	102	
	50·0	100	98	
	100·0	100	99	
			average 99·5	
Cu(II)	5·0	100	99	3·6
	5·0	100	97	
	50·0	100	105	
	50·0	100	98	
	100·0	100	100	
			average 99·8	
Fe(III)	5·0	100	104	1·3
	5·0	100	97	
	50·0	100	103	
	100·0	100	100	
	100·0	100	100	
	100·0	100	98	
	100·0	100	100	
			average 100·4	
	10·0	20	19·0	0·8
	10·0	20	20·0	
	10·0	20	19·5	
	10·0	20	19·5	
	20·0	20	20·0	
	20·0	20	21.7	
	20·0	20	20·5	
	20·0	20	20·0	
			average 20·0	

is dissolved in 0·5*M* hydrochloric acid, and the small precipitate of AgCl and SiO_2 is filtered off and washed with 0·5*M* hydrochloric acid. The filtrate and washings are treated as described above, on a reversible column.

RESULTS AND DISCUSSION

The investigations showed that chloraurate is completely eluted from Dowex 1 with a solution of thiourea at 50°, and this was confirmed by experiments with radioactive isotopes (not described here). The destruction of the thiourea complex and the excess of thiourea by ashing proceeds smoothly and completely. The residue of elemental gold (in some cases hardly noticeable) is readily dissolved in *aqua regia.*

The use of a reversible column is of significant advantage in the separation of minute amounts of gold, because the whole of the eluate can be used for the determination of the gold.

The accuracy and reproducibility of the photometric determination of gold after the anion-exchange separation of nickel, copper and iron was studied with synthetic samples, prepared by mixing a known amount of standard gold solution with pure solutions of the elements mentioned. The results are given in Table 1.

The method was applied to the determination of gold in anodic copper. The results, $63·9 \pm 2·3$ ppm (95% statistical certainty, six results) were in good agreement with those ($64·4 \pm 3·4$ ppm) obtained by co-precipitation of the gold with tellurium.

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Summary—Favourable conditions have been found for the elution of chloraurate ions, separated from base metals by sorption on Dowex 1. The elution is done at 50° with a hydrochloric acid solution of thiourea. A reversible column is proposed for the purpose, the use of which decreases the eluate volume. The conditions established have been applied in the separation of microgram amounts of gold from nickel, copper and iron as well as for determining gold in anodic copper.

Zusammenfassung—Zur Elution von Chloroaurat-Ionen, die durch Sorption an Dowex 1 von unedlen Metallen getrennt worden sind, wurden günstige Bedingungen gefunden. Die Elution wird bei 50° mit einer salzsauren Thioharnstofflösung ausgeführt. Für diesen Zweck wird eine in beiden Flußrichtungen verwendbare Säule vorgeschlagen; sie ermöglicht, das Volumen des Eluats kleiner zu halten. Die ermittelten Bedingungen wurden bei der Abtrennung von Mikrogrammengen Gold von Nickel, Kupfer und Eisen sowie bei der Bestimmung von Gold in Anodenkupfer verwendet.

Résumé—On a trouvé des conditions favorables pour l'élution des ions chloroaurate, séparés des métaux de base par sorption sur Dowex 1. L'élution est faite à 50° par une solution de thiourée dans l'acide chlorhydrique. On propose une colonne réversible à cette fin, dont l'emploi décroît le volume d'éluat. Les conditions établies ont été appliquées à la séparation de quantités d'or de l'ordre du microgramme des nickel, cuivre et fer, ainsi qu'à la détermination de l'or dans le cuivre anodique.

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A TWINNED MERCURY-FILLED GLASS ELECTRODE SYSTEM FOR ACID-BASE TITRATIONS IN A NUMBER OF NON-AQUEOUS SOLVENTS

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The mercury-filled electrode was first tested in 1932 by Thompson[1] for acid–base titrations in aqueous solutions. This indicator electrode was twinned with a classical saturated calomel electrode. Later, Ritchie and Uschold[2] used a similar system for titrations in dimethylsulphoxide, the reference electrode being the system Ag/Ag^+ (0·05M). More recently, Bottom and Covington[3] tested some mercury-filled electrodes for comparison with electrodes filled with water, water–ethanol and water–dioxan (the mercury-filled glass electrode contains pure mercury without any solvent).

Lately, workers in this laboratory have used a mercury-filled glass electrode for determinations in *N*-methylpyrrolidone,[4] glycol[5] and methanol,[6] the reference system being Hg/Hg_2^{2+} (0·01M) or $Ag/AgCl/KCl_{sat}$ in the corresponding solvent. These experiments showed that the response of the mercury-filled glass electrode to pH variations of the solutions in *N*-methylpyrrolidone, glycol and methanol media was linear, but that the slope of the line was not always 58 mV/pH unit. Although this makes the determination of acidity constants difficult, it is of little importance for titrations.

These results suggested the possibility of using the mercury-filled glass electrode for titrations in non-aqueous solvents or their mixtures with each other or with water, or to use a *pair* of such electrodes, the one operating as a conventional pH indicator whilst the second, immersed in a buffer solution, assumes a constant potential, thus behaving like a reference electrode.

EXPERIMENTAL

Apparatus

This is represented in Fig. 1. The platinum wire in the titration compartment of the cell connects the solution to the earth of the apparatus. The titration half-cell and the reference half-cell are connected by means of a liquid junction [Et_4NClO_4 (0·1M) in the solvent or in the mixture of solvents considered].

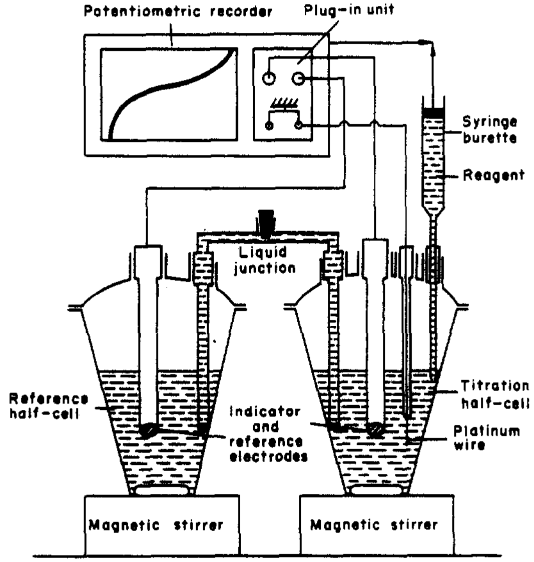

Fig. 1. Titration apparatus.

The potentiometric recorder is an EPL 1 Tacussel-Solea type fitted with a high input impedance differential voltage plug-in TD 11 G unit.

A "Scriptoburap" syringe-burette is linked to the chart-drive shaft for automatic recording of titration curves.

Reagents

A convenient buffer was a 0·1N solution of a strong acid in the titration medium. Perchloric acid, being a strong acid in quite a lot of solvents, was often employed. We also tested successfully a 0·1N solution of *p*-toluenesulphonic acid. In any case, any acid–base pair which is stable in the titration medium can fix the potential of the solution at the value E = constant − 0·058 pK_a.

RESULTS

The rapidity with which the mercury-filled glass electrode reaches equilibrium potential when immersed in a solution of constant acidity was first tested: the glass electrode was coupled with a conventional reference electrode prepared in the solvent considered and the difference of potential was recorded as a function of time.

When transferred from any solvent to water, the electrode instantly reached a stable potential; when transferred from any solvent to glycol or methanol the balance was obtained within a few minutes, but 20–30 min were necessary before equilibrium was reached in dimethylacetamide or *N*-methylpyrrolidone. This difference may be due to the nature, protic or aprotic, of the solvents.

When equilibrium is obtained in a solvent, the electrode response to the pH variations induced by titrations is much faster, and a whole titration curve can be recorded within 30 or 40 min; this time could be reduced by altering the rate of addition of titrant according to the stage reached in the titration.

Under these conditions, the electrodes can be used for successive titrations in various solvents. By way of example we titrated successfully an aqueous solution of acetic acid with sodium hydroxide; a solution of *p*-toluenesulphonic acid with imidazole in dimethylacetamide, dimethylacetamide–water, dimethylacetamide–glycol, water–glycol and dimethylacetamide–*N*-methylpyrrolidone media (mixtures 1 : 1 v/v). Reproducible curves were obtained even for the titration of maleic acid, oxalic acid and their mixtures in a dimethylacetamide–glycol mixture (Fig. 2).

The accuracy of the equivalence point was tested, using as example the titration of *p*-toluenesulphonic acid in a mixture of dimethylacetamide and glycol: 20 ml of 0·0985N acid solution were titrated with 0·1N

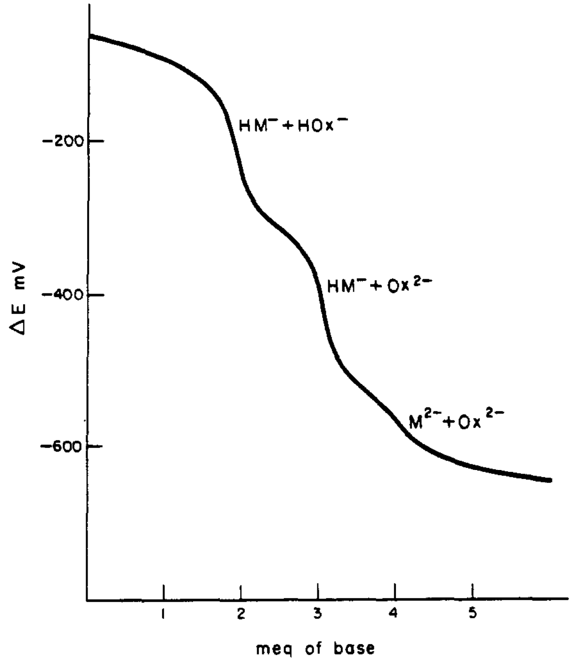

Fig. 2. Titration curve of a mixture of 10 ml each of 0·1N maleic acid (H_2M) and 0·1N oxalic acid (H_2Ox) with 0·1N tetrabutylammonium hydroxide in the solvent dimethylacetamide + ethylene glycol.

solution of imidazole in the titration medium; the titrant was added at 0·075 ml/min. Eighteen such titrations were performed and the results gave an average value for the acid concentration of 0·0985*N* with standard deviation 0·0008 (relative error ±0·4%).

CONCLUSION

Although only a few applications were tested it is thought likely that a pair of mercury-filled glass electrodes will be useful for acid–base titrations in a number of media and it is intended to pursue these trials.

The electrode system appears to be superior to the classical one in that the reference electrode is much simpler to prepare than say a conventional silver–silver chloride electrode and the same electrode pair can be used for successive titrations in both aqueous and non-aqueous solvents.

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Summary—A pair of mercury-filled glass electrodes is proposed for acid–base titrations in non-aqueous solvents or their mixtures with each other or with water.

Zusammenfassung—Ein Paar quecksilbergefüllter Glaselektroden wird für Säure–Basen-Titrationen in nichtwäßrigen Lösungsmitteln sowie ihren Gemischen untereinander und mit Wasser vorgeschlagen.

Résumé—On propose l'emploi d'un couple d'électrodes de verre à remplissage de mercure pour suivre les dosages acide–base dans les solvants non-aqueux, leurs mélanges et leurs mélanges avec l'eau.

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NON-AQUEOUS CERIMETRIC DETERMINATION OF THIOUREAS

(*Received* 8 *January* 1973. *Accepted* 27 *March* 1973)

Although considerable work has been done on acid–base titrimetry in non-aqueous media, redox titrations in such media have attracted limited attention. The importance of determination of organic compounds in industry and research, especially by functional group analysis, is well known. The application of non-aqueous redox titrimetry to such functional groups is therefore of interest.

Thioureas are of industrial, medicinal and analytical importance. Though various oxidimetric methods[1] have been developed for their determination in aqueous medium, such methods in non-aqueous medium are few. Copper(II) solutions in acetonitrile have been reported as suitable titrants for the potentiometric determination of thiourea[2–4] and some of its derivatives,[5] the thiol group being oxidized to disulphide. Kratochvil and Long[6] titrated thiourea potentiometrically with hydrated iron(III) perchlorate in acetonitrile medium. Suchomelová and Zýka[7] showed that though mercaptans could be smoothly and quantitatively titrated with lead tetra-acetate in acetic acid medium, the oxidation of thiourea with the oxidant occurred in 50% acetic acid and in the presence of sulphuric or hydrochloric acid.

Cerium(IV)[8] is one of the oxidants which in acidic solutions quantitatively oxidizes thiourea to formamidine disulphide, and its monosubstituted derivatives to their corresponding disulphides. The oxidation proceeds solution of imidazole in the titration medium; the titrant was added at 0·075 ml/min. Eighteen such titrations were performed and the results gave an average value for the acid concentration of 0·0985*N* with standard deviation 0·0008 (relative error ±0·4%).

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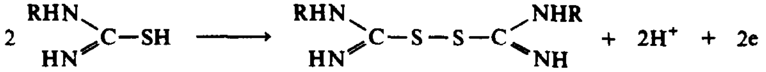
Cerium(IV)[8] is one of the oxidants which in acidic solutions quantitatively oxidizes thiourea to formamidine disulphide, and its monosubstituted derivatives to their corresponding disulphides. The oxidation proceeds smoothly and rapidly under specified conditions. No direct method to determine thiourea or its derivatives with cerium(IV) in non-aqueous medium appears to have been developed so far. Mruthyunjaya,[9] however, determined thiourea indirectly in acetic acid medium, using standard ammonium hexanitratocerate solution (in tri-n-butyl phosphate/carbon tetrachloride medium). The excess of cerium(IV) was titrated with standard hydroquinone solution in acetic acid medium. In the present work ammonium hexanitratocerate has been used as an oxidimetric reagent for the direct titrimetric determination of thiourea and its many alkyl derivatives, in acetonitrile medium, both visually and potentiometrically. Acetonitrile, because of its high dielectric constant and resistance to oxidation or reduction has been found to be quite promising as a non-aqueous solvent. Acetonitrile solution of ammonium hexanitratocerate(IV) is orange-red and imparts a distinct yellow tint to the solution at the end-point in visual titrations. The potentiometric titrations were performed with a platinum wire as indicator electrode and a modified calomel electrode as reference electrode. The method is simple, accurate, reliable and widely applicable. The results obtained agree well with those obtained by aqueous methods. The thioureas are oxidized to their corresponding disulphides with a single-electron change.



(R = hydrogen atom or alkyl group)

EXPERIMENTAL

Reagents

*Ammonium hexanitratocerate, 0·05*N *in acetonitrile.* Prepared by dissolving a little more than the calculated amount of dried analytical-grade oxidant in acetonitrile, and standardized by titration with ferrous ammonium sulphate in the presence of dilute sulphuric acid, with ferroin as indicator. The solution was stored in coloured glass-stoppered bottles and kept in a dry chamber.

A recrystallized sample of thiourea was used. The alkyl derivatives of thiourea were prepared from their corresponding isothiocyanates[10] by condensation with ammonia.

All other reagents were of guaranteed quality.

Procedure

Aliquots of solutions of each compound in acetonitrile were taken in conical flasks (for visual titrations) or beakers (for potentiometric titrations) and the volumes made up to 20–25 ml with the solvent. The solutions were cooled to room temperature (20°) and titrated visually and potentiometrically with ammonium hexanitratocerate solution (in acetonitrile) added from a microburette provided with guard-tube for protection from atomospheric moisture. The titration solution was magnetically stirred during potentiometric determinations. During titration white cerous nitrate was precipitated. The visual end-point was signalled by the yellow tint imparted by the first drop of oxidant in excess.

Table 1. Titrations of thiourea and its alkyl derivatives with standard ammonium hexanitratocerate(IV) in acetonitrile

	Amount of each compound taken, 8 *mg*		Amount of each compound taken, 30 *mg*	
	Amount found, *mg*		Amount found, *mg*	
Compound	Visual method	Potentiometric method	Visual method	Potentiometric method
	(Mean of 6 determinations, with standard deviation		(Mean of 6 determinations, with standard deviation)	
NH_2CSNH_2	7·94, 0·056	7·95, 0·051	30·09, 0·047	29·94, 0·044
$CH_2:CHNHCSNH_2$	8·01, 0·072	8·00, 0·043	29·96, 0·076	30·04, 0·048
$CH_3NHCSNH_2$	8·03, 0·061	8·02, 0·044	29·91, 0·065	29·92, 0·052
$CH_3CH_2NHCSNH_2$	7·95, 0·055	7·98, 0·045	30·09, 0·068	30·05, 0·031
$(CH_3)_2CHNHCSNH_2$	8·06, 0·045	8·02, 0·027	30·12, 0·076	30·10, 0·038
$CH_3CH_2CH_2NHCSNH_2$	7·96, 0·041	7·99, 0·028	29·88, 0·058	29·92, 0·031
$(CH_3)_2CHCH_2NHCSNH_2$	8·02, 0·068	8·00, 0·044	29·91, 0·090	29.95, 0·058
$CH_3CH_2CH_2CH_2NHCSNH_2$	8·03, 0·062	8·00, 0·027	30.13, 0·049	29.93, 0.031

RESULTS AND DISCUSSION

The results recorded in Table 1 show that thiourea, allyl thiourea, methyl thiourea, ethyl thiourea, isopropyl thiourea, n-propyl thiourea, isobutyl thiourea and n-butyl thiourea can be determined visually and potentiometrically with ammonium hexanitratocerate in acetonitrile medium. The overall standard deviations from pooled data of all the visual and potentiometric titrations performed with 8 mg samples of each compound were 0·058 and 0·039 mg respectively. For 30-mg samples they were 0·066 and 0·042 mg respectively. Pronounced fluctuations in potentials were observed when a saturated (aqueous) calomel electrode was used as reference electrode. With a modified calomel electrode (methanol saturated with potassium chloride used instead of saturated aqueous potassium chloride) the potentials attained stable values immediately on addition of the oxidant. A sharp jump in potential of 450–550 mV was observed at the end-point on the addition of 0·05 ml of 0·05*N* ammonium hexanitratocerate. The potentials of the inflection points for the listed compounds were 380–410 mV.

The use of acetic acid to economize in acetonitrile in these determinations is not recommended, as its presence makes the reaction slow and the end-point difficult to detect.

The effect of some typical compounds was studied in the determination of thioureas with Ce(IV) in acetonitrile medium by the recommended procedure in the usual way. No interferences were found from organic isothiocyanates, thiocyanates or isocyanates even when present in up to sixfold amounts relative to the thioureas. Cyanamide, thiosemicarbazide, urea, ammonium thiocyanate and amines interfered.

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Summary—Ammonium hexanitratocerate (in acetonitrile) solution has been used as an oxidimetric reagent for the visual and potentiometric determination of thiourea and its alkyl derivatives in acetonitrile medium. The thioureas are oxidized to their corresponding disulphides. The method is simple, accurate, reliable and widely applicable.

Zusammenfassung—Ammoniumhexanitratoceratlösung (in Acetonitril) wurde als oxidimetrisches Reagens zur visuellen und potentiometrischen Bestimmung von Thioharnstoff und seinen Alkylderivaten in Acetonitril-Medium verwendet. Die Thioharnstoffe werden zu den entsprechenden Disulfiden oxidiert. Die Methode ist einfach, genau, verläßlich und auf viele Probleme anwendbar.

Résumé—On a utilisé une solution d'hexanitratocérate d'ammonium (en acétonitrile) comme réactif oxydimétrique pour le dosage visuel et potentiométrique de la thiourée et de ses dérivés alkylés en milieu acétonitrile. Les thiourées sont oxydées en leurs disulfures correspondants. La méthode est simple, précise, sûre et largement applicable.

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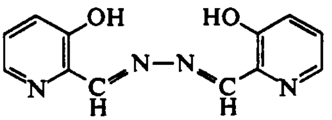
ANALYTICAL DATA

ANALYTICAL PROPERTIES OF 3-HYDROXYPICOLINALDEHYDE AZINE

(*Received* 20 *March* 1973: *Accepted* 17 *April* 1973)

Acyclic azines (R—CH═N—N═CH—R) are interesting as analytical reagents. The insolubility and fluorescence of salicylaldehyde azine (SAA) have been used for the detection of traces of hydrazine with salicyladehyde alicylaldehyde.[1] Picolinaldehyde azine (PAA) has been used in the photometric determination of Fe(II),[2] and its complexes with Co(II), Fe(II), Ni, and Cu have been also described.[3] 6-Methylpicolinaldehyde azine was used as a selective "cuproine" reagent for the estimation of copper.[4]

In this paper the synthesis, properties and analytical possibilities of a new compound, 3-hydroxypicolinaldehyde azine (3-OH-PAA) are described and a comparison is made with SAA and PAA.



3-OH-PAA

EXPERIMENTAL

Preparation of the compounds

3-OH-PAA. A solution of 1·5 g of 3-hydroxy-2-methoxypyridine hydrochloride in 150 ml of water with 0·8 g of manganese dioxide was heated together with chloroform (200 ml) to reflux (60°C), and 50 ml of 0·6*N* sulphuric acid were dropped into the mixture over a 30-min period. After 10 min more reflux, the solution was slightly cooled and the layers separated. The chloroform solution was dried over sodium sulphate and evaporated at 30–40° with a rotating film evaporator. The white solid (3-hydroxypicolinaldehyde) was dissolved in 30 ml of ethanol and added dropwise to 0·5 g of hydrazine sulphate and 0·5 g of potassium acetate dissolved in 50 ml of water. Fluorescent yellow crystals were separated, and recrystallized from ethanol (m.p. 162°). Found: C 59·3 %, H 4·3 %, N 23·2 %. Calculated for $C_{14}H_{10}N_4O_2$: C 59·5 %, H 4·1 %, N 23·0 %.

SAA. Prepared in a similar way to 3-OH-PAA, from salicylaldehyde. Yellow crystals (m.p. 270–75°) showing fluorescence in ultraviolet light. Found: C 69·9 %, H 5·0 %, N 11·9 %. Calculated for $C_{14}H_{12}N_2O_2$ C 70·0 %, H 5·0 %, N 11·7 %.

PAA. Picolinaldehyde, 2·5 g, dissolved in 25 ml of ethanol was added dropwise to 0·6 g of hydrazine hydrate in 90 ml of distilled water and 15 ml of concentrated ammonia solution. The mixture was stirred at room temperature for 3 hr. Yellow crystals were isolated and recrystallized from aqueous ethanol (m.p. 150°). Found: 68·6 %, H 5·0 %, N 26·6 %. Calculated $C_{14}H_{10}N_4$: C 68·6 %, H 4·8 %, N 26·6 %.

Properties

Some physicochemical properties are summarized in Table 1. The absorption spectra are shown in Fig. 1, with the effect of pH. The aqueous dilute solutions of the 3-OH-PAA and SAA were not stable, whereas PAA aqueous solutions were stable in weakly acid and neutral medium. A simultaneous potentiometric-photometric method[5] was used to measure the *pK* values.

Reactions with cations. The reactions of 36 ions with the three reagents were tested at pH 4·8, 8·6 and 11·3. The samples were prepared in 25-ml volumetric flasks, with 2 or 10 ppm of metal ion, buffer solution, and 10 ml of 0·05 % azine solution in dimethylformamide, and diluted to 25 ml with distilled water; the absorbance was measured from 350 to 700 nm against reagent blanks. The most important results are summarized in Table 2.

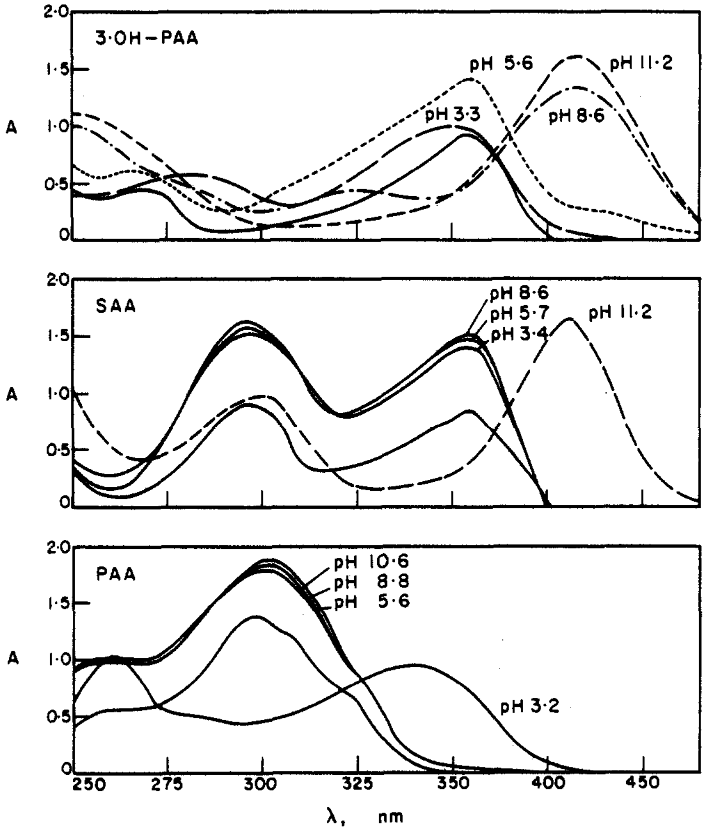


Fig. 1. Absorption spectra of 3·25 × $10^{-5}M$ 3-OH-PAA, SAA, and PAA in water at different pH values, and in ethanol.

Table 1. Physicochemical properties of the three azines

Property	3-OH-PAA	SAA	PAA
Solubility in ethanol, *g/l.*	0·85	0·2	26·0
Solubility in dimethylformamide, *g/l.*	14·4	20·6	33·6
C═N— stretching frequency, cm^{-1}	1622	1630	1631
pK_1 (pyridinium nitrogen)	3·92	—	4·60
pK_2 (phenol group)	7·97	9·63	—

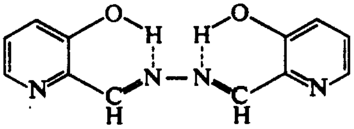
Table 2. Characteristics of azine complexes in solution

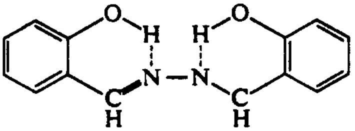
Ligand	Metal ion	pH	λ_{max} *nm*	ε, *l.mole.cm*$^{-1}$	p*D*	Colour
3-OH-PAA	Ag(I)	8·6	486–8	$1·9 \times 10^4$	6·5	orange yellow
	Cu(II)	4·6	500	$2·4 \times 10^4$	7·1	red
		10·8	460–70	$1·4 \times 10^4$	7·1	red
	Cu(I)	8·6	500–10	$1·4 \times 10^4$	7·0	red
	Hg(II)	4·6	460	$1·8 \times 10^4$	5·8	orange
		10·8	495	$1·2 \times 10^4$	5·4	orange
	Pt(IV)	4·6	490–510	$2·0 \times 10^3$	4·5	orange yellow
	Co(II)	4·6	545	$3·0 \times 10^4$	8·2	dark violet
		10·8	470	$2·6 \times 10^4$	6·0	orange yellow
	Ni(II)	4·6	430–40	$2·9 \times 10^4$	6·4	orange yellow
		10.8	485	$8·1 \times 10^3$	5·9	yellow
	Zn(II)	4·6	510–20	$1·1 \times 10^4$	5·3	orange
		10·8	490–96	$1·1 \times 10^4$	5·2	orange
	Pd(II)	4·6	450	$9·0 \times 10^3$	6·9	orange yellow
	Cd(II)	4·6	420–510	$4·5 \times 10^3$	5·1	orange
		10·8	490	$1·1 \times 10^4$		
	Mn(II)	10·8	495	$6·0 \times 10^3$	5·0	orange
	Fe(II)	4·6	430	$1·6 \times 10^4$	5·8	brown
	Fe(III)	4·6	430	$7·4 \times 10^3$	5·1	brown
SAA	Co(II)	8·6	490–500	$7·0 \times 10^2$	4·9	orange
		10·8	490	$2·4 \times 10^3$		
	Pd(II)	4·6	424	$8·5 \times 10^3$	5·4	yellow
		10·8				
	Fe(II)	4·6			5·0	brown
	Fe(III)	4·6	415	$4·5 \times 10^3$	5·7	yellow
PAA	Cu(I)	4·6	465–75	$3·4 \times 10^3$	4·9	red
	Co(II)	4·6	400–20	$2·9 \times 10^3$	4·8	yellow
		10·8	390	$6·3 \times 10^3$		
	Ni(II)	4·6	335	$1·0 \times 10^4$	4·2	yellow
		10·8	460	$8·3 \times 10^3$		
	Pd(II)	4·6	415	$7·4 \times 10^3$	5·4	yellow
	Fe(II)	4·6			5·3	brown
	Fe(III)	4·6			5·1	yellow

RESULTS AND DISCUSSION

3-Hydroxypicolinaldehyde is obtained by oxidation of 3-hydroxy-2-methoxypyridine with manganese dioxide in sulphuric acid medium. The aldehyde is continuously separated from the aqueous phase with chloroform in order to avoid further oxidation to acid. The earlier method[6] has been modified to increase the yield. The azine can also be obtained by methods similar to those for SAA[7] and PAA.[8]

Intramolecular hydrogen bonds exist in 3-OH-PAA and SAA both in the solid and in solution. In fact, in the infrared spectra of both azines, the typical vibration of the OH-group is suppressed so that no difference can be found from the infrared spectrum of PAA from 1800 to 4000 cm^{-1}. Although 3-OH-PAA and SAA, with a hydrophilic OH-group, would be expected to be more soluble than the corresponding benzaldehyde azine and PAA, this is not so, because of the hydrogen-bonding. In alkaline medium the solubility of SAA and 3-OH-PAA increases because the OH-groups are deprotonated.





The ultraviolet spectra of 3-OH-PAA and SAA in organic media are distinguished from the spectra of aromatic acyclic azines (BAA, PAA, 6-methyl-PAA) by a strong absorption band at 335–365 nm (Fig. 1). In aqueous solutions the presence of the hydroxyl groups in 3-OH-PAA and SAA produces bathochromic and hyperchromic shifts in alkaline media. The behaviour of PAA is quite different; in acid medium there is a bathochromic shift (Fig. 1).

In general, the acyclic azines are easily oxidized or reduced and in acid medium are easily hydrolysed to produce aldehyde and hydrazine. These facts limit the field of application. No strong redox agents can be used to change oxidation state of the metal ions, and the reagents cannot be used at pH < 1·5.

3-OH-PAA is more reactive than SAA and PAA with metal ions, probably because both hydroxyl and pyridine groups are present. Copper(II) in alkaline solution gives the same reaction as copper(I) because of reduction by the azine (*cf.* the 6-methylpicolinaldehyde azine system[4]).

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Summary—The synthesis and analytical properties of 3-hydroxypicolinaldehyde azine (3-OH-PAA), salicyladehyde azine and picolinaldehyde azine are described. 3-OH-PAA is isolated for the first time. The solubility, spectral characteristics, p*K* values and reactions with 36 cations were examined.

Zusammenfassung—Synthes und analytische Eigenschaften von 3-Hydroxypicolinaldehydazin (3-OH-PAA), Salicylaldehydazin und Picolinaldehydazin werden beschrieben. 3-OH-PAA wurde zum ersten Mal isoliert. Löslichkeiten, spektrale Eigenschaften, pK-Werte und die Reaktionen mit 36 Kationen wurdenuntersucht.

Résumé—On décrit la synthèse et les propriétés analytiques de l'azine du 3-hydroxypicolinaldéhyde (3-OH-PAA), de l'azine du salicylaldéhyde et de l'azine du picolinaldéhyde. Le 3-OH-PAA est isolé pour la première fois. On a examiné la solubilité, les caractéristiques spectrales, les valeurs de *pK* et les réactions avec 36 cations.

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CHELATING PROPERTIES OF α-OXIMINOCARBOXAMIDES—II*

syn-α-OXIMINOPHENYLACETAMIDE: COPPER(II) COMPLEXES

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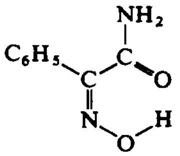
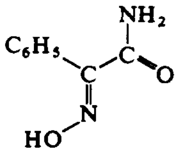
Two isomers (I and II) of α-oximinophenylacetamide (AOPA) can be obtained, depending on the synthetic route.[1]



(I)
syn



(II)
anti

The *syn* isomer gives coloured complexes with Cu(II), Ni(II) and Co(II), and the *anti* isomer does not. By application of the isosbestic-point,[2,3] continuous-variation[4,5] and molar-ratio methods[6] the nature and properties of the copper complexes have been established.

EXPERIMENTAL

Determination of the dissociation constants of α-oximinocarboxamides

The dissociation constants were determined potentiometrically by the method outlined by Albert and Sarjeant.[7] The measured pH was used to obtain a pK_a value from each titration point. Scatter was calculated as the largest deviation between the average value of K_a and any contributory value.

Determination of the formation constants of the metal chelates

Calvin and Wilson's[8] potentiometric procedure adapted from the method of Bjerrum[9] was adopted for determining formation constants. The constants log β_2 and log K_1 were calculated by the method of least squares by computer, and their difference gave a mean value for log K_2. Scatter was calculated by using the mean value of K_1 to obtain an individual value of β_2 from each titration point. The spread of K_1 was calculated from the series of individual values of K_1 obtained by use of the mean value of β_2 in the appropriate equation.

Preparation of syn-*α-oximinophenylacetamide-*O*-methyl ether*

To a solution of 8·2 g (0·05 mole) of *syn*-α-oximinophenylacetamide in 25 ml of methanol was added a solution of 2·0 g (0·05 mole) of sodium hydroxide in 2·5 ml of water and 25 ml of methanol. To this was added, dropwise, 7·2 g (0·05 mole) of methyl iodide. The mixture was set aside for three days and then the methanol was removed with a flash evaporator. The yellowish solid was treated with 30 ml of warm water, and the residue was collected by filtration and crystallized from chloroform, m.p. 102–104°. Analysis gave C 60·6%; H 5·7%; N 15·8%; Calculated for $C_9H_{10}N_2O_2$ C 60·65%; H 5·65%; N 15·72%.

RESULTS AND DISCUSSION

The Vareille isosbestic point method showed that the spectra of solutions ([Ligand]:[Cu] = 4:1) at pH 8·4 and below have λ_{max} at 625 nm. Increasing the pH above 8·4 leads to a hypsochromic shift and λ_{max} at 500 nm. The isosbestic point at 575 nm suggests the formation of two complex species.[2] Neither cupric chloride nor *syn*-AOPA shows absorption at 450–800 nm in the pH range 7·9–10·2. In acidic media, an aqueous solution of cupric chloride had λ_{max} at 700 nm. The molar absorptivity of the CuL_2 complex at 500 nm and pH 11·8 is 364 $l.mole^{-1}.cm^{-1}$.

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* Abstracted from the Doctoral Dissertation of H.M.E.F., University of Illinois at the Medical Center, Chicago, Ill., 1969.

The chelating properties of *syn*-AOPA were confirmed by spectroscopy on equimolar Cu(II) and *syn*-AOPA mixtures at various pH values. As the pH increased, the spectra showed a hypsochromic shift accompanied by a hyperchromic effect by complex formation. Further increase in pH caused precipitation of a green compound, making it impossible to obtain spectra. The green compound was isolated and its spectrum obtained in DMSO and acetone solutions, λ_{max} for both solutions being at 625 nm.

Stoichiometry of the complexes

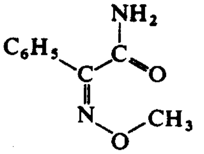
Job's method of continuous variation,[4,5] using the absorbance measured at 580 nm and pH 6·0, indicated a 1 : 1 complex. Similar measurements at 550 or 500 nm and pH 10 indicated the formation of 1 : 2 complex. Further confirmation of the stoichiometry of the 1 : 1 complex was obtained by the measurement of the concentration of hydrogen ions liberated in the complex formation, and construction of a Job plot. The molar-ratio method[6] was used to confirm the stoichiometry of the 1 : 2 complex.

Stability of the complexes

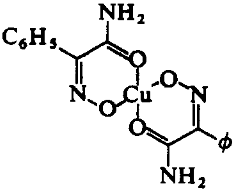
The dissociation constant (pK_a) of *syn*-AOPA was found to be 9·42 ± 0·04 (aqueous medium, 0·01*M* concentration, 25 ± 0·05°). The values of $\log \beta_2$ and $\log K_1$ were 14·32 ± 0·06 and 7·82 ± 0·07.

Structure of Cu(II) chelate of syn-*AOPA*

Since only the *syn* isomer has chelating properties, it was assumed that one point of attachment to Cu(II) is through the oxygen atom of the oxime group. This was confirmed by the fact that the *O*-methyl ether of *syn*-AOPA, III, lacks chelating properties. That the configuration of the oxime did not change during the transformation into the methyl ether was verified by regenerating the oxime from its sodium salt.



(III)



(IV)

The second site of attachment (closing the six-membered chelate ring) can be either the oxygen or the nitrogen atom in the amide group. The infrared spectrum of the 1 : 1 complex [isolated by addition of alkali to an aqueous solution containing equimolar quantities of Cu(II) and *syn*-AOPA] showed a carbonyl stretching frequency shifted to 1580 cm^{-1}, the frequency for the free carbonyl of *syn*-AOPA being at 1660 cm^{-1}. The shift to lower frequency suggests participation of the carbonyl group in metal chelate formation. Further, ethyl *syn*-α-oximinophenylacetate, the ester precursor of *syn*-AOPA, showed chelating properties. The results presented lead to the conclusion that the 1 : 2 Cu(II) chelate of *syn*-AOPA has the structure IV.

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Summary—*Syn*-α-oximinophenylacetamide forms two complexes with Cu(II), a CuL complex at pH $< 8{\cdot}4$ and CuL_2 at pH $> 8{\cdot}4$. $\log K_1 = 7{\cdot}82 \pm 0{\cdot}07$ $\log \beta_2 = 14{\cdot}32 \pm 0{\cdot}06$.

Zusammenfassung—Syn-α-oximinophenylacetamid bildet mit Cu(II) zwei Komplexe, bei pH $< 8{,}4$ einen CuL-Komplex und bei pH $> 8{,}4$ CuL_2. $\log K_1 = 7{\cdot}82 \pm 0{\cdot}07$ $\log \beta_2 = 14{\cdot}32 \pm 0{\cdot}06$.

Résumé—Le *syn*-α-oximinophénylacétamide forme deux complexes avec Cu (II), un complexe CuL à pH $< 8{,}4$ et CuL_2 à pH $> 8{,}4$. $\log K_1 = 7{\cdot}82 \pm 0{\cdot}07$ $\log \beta_2 = 14{\cdot}32 \pm 0{\cdot}06$.

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DETERMINATION OF CHROMIUM IN STEEL BY ATOMIC-ABSORPTION SPECTROMETRY WITH AN AIR-ACETYLENE FLAME

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Summary—A new atomic-absorption procedure is described for the determination of chromium, at levels up to 1%, in steel. The method involves the use of the air–acetylene flame and incorporates 8-hydroxyquinoline as a releasing agent to suppress metallic interferences. Chemical operations have been reduced to a minimum in order to provide a simple, rapid and accurate procedure.

In the steel production industry rapid analytical control of minor constituent concentrations is nowadays generally provided by either X-ray or optical emission spectrometry. However, other analytical techniques are still necessary as a standby, for checking analytical results, as a means of preparing standards, for non-routine analyses and to provide cheaper methods for use in smaller laboratories, particularly in the manufacturing industries using steel. In the past, these requirements have been largely met by wet chemical methods, including colorimetry or spectrophotometry, and polarography. However, for such applications, atomic-absorption spectrometry would appear to possess considerable advantages, and these are summarized in a review[1] of methods for the determination of many metals in steel. At the present time statistical information from single laboratories or from the results of collaborative studies between laboratories is unfortunately lacking for many otherwise satisfactory atomic-absorption procedures. The accuracy of an atomic-absorption procedure depends on the degree of interference by elements in the sample solution which are not present in the standards. For many determinations these effects are minimal but the atomic-absorption determination of chromium is subject to serious interference from other metals in all the commonly used premixed flames[2–6] and the signal is suppressed in particular by iron and nickel in the cooler flames.[2–4] Despite this, a number of procedures have been suggested for the determination of chromium in steel, using both the air–acetylene[2,3,7,8] and nitrous oxide–acetylene[6] flames in which either releasing agents or matrix matching or both are used to overcome interference effects. The most commonly used releasing agent is ammonium chloride[3,7,8] but in these cases it is still normal practice to add iron to the standard solutions to compensate for the iron in the sample solutions. Barnes[3] developed a method using ammonium chloride with aqueous standards without iron additions and his method appears to be the simplest and most rapid developed to date. Thomerson and Price[6] recently proposed a method using the nitrous oxide–

acetylene flame without releasing agent. This gives acceptable results for a wide range of steels (containing between 0·11 and 25·6% Cr) and illustrates the greater freedom from interference in this flame. Their method does, however, require metallic iron to be added to the standards to compensate for the iron in the sample solutions and the addition of potassium to the standards (*e.g.*, by use of potassium dichromate) must be avoided. Both iron and potassium interfere in chromium determination with this flame.

For the determination of low levels of chromium in steels the air–acetylene flame offers the advantages of greater sensitivity and reduced noise compared to the nitrous oxide–acetylene flame. It has been shown that the most sensitive absorption lines for chromium overlap with the CN band emission at 359 nm, which is most intense from the interconal zone of the nitrous oxide–acetylene flame and contributes significantly to noise levels in atomic absorption.[9] A method involving direct aspiration of the metal solution should therefore have better precision and a lower detection limit in an air–acetylene flame. The accuracy of the method will however depend on the degree to which interferences can be controlled when using this flame. During a detailed study of interferences in the determination of chromium by atomic absorption we have found that 8-hydroxyquinoline is more effective as a releasing agent for metallic interferences than ammonium chloride, sodium sulphate[10] or potassium pyrosulphate.[11] A procedure incorporating 8-hydroxyquinoline, for the determination of chromium in steel at levels below 1%, is described in this paper.

EXPERIMENTAL

Reagents

Reagents of the highest available purity were used to prepare 0·1% stock solutions of each metal. Where a particular anionic medium is specified, *e.g.*, sulphate, all metal solutions were prepared from the appropriate salts (*e.g.*, sulphates) and all solutions, both stock and diluted, were made up with the corresponding $10^{-3}M$ acid (*e.g.*, sulphuric acid). All solutions were prepared with water from a quartz still.

Apparatus

A Perkin–Elmer 290 Atomic Absorption Spectrophotometer was used with a single-slot tubular burner 50 mm long. A Perkin–Elmer Intensitron hollow-cathode lamp was used at a lamp current of 12 mA and a bandpass of 0·7 nm. The most sensitive line was found to be that at 357·87 nm with a sensitivity of 0·14 ppm for 1% absorption, and this was used throughout.

Interferences were studied under the optimum operating conditions of the instrument, *i.e.*, those giving the maximum absorption signal. These were established by using a 10-ppm chromium(VI) solution prepared from potassium dichromate dissolved in $10^{-3}M$ hydrochloric acid. The same absorbance was obtained for 10 ppm of chromium(VI) in hydrochloric, nitric or sulphuric acids or if the chromium solution was prepared from chromium trioxide or from chromium metal [to give chromium(III) solutions]. Maximum absorption was given at an optical-path height of 10–12 mm and 11 mm was usually selected. This height is measured at the middle of the focus of the light beam, which occurs approximately halfway along the burner and, owing to the spread of the beam (which was not restricted), represents an average of all the flame zones being irradiated.[12] The air pressure was regulated at 35 psig and the air flowmeter reading fixed at 14.00. With an acetylene pressure of 9 psig the flowmeter reading for acetylene was varied retween 14·10 (fuel-lean) and 13·50 (fuel-rich) as will be described. Maximum signal was obtained at a reading of 13·80, which is close to the position for stoichiometric flame composition.[12] Slight differences in signals were obtained for the different oxidation states of chromium and in different anionic media but only under conditions of lower observation height or a more fuel-rich flame than the optimum.

An Evans Electroselenium Ltd. 240 Atomic Absorption Spectrophotometer was also used for a series of determinations, with the same Perkin–Elmer hollow-cathode lamp at a lamp current of 8 mA. Flame conditions were optimized as described above at fixed feed-pressures of 20 psig for air and 10 psig for acetylene and a fixed air-flowmeter reading of 5·5. With the 100-mm single-slot air–acetylene burner the optimum height was found to be 6 mm and optimum acetylene flowmeter reading 1·6.

Procedure for the determination of chromium ($<1\%$) *in steel*

Stock chromium solution, 100 mg/l. Dissolve 0·2828 g of analytical-reagent grade potassium dichromate in water, transfer the solution to a 1-litre volumetric flask and dilute to the mark.

8-Hydroxyquinoline, 5% solution in 0·5M hydrochloric acid (oxine solution). Dissolve 25 g of 8-hydroxyquinoline in 25 ml of analytical-reagent grade hydrochloric acid by heating, and transfer the cooled solution to a 500-ml volumetric flask and dilute to the mark with distilled water.

Preparation of calibration solutions. Transfer by pipette 0, 5, 10, 15, 20 and 25 ml of the stock chromium solution into 100-ml volumetric flasks. To each flask add 16 ml of oxine solution and 1 ml of concentrated hydrochloric acid and dilute to the mark with distilled water. (These solutions contain the equivalent of 0, 0·05, 0·1, 0·15, 0·20 and 0·25% chromium in steel when 1 g of steel is used to prepare 100 ml of solution).

Preparation of sample solutions. Weigh 1·000 g of sample into a 150-ml beaker and dissolve it in 10 ml of concentrated hydrochloric acid. Heat for 5 min and then add dropwise 2 ml of nitric acid and heat for a further 30 min. Cool the solution and transfer to a 100-ml volumetric flask and dilute to the mark with distilled water. The small amount of material remaining undissolved at this stage may be filtered off if desired but this was found to be unnecessary.

(*a*) For steels containing less than 0·1% chromium pipette 20 ml of the sample solution into a 25-ml volumetric flask, add 4 ml of oxine solution and dilute to the mark with water.

(*b*) For steels containing 0·1–0·5% chromium, use 10 ml of sample solution and proceed as in (*a*).

(*c*) For steels containing 0·5–1% chromium, use 5 ml of sample solution and proceed as in (*a*).

Instrumental conditions. For the model PE290 the optimum conditions are as follows:

Wavelength 357·9 nm
Lamp current 12 mA
Bandpass 0·7 nm
Burner 50-mm air–acetylene, single-slot
Observation height 10–12 mm
Air flowmeter 14·00 (at 35 psig feed pressure)
Acetylene flowmeter 13·80 (at 8 psig feed pressure).

With other instruments the conditions recommended by the manufacturer should be used. The flame is correctly adjusted when the incandescence due to carbon species in the secondary reaction zone just disappears. The observation height should be slightly above the primary reaction zone.

Aspirate all solutions and plot % absorption (or absorbance) *vs* % chromium for the calibration solutions and determine the chromium content of the samples from the calibration graph. For procedure (*a*) multiply the result by $\frac{5}{4}$, for (*b*) by $\frac{5}{2}$ and for (*c*) by 5.

RESULTS AND DISCUSSION

Interferences in the determination of chromium

It is well known that many elements cause serious interference with the atomic-absorption signal of chromium in an air–acetylene flame.[2–4,7,11] In the determination of chromium in steels the most important interferences are the depressive effect due to iron and the effects of alloying elements such as nickel, vanadium, molybdenum, manganese, cobalt and titanium. Detailed studies[4,13] have shown that in nearly all cases the degree of interference is dependent on the concentration of the interfering element, the anions in the medium, the flame composition and the observation height at which absorption measurements are made. Typical interference results at a single concentration under optimum flame conditions are given in the first columns of Tables 1 and 2. Elements such as titanium and aluminium give enhancements at lower concentrations but the signal decreases at higher concentrations.[14,15] The depression due to iron is much less significant in a chloride medium than in a nitrate or sulphate medium (Fig. 1) and the same is true for the effects of nickel and cobalt. Interference effects are also confined to more fuel-rich air–acetylene flames. This is illustrated in Fig. 2 in which aluminium (100 ppm) can be observed to give a slight depression under the optimum flame condition (acetylene flowmeter reading 13·80) but an enhancement under more fuel-rich conditions. Under fuel-lean flame conditions no interference is observed for iron, aluminium or titanium and for many other elements, except at very high concentration.

Table 1. Releasing agents for the elimination of metallic interferences in the determination of 10 ppm of chromium

Interfering metals, 200 ppm, added as sulphate	% Absorption for 10 ppm of Cr			
	No releasing agent	With 2% NH_4Cl	With 1% Na_2SO_4	With 1% $K_2S_2O_7$
None	45	50	49	49
Cu(II)	28	50	49	49.5
Fe(III)	16	50	49	49
Ni(II)	21·5	50	48	48
Co(II)	17	49	49	49
Mn(II)	38	50	49	49
Mg(II)	26	50	41	42
Ti(IV)	18	21	48	48

Table 2. Effect of 0·8% 8-hydroxyquinoline as releasing agent on interferences in the determination of 10 ppm of chromium

Interferent*	% Absorption		Interferent*	% Absorption	
	No oxine	0·8% oxine		No oxine	0·8% oxine
None	45	50			
Fe(III)	42·5	50	Sr(II)	43·5	50
Fe(III), NO_3^-	18	50·5	Ba(II)	48·5	50·5
Ti(IV)	21	50	Mn(II)	42·5	50
Ti(IV), SO_4^{2-}	21	50	Mo(VI)	40·5	50
V(V)	27	50	Sn(II)	45	50·5
V(IV), SO_4^{2-}	26	43	U(IV)	49·5	50·5
Al(III)	45·5	50	Au(III)	51	50
Co(II)	42·5	50	Cd(II)	49	51
Ni(II)	42	50	*Acids*		
Cu(II)	49	51	HNO_3	44	50
Zn(II)	46	50	H_2SO_4	45	51
Na(I)	44	50	H_3PO_4	41	40
K(I)	45	50	$HClO_4$	46	51
Li(I)	45	50	HF	46	50·5
Mg(II)	42·5	50	HBr	45	51
Ca(II)	48·5	50	HI	44	51

* All metals 100 ppm in chloride medium unless otherwise specified; acids 0·1*M*.

This appears to be because the chromium species have been completely atomized under these conditions but the atomic population is depressed by conversion into chromium monoxide.[16] Interferences are therefore reduced to a minimum under fuel-lean conditions but the absorption of chromium is relatively low and poor sensitivity is obtained. The effect of observation height is analogous, with maximum interference at low flame-heights where the flame is relatively richer, and minimum interference high in the flame where the chromium signal is itself depressed owing to the formation of CrO by reaction of chromium atoms with entrained air.[16]

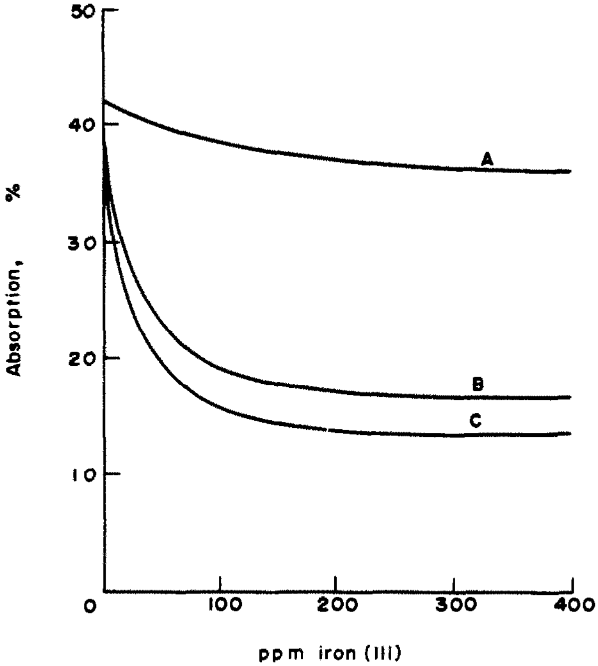

Fig. 1. Effect of increasing concentration of iron(III) on the absorption signal of 10 ppm of chromium in (*A*) chloride medium, (*B*) nitrate medium and (*C*) sulphate medium. Optimum operating conditions (PE 290).

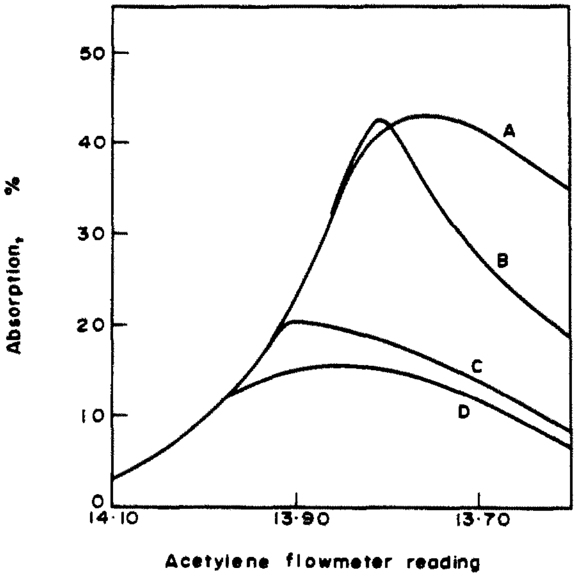

Fig. 2. Effect of flame composition on the interference of (*A*) 100 ppm of aluminium, (*C*) 100 ppm of iron(III), (*D*) 100 ppm of titanium on the absorption signal of 12 ppm of chromium (*B*). All solutions prepared in sulphate medium. PE 290 instrument.

Releasing agents

Methods which have been used to overcome these interferences include matrix matching in which the sample matrix is duplicated in the calibration standards,[2,6] use of the nitrous oxide–acetylene flame,[6] use of an oxidizing or fuel-lean air–acetylene flame, separation of chromium by extraction of chromium(VI) into organic solvents[17] and the use of releasing agents.[3,7,10,11] Matrix matching could be very complex with a wide range of steels of varying minor element content and would almost certainly lead to an overall depression with consequent loss of sensitivity. Use of the nitrous oxide–acetylene flame will give reduced sensitivity, and on its own, incomplete removal of interferences. Determination of chromium in a fuel-lean air–acetylene flame will also suffer from reduced sensitivity as will procedures based on the standard-addition technique. The introduction of a separation procedure is both tedious and liable to increase the possible sources of error and is not usually recommended unless preconcentration is also required. It is not surprising therefore that the use of releasing agents and the air–acetylene flame has proved to be the most popular technique.

Releasing agents which have been proposed include ammonium chloride,[3,7,8] sodium sulphate[10] and potassium pyrosulphate.[11] In our experience none of these is effective for all possible interfering elements, although all effectively remove the interference due to iron(III). In Table 1, some typical results are shown, which demonstrate that ammonium chloride is ineffective in removing the interference of titanium, and sodium sulphate and potassium pyrosulphate are ineffective for magnesium. Removal of the interference of other common alloying elements, Co, Ni, Cu and Mn, is, however, complete. The effect of oxine as a releasing agent is shown in Table 2 and all interferences are removed except those from vanadium in sulphate medium and from phosphoric acid. The effect of phosphoric acid also persists when ammonium chloride is used as releasing

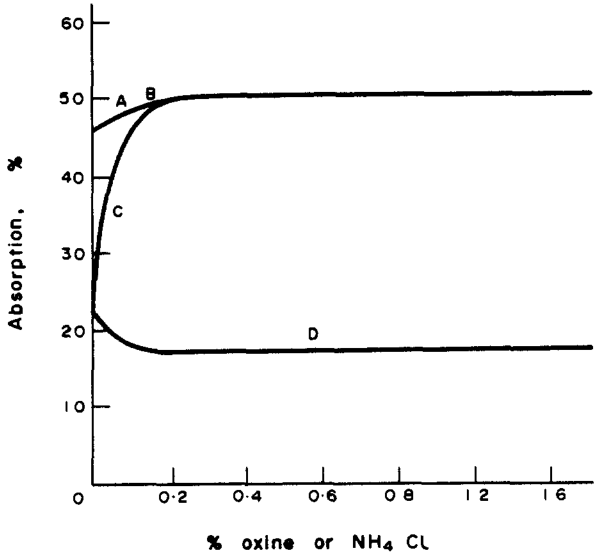

Fig. 3. Comparison of the efficiency of oxine and ammonium chloride as releasing agent in the presence of titanium.
(*A*) 10 ppm Cr + oxine, (*B*) 10 ppm Cr + NH_4Cl, (*C*) 10 ppm Cr + 100 ppm Ti + oxine, (*D*) 10 ppm Cr + 100 ppm Ti + NH_4Cl.

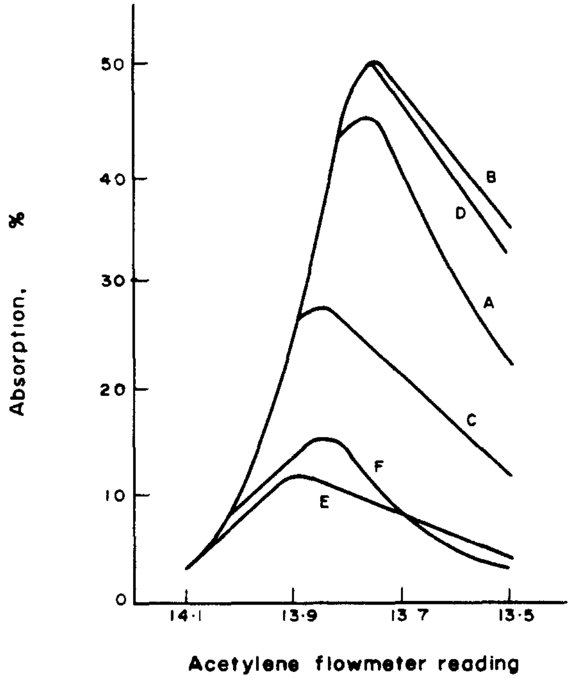

Fig. 4. Effect of flame composition on the interference of iron in determination of chromium. (*A*) 10 ppm Cr, (*B*) 10 ppm Cr + 0·8% oxine, (*C*) 10 ppm Cr + 0·5% Fe(III), (*D*) 10 ppm Cr + 0·5% Fe(III) + 0·8% oxine, (*E*) 10 ppm Cr + 0·5% Fe(II), (*F*) 10 ppm Cr + 0·5% Fe(II) + 0·8% oxine. PE 290 instrument.

agent and this acid should therefore be avoided in the preparation of sample solutions. The effect of vanadium is adequately controlled by adding at least *some* hydrochloric acid to the sample solutions. A comparison of the releasing effect of ammonium chloride and oxine on the interference of 200 ppm of titanium on 10 ppm of chromium is shown in Fig. 3. All the releasing agents, including oxine, increase the signal from chromium and therefore give a useful increase in sensitivity. The one important interference effect which is not removed by oxine or the other reagents is that due to iron(II). It can be seen in Fig. 4 that oxine has virtually no effect on the interference by iron(II). Complete oxidation of the sample solutions with nitric acid with conversion of iron into iron(III) is therefore essential. It should also be noted that the iron(III) interference is completely removed under the optimum and more fuel-lean flame conditions but not under fuel-rich flame conditions. Careful control of fuel-flow is therefore also essential. Under these conditions, the use of oxine as releasing agent is totally effective for the wide range of metallic elements and anions tested and a procedure using oxine should be both accurate and sensitive enough for the determination of traces of chromium in a wide range of steels as well as in other metals and alloys.

Determination of chromium in steels

Based on the observations above, the procedure described in the experimental section was developed and applied to a wide range of standard steels. The method was designed to be as simple and rapid as possible. Potassium dichromate is used to prepare the

Table 3. Determination of chromium in steels (PE 290 instrument)

Steel type	BCS No.	Cr found, %	Certificate value, %	Other major elements present
Mild	322	0·040, 0·041, 0·040, 0·040	0·039	—
Low alloy	401	0·075, 0·073, 0·074, 0·075	0·080	Mn, V
Mn–Mo	214/2	0·090, 0·091, 0·091 0·091, 0·090, 0·089	0·090	Mn, Mo
Mild	321	0·104, 0·104, 0·103, 0·103	0·106	Ti
Mild	320	0·130, 0·125, 0·128, 0·125	0·131	W
Low alloy	255/1	0·191, 0·191, 0·194, 0·194 0·190, 0·198	0·19	V, Ni, Mn
Low alloy	405	0·196, 0·195, 0·196, 0·198	0·21	Mn, V
Mild	325	0·213, 0·213, 0·210, 0·210	0.22	—
Low alloy	254/1	0·260, 0·265, 0·264, 0·263 0·265, 0·264	0·27	V, Ni
Low alloy	252/1	0·411, 0·415, 0·413, 0·415 0·413, 0·412	0·42	Ni, V
Low alloy	403	0·405, 0·406, 0·406, 0·400	0·42	V, Mn
Alloy	435	0·550, 0·545, 0·549, 0·545 0·550, 0·549	0·56	—
Ni–Cr–Mo	219/3	0·765, 0·770, 0·765, 0·750	0·76	Ni, Mo
Alloy	219/2	0·803, 0·800, 0·795, 0·792 0·795, 0·795	0·80	Ni, Mo
Cr–V	224/1	1·04, 1·07, 1·05, 1·06	1·06	V, Mn
Alloy	225/2	1·079, 1·080, 1·080, 1·080 1·080, 1·081	1·08	Ni, Mn
Low alloy	258/1	1·302, 1·302, 1·290, 1·288 1·290, 1·302	1·29	V
Low alloy	256	2·405, 2·381, 2·373, 2·400 2·373, 2·373	2·34	—
High-speed	241/2	5·25, 5·20, 5·23, 5·23	5·35	W, Co, V

standard solutions and no iron is added to these. The undissolved silica in the sample solutions is not filtered off but an aliquot of the final sample solution is taken and diluted with oxine solution and the appropriate amount of water. A single set of calibration solutions is used. Results are shown in Table 3, and show that the method is sufficiently accurate for a wide range of steels. Of those results which are slightly low all but one are within the range of the certificate values. The time required to complete the analysis of a batch of 9 samples was roughly 2 hr, most of the time being consumed in dissolution of the samples. The reproducibility of the method was tested on two standard steels, the results for 18 different analyses being given in Table 4. The precision shown would be considered adequate for most purposes.

Consistently low results were obtained when this procedure was tested with the EEL 240 instrument. For example, for BCS 322, 0·031% Cr was found, for BCS 214/2 0·14% Cr and for 252/1 0·29% Cr. The interference of iron in chromium determination is strongly dependent on the flame-height at which absorbance measurements are made. On the PE 290 instrument with the 50-mm burner head, a tall flame with fairly well-defined zones is obtained. Despite the vertical spread of the light beam, it is possible to select conditions where the effect of oxine completely removes the interference of iron, with the optical beam clear of the lower zones where release is incomplete. With the EEL 240 model, which has a longer and smaller flame and similar spread of the light beam, this is impossible and Fig. 5 illustrates that the signals for a chromium solution

Table 4. Reproducibility of the determination of chromium in steel (PE 290 instrument)

	BCS 255/1	BCS 225/2
Results, % Cr	0·191, 0·191, 0·194 0·194, 0·190, 0·188 0·189, 0·191, 0·190 0·190, 0·188, 0·188 0·188, 0·188, 0·186 0·186, 0·187, 0·187	1·079, 1·080, 1·080 1·080, 1·080, 1·081 1·078, 1·078, 1·075 1·085, 1·080, 1·080 1·075, 1·075, 1·075 1·080, 1·080, 1·080
Mean, % Cr	0·189	1·079
Certificate value, % Cr	0·190	1·08
Standard deviation, % Cr	0·0023	0·0025
Relative standard deviation, %	1·2	0·2
95% Confidence limits, % Cr	±0·0048	±0·0052

containing oxine and for the same solution with 0·8% iron present are not identical at any fuel-flow. The difference is smallest in a fuel-lean flame but a residual depression is still present under these conditions. For analysis using instruments of this type it is therefore recommended that the standard solutions be made up with oxine as in the procedure described above but also containing an amount of iron equivalent to that in the sample solutions. Results are then obtained which are just as adequate as those obtained with the PE 290 and the original procedure (Table 5) although analysis for a batch of samples takes a little longer.

The phenomenon above illustrates the danger of taking a procedure developed on one instrument and expecting it to give accurate results on another instrument. In either

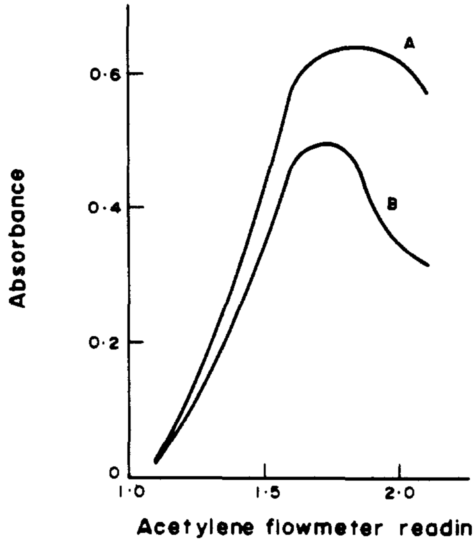

Fig. 5. Effect of flame composition on the releasing effect of oxine in the presence of iron (EEL 240 instrument).
(*A*) 25 ppm Cr + 0·8% oxine, (*B*) 25 ppm Cr + 0·5% iron(III) + 0·8% oxine.

Table 5. Determination of chromium in steels (EEL 240 instrument)

BCS No.	Cr found, %	Certificate value, %
322	0·040, 0·040, 0·040	0·039
214/2	0·091, 0·089, 0·090	0·09
255	0·195, 0·195, 0·192	0·19
252/1	0·420, 0·422, 0·427	0·42
225/2	1·080, 1·085, 1·040	1·08

case the procedure is more sensitive than the equivalent nitrous oxide–acetylene flame procedure and has a detection limit of 0·001% chromium although there are few steel or iron samples for which analysis at this level is necessary.

Acknowledgements—We wish to thank Evans Electroselenium Ltd for the loan of the EEL 240 Atomic Absorption Spectrophotometer used for part of this work. We would also like to thank Mrs. B. J. Craik for technical assistance with part of the work.

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Zusammenfassung—Zur Bestimmung von Chrom in Mengen bis herauf zu 1% in Stahl wird ein neues Atomabsorptionsverfahren beschrieben. Dabei wird eine Luft-Acetylen-Flamme verwendet; 8-Hydroxychinolin dient als freisetzendes Agens zur Unterdrückung von Strörungen durch andere Metalle. Um ein einfaches, rasches und genaues Verfahren zu gewährleisten, wurden die chemischen Operationen auf ein Minimum verringert.

Résumé—On décrit une nouvelle technique d'absorption atomique pour le dosage du chrome, à des teneurs montant jusqu'à 1% dans l'acier. La méthode comprend l'emploi de la flamme air-acétylène et incorpore la 8-hydroxyquinoléine comme agent destiné à supprimer les interférences métalliques. Les opérations chimiques ont été réduites à un minimum afin de fournir une technique simple, rapide et précise.

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PHOTOMETRIC COMPLEX-FORMATION TITRATIONS OF SUBMICROMOLE AMOUNTS OF METALS—III

BACK-TITRATIONS

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Summary—In this paper the theoretical considerations on photometric complex-formation titrations of submicromole amounts of metals in the presence of an approximately equivalent amount of indicator are completed by considering the back-titration of a metal in the presence of another metal which is displaced by the titrant. The simultaneous formation of different metal-indicator complexes M_pI_q is taken into account. Titration conditions have been derived, with which optimal experimental conditions can be selected. Optimum conditions for the analysis of an indium-ytterbium alloy are deduced from the theory.

The first paper of this series[1] discussed the photometric titration of a metal M with a ligand L in the presence of an approximately equivalent amount of indicator I which formed a 1 : 1 complex, MI. A tangent procedure was adopted for the determination of the end-point and optimum titration conditions were deduced from graphs.

In the second paper[2] the presence of two other metals P_1 and P_2 was discussed. It was found that the end-point can only be determined when the reaction of P_1 and P_2 with L during the titration of M is negligible. Either metal or both may react either before the titration starts or after the titration has been completed.

The formation of different metal–indicator complexes was considered elsewhere. It was found that systematic deviations may be expected when M_2I_n complexes are formed ($n = 1$ or 2).[3,4] In spite of lack of data about the molar absorptivities and the conditional constants of the different complexes MI, MI_2, M_2I and M_2I_2 it proved possible to draw quantitative conclusions if the different complexes were formed simultaneously.[5]

The object of this paper is to present rules which enable optimum conditions for back-titrations to be selected.

Some investigators[6,7] have discussed back-titrations, but their papers merely deal with the calculation of titration errors and are meant for titrations in the presence of negligible amounts of indicator. To the best of our knowledge no complete system of equations has been published for back-titrations in which species M_pI_q, where p and $q = 1$ or 2, are involved, although such species are common. Therefore this also will be dealt with. The case to be considered is of a metal N that is determined by back-titrating L with a metal M in the presence of P. It is supposed that the conditional constants of the metal complexes with the ligand L decrease in the sequence N, M, P and that P and I do not complex. An excess of L with respect to N is added together with an amount of indicator I roughly equivalent to the total amount of L (or N). When M is added, free L, if present, will be complexed first, after which P will be displaced from its complex with L near the end-point. The end-point is found by the tangent procedure; the intersection of the tangent drawn just after the equivalence point, with the extrapolated linear portion of the curve before the equivalence point, is taken. This procedure is well suited for a mathematical treatment, which can be related directly to the titration conditions.

It will be shown that the titration conditions specific for the metal–indicator complexes are actually independent of the presence of N and P, and that these conditions are exactly the same as for the direct titrations.[5] When the conditions are specific for the back-titrations it can be shown that the conclusions about the presence of N and P are not affected when the restriction $p = q = 1$ is imposed. Therefore, in the first part of the paper the possible existence of different metal–indicator complexes is taken into account; in the second part MI is the only metal–indicator species considered.

At the end of this paper the selection of experimental conditions for the analysis of a Yb–In alloy will be used to illustrate the application of the theory.

THEORY

Symbols and terminology are similar to those used previously.[1–4] In back-titrations the total concentration of the ligand C_L is kept constant, while C_M changes during the titration. Therefore, in contrast with the theory for direct titrations, C_L instead of C_M is used to make the different quantities dimensionless.

We introduce

(*a*) reduced concentrations $m = \frac{[M]}{C_L}$, $l = \frac{[L]}{C_L}$, $mi = \frac{[MI]}{C_L}$, $m_2 i = \frac{[M_2I]}{C_L}$, $mi_2 = \frac{[MI_2]}{C_L}$,

$m_2 i_2 = \frac{[M_2I_2]}{C_L}$, $i = \frac{[I]}{C_L}$, $ml = \frac{[ML]}{C_L}$, $pl = \frac{[PL]}{C_L}$, $p = \frac{[P]}{C_L}$ *etc.*

$\beta = C_I/C_L$ = relative amount of indicator.

$\gamma_P = C_P/C_L$ = relative amount of metal P, and so on.

$f = C_M/C_L$ = titration parameter.

f_n is the value of the nth term in the equation $f = f_1 + f_2 + \cdots + f_n + \cdots$.

(*b*) reduced conditional constants

$$Z_L = C_L \,.\, K_{ML} = \frac{ml}{m \times l} \tag{1}$$

$$Z_{M_pI_q} = C_I^{(p+q-1)} \,.\, K_{M_pI_q} = \beta^{(p+q-1)} \,.\, \frac{m_p i_q}{m^p \times i^q} \tag{2}$$

$$Z_{PL} = C_P \,.\, K_{PL} = \gamma_P \,.\, \frac{pl}{p \times l} \quad \text{and} \quad Z_{NL} = C_N \,.\, K_{NL} = \gamma_N \,.\, \frac{nl}{n \times l} \tag{3}$$

It is assumed that N and P do not react with the indicator.

The reactions between M and I, and P, N and L are separately taken into account as "competing main reactions." This means that no side-reaction coefficients for these reactions should be introduced in the conditional constants mentioned above. All other side-reactions in which the reactants are involved must be incorporated.

The following mass balances hold:

$$\beta = i + mi + m_2 i + 2mi_2 + 2m_2 i_2 \tag{4}$$

$$1 = l + ml + nl + pl \tag{5}$$

$$f = (mi + mi_2 + 2m_2 i + 2m_2 i_2) + m + ml \tag{6}$$

$$\gamma_P = p + pl \quad \text{and} \quad \gamma_N = n + nl \tag{7}$$

The most convenient way to represent the relation between the titration parameter f and the different variables $m_p i_q$ is by means of a parameter representation. In this paper l is used as the parameter which leads to the following sequential calculation scheme.

Elimination of p and n from (3) and (7) yields

$$pl = \gamma_P\left(\frac{l}{l + \gamma_P/Z_{PL}}\right) \quad \text{and} \quad nl = \gamma_N\left(\frac{l}{l + \gamma_N/Z_{NL}}\right) \tag{8}$$

Rearranging (5) gives

$$ml = 1 - l - nl - pl \tag{9}$$

and (1) gives

$$m = \frac{ml}{l} \cdot \left(\frac{1}{Z_L}\right) \tag{10}$$

From (2) and (4) we derive

$$\left(2m^2 \frac{Z_{M_2I_2}}{\beta^3} + 2m \frac{Z_{MI_2}}{\beta^2}\right) i^2 + \left(1 + m \cdot \frac{Z_{MI}}{\beta} + m^2 \cdot \frac{Z_{M_2I}}{\beta^2}\right) \cdot i - \beta = 0 \tag{11}$$

from which i can be found as a function of m and so of l. From

$$mi = m \cdot i \cdot (Z_{MI}/\beta) \tag{12}$$

$$mi_2 = m \cdot i^2 \cdot (Z_{MI_2}/\beta^2) \tag{13}$$

$$m_2 i = m^2 \cdot i \cdot (Z_{M_2I}/\beta^2) \tag{14}$$

$$m_2 i_2 = m^2 \cdot i^2 \cdot (Z_{M_2I_2}/\beta^3) \tag{15}$$

and equation (6) we can finally compute mi, mi_2, $m_2 i$, $m_2 i_2$ and f as a function of l. The calculation scheme has been used as the basis for an iterative procedure in a computer programme, with which mi, mi_2, $m_2 i$ and $m_2 i_2$ can be calculated for given values of f. The programme has been used for checking whether the approximations in the relations derived hereafter are justifiable. Approximate relations are used because they reveal the magnitude of the titration error and the shape of the curve more readily than the exact relationships do. Therefore ml is eliminated from equations (5) and (6) to give

$$f = 1 + (mi + mi_2 + 2m_2 i + 2m_2 i_2) + (m - 1) - nl - pl \tag{16}$$

which in the absence of N and P becomes

$$f = 1 + (mi + mi_2 + 2m_2 i + 2m_2 i_2) + (m - l) \tag{17}$$

Previously[5] titration conditions were derived from the analogous equation

$$\begin{aligned} f &= 1 - (mi + mi_2 + 2m_2 i + 2m_2 i_2) - (m - l) \\ &= f_1 + f_2 + f_3 \end{aligned} \tag{18}$$

by calculating the systematic error with

$$f_e = f_0 - (m_p i_q)_0 \cdot \left(\frac{\mathrm{d}f}{\mathrm{d}m_p i_q}\right) \tag{19}$$

A similar procedure will be followed with respect to equations (17) and (16). There are some essential differences, however, between equations (18) and (17).

First, C_L was introduced to make the variables in equation (18) dimensionless, while C_M was used in equation (17). It implies that equation (19) has correspondingly to be adapted before it can be applied to equation (17). The adapted version, however, is identical to (19), as $m_p i_q$, which is proportional to $M_p I_q$ appears both in the numerator and in the denominator. So (19) can be used directly in combination with (17) and (16).

Secondly the different terms in (17) have different signs in comparison with (18). The titration conditions, however, do not depend upon the sign of the terms f_1, f_2 and f_3. In equation (19) f_e is linearly related to f, so the total systematic deviation Δf_e, differing from f_e only by a constant, is additively composed from the contributions of the separate terms f_1, f_2 and f_3. It was proposed in the previous paper that the absolute values of the separate contributions Δf_1, Δf_2 and Δf_3 should each be smaller than 0·5‰, because small values of Δf_e which are caused by compensation of large Δf_i-values can generally be neglected. It ensures that the derivation of the titration conditions, which, as previously,[5] will be based on $|\Delta f_i| <$ 0·5‰, is irrespective of the sign of the terms f_1, f_2 and f_3. It follows that equation (17) will provide analogous information, in an identical notation, the only difference being that C_M should be replaced by C_L for application to back-titrations. It implies that general conclusions, such as about a possible systematic error when M_2I_n predominates, remain valid. Furthermore, as C_L does not occur in the titration conditions following from f_2 in (17), analogously identical conditions will follow from the term f_2 in equation (16).

The contributions to the systematic error originating from the third and fourth term in (16) (Δf_3 and Δf_4) will generally be a function of m, as pl, nl and m are functions of l [(equations (8)–(10)] from which l can be calculated. From equation (11) and each of the equations (12)–(15) it follows that the predominantly occurring species $m_p i_q$ is a function of only m [and reversely $m = f(m_p i_q)$]. This gives us the possibility of calculating first Δf_3 and Δf_4 as a function of m and afterwards to replace m. It is a rather complicated procedure and will not be followed here. A more convenient way is to consider first the case where only MI is formed. In this case equation (16) simplifies to

$$f = 1 + mi + m - l - nl - pl \tag{20}$$

In order to get an idea about the influence of the metals N and P on the titration a number of titration curves have been computed. For convenience this was done for the case of only one metal, Q, in solution, to which L is added in excess ($\gamma = 0{\cdot}8$). It is supposed that $\beta = 0{\cdot}5$, $\log Z_L = 8$ and $\log Z_{MI} = 2$. The result for different values of Z_{QL}

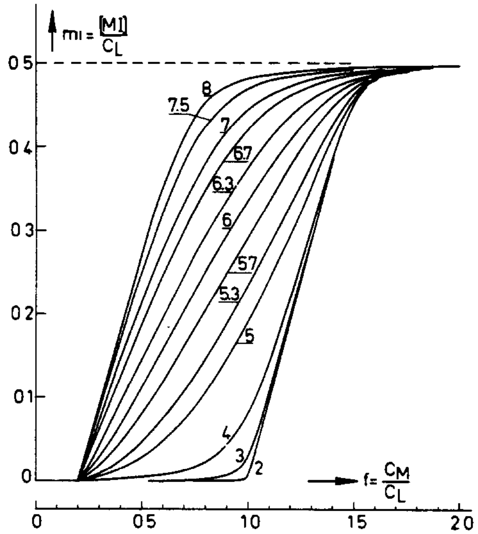

Fig. 1. Theoretical titration curves for the back-titration of one metal Q by a metal M. The curves were all found by computer and based on $Z_L = 10^8$, $Z_{MI} = 100$, $\beta = C_I/C_L = 0{\cdot}5$ and $\gamma = C_Q/C_L = 0{\cdot}8$ (25% excess of ligand). The numbers near the lines correspond to the log Z_{QL} values.

is represented in Fig. 1. It can be concluded that an end-point can only be determined when Z_{QL} is about 10 times Z_L/Z_{MI} or when Z_{QL} is small with respect to Z_L/Z_{MI}. The first situation is assumed to occur with N and the second with P. It will be obvious that when both metals are present in solution an end-point will only be found with sufficient accuracy when N is not displaced by M and P is completely displaced from PL.

In what follows, titration conditions will be derived which are based on these two cases and which have simultaneously to be satisfied.

First the corresponding approximate relation between f and mi will be derived. For reasons previously stated,[2] pl in equation (8) may be approximated by

$$pl = Z_{PL}\,.\,l \tag{21}$$

Substitution in (9) gives

$$\begin{aligned} ml &= 1 - l(1 + Z_{PL}) - \gamma_N\left(\frac{l}{l + \gamma_N/Z_{NL}}\right) \\ &= (1 - \gamma_N) - l(1 + Z_{PL}) + \gamma_N\left(\frac{1}{Z_{NL}\,l/\gamma_N + 1}\right) \end{aligned} \tag{22}$$

Equation (10) can be written as

$$ml = l\,.\,Z_L\,.\,m \tag{23}$$

Substitution of l from (23) in the second term in (22) leads to

$$ml = \frac{(1 - \gamma_N)}{1 + \dfrac{(1 + Z_{PL})}{Z_L}\cdot\dfrac{1}{m}} + \frac{\gamma_N}{\{l\,.\,Z_{NL}/\gamma_N + 1\}\left\{1 + \dfrac{(1 + Z_{PL})}{Z_L}\cdot\dfrac{1}{m}\right\}} \tag{24}$$

It is rather laborious to eliminate l from the last term. In connection with the tangent procedure we are only interested in the region just after the equivalence point, when the last term of equation (24) and its derivatives are small in comparison with the first term. Substitution of a proper approximation of l in equation (24) is satisfactory in practice. A convenient way to estimate l is by means of an iterative procedure from equations (23) and (24). From the approximate ml equation, equation (9) and equation (20) the following mi–f relation has finally been derived

$$f = \{(1 - \gamma_N) + mi\} + \frac{mi}{Z_{MI}(1 - mi/\beta)} - \frac{(1 - \gamma_N)}{mi} \cdot \frac{(1 + Z_{PL})Z_{MI}}{Z_L} + \gamma_N \left\{ \frac{a\left(\frac{mi}{1 - mi/\beta}\right)}{b\left(\frac{mi}{1 - mi/\beta}\right) + 1} \right\} = f_1 + f_2 + f_3 + f_4 \quad (25)$$

in which

$$a = \left(\frac{\gamma_N}{1 - \gamma_N}\right)\left(\frac{Z_L}{Z_{MI} Z_{NL}}\right) \quad (26)$$

and

$$b = a/(1 - \gamma_N) \quad (27)$$

[The approximation used for l is $l = (a/b + aZ_{MI} \,.\, m)/Z_L m$.]

Apart from a constant factor $(1 - \gamma_N)$ and their sign, the terms f_1, f_2 and f_3 in equation (25) are identical to those in previous papers.[1,2] As we discussed earlier in this paper the sign does not influence the derivation of the titration conditions and so analogous conditions can be derived, differing only by a factor $(1 - \gamma_N)$ [see equations (31) and (32)].

The term f_4 reflects the possible replacement of N from NL by M and does not depend linearly on mi, so it gives a contribution to the systematic deviation which can be found with equation (19). We obtain

$$\Delta f_4 = \gamma_N \cdot a\left(b - \frac{1}{\beta}\right)\left(\frac{mi}{b \cdot mi + 1}\right)^2 \quad (28)$$

It is difficult to be sure that the approximations used to derive (25) and (28) are reasonable. For this reason we calculated the systematic deviations Δfe from the ideal value $(1 - \gamma_N)$ for a variety of cases, by computer, with a programme based on the original set of equations (4)–(15). The results are shown in Table 1.

It was found that when $a \ll 1$, which occurs when $\gamma_N \ll 1$ or $Z_{NL} \gg Z_L/Z_{MI}$, the exact value of Δf_e agreed with the approximate value of $(\Delta f_1 + \Delta f_2 + \Delta f_3)$ for all cases of practical interest ($\Delta f_e < 1\%$) with respect to variation of Z_{NL}, Z_L and Z_{MI}. So Δf_4 is negligible in these cases.

Secondly it can be noted that when $(\Delta f_1 + \Delta f_2 + \Delta f_3)$ is negligible, $\Delta f_e \sim \Delta f_4$. In Table 1 a particular combination of Z_{NL}, Z_{MI}, Z_L and γ_N is presented, related to this case. The importance of the table is that if Δf_1, Δf_2 and Δf_3 remain sufficiently small ($<0.5\%$) and this occurs when the titration conditions (31) and (32) are satisfied as they should

Table 1. Comparison of values obtained by exact and approximate methods of calculation

		$\beta = 0{\cdot}5$		$\beta = 2$		$\beta = 5$	
$\log Z_{NL}$	a	Exact solution	Eq. (28)	Exact solution	Eq. (28)	Exact solution	Eq. (28)
8·0	0·04	−0·001	−0·001	0	0	0	0
7·5	0·1	−0·003	−0.002	0	0	0	0
7·0	0·4	−0·002	0	+0·003	+0·003	+0·003	+0·004
6·7	0·8	+0·002	+0·007	+0·009	+0·011	+0·010	+0·012
6·3	2	+0·019	+0·034	+0·030	+0·038		
6·0	4	+0·047	+0·07				
5·7	8	+0·093	+0·10				

The systematic deviations Δf_e from the value $(1 - \gamma_N)$ have been calculated with $Z_L/Z_{MI} = 10^6$, $Z_{MI} = 100$, and $\gamma_N = 0{\cdot}8$. The tangent point is chosen as usual at $mi = 0{\cdot}1$. By the proper choice of these values the contribution of f_1, f_2 and f_3 to Δf_e is negligible. Therefore the values of Δf_e in the columns headed "exact solution" which are found with the original set of equations, can be directly compared with the other columns representing Δf_4, found with equation (28).

be in practice, the Δf_e values hardly change when for a fixed value of a other combinations of Z_{NL}, Z_{MI}, Z_L and γ_N are chosen. Even around the borderline case $\Delta f_2 \sim \Delta f_3 \sim \Delta f_4 \sim 0{\cdot}2\%$, which has a low probability, the difference between the exact and the approximate values for Δf_e is less than 10%. So it can be concluded that equations (25) and (28) are satisfactory approximations in all cases of practical interest ($\Delta f_e < 1\%$).

From equation (28) it can be concluded that with $mi \sim 0{\cdot}1$ and $0{\cdot}5 < \gamma_N < 0{\cdot}8$ as usual, the limiting value of a will be $\sim 0{\cdot}4$ (see Table 1). From this the following titration condition follows

$$R = \log Z_{NL} - \log(Z_L/Z_{MI}) > 1 \tag{29}$$

It can be remarked that the limit of 1 in (29) is somewhat arbitrary. In some cases 0·7 may also be satisfactory. For practical purposes this is not important because the uncertainty in the logarithms of the conditional constants and consequently in the value of R is usually larger than 0·3. This also means that for practical purposes the difference between C_L and C_N can be neglected in equation (29) which then can be transformed into the more suitable equation[1,2]

$$R = \log K_{N'L'(NL)'} - \log {}^{\text{Ind}}K_{ML} > 1 \tag{30}$$

where

$${}^{\text{Ind}}K_{ML} = K_{M'L'(ML)'}/Z_I = K_{M'L'(ML)'}/\chi_I$$

The titration conditions following from the other terms are[1,2]

$$Z_{MI} > 10 \tag{31}$$

$$T = \log\left\{\frac{Z_L}{(1-\gamma_N)(1+Z_{PL})Z_{MI}}\right\} = \log\left\{\frac{C_L\,{}^{\text{Ind}}K_{ML}}{(1-\gamma_N)(1+Z_{PL})}\right\} > 3{\cdot}5 \tag{32}$$

It can be noted that from (29) and (32) it still follows that

$$\log Z_{NL} - \log Z_{PL} > 4{\cdot}5 + \log(1-\gamma_N) \sim 4 \tag{33}$$

which implies that when the difference in conditional constants for P and N is too small, the search for a suitable back-titrant is useless.

It must be noted that the term f_4 in (25) has been derived as a function of m in which finally $m = f(mi)$ has been substituted. This means first that (25) [and (28) too], when written as $f(m)$, does not change when other metal–indicator complexes occur in amounts small relative to MI. It only has to be kept in mind that the actual systematic deviation will be smaller than (or equal to) the value calculated for the most unfavourable situation.[5] Secondly it implies that when other metal-indicator complexes predominate, the fourth term in equation (25) changes correspondingly. In the case of MI_2 the factor $(1 - mi/\beta)$ has to be replaced by $(1 - 2mi/\beta)^2$ and Z_{MI} by Z_{MI_2}. Equation (28) then becomes

$$\Delta f_4 = \gamma_N \cdot a\left(b - \frac{4}{\beta}\right)\left(\frac{mi_2}{b \cdot mi_2 + 1}\right)^2 \tag{34}$$

For values of β four times larger than in the previous case the same conclusions can be drawn. Usually, when MI_2 is formed more indicator will be added so analogous titration conditions can be deduced; only Z_{MI} has to be replaced by Z_{MI_2} in the conditions (30)–(32).

When M_2I_2 (or M_2I) predominates, equation (29) will change into

$$R = \log Z_{NL} - \log(Z_L/\sqrt{Z_{M_2I_2}/\beta}) > 1 \tag{35}$$

as can be proved in the same way as for equation (29). The replacement of Z_{MI} by Z_{MI_2} or $(Z_{M_2I_2/\beta})^{1/2}$ is a familiar one if the titration conditions (43), (49), (59) and (63) in reference 5 are compared with each other. In most cases the formation of M_2I_2 leads to systematic deviations, as the condition (60) in ref. 5 is not satisfied for most metals. Only Ce(III) in combination with Xylenol Orange seems to be an exception. Ce(III) is found to be a very suitable back-titrant as Z_L is relatively small and $\varepsilon_{M_2I_2}$ is rather high.

If more than two metals are present in solution the theory can be extended correspondingly. The result will be similar to that for the direct titrations. For every metal belonging to the class P, titration condition (32) has to be extended.[2] For every metal belonging to the class N, an extra R-condition will arise.

In this section it has been assumed that the indicator does not react with the metals N or P. This is a necessary condition for P, as otherwise the absorption of PI interferes in the end-point determination. When the metal belongs to the class N the excess of L will mostly prevent the formation of NI. The tendency to form NI then does not interfere; it has only to be taken into account by introducing a side-reaction coefficient in Z_{NL} in equation (30).

The selection of experimental conditions

As has already been demonstrated,[1,2] the diagrams enable optimum experimental conditions to be selected. This will be illustrated for the analysis of an ytterbium–indium alloy. It was found that bismuth is suitable for back-titration in determination of indium, and lead is suitable for total ytterbium plus indium. The stability constants of the complexes In–EDTA and Yb–EDTA are $\log K_{InY} = 25{\cdot}0$, $\log K_{YbY} = 19{\cdot}5$ and $\log K^{H}_{YbY} = 2{\cdot}7$.[7] According to equation (33) the difference is sufficiently large for a back-titration. In Fig. 2 the combined diagram is presented for the metals In, Yb and Bi[8] in combination

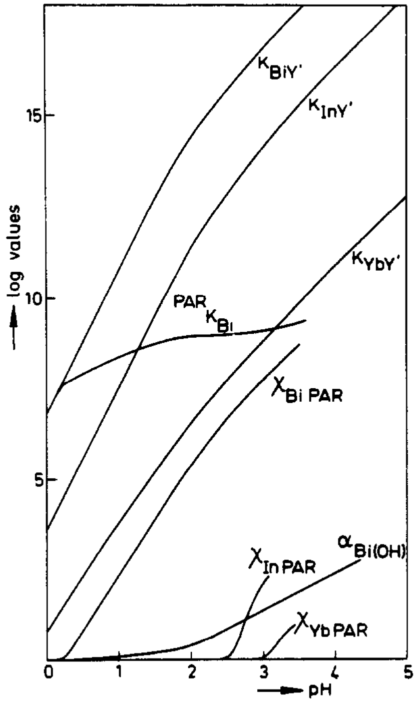

Fig. 2. Diagram representing the influence of the medium on the K', χ and α-values for indium, ytterbium and bismuth. $C_{PAR} = 10^{-4}M$. In calculation of log K' only side-reactions in which ML and L involved are taken into account.

with PAR, based on results obtained by Sommer and co-workers.[9-11] The χ-lines[1] are based on a PAR concentration of $10^{-4}M$. Bismuth and PAR mainly form two complexes BiPAR and BiHPAR in the range pH = 0·5–3, which need not be distinguished.[5] The other complexes[9] are formed to a negligible extent and need not be taken into account.[5] In the range pH > 0·5 Z_{BiPAR} exceeds 10. In Fig. 3 the values of Z_{BiPAR}, T and R from equations (30), (31) and (32) are presented for the particular case $C_{Yb} = 0{\cdot}5 \times 10^{-4}M$, $C_{In} = 1{\cdot}5 \times 10^{-4}M$, $C_L = 2 \times 10^{-4}M$ (thus $\gamma_N = 0{\cdot}75$) and $C_{PAR} = 10^{-4}M$ (so $\beta = 0{\cdot}5$).

It follows that the titration conditions are only simultaneously satisfied in the pH-range 1·6–2·0. It was found experimentally that the titrations could conveniently be performed between pH 1·3 and 1·9.

The sum of ytterbium and indium has also been determined by back-titration, as the direct titration of ytterbium with PAR or Xylenol Orange as indicator is rather slow. The back-titration can conveniently be performed with lead or cerium(III) and Xylenol Orange. Ytterbium and indium both form complexes with Xylenol Orange. No data are available about their conditional constants. From some preliminary investigations we found that the complexes are weaker than the corresponding PAR complexes. This implies that both $^{XO}K_{In}$ and $^{XO}K_{Yb}$ remain sufficiently large to satisfy both R conditions (log $^{XO}K_{Pb}$ = 8·5 at pH 5·5[1]).

The ytterbium–indium ratio can be determined with a precision of 0·8% from 10 titrations of indium and 10 titrations of (indium + ytterbium). For each titration 2-ml quantities from an acid stock solution containing about 10 mg of alloy in 100 ml were titrated in a 12-ml spectrophotometer cell (2 × 2 cm cross-section).

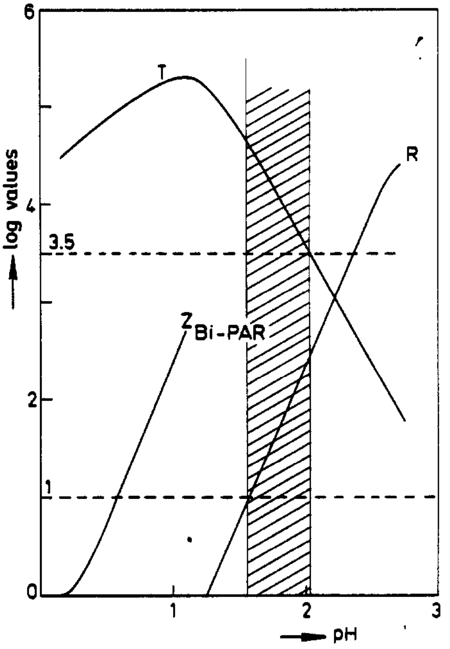

Fig. 3. Graphical representation of T, R and Z_{MI} for a proper selection of final pH in combination with the titration conditions (30), (31) and (32).

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Zusammenfassung—Die theoretische Erörterung der photometrischen Komplexbildungstitration von Submikromol-Mengen Metall in Gegenwart einer etwa äquivalenten Indikatormenge wird vervollständigt durch die Betrachtung der Rücktitration eines Metalls in Gegenwart eines anderen Metalls, das durch den Titranten verdrängt wird. Die gleichzeitige Bildung verschiedener Metall-Indikator-Komplexe M_pI_q wird berücksichtigt. Es wurden Titrationsbedingungen abgeleitet, mit denen optimale Versuchsbedingungen ausgewählt werden konnen. Aus der Theorie werden die optimalen Bedingungen für die Analyse einer Indium–Ytterbium–Legierung entnommen.

Résumé—Dans ce mémoire, on complète les considérations théoriques sur les titrages photométriques par formation de complexe de quantités submicromolaires de métaux en la présence d'une quantité approximativement équivalente d'indicateur en envisageant le titrage en retour d'un métal en la présence d'un autre métal qui est déplacé par l'agent de titrage. On tient compte de la formation simultanée de différents complexes métalindicateurs M_pI_q. On en a déduit des conditions de titrage, avec lesquelles on peut choisir des conditions expérimentales optimales. On déduit de la théorie les conditions optimales pour l'analyse d'un alliage indium–ytterbium.

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ELECTROANALYTICAL STUDY OF THE CATALYTIC ENHANCEMENT BY ANTIMONY(III) OF THE ANODIC WAVE FOR BROMIDE IN ACIDIC MEDIA

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Summary—The results are given of a study using a rotating disk electrode to develop an amperometric method for the determination of Sb(III) in acidic media, based on the catalytic increase of the limiting anodic current for Br^-. Analytical application was successful provided the bulk concentration of antimony(III) was less than that of bromide. The enhancement technique was also applied to the determination of Sb(III) injected into a stream of electrolyte passing through a platinum coulometric detector.

Instrumental methods of chemical analysis based on electrochemical measurement of Faradaic current offer the advantages of simplicity and low cost for instrumentation, and a very high sensitivity which is nearly uniform for determinations of all electroactive species. As a result, there is renewed interest in electroanalysis as the basis for automatic continuous analysis such as monitoring of effluent streams. There are numerous electroanalytical procedures for determination of ions of transition elements and heavy metals in a large variety of aqueous media, with electrodes of various types, but relatively few for elements in Groups IVA, VA, and VIA which show amphoteric behaviour in aqueous solution. Species which hydrolyse extensively are frequently electrolysed by irreversible processes. For example, the oxidation of antimony(III) to antimony(V) is totally irreversible at a platinum electrode in acidic media.

A few electroanalytical methods for determining antimony(III) have been described. Coulometric determinations with electrogeneration of bromine at constant current in $2M$ hydrochloric acid were reported by Brown and Swift.[1] Lingane and Bard[2] and Wise and Williams[3] determined antimony(III) coulometrically at pH 7–8 with electrogenerated iodine. Kostromin and Akhmentov[4] determined antimony(III) in $2M$ sulphuric acid and $1M$ hydrochloric acid with electrogenerated dichromate. Elemental antimony can be electrodeposited on platinum and mercury cathodes by reduction of antimony(III) in suitable media, and polarographic,[5,6] electrogravimetric,[7] and electrolytic[8–11] methods have been based on this reaction. We have judged the use of dropping mercury electrodes and mercury pool electrodes to be unsuitable for analysis of effluent streams because of the physical instability of the liquid electrodes at high stream velocities. Deposition of elemental antimony at a platinum electrode,[7] is also not useful for amperometric determination of antimony(III) in acidic media because of the simultaneous evolution of hydrogen.

We report here the results of a study to develop an electrolytic method for the determination of antimony(III) by using a platinum electrode which does not require deposition of elemental antimony and which can be applied for continuous analysis of effluent streams. The technique is based on the measured increase, caused by antimony(III), of the limiting current for the oxidation of bromide to bromine in acidic media. The mechanism for the Faradaic reaction is described by equations (1) and (2). According to this mechanism, bromide serves essentially as a catalyst for the electrolysis of antimony(III).

$$\text{Platinum electrode: } 2Br^- \longrightarrow Br_2 + 2e \tag{1}$$

$$\text{Diffusion layer: } Sb(III) + Br_2 \overset{k}{\rightleftharpoons} 2Br^- + Sb(V) \tag{2}$$

Such a phenomena is commonly known as a catalytic enhancement. The use of catalytic enhancement for electroanalytical determinations of many electro-inactive species was described by Mairanovskii.[12]

A rotating platinum disk electrode was chosen because the hydrodynamics at a rotating disk are known and because the rates of convective transport can be precisely controlled and easily changed by controlling the rate of rotation of the electrode.[13] It is necessary to study the effect of variations of fluid velocity on the applicability of any detector used in a fluid stream. If the rate of the forward reaction in equation (2), k, is fast relative to the rate of mass transport in the vicinity of the electrode, and if the equilibrium constant for the homogeneous reaction is large, the concentrations of bromide and antimony(III) at the surface of the electrode are zero for an electrode potential in the region of the limiting anodic wave for bromide. Thus the total current in the electrode is limited by the rates of convective-diffusional transport of bromide and antimony(III) and independent of the rate constant, as described by equation (3).

$$I_{tot} = n_{Br^-} FA[\text{flux } Br^-] + n_{Sb(III)} FA[\text{flux } Sb(III)] \tag{3}$$

For a rotating disk electrode, equation (3) is written as

$$I_{tot} = 0{\cdot}62 FA\nu^{-1/6}\omega^{1/2}[n_{Br^-} D_{Br^-}^{2/3} C_{Br^-}^{b} + n_{Sb(III)} D_{Sb(III)}^{2/3} C_{Sb(III)}^{b}] \tag{4}$$

where

I = Faradaic current limited by rate of convective-diffusional mass transport
F = Faraday's constant
A = area of the disk electrode
ν = kinematic viscosity of the solution
ω = angular velocity of electrode rotation
n_i = number of electrons transferred in reaction of the ith species
D_i = diffusion coefficient of the ith species
C_i^b = concentration of the ith species in the bulk of the solution

If k for equation (2) is zero, the observed current is due only to the oxidation of bromide and is predicted by equation (5).

$$\begin{aligned} I_{tot} &= I_{Br^-} \\ &= 0{\cdot}62 FA\nu^{-1/6}\omega^{1/2} n_{Br^-} D_{Br^-}^{2/3} C_{Br^-}^{b} \end{aligned} \tag{5}$$

The solution of the equation of convective diffusion for the case of intermediate values of k has been discussed by Haberland and Landsberg[14] and by Prater and Bard.[15] We have found that equation (4) is applicable for the determination of antimony(III) in $4{\cdot}0M$ sulphuric acid and $4{\cdot}0M$ perchloric acid for low values of ω when $C_{Sb(III)}^{b} < C_{Br^-}^{b}$

The analytical technique is subject to interferences by species which are oxidized by bromine or which form slightly dissociated complexes with bromide.

The enhancement technique was applied in the use of a coulometric detector for determining antimony(III) present in small volumes of sample injected into a stream of electrolyte flowing through the detector. For the detector,[16] the electrolytic efficiency was 100% and the area of the antimony(III) peak on the current–time curve, $Q_{\mathrm{Sb(III)}}$, was related to the number of gram-equivalents of antimony(III) by

$$Q_{\mathrm{Sb(III)}} = -F\{\text{equiv Sb(III)}\} \tag{6}$$

We also report here the results of determinations of antimony in several lead- and tin-based alloys by coulometry at constant current with electrogeneration of bromine in 4·0*M* sulphuric acid. The procedure does not require prior separations. An electronic device is described which automatically shuts off the coulometer at the end-point.

EXPERIMENTAL

Instrumentation

Electronic circuitry. The electronic instrument used was that for the simultaneous and independent potentiostatic control of two electrodes, described earlier.[17] The portion of the circuit for potentiostatic control of electrode I-1 in Fig. 1 of reference 17 was modified according to the design described in reference 18. The modification permitted the control of potential or current in electrode I-1 with simultaneous potentiostatic control of electrode I-2. The circuit was constructed in our laboratory but an equivalent instrument is available commercially from Pine Instrument Co., Grove City, Pa. Instead of a recorder with potentiometric input for recording the current in electrode I-2,[17] a difference amplifier was used to monitor the difference in the voltages at the outputs of amplifiers A-2 and F-2.

Voltages were measured with a digital voltmeter, Model 345, from Data Technology, Inc., Palo Alto, Cal. The voltmeter was equipped with BCD output and was interfaced to a digital printer, Model DP12, Mechanics For Electronics, Inc., Wilmington, Mass. Current-potential curves were recorded on an X-Y recorder, Model 815, Bolt, Beranek, and Newman, Inc., Santa Ana, Cal. Instruments used for determining values of current, voltage, and resistance were calibrated with standards from the Physics Instrument Services of Iowa State University.

Coulometry. Coulometric determinations of arsenic(III) and antimony(III) by electrogeneration of bromine at constant current were performed by using a glass cell constructed with three chambers separated by fritted glass disks. The largest chamber contained a platinum generator electrode, a platinum indicating micro-electrode, and a Beckman, Model 39270, Saturated Calomel Electrode (SCE). The electrolyte in this chamber was 4·0*M* sulphuric acid, 0·10*M* sodium bromide. A coil of 21-gauge platinum wire in 4·0*M* sulphuric acid was used as the counter-electrode. The chamber for the counter-electrode was separated from the chamber containing the generator electrode by an intermediate compartment filled with 6·0*M* sulphuric acid.

For coulometric determinations the circuit described in the previous section was used, with galvanostatic control of the generator electrode and simultaneous potentiostatic control of the platinum indicating electrode. An electrical current of approximately 20·0 mA was used for the electrogeneration of bromine with the exact value determined at the time of each analysis by measuring the IR-drop produced by the constant current across a standard resistor. During the coulometric analyses the electrolyte in the generator compartment was stirred with a magnetic stirrer and a Teflon-coated bar. The potential of the indicating electrode was 0·40 V *vs.* SCE. The residual current in the indicating electrode was typically $< 0{\cdot}02\ \mu$A throughout the coulometric determinations. The current corresponding to the end-point was arbitrarily taken as 0·10 μA and was due to the reduction of excess of bromine. The clock used for determining the time required to reach the end-point was Model 1029, McKee Pederson Instruments, Danville, Cal.

The timer and the constant current in the generator electrode were shut off automatically at the end-point of the coulometric analyses by a device described schematically in Fig. 1. A positive voltage proportional to the indicator current, E_{ic}, was continuously applied to resistor R_1 by the output of the difference amplifier described previously. At the end-point, $E_{ic} = E_{ep}$. The control amplifier, C-1, was wired with positive feedback with the result that the output voltage was stable only at the saturation limits, ± 12 V. A bias voltage equal to $-E_{ep}$ was applied to resistor R_2. Before the end-point, $E_{ic} < E_{ep}$, and the output state of C-1 was $+12$ V. At an infinitesimal time past the end-point, $E_{ic} > E_{ep}$, resulting in the state of the output of C-1 changing to -12 V. Electrical current was then conducted by the diode, actuating a relay which stopped the timer and shut off the current in the generator electrode. At the beginning of a coulometric determination, $E_{ic} < E_{ep}$, and the momentary opening of the switch resulted in the output voltage of C-1 reverting to $+12$ V. The clock and the flow of current in the generator electrode were thus started.

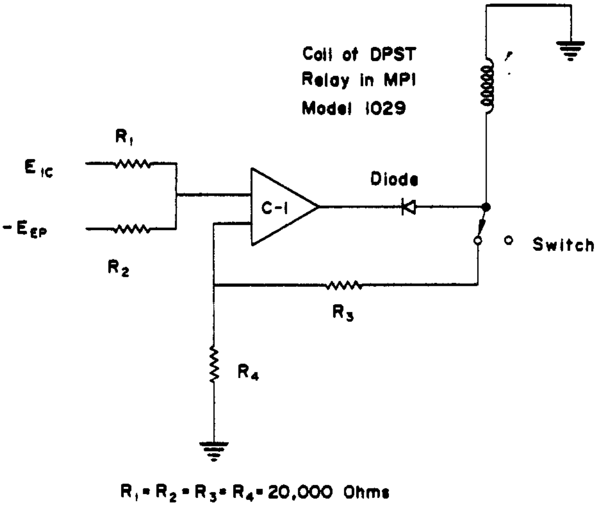

Fig. 1. Device for automatic detection of end-point.
Amplifier C-1 is Zeltex ZEL-1C.

Voltammetry. Voltammetric studies of catalytic enhancement were performed with a rotating platinum-disk electrode (RPDE), Pine Instrument Co., Grove City, Pa. The area of the disk electrode was 0·3135 cm^2. The RPDE was rotated by a variable speed rotator, Model PIR, Pine Instrument Co. The glass cell used for voltammetric studies was described elsewhere.[19] The cell temperature was kept within ±0·2° by circulating water from a thermostatic bath through the water jacket.

The RPDE was polished with Buehler Handimet 600 paper strips followed by 30, 6, and 1 μm Buehler AB Metadi Diamond on nylon lubricated with Buehler Metadi Fluid. After each step in the procedure, the electrode was washed carefully with detergent on a cotton swab and was then rinsed thoroughly with distilled water. At the beginning of each day, the electrode was polished with 0·3-μm alumina on Buehler microcloth, with distilled water as lubricant, and the electrode was cleaned as described above. The electrode was then treated at constant potential in 4·0*M* sulphuric or perchloric acid for 3 min at +1·5 V, −1·5 V, and 0·0 V.

All solutions were deaerated with Air Products prepurified (99·999%) nitrogen. All potentials of the electrode were measured and are reported in V *vs.* SCE.

Values of the limiting current for oxidation of bromide in the absence and presence of antimony(III) were obtained by a potential-step method. Following the pretreatment of the electrode, the potential was set at 0·300 V and the residual current allowed to decrease to less than 2 μA. The potential was then stepped to 1·100 V which is in the region of the limiting current for oxidation of bromide. The currents for charging of the double layer and oxidation of the platinum surface were allowed to decay and the value of current printed. The potential was then returned to 0·300 V. All additions of reagents were made with the potential of the electrode at 0·300 V.

Coulometric electrode

The coulometric electrode used was described elsewhere.[16] The electrode was used with the associated apparatus described but without the chromatographic column and mixing chamber. Deaerated 1·0*M* sulphuric acid that was 1·00 m*M* in sodium bromide was pumped through the apparatus at flow-rates from 0·75 to 1·25 ml/min with compressed helium. The electrode was pretreated by potentiostatic treatment for 3 min at +1·5 V, −1.5 V and 0·0 V. The electrode potential was maintained at a value of 1·100 V for measurement of current *vs.* time results. The areas of the peaks resulting from oxidation of antimony(III) injected into the electrolyte stream were determined by using a Keuffel and Esser planimeter. Current *vs.* time results were recorded on a Leeds and Northrup Speedomax strip-chart recorder.

Reagents

Primary Standard As_2O_3 from the National Bureau of Standards, antimony metal (Coleman and Bell Technical Grade) and Sb_2O_3 (J. T. Baker, Reagent Grade) were used. All other chemicals were Reagent Grade from J. T. Baker, Inc. All water used was triply distilled with a demineralization between the first and second distillations and the second distillation being from alkaline permanganate.

Coulometric determinations of antimony(III) with electrogenerated bromine in 4·0*M* sulphuric acid medium were performed for two standard alloys from the National Bureau of Standards and two standard alloys prepared by Dr. John D. Verhoeven of the Department of Metallurgy at Iowa State University and Ames Laboratory of the Atomic Energy Commission. The certificate values of the standards were as follows: NBS-54D contained 88·57% Sn, 7·04% Sb, 3·62% Cu, 0·62% Pb and < 0·1% of As, Bi, Fe, Ag, and Ni. NBS-53 contained 78·87% Pb, 10·91% Sn, 10·09% Sb, and < 0·1% of Bi, Cu, Fe, and As. ISU-1 contained 96·00% Pb and 4·00% Sb. ISU-2 contained 56·00% Sn, 40·00% Pb, and 4·00% Sb.

Arsenic(III) solution. Arsenious oxide was dissolved in 20 ml of 5*M* sodium hydroxide, transferred to a 1-litre volumetric flask, and 200 ml of water were added followed by 225 ml of conc. sulphuric acid added with mixing; the solution was cooled to room temperature, and diluted to the volume with distilled water.

Antimony(III) solution. Antimony metal or antimonious oxide was dissolved in 30 ml of conc. sulphuric acid at 250–275°.Prepurified nitrogen was bubbled through the solution, during cooling, to remove dissolved sulphur dioxide. The solution was transferred to a 1-litre volumetric flask and 200 ml of distilled water were added with vigorous mixing to prevent hydrolysis and precipitation of antimony(III); 225 ml of conc. sulphuric acid were added, and the solution was cooled and diluted to volume with distilled water. The stock solutions were standardized coulometrically by electrogeneration of bromine at constant current in 4·0*M* sulphuric acid.

Dissolution of alloys

Lead alloys (procedure A). The procedure was similar to that already described for lead-based alloys.[20,21] Sufficient alloy to prepare a solution 3–5m*M* in antimony(III) was dissolved in 30 ml of conc. sulphuric acid at 250–275°. The solution was cooled to room temperature, 70 ml of water were added slowly with vigorous stirring and the solution was again cooled. The solution was decanted from the precipitate of lead sulphate and heated to gentle boiling to remove dissolved sulphur dioxide. The lead sulphate was boiled with 10 ml of conc. hydrochloric acid until the gray precipitate was converted into white, crystalline lead chloride. The process resulted in the dissolution of all antimony. The lead chloride was filtered off on Whatman No. 41 paper and rinsed with 50 ml of 40% sulphuric acid. The combined solutions were diluted with sufficient sulphuric acid and water to give a final acidity of 4·0*M* sulphuric acid.

Tin alloys (procedure B). Sufficient sample to prepare a solution 3–5m*M* in antimony(III) was dissolved in 30 ml of conc. sulphuric acid at 250–275°; 70 ml of water were added and nitrogen was bubbled through the solution during cooling to remove dissolved sulphur dioxide. The solution was transferred to a volumetric flask and diluted, with vigorous mixing, with conc. sulphuric acid and water so that the final acidity was 4·0*M* sulphuric acid.

Solutions of tin-based alloys prepared according to procedure *B* became yellow within a few days of preparation and gave a yellow precipitate after 2–4 weeks. The yellow colour and precipitate were concluded to be the products of the slow hydrolysis of tin(IV) since the same phenomena occurred for solutions containing only tin(IV) and prepared according to procedure *B*. Solutions of tin-based alloys were stable if 5–10 ml of conc. hydrochloric acid were added after the first addition of water. The modification of procedure *B* by the use of hydrochloric acid will be referred to as procedure *B* + HCl.

Coulometry

Titration efficiency. This was determined by coulometric titration of aliquots of arsenic(III) solution containing 25–50 μmole of arsenic(III). A total of 29 determinations were made over a period of 5 months. The average efficiency was 100·0% with a standard deviation of 2 ppt.

Lead and tin-based alloys. The results of the coulometric determinations of antimony in the four standard alloys are summarized in Table 1. The success of the procedures for dissolution and coulometric determination

Table 1. Determination of Sb in standard alloys

Alloy	Dissolution procedure	Certificate value, %	No. of determinations	Sb found, %	Rel. std. devn., ppt
ISU-1	*A*	4·00	3	3·98	4
NBS-53	*A*	10·09	3	10·10	2
NBS-54D	*B**	7·04	4	7·04	4
NBS-54D	*B*†	7·04	2	3·56	—
NBS-54D	*B* + HCl†	7·04	4	7·03	4
ISU-2	*B* + HCl	4·00	3	4·00	3

* Solution analysed immediately after preparation.

† Solution analysed 4 days after preparation.

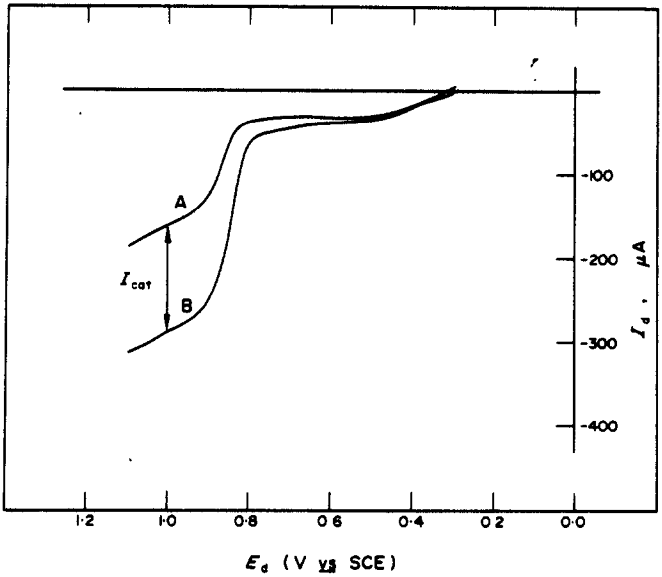

Fig. 2. I–E curves for Br^- in 4·0M H_2SO_4.
Scan-rate 1·0 V/min. Temperature 24°C. Rotational velocity 41·9 rad/sec. A—0·63mM Br^-.
B—0·63mM Br^- and 0·524mM Sb(III).

is evident from an inspection of the results. No difficulty was experienced in precisely applying procedure A for lead-based alloys. It was stated above that solutions of tin-based alloys prepared without the use of hydrochloric acid were not stable, owing to hydrolysis of tin(IV). The results of coulometric determinations of antimony(III) in solutions which were yellow were distinctly low. The modification of procedure B by the addition of conc. hydrochloric acid is recommended.

Large positive errors occurred in preliminary tests of the procedures for dissolution and analysis when no special precaution was made for removal of dissolved sulphur dioxide. For the lead-based alloys containing no tin, sulphur dioxide was removed by gentle boiling. The same technique was not applicable to solutions containing tin(IV). Boiling resulted in the solutions quickly becoming yellow owing to hydrolysis of tin(IV) and subsequent coulometric analysis gave low results for antimony(III). Dissolved sulphur dioxide was removed from solutions containing tin(IV) by passing nitrogen through the solution during cooling.

Catalytic enhancement

Current–potential curves. Current-potential (I–E) curves for platinum electrodes in sulphuric and perchloric acid were shown and discussed earlier.[22] I–E curves obtained in this study for rotating platinum disk electrodes (RPDE) were consistent with that discussion. The I–E curves obtained for the supporting electrolytes made 0·1mM in antimony(III) showed no appreciable wave for the electrochemical oxidation of antimony(III). The irreversibility of the oxidation of antimony(III) prevents determination of antimony(III) by a direct amperometric method other than by electrodeposition of antimony.

The anodic portion of the I–E curve obtained with the RPDE at $\omega = 41{\cdot}9$ rad/sec for 0·63mM bromide in 4·0M sulphuric acid is shown in Fig. 2. Following pretreatment of the electrode, the potential of the RPDE, E_d, was set at 0·300 V and the current allowed to decay to approximately 2 µA. E_d was then scanned at 1·0 V/min and the I–E curve recorded. The oxidation of bromide in acidic media was discussed earlier.[23] The $E_{1/2}$ for the oxidation is approximately 0·85 V and the anodic current is limited by the rate of convective-diffusional mass transport at $E_d > 0{\cdot}9$ V. The process resulting in the small anodic wave at $E_d \sim 1{\cdot}0$ V is the oxidation of the surface of the platinum electrode.[23]

According to equation (5), the current for the electrochemical reaction of a species at a rate limited by convective-diffusional processes is proportional to $\omega^{1/2}$. The results of a study of the limiting current for the oxidation of bromide, I_{Br^-}, as a function of $\omega^{1/2}$ confirmed this dependency for 6·47 (rad/sec)$^{1/2} < \omega^{1/2} < 32{\cdot}4$ (rad/sec)$^{1/2}$ in 4·0M sulphuric or perchloric acid. These results are consistent with those reported before.[23] The value of D_{Br^-} was calculated from equation (5) and the slopes of the plots of I_{Br^-} vs. $\omega^{1/2}$. The values determined are $0{\cdot}76 \times 10^{-5}$ cm^2/sec in 4·0M sulphuric acid and $1{\cdot}4 \times 10^{-5}$ cm^2/sec in 4·0M perchloric acid.

The I–E curve obtained for 0·524mM antimony(III) and 0·63mM bromide in 4·0M sulphuric acid is also shown in Fig. 2. The mechanism resulting in the increase of the anodic current at $E_d = 1{\cdot}1$ V is given by

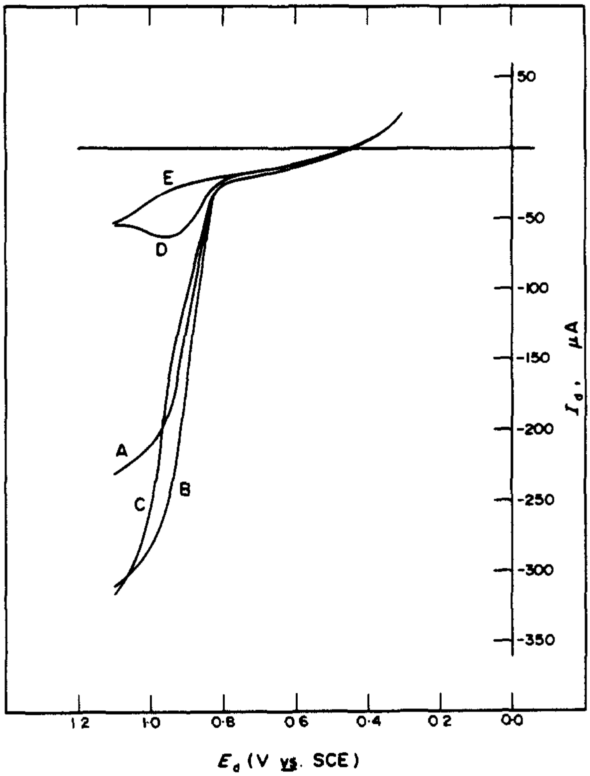

Fig. 3. I-E curves for Br^- in 4·0M $HClO_4$.
Scan-rate 1·0 V/min. Temperature 25°C. Rotational velocity 41·9 rad/sec. A—1·22mM Br^-. B—1·22mM Br^- and 0·44mM Sb(III). C—1·22mM Br^- and 0·54mM Sb(III), first scan. D—1·22mM Br^- and 0·54mM Sb(III), second scan. E—1·22mM Br^- and 0·54mM Sb(III), third scan.

equations (1) and (2) and was discussed in the introductory paragraphs. This increase, I_{cat}, for the case when k in equation (2) is large, is found by subtracting equation (5) from equation (4), as shown by equation (6).

$$\begin{aligned} I_{cat} &= I_{tot} - I_{Br^-} \\ &= 0{\cdot}62FA\nu^{-1/6}\omega^{1/2}n_{Sb(III)}D^{2/3}_{Sb(III)}C^b_{Sb(III)} \end{aligned} \tag{6}$$

I-E curves obtained in 4·0M perchloric acid media for 1·22mM bromide (A) and for 1·22mM bromide plus 0·44mM antimony(III) (B) are shown in Fig. 3. Also shown in Fig. 3 are the anodic portions of three consecutive I-E curves obtained after $C^b_{Sb(III)}$ was increased to 0·54mM (C, D and E). The anodic wave for the first of these scans was shifted towards positive potentials relative to the normal curve. The anodic current for the second of these scans did not achieve a value as great as that in the absence of antimony(III) and the third and subsequent scans produced I-E curves virtually identical to the residual curve obtained in the absence of bromide and antimony(III). I-E curves for fresh solutions of bromide, obtained at the RPDE after recording the curves in Fig. 3 were virtually identical to the residual curves. All efforts to reactivate the electrode by repeated anodization and cathodization were futile. The electrode was removed from the solution, polished according to the procedure described previously and an I-E curve obtained for a fresh solution of 1·22mM bromide. This curve was normal for bromide in 4·0M perchloric acid. Deactivation in 4·0M sulphuric acid that was 0·63mM in bromide also occurred during successive scans with $C^b_{Sb(III)}$ = 1·25mM.

The values of I_{cat} were found to be dependent on the temperature of the solution. The dependence in the range 20–35° was +2·1 μA/deg for 4·0M sulphuric acid and +1·9 μA/deg for 4·0M perchloric acid. For maximum precision, all measurements were made with thermostatic control to within ±0·2°.

Plots of I_{cat} obtained by the potential-step method as a function of $\omega^{1/2}$ for 1·22mM bromide and two values of $C^b_{Sb(III)}$ are shown in Fig. 4 for 4·0M sulphuric acid and in Fig. 5 for 4·0M perchloric acid. The value of $D_{Sb(III)}$ was calculated by using equation (5) and the slopes of the linear portions of the plots in

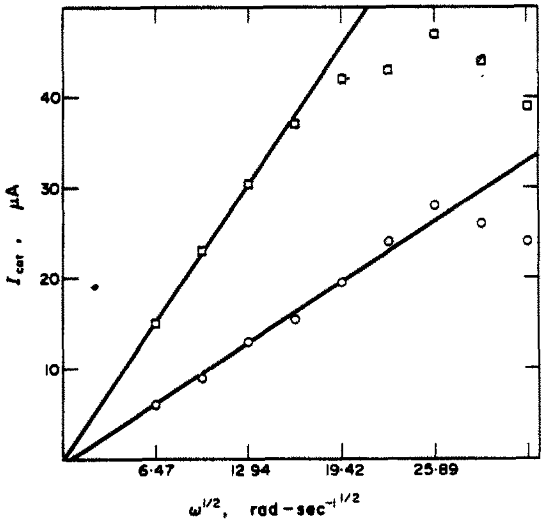

Fig. 4. I_{cat} vs. $\omega^{1/2}$.
1·22mM Br^- in 4·0M H_2SO_4. Temperature 25·0°C. ○—0·0988mM Sb(III); □—0·198mM Sb(III).

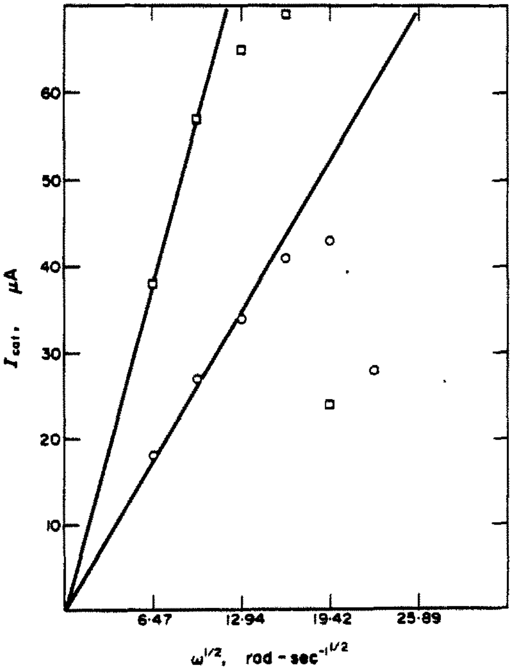

Fig. 5. I_{cat} vs. $\omega^{1/2}$.
1·22mM Br^- in 4·0M $HClO_4$. Temperature 25·0°C. ○—0·0988mM Sb(III); □—0·198mM Sb(III).

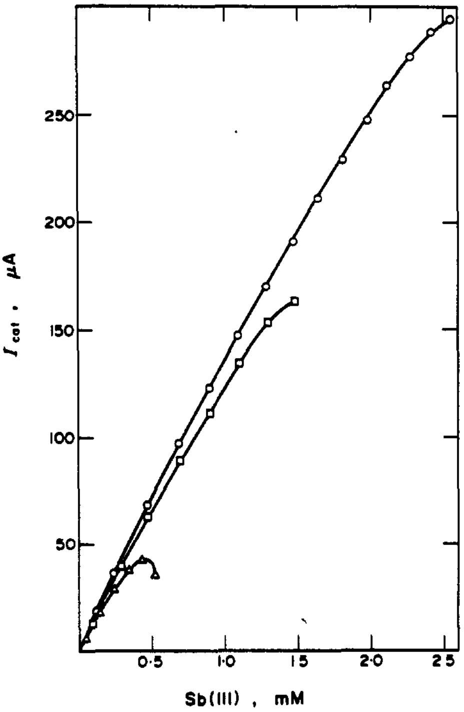

Fig. 6. I_{cat} vs. $C^b_{Sb(III)}$.
4·0*M* H_2SO_4. Temperature 25·0°C. Rotational velocity 41·9 rad/sec. △—0·12m*M* Br^-. □—0·63m*M* Br^-. ○—1·22m*M* Br^-.

Figs. 4 and 5. In 4·0*M* sulphuric acid, $D_{Sb(III)} = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{-6}$ cm^2/sec which is in good agreement with the literature value[24] of $2{\cdot}7 \times 10^{-6}$ cm^2/sec. In 4·0*M* perchloric acid, $D_{Sb(III)} = 6{\cdot}4 \pm 0{\cdot}3 + 10^{-6}$ cm^2/sec

Calibration curves. Values of I_{cat} as a function of $C^b_{Sb(III)}$, obtained by the potential-step method for three values of $C^b_{Br^-}$, are shown in Fig. 6 for 4·0*M* sulphuric acid. The results for perchloric acid medium are similar. As $C^b_{Sb(III)}$ increases so does the deviation from linearity, and I_{tot} finally falls to the residual value. For larger values of $C^b_{Br^-}$ a larger value of $C^b_{Sb(III)}$ is necessary to deactivate the electrode.

Loss of electrode activity. Figures 3 and 6 show loss of activity of the platinum electrode when $C^b_{Sb(III)}$ is increased beyond a certain value. Figures 4 and 5 reveal deactivation at large values of $\omega^{1/2}$. These results are consistent with a mechanism by which deactivation occurs when antimony(III) is irreversibly adsorbed at the electrode surface during formation of platinum oxide. Bromide is known to be strongly adsorbed at platinum electrodes in 1·0*M* sulphuric acid.[23] Adsorbed bromide is not desorbed at $E = 1{\cdot}0$ V, which is in the region of the limiting anodic wave. The oxidation of the platinum surface occurs at $E > 1{\cdot}1$ V in 1·0*M* sulphuric acid and the adsorbed bromide is oxidized and desorbed as HOBr at $E > 1{\cdot}2$ V.

The RPDE was rotated at 41·9 rad/sec in 4·0*M* perchloric acid. The solution was made 0·76m*M* in antimony(III) and the value of E_d was stepped from 0·300 to 1·100 V. At $E_d = 1{\cdot}100$ V the platinum surface is oxidized in this medium. After 5 min, E_d was stepped to 0·300 V. The solution was then made 1·00m*M* in bromide and E_d stepped to 1·100 V. The anodic current quickly decayed to a residual value which was characteristic of a deactivated electrode. It was again necessary to polish the electrode surface to restore activity. The electrode was then rotated in a fresh solution of 4·0*M* perchloric acid that was 0·74m*M* in antimony(III) and potentiostatically treated at 0·300 V. E_d was maintained at 0·300 V for 5 min and the solution then made 1·00m*M* in bromide. E_d was stepped to 1·100 V and the anodic current observed was the expected, steady-state value of I_{tot}, indicating no deactivation had occurred. When these experiments were repeated with antimony(V) instead of antimony(III), no deactivation of the electrode resulted.

In the experiments for which results are shown in Figs. 4–6, deactivation did not occur when E_d was stepped to 1·100 V provided the oxidation of antimony(III) by electrogenerated bromine was fast and quantitative so that the concentration of antimony(III) was zero at the electrode surface. For large values of $C^b_{Sb(III)}$ or $\omega^{1/2}$, the rate of the homogeneous reaction was not sufficiently fast to bring about quantitative oxidation of antimony(III) in the diffusion layer. Consequently, antimony(III) was present at the electrode surface during oxidation of the

Table 2. Analytical applications of calibration curves

Total Sb added, mg	Total Sb found ($HClO_4$), mg	Rel. error, %	Total Sb found (H_2SO_4), mg	Rel. error, %
3·01	3·01	0·0	2·87	−4·7
6·02	5·86	−2·7	6·02	0·0
9·03	8·78	2·8	8·81	−2·4
12·04	12·16	1·0	11·98	−0·5
15·05	15·26	1·4	14·65	−2·7
3·01	2·68	−11·0	3·14	4·3
6·02	5·58	−7·3	6·07	0·8
9·03	8·76	−3·0	9·00	−0·3
12·04	11·81	−1·9	11·90	−1·2
15·05	14·76	−1·9	14·87	−1·2
	Avg. rel. error	3·3		1·8

($\omega^{1/2} = 6{\cdot}47\ (\mathrm{rad/sec})^{1/2}$; $C^b_{\mathrm{Br}^-} = 1{\cdot}22\mathrm{m}M$; Temp. = 25·0°C)

platinum and its irreversible adsorption simultaneously with the formation of the layer of platinum oxide resulted in deactivation. The stoichiometry of this stable layer containing antimony was not determined.

It was also found necessary to restrict the values of E_d if the activity of the electrode was to be maintained in a mixture of antimony(III) and bromide. For $E_d < 0{\cdot}3$ V, some antimony was deposited at the electrode surface. Although stripping of the deposit apparently occurred on the anodic sweep, the activity of the electrode was lost. Deactivation also resulted if potentials more positive than 1·1 V were applied.

ANALYTICAL APPLICATIONS

Rotating disk electrode

The potential-step method was used for obtaining values of I_{cat} for solutions prepared by standard addition of stock solutions of antimony(III) to 1·22m*M* bromide in 4·0*M* sulphuric or perchloric acid. The values of $C^b_{\mathrm{Sb(III)}}$ were determined by using the calibration curves in Figs. 6 and 7 and the results are tabulated in Table 2. The average relative error for the determinations is larger than expected for electroanalytical methods and results from the fact that evaluation of I_{cat} involves taking the difference of two relatively large numbers, $I_{\mathrm{tot}} - I_{\mathrm{Br}^-}$. The relative error decreases as $C^b_{\mathrm{Sb(III)}}$ increases.

A large number of cations were found to interfere, causing negative errors. The concentrations of the interfering species producing a 5% change in I_{cat} for 1·22m*M* bromide with 0·43m*M* antimony(III) are given in Table 3.

None of the species listed in Table 3 is oxidized by bromine. The interference was greatest for those cations forming the strongest bromide complexes. Because of the severe interference caused by tin(IV), tin-base alloys cannot be analysed by the catalytic method without prior separation. If hydrochloric acid is added to solutions of lead-base alloys, these samples cannot be analysed because chloride is oxidized at values of E_d in the region of the limiting wave for bromide. Several masking agents were used, including phosphate, oxalate, and EDTA. None successfully prevented interference by the cations, probably because of the high acidity of the solution. Interferences not listed in Table 3 are from species which are oxidized by bromine or which react directly at the electrode at the potential used.

Table 3. Concentration of interfering species producing a 5% decrease in I_{cat}

Cation	Concentration, mM (H$_2$SO$_4$)	(HClO$_4$)
Bi(III)	0·20	0·066
Sn(IV)	0·33	0·28
Cd(II)	1·0	0·47
Fe(III)	1·2	2·1
Zn(II)	5·7	3·7
Cu(II)	6·0	2·4
Ni(II)	6·8	2·0

($C^b_{Br^-}$ = 1·22mM; $C^b_{Sb(III)}$ = 0·43mM; $\omega^{1/2}$ = 6·47 (rad/sec)$^{1/2}$; temp. = 24·0°C)

Table 4. Determination of Sb(III) with the coulometric detector

Sb(III), μg	Q_{calc}, mC	Q_{exp}, mC	Rel. error, %
0·0616	0·0977	0·146	49
0·123	0·196	0·203	3·6
0·308	0·489	0·506	3·5
0·771	1·22	1·30	6·6
1·54	2·44	2·50	2·5
3·08	4·89	4·80	−1·8
6·17	9·78	9·70	−0·8
12·3	19·6	19·6	0·0

($C^b_{Br^-}$ = 1·00mM; flow-rate = 0·75 − 1·25 ml/min)

Use of coulometric electrode

The coulometric electrode[16] was used in conjunction with the enhancement technique for the determination of antimony(III) injected into a stream of 1·0M sulphuric acid that was 1·00mM in sodium bromide. The detector was connected directly to the sample-injection valve described in reference 16, without any intervening chromatographic column. The potential of the electrode was set at 1·100 V. The volume of the sample loop was 0·5065 ml and the concentrations of sulphuric acid and sodium bromide in the sample were identical to those in the electrolyte stream. The current in the electrode was recorded as a function of time, and gave a peak, due to oxidation of injected antimony(III), on the baseline due to oxidation of bromide. Results obtained for a series of injections are shown in Table 4. The ability to determine accurately very small quantities of antimony(III) was improved significantly when $C^b_{Br^-}$ was decreased. The large relative error for those determinations was due primarily to electrical and convective noise on the baseline.

CONCLUSIONS

On the basis of the results described here, we conclude that the catalytic enhancement by antimony(III) of the limiting anodic current for bromide can be used for the determination of antimony(III) provided numerous interfering species have been separated by appropriate chromatographic techniques. For the determination of antimony(III) in the effluent from a high-speed liquid chromatograph by using a coulometric detector, a stream of supporting electrolyte containing bromide is mixed with the effluent stream ahead of the detector. Because the coulometric electrode operates with 100% efficiency according to equation (6), there is no need to determine any calibration constants such as diffusion coefficients.

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Zusammenfassung—Mit Hilfe einer rotierenden Scheibenelektrode wurde versucht, ein amperometrisches Verfahren zur Bestimmung von Sb(III) in sauren Medien zu entwickeln, das auf dem katalytsichen Anwachsen des anodischen Grenzstroms von Br^- beruht. Die analytische Anwendung war erfolgreich, wenn die Konzentration von Antimon(III) in der Lösung kleiner war als die von Bromid. Die Verstärkungstechnik wurde auch auf die Bestimmung von Sb(III) angewandt, das in einen Elektrolytstrom injiziert wurde, der durch einen coulometrischen Platindetektor passierte.

Résumé—On donne les résultats d'une étude utilisant une électrodedisque tournante pour mettre au point une méthode ampérométrique pour le dosage de Sb(III) en milieu acide, basée sur l'accroissement catalytique du courant anodique limitant pour Br^-. L'application analytique a été couronnée de succès, étant entendu que la concentration globale de l'antimoine (III) était moindre que celle du bromure. On a aussi appliqué la technique d'accroissement au dosage de Sb(III) injecté dans un courant d'électrolyte passant à travers un détecteur coulométrique de platine.

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FORCED-FLOW LIQUID CHROMATOGRAPHY WITH A COULOMETRIC DETECTOR

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Summary—A tubular platinum electrode packed with small chips of platinum is described which was shown to function with 100% electrolytic efficiency. Application of the electrode is described for the coulometric determination of electroactive species in the effluent from a liquid chromatograph. Cu and Fe were determined in a series of standards. An average relative deviation of less than 2 ppt was obtained for analysis of samples containing 5 μg of Cu(II) and 5 μg of Fe(III).

The characteristics of an ideal detector for high-speed column chromatography include the following:

1. High sensitivity,
2. Low limit of detection,
3. Large, linear dynamic range,
4. Continuous operation,
5. Low internal volume (*i.e.*, high resolution),
6. Independence of column parameters such as the rate of flow of the eluent.

Detectors operating on the basis of controlled-potential electrolysis of the column effluent can satisfy these criteria. Many designs have been reported, for electrodes to be used in electrolysis cells for flowing solutions. These include types which electrolyse only a small fraction of the electroactive species passing through the cell, as well as some for which the electrolytic efficiency is 100%, *i.e.*, all electroactive species passing through the cell are electrolysed. For each of these electrodes, convective-diffusional processes result in the transfer of electroactive species from the fluid to the surface of the electrode.

Levich[1] studied many electrolytic systems under various hydrodynamic restraints and showed that the general relationship between the limiting electrical current, I_l, the concentration of the electroactive species in the bulk of the solution, C^b, and the velocity of fluid in the vicinity of the electrode, v, is that given by equation (1)

$$I_l = knFv^{\alpha}C^b \tag{1}$$

where n and F have their usual electrochemical significance. The coefficient k is frequently a function of experimental parameters such as the kinematic viscosity of the fluid, the diffusion coefficient of the electroactive species, the geometry of the electrode, *etc.* The exponent of the velocity, α, is dependent on the nature of the convection and the boundary conditions used for solving the equation of convective-diffusional mass transfer. When using an electrode as a detector in a fluid stream, it is usually more convenient to relate the velocity term in equation (1) to the net rate of fluid flow past or through the detector, v_f. Equation (1) is then written as equation (2).

$$I_l = k'nFv_f^{\alpha}C^b \tag{2}$$

For a detector operating with an electrolytic efficiency of 100%, k' and α are unity. Such a detector is called a coulometric detector since the time integral of the current in the electrode is related by Faraday's law of electrolysis to the number of equivalents of electroactive species flowing in the stream. The possible limit of detection for a coulometric detector can be appreciated from the following calculation. With simple electronic circuitry, it is possible to measure accurately an electrical signal of 10^{-9} A or 10^{-9} C/sec. This corresponds to approximately 10^{-14} eq/sec or, for Ag^+, approximately 10^{-12} g/sec.

Müller,[2] in 1947, first reported the use of an electrode in a flowing stream for electroanalysis. The limiting current in a platinum microelectrode sealed in the constricted portion of a glass tube was found to be a linear function of the bulk concentration of an electroactive species in the fluid stream, and log I_l was a linear function of log v_f as predicted by equation (2). Most applications of microelectrodes for electroanalysis of streams have involved use of the dropping mercury electrode (DME). Kemula,[3] in 1952, was the first to use a DME for continuous analysis. His application was to the analysis of the effluent stream from a liquid chromatographic column. Other workers have since reported various designs for flow-through cells based on the use of a DME.[4-10] These devices have been used for the monitoring of sulphur dioxide[11] and uranium[12] in process streams, the determination of inorganic anions,[13] metal ions,[9, 14-20] nitro-compounds,[21] amino-acids,[22, 23] proteins,[24] aldehydes and ketones,[25] alkaloids,[26] DDT,[21] and other pesticides.[27, 28]

The major disadvantages of using a DME as a detector in a stream are (*i*) the drop-time is likely to be irregular when the stream velocity is high, owing to turbulence in the vicinity of the drop, (*ii*) the periodic nature of the DME prevents accurate measurement of transients in the composition of the stream such as are likely in high-speed chromatography, and (*iii*) the sizable charging-current background for the dropping electrode prevents application to the determination of very low concentrations. Use of a mercury pool in place of the DME does not satisfactorily eliminate these problems. The motions in the pool caused by the flowing stream causes an irregular limiting current and a large charging-current background.[29]

One obvious benefit of using a mercury electrode is the availability of an extensive cathodic range of polarization due to the large over-potential for the evolution of hydrogen. Solid electrodes also characterized by a large cathodic working range can be made of carbon. Joyness and Moggs,[30] and Pungor *et al.*[31, 32] used a planar, silicone rubber-based, glassy-carbon electrode for the determination of Cd^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, and "Propylon hydrochloride" [3,4-dihydroxy-α-(isopropylaminomethyl)benzyl alcohol hydrochloride] in a stream.

Another type of electrode for continuous electroanalysis is a tubular electrode through which the fluid passes, with the electrolysis occurring at the inner surface of the tube. Levich[1] solved the equation of convective-diffusional mass transfer for the tubular electrode under conditions of Poiseuille flow and negligible consumption of electroactive species from the fluid. The analytical relationship between I_l, C^b, and the length of the tubular electrode, L, is that given by equation (3). Blaedel *et al.*[33] constructed such an electrode, having a bore

$$I_l = (5{\cdot}24 \times 10^5)D^{2/3}L^{2/3}nv_f^{1/3}C^b \tag{3}$$

of 0·03 in. and $L = 1{\cdot}0$ in., and confirmed the validity of equation (3) for $v_f \leqslant 10$ ml/min. Blaedel and Klatt[34] derived the complete current-voltage curve for a reversible process at a tubular electrode and they also[35] investigated the use of a tubular electrode for the study of catalytic reactions. Blaedel and Boyer[36] demonstrated the applicability of a tubular electrode made of platinum for the determination of $Fe(CN)_6^{3-}$ in an aqueous stream at concentrations down to $0{\cdot}01 \mu M$. Sharma and Dutt[37-39] verified equation (3) for the determination, with a tubular graphite electrode, of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, Ag^+, Fe^{3+}, Fe^{2+}, MnO_4^-, Mn^{2+}, Tl^{3+} and Tl^+.

Applications of all the detectors described above result in the electrolysis of negligible amounts of the electroactive species in flowing streams. Consequently, the maximum sensitivity of the electrolytic method is not realized. The value of I_l for the polarographic detector of Takemori and Honda[9] was 0·13% of the maximum value calculated on the basis of 100% electrolysis at $v_f = 3{\cdot}0$ ml/min. The tubular electrode of Blaedel and Boyer[36] electrolysed 0·4% of all electroactive species at $v_f = 3{\cdot}15$ ml/min. The use of such inefficient devices as detectors for liquid chromatography requires precise control of rates of eluent flow. The area under the chromatographic peak, Q, is found by integrating equation (2).

$$Q = k'nF \int v_f^{\alpha} C^b(t)\,\mathrm{d}t \tag{4}$$

If v_f is constant, equation (4) can be written as equation (5). The total number of moles eluted is given by equation (6).

$$Q = k'nFv_f^{\alpha} \int C^b(t)\,\mathrm{d}t \tag{5}$$

$$\text{No. of moles} = v_f \int C^b(t)\,\mathrm{d}t = x \tag{6}$$

Combining equations (5) and (6) yields equation (7)

$$Q = xk'nFv_f^{\alpha-1} \tag{7}$$

A plot of log Q *vs.* log v_f has a slope of $\alpha - 1$. The value of $\alpha - 1$ for the tubular detector of Blaedel *et al.*,[33-36] for example, is $-0{\cdot}667$. This rather large dependence of Q on v_f necessitates either accurate knowledge or precise control of v_f during the processes of standardization and analysis.

The sensitivity of Q to change in v_f is eliminated for a detector operating with an electrolytic efficiency of 100%. For such a device, k' and α in equation (2) are unity and equation (7) becomes equation (8).

$$Q = xnF \tag{8}$$

The need for calibration is eliminated except as used to determine n. The first reported application of a coulometric detector was by Shaffer, Briglio and Brockman[40] in 1948 for the continuous analysis of a gas stream. The technique involved the continuous dispersion of a gas stream into an electrolytic solution in the zone of electrolysis. Patents were issued in 1952[41] and 1956[42] to Eckfeldt for detectors operating on this principle for use in analysis of gas streams. Eckfeldt and Shaffer[43] described a flow-through electrode of silver particles for determining dissolved oxygen. Hersch has reviewed the principles of various designs of electrodes for continuous gas analysis.[44]

Efforts to develop coulometric detectors for application to fluid streams at high values of v_f have centered on the need to increase the surface area of the electrode while decreasing the volume of mobile phase entrained by the detector and the thickness of the diffusion layer at the electrode–solution interface.[45] Eckfeldt[46] described an electrode having an appearance similar to a rat-maze in which the fluid passed through a labyrinth in contact with a circular gold electrode. Bard[45] proposed the use of an ultrasonic transducer adjacent to a gauze electrode placed in the stream to disrupt the laminar flow patterns, thereby decreasing the effective thickness of the diffusion layer. Johansson[47] described an elaborate and impractical device for increasing the rate of convective mass transfer by rotating at high velocities a cylindrical or disk electrode within the confinement of cells having minimal volumes.

The most successful designs of coulometric detectors, in terms of ease of construction and successful operation with an efficiency of 100% at high values of v_f, have been electrodes constructed by packing a section of the stream channel with (*i*) finely divided materials suitable for use as electrodes,[43, 48–54] (*ii*) plugs of wire or metallic gauze,[55] and (*iii*) porous or fritted metals.[56] The only mode of convective transport within these detectors is that due to the flow of the stream around the particles of the packing material as the fluid passes through the detector. Voorheis and Davis[48] removed traces of organic materials from solutions by passage through a column packed with graphite. The graphite was then made the anode of an electrolysis cell and the adsorbed organics were determined by chronopotentiometry. Molnar[49] used a column filled with platinum chips maintained at a constant potential for removal of traces of heavy metals from aqueous solutions. Blaedel and Strohl[50] electro-deposited traces of metals from aqueous streams onto an electrode of granular glassy carbon and then determined the metals by anodic stripping voltammetry. Strohl *et al.*[52 53] used a granular carbon electrode for determination of Fe(III), Cu(II), *p*-nitrophenol, hydroquinone, and *p*-phenylenediamine. Roe described the construction of a granular mercury electrode[54] prepared from amalgamated chips of nickel. Sioda used a granular graphite electrode[51] for the determination of $Fe(CN)_6^{3-}$ and discussed the theory of that detector, and electrodes constructed from rolled 80-mesh platinum gauze, with regard to the value of α in equation (2).[55] Shropshire[56] used an electrode prepared by depositing Ag and Pt-black on fritted-glass spargers for the coulometric determination of Mo(VI) and Re(VII). Recently, Kihara *et al.*[57] used a coulometric electrode to study the changes in the oxidation state of plutonium. Rogers[58] pointed out the similarity between electrodeposition at a potentiostated detector and the partitioning between the mobile and stationary phases in a chromatographic column. The use of coulometric detectors for electrochromatography was later discussed by Roe.[54] Fujinaga[59] has reviewed the use of coulometric detectors and electrochromatography.

It is our goal to develop a series of procedures utilizing high-speed liquid chromatography with coulometric detection for routine chemical analysis of solid and liquid samples. Here we report the design of our chromatograph and detector, and verify that the detector functions with virtually 100% efficiency for a large range of flow-rates to be used in the chromatographic procedures. The design and construction of the detector described here is simple, relative to that of many of the coulometric detectors proposed in the chemical literature. Results are given for the analyses of a synthetic liquid sample containing Cu(II) and Fe(III) and for two NBS standard alloys.

EXPERIMENTAL

Instrumentation

Detectors. The diagram of a cross-section of the detector used in this study is shown in Fig. 1. The detector was assembled for this work by Pine Instrument Co. of Grove City, Pennsylvania. In the construction, a platinum rod having a diameter of approximately 4 mm and a length of 1·5 cm was drilled to an inside diameter of 2·79 mm. The resulting platinum tube was press-fitted into the Teflon cell previously machined to the appropriate dimensions. The reference electrode was a Beckman Model 39270 fibre-junction calomel electrode and the counter electrode was a coil of 21-gauge platinum wire placed over the probe of the reference electrode. The fibre tip of the calomel electrode was within 2 mm of the end of the platinum tube when inserted into the Teflon cell. Electrical contact to the platinum electrode was made through the wall of the Teflon cell. Teflon tubing and tube-end fittings were from Chromatronix, Inc., of Berkeley, Cal. Waste fluid was drawn from the cell through tubing to a safety trap connected to a water aspirator. The interior of the platinum tube was packed according to various designs, as described below, to determine the correspondence between the manner of packing and the efficiency of electrolysis.

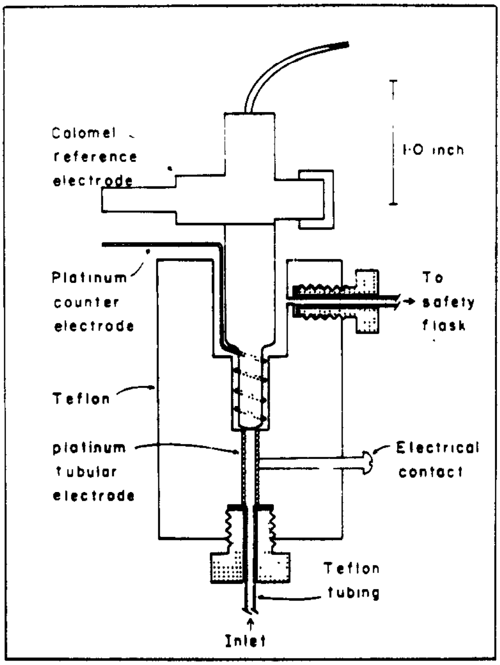

Fig. 1. Cross-section of detector for forced-flow liquid chromatography.

Detector A. No solid material was inserted into the platinum tube.

Detector B. Thirty-three 1·5-cm lengths of 26-gauge platinum wire were inserted lengthwise into the platinum tube. This was the maximum number that could be inserted with reasonable effort.

Detector C. The platinum tube was packed with short pieces (approximately 0·1 mm) of platinum wire ranging from 26 to 31 gauge, Small plugs made by wadding 31-gauge platinum wire were inserted into each end of the tube to prevent the platinum chips from being forced out of the tube at high values of v_f. The design and construction of this detector is very simple, resulting in very low cost.

Liquid chromotagraph. The liquid chromatograph was constructed in a manner similar to a design described by Seymour, Sickafoose and Fritz[60] and is shown schematically in Fig. 2. Many of the components of the chromatograph were obtained from Chromatronix, Inc. All tubing was made of Teflon having an inside diameter of 0·060 in. The sample-injection valve (type SV-8031) was constructed of Kel-F. The eluent-selector valve (type R60V6K) was a six-position rotary valve also made of Kel-F. Rates of eluent flow were monitored with a Gilmont (model F 1100) flowmeter. The flowmeter was calibrated by determining the volume, calculated from the weight, of eluent passed at a constant rate for a known period of time. Eluents were contained in glass bottles which were pressurized with compressed helium. A mixing chamber, model

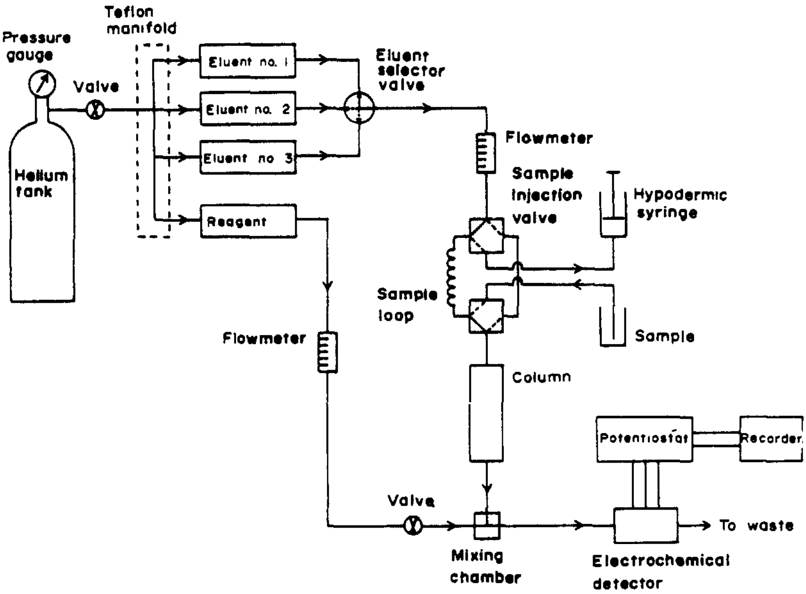

Fig. 2. Schematic diagram of liquid chromatograph.

2MC constructed by Pine Instrument Co., was used to mix reagents with the effluent stream before it passed through the detector. The two streams entering the chamber were divided and directed tangentically through the wall of the cylindrical mixing cavity. The combined streams made their exit through an end wall of the mixing cavity. The volume of the cavity was estimated to be 0·01 ml.

Electronics. The potentiostat and analogue integrator were constructed according to established designs[61] using operational amplifiers. The strip-chart recorder was model 2801 from Laboratory Data Control. All voltage signals and resistances used were calibrated against references standardized by the Physics Instrument Services at Iowa State University. All electrode potentials were measured and are reported in V *vs.* SCE. Values of current-time integrals, Q, are given in mC.

Reagents

Water. All solutions were prepared with water which was triply distilled with a demineralization following the first distillation, and the second distillation being from alkaline permanganate.

Sodium iodide solution in 1·0M sulphuric acid. Prepared from Baker "Analyzed Reagent" sodium iodide and Mallinckrodt "Analytical Reagent" acid, and standardized by potentiometric titration with a standard solution prepared from dry Mallinckrodt "Analytical Reagent" silver nitrate.

Hydrobromic acid. A stock solution of 24% hydrobromic acid was prepared by 1:1 dilution of the Baker "Analyzed Reagent" (47–49%) acid. The solution was deareated for 1 hr with dispersed helium (99·999% pure) while being stirred with a magnetic stirrer. The solutions consistently had a yellowish colour due to the presence of bromine; dissolved oxygen oxidizes bromide in an acidic solution. The presence of residual bromine resulted in large baseline currents in the chromatographic determinations and had to be eliminated. Mossy zinc was amalgamated with a solution of mercury chloride, washed with several small portions of distilled water and placed in the stock hydrobromic acid. The mixture was stirred for a minimum of 2 hr with continuous passage of helium. All colour due to bromine disappeared during this reduction process. The reduced solution was decanted and filtered through a plug of glass wool into a bottle previously deareated with helium. The stock solution was further deareated to remove any dissolved hydrogen and was stored under helium. Dilute hydrobromic acid was prepared by dilution of the stock solution with distilled water previously reduced with amalgamated zinc and deareated with helium.

Standard Cu(II) and Fe(III) solutions. A standard solution containing 10·000 µg/ml each of Cu(II) and Fe(III) was prepared with copper (Baker Chemical Co.) and iron (G. F. Smith Chemical Co.) dissolved in conc. hydrochloric acid at room temperature. A few ml of hydrogen peroxide were added to the solution to ensure that all iron existed as Fe(III). The solution then was warmed to destroy excess of peroxide, cooled, and diluted to volume with 0·1*M* hydrochloric acid.

Ion-exchange resin. Ion-exchange separations were performed with Amberlite IRA-200 cation-exchange resin (Rohm and Haas Co.). This is a macroreticular, strong-acid resin. Several grams of the water-moist resin were washed with acetone and air-dried, then ground with an agate mortar and pestle and sieved. The 140–200 mesh fraction was slurried in water and the fines, not eliminated by sieving, were decanted. The remaining slurry was poured into a 3-mm bore glass tube and allowed to settle by gravity. Compressed helium was applied to produce moderately tight packing. The dimensions of the cation-exchange bed were 3·0 mm × 8·0 cm. The resin was prevented from leaving the column under the pressure of the eluent by a plug of glass wool placed at the end of the glass tube.

Standard materials

An aluminium-base standard alloy from the National Bureau of Standards (NBS 87) was analysed for copper and iron. The certificate composition for NBS 87 is 6·22% Si, 0·46% Fe, 0·59% Ni, 0·39% Mg, 0·30% Cu, 0·30% Mn, 0·17% Cr, 0·16% Ti, 0·075% Zn, 0·07% Pb, and 0·061% Sn. About 4 g of NBS 87 were accurately weighed and dissolved at room temperature by slow addition of 30 ml of 8*M* hydrochloric acid. Then 100 ml of conc. perchloric acid were added and the solution was heated to boiling under reflux to dehydrate the silica. The solution was filtered through a fine fritted-glass disk to remove the silica and diluted to 500·0 ml, and 100·0 ml of this solution were further diluted to 500 ml, producing a stock solution of NBS 87.

A nickel-base standard alloy (NBS 169) was also analysed for copper and iron. The certificate composition is 20·26% Cr, 1·42% Si, 0·54% Fe, 0·19% Co, 0·059% Al, 0·073% Mn, 0·042% Zr, 0·018% V, 0·015% Ca, and 0·015% Cu. About 1 g was accurately weighed and in dissolved 40 ml of *aqua regia* with low heat for several hours. The solution was then evaporated to 20 ml and diluted to 200·0 ml.

Separation procedure

Samples were injected into a stream of 0·3*M* hydrobromic acid flowing at a rate of 0·5 ml/min. After a waiting period of 4–6 min, the eluent was changed to 1·5*M* hydrobromic acid. Elution was continued until the copper(II) was completely eluted from the column, usually 15 min. The eluent was then switched to 25% hydrobromic acid to elute iron(III).

Pretreatment of the detector at the start of each day consisted of alternate potentiostating at potentials for evolution of hydrogen and oxygen. The detector was potentiostated at 0·150 V for the detection of copper (II) and iron(III). To stabilize copper(I) as the product of the electrochemical reduction of copper(II), a stream of 25% hydrobromic acid at a flow rate of 2 ml/min was mixed with the effluent stream just ahead of the detector. The products of the electrochemical reactions in the detector were the bromide complexes of copper(I) and iron(II).

Flow-rates were regulated with screw clamps to restrict the flow in the Teflon tubes leading from the exchange column and the bottle of 25% hydrobromic acid. The pressure applied to the eluent bottles was approximately 25 psig.

EXPERIMENTAL RESULTS

Volume of the sample loop

The volume of the sample loop of the sample-injection valve was calculated on the basis of the volume of 0·1*M* sodium hydroxide required to titrate, to the phenolphthalein end-point, the quantity of 5*M* hydrochloric acid delivered in two aliquots from the injection valve. The procedure was standardized by titration of the quantity of the 5*M* acid delivered by a 1·00-ml pipette, itself calibrated by determining the weight of water delivered. The density of water at room temperature (27·5°) was taken as 0·9920 g/ml. After correcting for bouyancy, the apparent density of water is 0·9952 g/ml. In a series of 4 measurements, the volume found for the pipette was 1·0018 ± 0·0002 ml. From a series of 5 calibrations of the sample loop, its volume was calculated to be 0·5040 ± 0·0002 ml.

Current–potential curves for iodoide in 1·0M sulphuric acid

Current–potential (I–E) curves were obtained with detectors A and C for 1 × $10^{-4}M$ sodium iodide in 1·0*M* sulphuric acid at v_f = 5 ml/min. I–E curves are shown in Fig. 3 for the anodic scan potential at a sweep rate of 0·10 V/min. The large difference in the values of the limiting anodic current for iodide is due to the large difference in the electrolytic efficiency of the two detectors. The electrochemistry of iodide at platinum electrodes in 1·0*M* sulphuric acid is discussed in reference 62. The sweep rate used for obtaining the curves in Fig. 3 was sufficiently low for currents due to surface processes, such as charging of the electrical double-layer and generation of adsorbed iodine, to be negligible. The observed value of $E_{1/2}$ for the oxidation of iodide in detector A was 0·48 V and for detector C it was 0·51 V, which are both in fairly good agreement with the value of 0·46 V obtained using a rotating platinum disk electrode.[62] That the observed values of $E_{1/2}$ for the two curves were within 30 mV clearly demonstrates that the electrical resistance of the packed electrode (C) was not significantly greater than that of the unpacked electrode (A).

Electrolytic efficiency of the detectors

Studies to characterize the efficiency of the three electrodes for various values of v_f were conducted by injecting 0·5040-ml aliquots of $4{\cdot}73 \times 10^{-5}M$ sodium iodide in 1·0*M* sulphuric acid into a stream of 1·0*M* sulphuric acid passing through the electrodes. The electrodes were potentiostated at 1·00 V and the anodic peaks integrated electronically for the electrochemical oxidation of iodide. The number of mC calculated for 100·0% efficient electrolysis was 2·30. Before each experiment, the potential of the electrode was set at 0·20 V to reduce any oxide present at the platinum electrode surface. Several aliquots of $10^{-3}M$ sodium iodide in 1·0*M* sulphuric acid were injected into the stream of 1·0*M* sulphuric acid. At a potential of 0·20 V, iodide is adsorbed at the surface of the platinum electrode.[62] The adsorption is irreversible and prevents oxidation of the surface of the platinum electrode at 1·00 V. Adsorbed iodide is not oxidized at 1·00 V.

Plots of log *Q* *vs.* log v_f are shown in Fig. 4 for the three detectors with $0{\cdot}12 \leqslant v_f \leqslant 4{\cdot}0$ ml/min. The slope of the plot for detector A is $-\frac{2}{3}$ which is in agreement with that predicted for an open-tubular electrode according to equation (7). The efficiency of detector B was

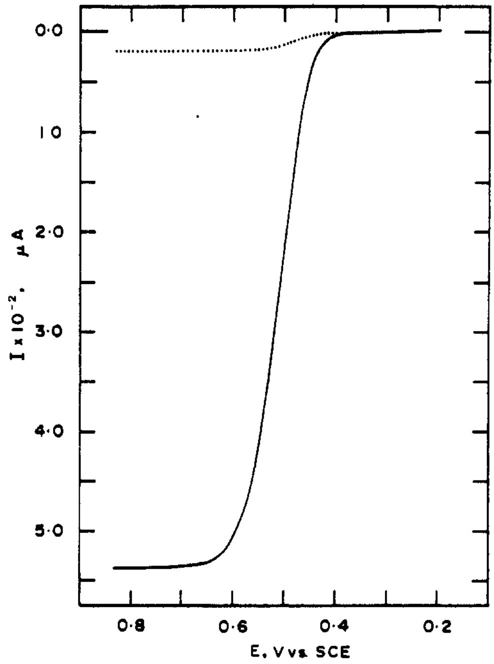

Fig. 3. Current–potential curves for I^- in 1·0*M* H_2SO_4. Scan rate = 0·1 V/min; $[I^-] = 1 \times 10^{-4}M$; v_f = 5 ml/min; ..... detector A;— detector C.

significantly greater than that of detector A, owing to the greater internal surface area. For very small values of v_f, the observed electrolytic efficiency of detector B approached 100%. Negligible change in Q was observed for detector C over the range of values of v_f, as expected for a coulometric electrode on the basis of equation (8).

A determination of the precision possible for combined use of the sample-injector valve with detector C was made from the results for a series of 8 injections of 1·0M sulphuric acid that was 4·73 × $10^{-5}M$ in sodium iodide into the stream of 1·0M sulphuric acid. Values of v_f were in the range 1·1–2·1 ml/min. The average value of electrolytic efficiency was 100·0%, with an average relative deviation of 1·3 ppt.

Calibration plot for oxidation of iodide

A log–log plot of Q *vs.* $[I^-]$ was linear for a series of 0·5040-ml aliquots of 1·0M sulphuric acid containing sodium iodide which were injected into a stream of 1·0M sulphuric acid passing through detector C with $v_f = 3$ ml/min. The range of $[I^-]$ was 2·50 × 10^{-8}–1·82 × $10^{-4}M$. The results agreed very well with those predicted from equation (8). The upper limit for the concentration range was due to the limited output current for the amplifiers in the potentiostat. Results for concentrations lower than 2·50 × $10^{-8}M$ were not used because repeated integrations gave results varying by more than 10%. The excellent linear correspondence of the experimental results with theory over four decades satisfies the requirement of chromatographic detectors that they function with a large linear dynamic range. Similar response is expected for all electroactive species which react at the electrode by processes limited by convective-diffusional mass transport.

Analysis of standards

Cu(*II*) *and* Fe(*III*). A 0·5040-ml aliquot of the 10·000-μg/ml standard solution of copper(II) and iron(III) was analysed by forced-flow liquid chromatography, using detector C with the separation procedure described in an earlier section. The chromatogram is shown in Fig. 5. The resolution of the peaks was excellent and the baseline was typically less than 0·3 μA. The peak for iron(III) showed considerable tailing. This situation was not improved by cathodic adjustment of electrode potential, use of more peroxide in sample preparation, increase in the hydrobromic acid concentration, or decrease of v_f in the chromatograph and detector. The cause of tailing might be the formation of some iron(III) species which is only slowly desorbed from the ion-exchanger. For the sake of expediency, the integrations of the iron(III) peaks were terminated exactly 8 min after the appearance of the peak maximum. Consequently, the determination of iron(III) on the basis of the time-integral of electrode current and equation (8) yielded low results. The results of the integrations of chromatographic peaks for a series of 5 injections are shown in Table 1. The precision of the results both for copper and iron was excellent. The relative error was 4 ppt for copper(II) and 34 ppt for iron.

NBS 87. NBS 87 presented some interesting challenges for analysis. The high level of trivalent aluminum initially resulted in overloading of the ion-exchange column; the copper(II) was partially displaced from the column by it. The very great sensitivity of the detector, however, allowed injection of very small quantities of the sample without sacrifice in accuracy for the determination of copper and iron. The 6·22% Si resulted in the need to filter off the silica following sample dissolution and dehydration. Failure to do this resulted in plugging of the ion-exchange column by the fine particles. The results for analyses of

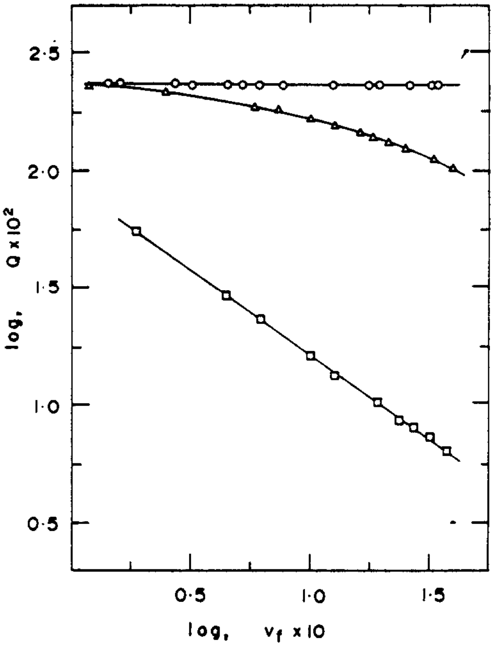

Fig. 4. Log Q *vs.* log v_f for detectors. Injections of 0·5040 ml of $4 \cdot 73 \times 10^{-5}M$ NaI; log ($Q \times 10^2$) calculated for 100·0% efficient electrolysis = 2·36; □—detector A; Δ—detector B; ○—detector C.

5 aliquots of the solution of NBS 87 are given in Table 2. They were calculated by using the calibration constant from Table 1 and on an absolute basis by using equation (8). The copper value calculated by either method was in excellent agreement with the certificate value. The iron value calculated from the calibration was in excellent agreement with the certificate value but that calculated on an absolute basis was 40 ppt low.

NBS 169. NBS 169 was chosen for analysis because of the small amount of copper present (0·015%) and the large ratio of iron to copper (36:1). The results for analyses of

Table 1. Results for standard Cu(II) and Fe(III) sample = 5·040 μg of Cu(II) + 5·040 μg of Fe(III)

Injection	$Q_{Cu(II)}$, mC	$Q_{Fe(III)}$, mC
1	7·59	8·39
2	7·61	8·42
3	7·64	8·40
4	7·62	8·42
5	7·62	8·43
Average	7·62 ± 1·6 ppt	8·41 ± 1·7 ppt
Theoretical [equation (8)]	7·65	8·71
Relative error, ppt	4	34
Calculated calibration constant	1·51 mC/μg	1·67 mC/μg

Table 2. Results for NBS 87 (sample = 809·4 μg)

Injection	$Q_{\mathrm{Cu(II)}}$, *mC*	$Q_{\mathrm{Fe(III)}}$, *mC*
1	3·66	6·11
2	3·66	6·13
3	3·70	6·13
4	3·68	6·14
5	3·69	6·16
Average	3·68 ± 3·9 ppt	6·13 ± 2·1 ppt
% calculated using calibration from Table 1	0·30$_2$ %	0·45$_4$ %
% from certificate	0·30 %	0·46 %
% calculated on absolute basis using equation (8)	0·30$_0$ %	0·43$_9$ %

Table 3. Results for NBS 169 (sample = 2086 μg)

Injection	$Q_{\mathrm{Cu(II)}}$, *mC*	$Q_{\mathrm{Fe(III)}}$, *mC*
1	0·455	18·31
2	0·503	18·23
3	0·459	18·27
4	0·439	18·27
5	0·455	18·39
Average	0·462 ± 35 ppt	18·29 ± 2·2 ppt
% calculated using calibration from Table 1	0·014$_7$ %	0·52$_5$ %
% from certificate	0·015 %	0·54 %
% calculated on absolute basis using equation (8)	0·014$_6$ %	0·50$_8$ %

5 aliquots of the solution of NBS 169 are given in Table 3. The composition was again calculated by the two methods and the agreement with certificate values was similar to that for NBS 87.

DISCUSSION

Several advantages should be noted for the application of coulometric electrodes as detectors for liquid chromatography as reported here. First, 100·0 % electrolytic efficiency results in very high sensitivity and a very low detection limit for applications of the detector. For example, the *I–t* peak for the injection of a 0·5040-ml aliquot of $2{\cdot}5 \times 10^{-8}M$ sodium iodide was integrated with an uncertainty of 10 %. That sample contained only 1·59 ng of iodide. Including consideration of the fact that the ion-exchange column can remove and effectively concentrate species present at the trace level in a large volume of sample, we conclude that the instrumental technique will be useful for determination at the ppb level. Secondly, the great sensitivity and large linear dynamic range for application of the detector make possible its use for multicomponent analysis when the species are present at highly differing levels. Very good results were obtained for the analysis of NBS 169 which contained a 36:1 ratio of iron to copper. Thirdly, analyses performed were of a precision comparable to that expected for volumetric techniques (see Tables 1–3), and achieved even with indeterminate variation of eluent flow-rate, because of the 100·0 % efficiency for the electrolysis reactions. Fourthly, the design of our detector is very simple and the construction very inexpensive. Furthermore, the simplicity of its use in connection with the liquid chromatograph makes the total instrumental method well suited to automation.

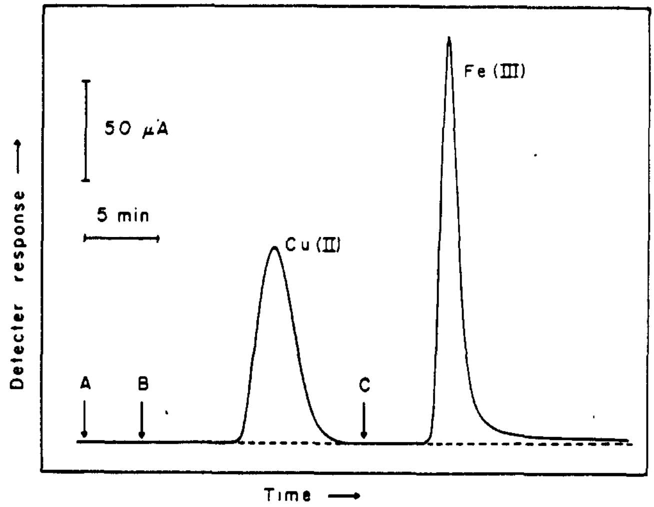

Fig. 5. Chromatogram for standard Cu(II) + Fe(III), using detector C.
Sample = 5·040 μg of Cu(II) + 5·040 μg of Fe(III);
A—injection of sample into stream of 0·3*M* HBr;
B—change of eluent to 1·5*M* HBr;
C—change of eleunt to 25% HBr.

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Zusammenfassung—Es wird eine mit kleinen Platinstückchen vollgestopfte Platinrohrelektrode beschrieben. Es wurde gezeigt, daβ diese mit einem elektrolytischen Wirkungsgrad von 100% arbeitet. Die Anwendung der Elektrode bei der coulometrischen Bestimmung electroaktiver Spezies im Auslauf eines Flüssigkeitschromatographen wird beschrieben. Cu und Fe wurden in einer Anazhl von Standards bestimmt. Eine mittlere relative Abweichung von weniger als 2 ppt wurde bei der Analyse von Proben erhalten, die 5μg Cu(II) und 5μg Fe(III) enthielten.

Résumé—On décrit une électrode de platine tubulaire garnie de petits copeaux de platine, dont on a montré qu'elle fonctionne avec une efficacité électrolytique de 100%. On décrit l'application de l'électrode pour le dosage coulométrique d'espèces électro-actives dans l'effluent d'un chromatographe en phase liquide. On a dosé Cu et Fe dans une série d'étalons. On a obtenu un écart relatif moyen de moins de 2 ppt pour l'analyse d'échantillons contenant 5 μg de Cu(II) et 5 μg de Fe(III).

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NMR DETERMINATION OF THE MICROSCOPIC CONSTANTS OF DIPROTONATED DIAMINES IN AQUEOUS SOLUTION

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Summary—The microscopic acidity constants of the diprotonated asymmetric N-methyl-substituted ethylenediamines and N-methylpiperazine were determined by using the change of the chemical shift of the methyl protons with varying acidity. The determination was carried out at 25° in aqueous solution and in an ionic medium of $1M$ KNO_3. The basicity of the amino-functions follows the expected sequence: secondary > primary ≫ tertiary. The influence of the substituent on the basicity of the end-group is primary > secondary ≫ tertiary.

The dissociation of asymmetric diprotic acids can be described in terms of microscopic constants. In this study the microscopic constants of N-methyl-substituted ethylenediamines and N-methylpiperazine were investigated. According to King,[1] the dissociation scheme can be represented as follows:

$$\begin{tikzcd}
 & A\text{-}B\overset{+}{H} \arrow[dr, "k_c"] & \\
\overset{+}{H}A\text{-}B\overset{+}{H} \arrow[ur, "k_a"] \arrow[dr, "k_b"'] & & A\text{-}B \\
 & \overset{+}{H}A\text{-}B \arrow[ur, "k_d"'] &
\end{tikzcd}$$

where A–B is the unprotonated molecule, A stands for the basic site that is the less substituted, and B for the basic site that is the more substituted by the methyl group.

Many methods such as ultraviolet and infrared spectrophotometry,[2–5] potentiometry,[6] calorimetry[7,8] and NMR[3,9,10] have been used to determine microscopic constants. The last named method seems to be very appropriate.

In this investigation proton resonance may be expected from the methylene and methyl groups. These protons attached to nitrogen are labile and their resonance is combined with that of water, which is used as a solvent. In some studies,[10] methylene proton chemical shifts were used for determining microscopic constants. A preliminary investigation revealed that resonance of the methylene protons turned out to be second order at higher pH values. Since low concentrations were used here, it was difficult to distinguish some of the response signals from the noise. This second-order phenomenon has been confirmed by using higher concentrations, as illustrated in Fig. 1.

The resonance signal from the methyl group is one sharp peak over the whole pH range, indicating a fast equilibrium between the different species. Moreover the resonance is influenced only by changes in the protonation of the nitrogen atom adjacent to the

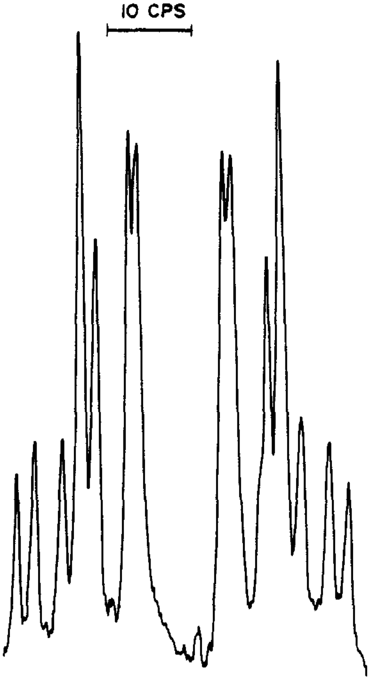

Fig. 1. Proton magnetic resonance of methylene groups in unprotonated *a*-dimen at high concentration (1·5*M*), showing second-order spectrum.

methyl group. Therefore in this investigation microscopic constants were determined from the chemical shift of the methyl group(s) as a function of pH.

EXPERIMENTAL

NMR spectra were recorded on a HFX-5 Bruker Physik spectrometer at a proton frequency of 90 MHz. Tetramethylsilane was used as an external standard. Sample tubes were rotated at a speed of about 4500 rpm. The sample temperature was 25 ± 1°. Shifts were recorded in Hz units. The reproducibility was estimated to be better than 0·2 Hz.

The diprotic acids were prepared from the corresponding amines and nitric acid as described previously.[11]

The following abbreviations are used: en (ethylenediamine), men (*N*-methylethylenediamine), *s*-dimen (symmetric dimethylethylenediamine or *N*,*N*′-dimethylethylenediamine), *a*-dimen (asymmetric dimethylethylenediamine or *N*,*N*-dimethylethylenediamine), trimen (*N*,*N*,*N*′-trimethylethylenediamine), tetramen (*N*,*N*,*N*′,*N*-tetramethylethylenediamine), pip (piperazine), mpip (*N*-methylpiperazine) and dimpip (*N*,*N*′-dimethylpiperazine).

For each asymmetric diprotic acid and for *s*-dimen 10–15 solutions were prepared, with total concentration of 0·05*M* for the protonated diamines, 1*M* potassium nitrate as an indifferent electrolyte, and a varying amount of potassium hydroxide. To the first solution no potassium hydroxide was added. The last solution of each series contained an excess of base to ensure the full deprotonation of the acid. For the symmetric acids only two solutions were prepared: one without potassium hydroxide, and a second with an excess of base. The concentration of the diprotic acid should be low in comparison with the concentration of the indifferent electrolyte, so that the macroscopic acidity constants determined in 1*M* potassium nitrate can be used in the calculations. Otherwise large errors can be made as mentioned by Martin.[12] Calculations were performed with a Siemens computer model 4004/150 and appropriate programmes were written in Fortran IV.

Method

The dissociation of the diprotic acid can be described by

$$H_2L^{2+} \rightleftharpoons H^+ + HL^+ \tag{1}$$

$$HL^+ \rightleftharpoons H^+ + L \tag{2}$$

The acidity constants are defined as

$$K_1 = \frac{a_{\mathrm{H}}[\mathrm{HL}]}{[\mathrm{H_2L}]}$$

$$K_2 = \frac{a_{\mathrm{H}}[\mathrm{L}]}{[\mathrm{HL}]}$$

charges being omitted for simplicity.

The values of these "mixed" acidity constants have been reported elsewhere.[11] The relation between the acidity constants and the microscopic constants can be expressed by

$$K_1 = k_a + k_b \tag{3}$$

$$\frac{1}{K_2} = \frac{1}{k_c} + \frac{1}{k_d} \tag{4}$$

The method for determining the microscopic constants is based upon two assumptions:

(*i*) the shielding of the basic site adjacent to the methyl group is linearly related to the fraction of time it is protonated;

(*ii*) the other basic site has no influence on the shielding.

Assumption (*i*) was proved by Grunwald et al.;[13] (*ii*) seems to be a fairly good assumption since the methyl protons are five atoms away from the non-adjacent basic site. Thus protonated *s*-dimen will act as a monoprotic acid with concentration twice the concentration of the original acid. In this case:

$$\delta = \frac{[\mathrm{HL}] + 2[\mathrm{H_2L}]}{2C_{\mathrm{L}}}\,\Delta\delta_t + \delta_b \tag{5}$$

in which δ is the chemical shift of the methyl protons, $\Delta\delta_t$ is the difference of the chemical shift between the fully protonated and deprotonated acid and δ_b is the chemical shift of the fully deprotonated acid. In order to check equation (5), a_{H} was calculated from the relation

$$C_{\mathrm{B}}a_{\mathrm{H}}^3 + (C_{\mathrm{B}}K_1 - K_{\mathrm{W}} - C_{\mathrm{L}}K_1)a_{\mathrm{H}}^2 + (C_{\mathrm{B}}K_1K_2 - K_{\mathrm{W}}K_1 - 2K_1K_2C_{\mathrm{L}})a_{\mathrm{H}} - K_{\mathrm{W}}K_1K_2 = 0 \tag{6}$$

where $K_{\mathrm{W}} = a_{\mathrm{H}}[\mathrm{OH}]$ and was obtained experimentally for this medium, as reported earlier.[11] By use of the known macroscopic acidity constants[11] [L], [HL] and $[\mathrm{H_2L}]$ were calculated. The value of δ as a function of $([\mathrm{HL}] + 2[\mathrm{H_2L}])$ gives a straight line with correlation coefficient 0·991; $\Delta\delta_t$ calculated from the slope was 46·8 Hz, and from the intercept and the δ value for total protonation it was 46·4 Hz, so assumptions (*i*) and (*ii*) can be considered as sufficiently valid, and formulae can be established in order to calculate the microscopic constants of the asymmetric diprotic acids. If there is only one substituted nitrogen atom the difference of the chemical shift from δ_b, $\Delta\delta$, is given by

$$\Delta\delta = \frac{[\mathrm{HA\text{-}B}] + [\mathrm{H_2L}]}{C_{\mathrm{L}}}\,\Delta\delta_t \tag{7}$$

Then, from this equation, and considering the dissociation scheme:

$$k_a = \frac{a_{\mathrm{H}}}{[\mathrm{H_2L}]}\left(\frac{\Delta\delta C_{\mathrm{L}}}{\Delta\delta_t} - [\mathrm{H_2L}]\right) \tag{8}$$

$$k_c = \frac{a_{\mathrm{H}}[\mathrm{L}]\,\Delta\delta_t}{\Delta\delta C_{\mathrm{L}} - \Delta\delta_t[\mathrm{H_2L}]} \tag{9}$$

The values of k_b and k_d can be calculated from k_a, k_c and equations (3) and (4). In the case of trimen where both basic sites are substituted, k_b and k_d can be calculated from equations similar to relations (8) and (9).

RESULTS AND DISCUSSION

Table 1 summarizes the chemical shift values of the symmetric and asymmetric diprotic acids: $n = 0$ and $n = 2$ mean fully unprotonated and fully protonated acid respectively.

It is remarkable that for tertiary amines the chemical shift is about 10 Hz units lower for $n = 0$ than for the secondary amines, and about 15 Hz units higher for $n = 2$. As

Table 1. Chemical shift values of fully unprotonated ($n = 0$), and protonated ($n = 2$) acids, in Hz *vs.* TMS

Acid		$n = 0$	$n = 2$
men		249·2	294·6
s-dimen		249·5	294·4
trimen	$-NHCH_3$	249·9	295·2
	$-N(CH_3)_2$	239·0	309·7
a-dimen		238·7	308·6
tetramen		239·1	309·2
mpip		238·7	311·5
dimpip		240·5	313·5

a result, in the case of trimen, with decreasing pH, the value of the resonance peak due to the methyl groups belonging to the tertiary amino function will shift to the other side of the resonance peak due to the methyl group of the secondary amino function.

The results of the calculations of microscopic constants from equations (8) and (9) are shown in Table 2. The α-values given in the last column are defined as

$$\alpha = \frac{[A\text{–}BH]}{[A\text{–}BH] + [HA\text{–}B]} = \frac{k_b}{k_a + k_b} = \frac{k_c}{k_c + k_d}$$

Table 2. Microconstants with standard deviations and α-values, for asymmetric acids

Acid	pk_a	pk_b	pk_c	pk_d	α*
men	7·677 ± 0·008	7·899 ± 0·013	10·076 ± 0·008	9·854 ± 0·013	0·38(0·42)
trimen	7·500 ± 0·019	6·972 ± 0·008	9·306 ± 0·019	9·834 ± 0·008	0·77(0·79)
a-dimen	7·342 ± 0·025	7·135 ± 0·015	9·417 ± 0·024	9·623 ± 0·014	0·62(0·62)
mpip	5·721 ± 0·015	5·354 ± 0·007	8·794 ± 0·016	9·162 ± 0·007	0·70(0·68)

* Values in brackets are those obtained by calorimetry.[11]

These values agree quite well with those reported earlier[11] and obtained by a calorimetric method described by Paoletti *et al.*[14] The hypothesis, made by Paoletti, that the enthalpy change involved in the dissociation of a proton is dependent on the dissociating group, therefore seems valid, and thus for primary amino-functions the values from en may be used, and similarly those from *s*-dimen for the secondary amino-function and from tetramen for the tertiary. This means that the influence of the substituent seems to be an entropy effect. This is confirmed by the fact that the second method mentioned by Paoletti *et al.*[14] for calculating microscopic constants from macroscopic constant values, gives results which deviate to a large degree from the results obtained here and earlier.[11] This could be explained by the fact that the values of the macroscopic constants are more influenced by the substituents than the values of the enthalpy changes.

For securing more insight, the results of Table 2 are rearranged in Table 3 as a function of the acidic group and of the substituent on the second site. They are completed with the microscopic constants of the symmetric diprotic acids. The latter have been obtained from the macroscopic constants[11] by taking into account the contribution of the symmetry effect.

For symmetric diamines both acidic groups are equivalent, thus $k_a = k_b$ and $k_c = k_d$. Then it follows from equations (3) and (4) that

$$\mathrm{p}k_a = \mathrm{p}k_b = \mathrm{p}K_1 + \log 2$$

$$\mathrm{p}k_c = \mathrm{p}k_d = \mathrm{p}K_2 - \log 2$$

Thus, microscopic constants of symmetric acids can be obtained directly from the macroscopic constants.[11] In Table 3 the microscopic constants for symmetric and asymmetric diamines are given as a function of the acidic group and the substituent on the second site. In that table the acidity constants are given for all possible dissociations of the *N*-methyl-substituted ethylenediamines and piperazines. Table 3 can be interpreted in the following way: *e.g.*, for $CH_3NH_2^+CH_2CH_2NH_3^+$ there is the possibility of considering two dissociations; if NH_3^+ is the dissociating group then $CH_3NH_2^+$ is the substituent and the *pK* values is 7·68; if $CH_3NH_2^+$ is the dissociating group then NH_3^+ is the substitutent and the *pK* value is 7·90. For a protonated form, *e.g.*, $NH_2CH_2CH_2NH_2^+CH_3$ there is only one possibility: $CH_3NH_2^+$ is the dissociating group and NH_2 the substituent.

Table 3. Microconstants of acids as a function of acidic group and substituent

Ethylenediamine and derivatives

Substituent \ Acidic group	$-\overset{+}{N}H_2CH_3$	$-\overset{+}{N}H_3$	$-\overset{+}{N}H(CH_3)_2$
$-\overset{+}{N}H_3$	7·90	7·84	7·14
$-\overset{+}{N}H_2CH_3$	7·83	7·68	6·97
$-\overset{+}{N}H(CH_3)_2$	7·50	7·34	6·66
$-NH_2$	10·08	9·93	9·42
$-NHCH_3$	9·96	9·85	9·31
$-N(CH_3)_2$	9·83	9·62	9·15

Piperazine and derivatives

	$>NH_2^+$	$>\overset{+}{N}HCH_3$
$>NH_2^+$	6·34	5·35
$>\overset{+}{N}HCH_3$	5·72	4·93
$>NH$	9·70	8·79
$>NCH_3$	9·16	8·24

Several trends can be noted in the values of the microscopic constants in Table 3. In each case, the secondary amino-function is a stronger base than the primary, which itself is a much stronger base than the tertiary amino-function. This is demonstrated by the horizontal lines of Table 3. The vertical lines of Table 3 show the influence of the substituent. It is noteworthy that here the sequence between primary and secondary amino-functions has changed. Indeed, the primary amino-function as a substituent strengthens in each case the basicity of the end-group more than the secondary amino-function does. This is true for both the series of protonated and unprotonated substituents, and could be an explanation for the roughly equal values for the macroscopic constants of en and *s*-dimen.

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Zusammenfassung—Die mikroskopischen Aciditätskonstanten der zweifach protonierten asymmetrisch *N*-methylsubstituierten Äthylendiamine und von *N*-Methylpiperazin wurden bestimmt durch Messung der Änderung der chemischen Verschiebung der Methylprotonen mit der Änderung der Acidität. Die Bestimmung wurde in wäßriger Lösung bei 25° und in einem Ionenmedium von 1 *M* KNO_3 ausgeführt. Die Basizität der Aminofunktionen zeigt den erwarteten Gang: sekundär > primär ≫ tertiär. Der Einfluß des Substituenten auf die Basizität der Endgruppe ist primär > sekundär ≫ tertiär.

Résumé—On a déterminé les constantes d'acidité microscopiques des éthylènediamines *N*-méthyl substituées diprotonées asymétriques et de la *N*-méthylpipérazine en utilisant le changement du déplacement chimique des protons du méthyle avec l'acidité variable. Le dosage a été mené à 25° en solution aqueuse et dans un milieu ionique de KNO_3 1*M*. La basicité des fonctions amine suit la séquence attendue: secondaire > primaire ≫ tertiaire. L'influence du substituant sur la basicité du groupe terminal est primaire > secondaire ≫ tertiaire.

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ANALYTICAL APPLICATION OF ORGANIC REAGENTS IN HYDROPHOBIC GEL MEDIA—I

GENERAL PRINCIPLE AND THE USE OF DITHIZONE GEL*

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Summary—Two types of hydrophobic gel particles containing dithizone were prepared, either by the swelling of low cross-linkage polystyrene beads with a dithizone solution in chlorobenzene, or by the gelatinization of a dithizone solution with dibenzalsorbitol. The extraction capacity of the gel particles for metal ions such as mercury, cadmium, zinc and lead from dilute aqueous solution, was investigated at various dithizone concentrations and pH values. A column packed with such gel particles is found to be useful for the selective preconcentration or the selective trapping of specific metal ions at low concentration levels.

Solvent extraction of inorganic ions from the aqueous into the organic phase with various organic reagents has been extensively investigated.[1] If the organic solvent phase containing an organic reagent is frozen in the form of small particles, the solvent extraction process can be replaced by a flow process, in which the aqueous phase moves through a column packed with such frozen organic liquid particles. However, as it is not practical to use frozen particles, hydrophobic gel particles containing organic reagents can be employed instead. Such gel particles can be prepared either by the swelling of low cross-linkage synthetic polymer beads or by the gelatinization of organic solvent with a suitable gelatinizing agent, and various organic reagents can be incorporated into such gel particles. With the use of a column packed with such hydrophobic gel particles containing various organic reagents, inorganic ions in the mobile aqueous phase can be extracted into the stationary phase of gel particles.[2]

The use of polystyrene beads as a solid support for the stationary phase in reversed-phase partition chromatography has been reported.[3,4] In that work, however, porous polymers with relatively higher cross-linkage were employed, so that a high content of stationary phase liquid cannot be expected since the polymer beads support the liquid only mechanically, without swelling.

The idea of using low cross-linkage polystyrene beads swollen with solvent as a stationary phase was once the subject of a patent.[5] Later, columns packed with swollen polystyrene beads containing various organic reagents were proposed for the concentration and the chromatographic separation of metal ions.[6,7]

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The purpose of our investigation is to improve the gel–liquid extraction system as well as to prepare a wider variety of such gel particles. In this paper, we report on the construction of such a system, the preparation of gel particles containing dithizone as an extraction reagent and their application in analytical chemistry.

EXPERIMENTAL

Preparation of polystyrene gel beads

Spherical beads (2 g) of styrene–divinylbenzene copolymer (2% divinylbenzene)*, which had been previously dried at 90°, were soaked with 10 ml of 0·3% dithizone solution in chlorobenzene for 24 hr at room temperature. The excess of solvent was removed from the green gel beads by centrifugation. The amount of solution soaked into the polymer was determined from the weight increase of the gel beads after swelling, and was found to be 2·3–2·5 ml/g, referred to dry polymer beads. The diameter of the swollen gel beads was in the range 50–200 μm. The gel beads were packed into a column 13 mm in diameter and 75 mm in height to give a gel bed volume of about 10 ml. As the green gel is fairly unstable, owing to air oxidation, the gel column was best stored under 0·1% ascorbic acid solution in a dark cool place. Alternatively, the green gel beads were suspended in 1% aqueous zinc sulphate solution to convert them into the pink zinc dithizonate gel beads which are stable for many months at room temperature. The pink gel beads were packed in a column which was eventually treated with a dilute mineral acid solution to regenerate the green dithizone gel immediately before use.

Preparation of gel particles by gelatinization of organic solvents

A hot mixture (about 90°) of 5 ml of 0·3% dithizone solution in chlorobenzene and a solution of 1 g of dibenzalsorbitol† in 3 ml of dimethylformamide, was poured through a narrow nozzle into 200 ml of cold water with vigorous stirring. The resulting amorphous gel particles were collected by filtration and were packed into a column 11 mm in diameter and 110 mm in height to give a gel bed volume of 11–12 ml. The gel particles thus obtained were pinkish green and gradually turned to pink upon standing for a few days, probably owing to complex formation with dimethylformamide. Accordingly, the column was treated with dilute mineral acid solution to regenerate the green dithizone gel before use.

Column operation

An aqueous solution of known metal ion concentration, which had been saturated with chlorobenzene, was passed continuously through a column packed with the gel particles until the column came to complete saturation. The effluent was collected in 10-ml fractions, which were analysed for metal ions by using dithizone as a colorimetric reagent. Some of the results are shown in Figs. 1 and 2.

Metal ions were eluted from the column in a fashion similar to that for the extraction process, with 1*N* hydrochloric acid as eluent for the metal ions except mercury, for which sulphuric acid–potassium bromide mixture (50 ml of 1*N* acid plus 10 ml of 40% bromide solution) was used. Each fraction of eluate was analysed for metal ions.

As the recovery of metal ions from the column was found to be almost quantitative, the extraction capacity of the column was estimated from the extraction curve, as the difference of the amount of metal ion in the inflowing and outflowing solutions.

RESULTS AND DISCUSSION

The purpose of this investigation is to replace the conventional solvent extraction process with a column operation using hydrophobic gels containing organic reagents. With the use of such a column, inorganic ions in dilute solution can be selectively extracted and concentrated on the column. Although this process is seemingly similar to reversed-phase chromatography, it differs from it in that the capacity of the stationary phase is much greater, so that a higher extraction capacity per unit volume of gel bed is expected. Accordingly, the process may be useful in the selective concentration or trapping of metal ions

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* Polymer beads were obtained by courtesy of Mitsubishi Kasei Kogyo Co.

† A commercial product, E-Gel Type P, which was obtained by courtesy of E. C. Chemical Co. (Minami-Funabashi, Hirakata-shi, Osaka), was used throughout this investigation. However, laboratory preparations of dibenzalsorbitol gave the same results. For the preparation, refer to L. V. Vargha, *Ber.*, 1935, **68**, 1337 or S. J. Angyal and J. V. Lawler, *J. Am. Chem. Soc.*, 1944, **66**, 837.

from a large volume of dilute aqueous solution, whereas reversed-phase chromatography is useful in the chromatographic separation of metal ions. However, the present process may again become advantageous when such separations on a preparative scale.

Preparation of hydrophobic gel particles

The hydrophobic gel particles for use in this process have been prepared by two methods. The first is based on the use of low cross-linkage synthetic polymer beads which swell easily with hydrophobic organic solvents, *e.g.*, polystyrene or poly(vinyl acetate) beads. The solvent is kept in the network of the polymer matrix, as indicated by the swelling of the beads. Hereafter, this type of gel bead will be designated as PST-gel.

The second method is based on gelatinization of the solvent with, for example, a dimethylformamide solution of dibenzalsorbitol. The gelatinizing properties of dibenzalsorbitol and related compounds have been investigated in detail.[9] Efforts to obtain spherical gel particles by use of suitable surfactants have so far been unsuccessful. The hardness of the gel particles depends upon the kind of solvent and the concentration of the gelatinizing agent. The hardness of chlorobenzene gels was found to increase almost linearly with the concentration of gelatinizing agent and gel particles containing 20% of dibenzalsorbitol were found to be hard enough to be used for the column operation. Hereafter, this type of gel particle will be designated as DBS-gel.

Incorporation of organic reagents into gel particles

If the hydrophobic solvent used for the preparation of the gel particles contains an organic reagent the latter can be incorporated into the hydrophobic gel medium. Various chelating agents or liquid ion-exchangers may be used for this purpose. For the extraction of metal ions, chelating agents such as dithizone, thenoyltrifluoroacetone, thiothenoyltrifluoroacetone or 8-hydroxyquinoline may be incorporated into the gel particles. For the extraction of anions, oil-soluble liquid anion-exchangers such as Aliquat 336 (methyltrioctylammonium chloride), may be incorporated into the gel.

The criteria for choosing organic reagents for this purpose are the distribution coefficients of the organic reagents and their complexes into an organic phase. In the case of the column operation, even a slight distribution of an organic reagent into the aqueous phase results in a considerable loss of the reagent from the gel particles because the organic phase is continuously washed with fresh aqueous phase. Similarly, a slight distribution of complexes into the aqueous phase may result in the incomplete extraction of ions from the aqueous phase, especially at very low concentration levels.

Thus, by use of a column packed with gel particles containing a suitable organic reagent, various inorganic ions at low concentration level can be concentrated on the gel column. Proper adjustment of pH of the aqueous phase, with simultaneous use of masking agents, may increase the selectivity of extraction of inorganic ions into a gel column, just as in the conventional solvent extraction process.

For example, chlorobenzene gel particles containing dithizone extract only mercury, silver and copper from a mixture of common heavy metal ions at pH 1 or lower. However, at higher pH, other heavy metal ions such as lead, cadmium and zinc can also be extracted.

Comparison of the two types of gel

In ease of preparation, PST-gel is superior to DBS-gel, because it can be obtained by simply swelling the dry polymer beads in the appropriate solution of organic reagent.

PST-gel particles are more uniform in size and they are almost spherical if the starting polymer beads are carefully prepared and sieved. The size of DBS-gel, on the other hand, depends upon the conditions of preparation, and the particles are more or less irregular in shape.

When the polystyrene beads are swelling in the solution of organic reagent, the solvent molecules penetrate more easily into the polymer matrix than the solute molecules, if an organic reagent of higher molecular weight is employed. Although segregation of the solute molecule can be neglected for organic reagents of low molecular weight such as dithizone, thenoyltrifluoroacetone or 8-hydroxyquinoline, it becomes significant for solutes such as Aliquat 336. For example, when 2 g of polystyrene beads were soaked with 10 ml of 2% Aliquat 336 solution in chlorobenzene, the concentration of Aliquat in the gel particles was only a quarter of the original concentration in the solvent. Similar segregation of the solute molecule must have occurred in the preparation of the gel beads from polystyrene beads (4% DVB) and a solution of high molecular-weight liquid ion-exchanger, although the authors did not mention this problem.[7] In the case of DBS-gel, however, the entire solution can be completely gelatinized, so that there is no chance of segregation of the solute molecule.

Column operation with dithizone gel

In the preparation of DBS-gel, organic solvents such as *o*-dichlorobenzene or tetrachloroethylene were substituted for chlorobenzene, and the extraction capacity of such DBS-gels for mercury(II) was investigated. The result, as shown in Fig. 1, indicates that the extraction capacity is maximum for chlorobenzene, probably because of the solubility of mercury dithizonate is higher in chlorobenzene than in other solvents.

Mercury(II) is known to give an orange primary dithizonate, $Hg(HDz)_2$, at low pH, and a pink secondary dithizonate, $Hg_2(Dz)_2$, at neutral or high pH. When mercuric nitrate

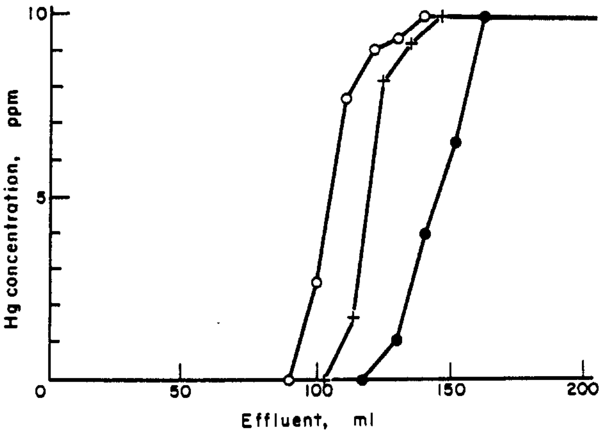

Fig. 1. Relationship between solvent and extraction capacity.
—●— chlorobenzene
—+— *o*-dichlorobenzene
—○— tetrachloroethylene
Composition of gel: gelatinizer 1 g, dimethylformamide 3 ml, solvent 5 ml, dithizone 2·56 mg.
Column conditions: pH 1·1; column height, *ca.* 12 cm; gel bed volume, *ca.* 11 ml; flow-rate 50 ml/hr.

solution containing 10 ppm of Hg, adjusted to pH 1 with nitric acid, was passed through the column, the original green colour of the DBS-gel changed to orange from the top of the column, indicating the formation of primary mercuric dithizonate. As the solution flowed through the column, the orange band elongated downward and a new narrow pink zone appeared at the top, showing the formation of secondary dithizonate even at pH 1. This may be attributed to the higher mercuric ion concentration relative to the dithizone concentration in the gel particles on the upper part of the column. When the orange zone reached the bottom of the column, the top 20% was pink and rest orange. Thus, about 33% of the mercury(II) had been extracted as a secondary dithizonate at this stage.

When the sample solution in pH 6 acetate buffer was passed through the column, the green gel particles turned to pink at the top, indicating the immediate formation of a secondary dithizonate at this pH value. As the solution flowed through the column, the pink zone elongated downward, indicating that mercuric ion was extracted almost exclusively as a secondary dithizonate at pH 6, as expected from the solvent extraction study.

The result of column operation at various pH values indicated the increased extraction capacity at higher pH, which agrees well with the complexing behaviour of dithizone with mercury(II). The calculated amounts of mercury that can be extracted with dithizone on the column are 1·0 and 2·0 mg for the primary and secondary dithizonate respectively. The observed values for complete saturation of the column are 1·4 mg (pH 1·1), 1·5 mg (pH 4·6) and 1·85 mg (pH 6·2), which lie in the range of expected values. The difference between observed and calculated values at pH 6·2, where mercury(II) is expected to form a secondary complex exclusively, may be partly due to the decomposition of dithizone and partly due to the slow diffusion of metal ion in the gel matrix.

The extraction capacity of DBS-gel is nearly proportional to the dithizone concentration in the gel particles, as shown in Fig. 2. A sample solution containing 10 or 20 ppm of

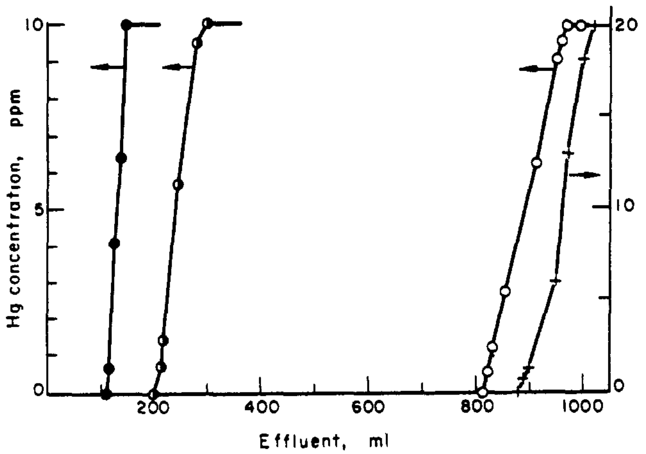

Fig. 2. Relationship between dithizone concentration and extraction capacity.
—●— 2·4 mg (*ca.* 0·05%); —◑— 5·1 mg (*ca.* 0·1%); flow-rate of 50 ml/hr.
—○— 15·0 mg (*ca.* 0·3%); —+— 29·5 mg (*ca.* 0·6%); flow-rate of 100 ml/hr
Composition of gel: same as for Fig. 1, except dithizone concentration.
Column conditions: same as for Fig. 1, except flow-rate.

mercury was passed through the column until the latter was completely saturated. The amounts of mercury(II) extracted into the gel particles were estimated from Fig. 2, and were 0·53, 0·44, 0·59 and 0·65 mg per mg of dithizone at pH 1·1 on DBS-gel columns of 0·05, 0·1, 0·3 and 0·6% dithizone concentration respectively. The extraction capacity was higher for the more concentrated dithizone gel column, which may be explained by the decomposition of dithizone being relatively lower in the gel particles of higher dithizone concentration. The observed extraction capacity of DBS-gel of 0·6% dithizone concentration is 9 μeq per ml of apparent gel bed volume, whereas the corresponding values calculated from the amount of dithizone used are 6 and 12 μeq/ml for the primary and secondary complexes respectively.

PST-gel columns and the extraction of other metal ions such as cadmium, zinc and lead, were similarly investigated.

PST-gel prepared by the standard procedure using 0·1% dithizone solution in chlorobenzene, was found to contain 0·47 mg of dithizone per ml of apparent gel bed volume. As the dithizone concentration in the supernatant solution after the swelling of the polymer beads was found to be same as that before the swelling, the dithizone concentration did not change during the preparation of PST-gel.

With PST-gel of higher dithizone concentration (0.3% or higher), the mercury dithizonate complex was found to pass into the aqueous phase before the column was saturated with mercury(II). Accordingly, PST-gel containing 0·1% dithizone was used throughout this investigation. With lower dithizone concentrations, the extraction capacity of the gel beads is approximately proportional to the dithizone concentration as in the case of DBS-gel.

Mercury(II) extracted into the PST-gel column can be eluted with sulphuric acid–potassium bromide mixture, leaving free dithizone in the gel beads. The mercuric dithizonate complex can also be recovered by flushing the column with organic solvents such as methyl isobutyl ketone until the gel beads become colourless.

The extraction behaviour of dithizone PST-gel towards other metal ions such as cadmium, zinc and lead, was also investigated with a 0·1% dithizone gel column, and found to be similar to that obtained in the solvent extraction study. With increasing pH of the aqueous phase, the extraction capacity of the gel increased. The minimum pH values for optimum extraction capacity are 3·5 for Cd, 4·0 for Zn and 5·2 for Pb. The degree of extraction (amount actually extracted, as fraction of that equivalent to the amount of dithizone used) was 50–70%. The calculation was based on the formation of a primary complex, $M(HDz)_2$, which is known to be the only complex formed with these metal ions. The rather poor extraction capacity may again be attributed to the decomposition of dithizone during preparation of the gel and to the slow diffusion of metal ions in the gel matrix.

The metal ions in the column can easily be eluted by passing 1*N* hydrochloric acid through the column, the recovery being almost quantitative. Though free dithizone PST-gel is rather unstable, its complexed form is very stable, and the column can be used repeatedly if the column is stored in the complexed form. For example, the column was used repeatedly for the extraction and elution of zinc for ten cycles during a period of two weeks, without showing any decrease of extraction capacity.

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Zusammenfassung—Zwei Typen von hydrophoben Gelteilchen wurden hergestellt, die Dithizon enthalten. Entweder wurden schwach vernetzte Polystyrol–Perlen mit einer Lösung von Dithizon in Chlorbenzol gequollen, oder es wurde eine Dithizonlösung mit Dibenzalsorbit gelatiniert. Die Extraktionskapazität der Gelteilchen für Metallionen wie Quecksilber, Cadmium, Zink und Blei aus verdünnter wäßriger Lösung wurde bei verschiedenen Dithizonkonzentrationen und pH-Werten ermittelt. Eine mit solchen Gelteilchen beschickte Säule erweist sich als nützlich für die selektive Voranreicherung oder zum selektiven Abfangen bestimmter Metallionen, die in geringen Konzentrationen vorliegen.

Résumé—On a préparé deux types de particules de gel hydrophobe contenant de la dithizone, soit par le gonflement de perles de polystyrène à faible enchaînement par liaison transversale avec une solution de dithizone en chlorobenzène, soit par gélatinisation d'une solution de dithizone avec le dibenzalsorbitol. On a étudié la capacité d'extraction des particules de gel pour des métaux tels que mercure, cadmium, zinc et plomb à partir de solution aqueuse diluée, à diverses concentrations en dithizone et valeurs de pH. On a trouvé qu'une colonne garnie avec de telles particules de gel est utile pour la préconcentration sèlective ou la fixation sélective d'ions métalliques spécifiques à de faibles niveaux de concentration.

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FLUORIMETRIC METHOD FOR THE DETERMINATION OF LONG-CHAIN AMINES IN WATER

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Summary—A method is presented for the determination of long-chain quaternary ammonium salts, tertiary amines and secondary amines in water or aqueous raffinates, based on their extraction and fluorimetric determination as amine salts with Eosine Yellowish in toluene–hexanol (4 : 1) as solvent. No interferences were obtained from metal ions, or chloride, nitrate or phosphate ions when a back-washing method was applied to the sample extract. The method allows the determination of long-chain tertiary amines down to 4 ppM.

Until recently there existed no satisfactory analytical method for the determination of traces of long chain amines in water. Milun and Moyer[1] in 1956 reported a method based on the titration with an anionic detergent of the pink colour formed by the reaction of amines with eosin. This method allows concentrations of amines greater than 0·5 ppm to be determined. The current awareness of the need to protect the environment from chemical pollutants has created the need for more sensitive analytical methods. The necessity to determine traces of amines at the parts per milliard (ppM) level in the raffinate wastes from mineral processing involving amine solvent-extraction stages, has already been stressed.[2] Recent research in these laboratories[2] has resulted in a method based on the extraction of the amines as ion-association complexes with chromate, which allows the determination of down to 0·01 ppm of amines in natural waters or processing raffinates.

Following this study, we examined the possible application of fluorimetric methods to the determination of traces of amines to decrease further the limits of detection, and studied methods based on the formation of fluorescent salts of amines with phthalein dyes.[3] The formation of such salts has been known for some time. Davis *et al.*[4] in 1948 referred to the use of Bromophenol Blue in the spectrophotometric determination of di-n-butylamine by its salt formation in benzene. Palit[5] reported highly sensitive qualitative tests for organic bases and salts based on their extraction as complexes with phthalein dyes. The application of fluorimetry to such reactions appears to have been neglected despite the fact that the increasing sophistication of modern fluorimeters and the inherent sensitivity of the fluorimetric method should make it possible to considerably lower the limits of detection of methods based on a spectrophotometric measurement of a fluorescent complex.

This paper reports the application of fluorimetry to the determination of traces of long-chain amines as an ion-association complex with Eosine Yellowish. Optimization of the conditions for extraction and measurement of this complex has resulted in a limit of detection of 4 ppM for the commercial tertiary amine, Alamine 336.

EXPERIMENTAL

Apparatus

Fluorimetric measurements were carried out in 1-cm cells with a Farrand spectrofluorimeter, using slits giving a 10-nm bandwidth. Separating funnels and flasks were siliconed with Beckman "Desicote" to minimize adsorption of amines.

Reagents

Eosin solution. Weigh 10·0 mg of Eosine Yellowish (Merck) into a 50-ml volumetric flask. Add n-hexanol to the mark and shake to dissolve. Transfer 20 ml of this solution into a 100-ml volumetric flask and dilute to volume with toluene. Remove the pink-yellow colour of the solution by adding 1 g of citric acid and shaking for several minutes. Decant the solution from the undissolved acid.

Buffer solution. A 1*M* citrate buffer is prepared by dissolving 21·0 g of citric acid in water, adjusting to pH 4·0 with 1*M* sodium hydroxide, then diluting to volume in a 100-ml volumetric flask.

Amines. Alamine 336 (a mixture of tri-n-octylamine and tri-n-decylamine) and Aliquat 336 (the quaternary ammonium chloride of Alamine 336) were supplied by General Mills Inc., Ill., U.S.A. Amberlite LA-1, a secondary amine with 12–14 carbon atoms, and Primene JM-T, a primary amine with 18–24 carbon atoms, were supplied by Rohm and Haas Co., Penn., U.S.A.

Standard Alamine 336 solution. Accurately weigh about 50 mg of amine into a 100-ml volumetric flask and dilute to volume with dioxan. Shake thoroughly, then dilute 1 ml of this solution with dioxan to 10 ml in a volumetric flask.

Recommended procedure

By pipette take 10 ml or less of the amine sample (containing *e.g.*, 0·5–10 μg of Alamine 336) into a 50-ml separating funnel. If the amine solution is strongly acid or alkaline it must first be neutralized to about pH 4. Add 1 ml of 1*M* citrate buffer, pH 4·0, and distilled water so that the total volume is 11 ml. Add 5 ml of eosin solution in toluene–hexanol, stopper the funnel and shake vigorously for 2 min. After the phases have separated, withdraw a sample of the organic layer and transfer it to a 10-ml conical flask containing a small quantity of anhydrous sodium sulphate. When the sample has lost all turbidity transfer it to a 1-cm cell and measure its fluorescence intensity as rapidly as possible, using an excitation wavelength of 495 nm and an analyser wavelength of 556 nm.

In the presence of greater than 100 ppm of metal ions or for sea-water samples the following back-washing procedure should be used after the first extraction. After the phases have separated, withdraw 4 ml of the organic layer and transfer it to a second 50-ml separating funnel containing 10 ml of distilled water and 0·1 ml of citrate buffer, pH 4·0. Shake for 2 min and remove a sample of the organic layer to a 10-ml conical flask containing anhydrous sodium sulphate. When all turbidity is lost, transfer the solution to a 1-cm cell and measure as before.

Prepare a calibration graph by applying the method to aliquots of standard amine solution containing 1, 1·0, 2·5, 5·0 and 10·0 μg of amine.

RESULTS AND DISCUSSION

Calibration graph

A calibration graph for Alamine 336 is linear but gives an intercept on the ordinate. Since discontinuous operation of the spectrofluorimeter can result in changes in the fluorescence intensity, the calibration graph must be checked for each day's operation of the instrument. Having established that this graph is linear it is possible to correct for variations in its slope by measuring the fluorescence intensity for two amine concentrations (we chose 2·5 and 5 μg) at the start of each day's operation.

The recommended procedure outlined above is based on the extraction of up to 10 ml of an amine-containing solution. It is possible however to extract all the amine from a 50-ml volume but extraction from the smaller volume is more efficient. Extractions from volumes larger than 50 ml resulted in dissolution in the aqueous phase of part of the hexanol from the organic phase, with an accompanying decrease in the fluorescence intensity of the extract.

Fluorescence spectrum

The fluorescence spectrum of the amine salt of Eosine Yellowish in 80% toluene–20% hexanol is shown in Fig. 1. An excitation wavelength of 495 nm was found to be satisfactory, and was chosen in preference to an excitation wavelength of 530 nm to avoid any contribution of the excitation peak to the emission intensity at 556 nm, the wavelength at which the fluorescence peak occurs.

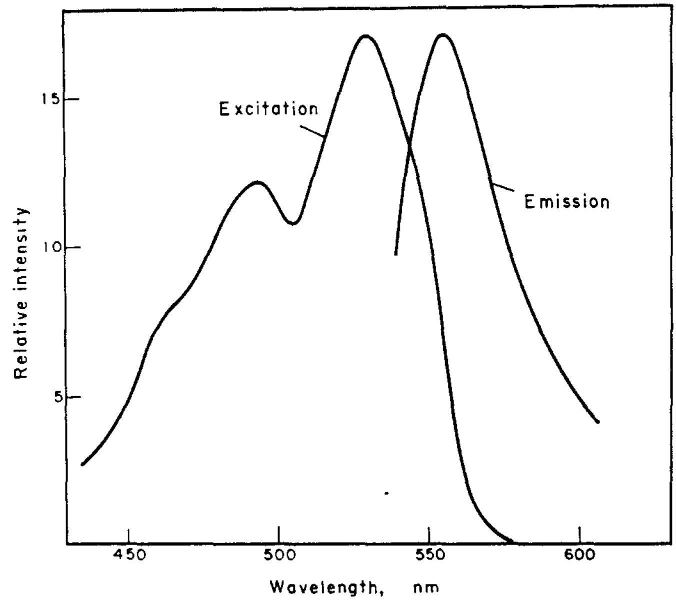

Fig. 1. Excitation and emission spectra (uncorrected) for the Alamine 336 complex of Eosine Yellowish in 80% toluene–20% hexanol.
Excitation wavelength 495 nm, amine concentration 0·7 μg/ml.

Choice of solvent

Because the fluorescence intensity varies considerably as the solvent system is altered, the fluorescence of the Eosine Yellowish–amine complex in a number of solvents was studied. A system was sought in which a stable emission spectrum having high-intensity fluorescence was obtained. The fluorescence of the solvent in the absence of the complex should be of minimum intensity.

Table 1 shows the effect of different solvent systems on the fluorescence intensity. In many cases the blank values were too high to be useful. In chlorinated solvent systems, the eosin–amine extract underwent photochemical dissociation when illuminated with light of the excitation wavelength, 495 nm. In carbon tetrachloride–acetone-medium the fluorescence for a solution containing 5 μg of Alamine 336 decayed to the blank value in less than 3 min. This type of phenomenon is not unknown in fluorescence studies[6] and in this case is probably due to photochemical instability of the solvent with subsequent decomposition of the fluorescent complex.

The toluene–hexanol system was found to be the most satisfactory, giving a low blank and a comparatively stable fluorescence intensity for the amine complex, although a slow decay of the signal did occur. The effect of increasing temperature is to decrease the fluorescence

Table 1. Effect of solvent on the fluorescence intensity at 556 nm of the Eosine Yellowish–Alamine 336 complex

Solvent	Fluorescence intensity blank	 5 μg of Alamine 336*
20% acetone + 80% butanol	7·45	18·30
20% acetone + 80% octanol	8·83	20·70
20% acetone + 80% methyl isobutyl ketone	2·30	7·60
20% acetone + 80% ethylene dichloride	5·45	16·00
20% acetone + 80% carbon tetrachloride	1·25	11·50
20% acetone + 80% n-hexane	0·13	2·85
20% acetone + 80% toluene	2·05	8·05
20% n-hexane + 80% toluene	1·65	7·03

* Measured rapidly.

intensity, and heating of the sample solution in the cell compartment by the exciting radiation could therefore have been responsible for the observed intensity decrease.

Effect of pH

The pale yellow acid form of Eosine Yellowish is extractable as a colourless extract into non-aqueous solvents. In alkaline solution the anionic form of the dye is not extractable. The efficiency of the amine–eosin extraction was studied over a range of pH values from 2 to 6. The graph of fluorescence intensity *vs.* pH (Fig. 2) showed a maximum at pH 4·5.

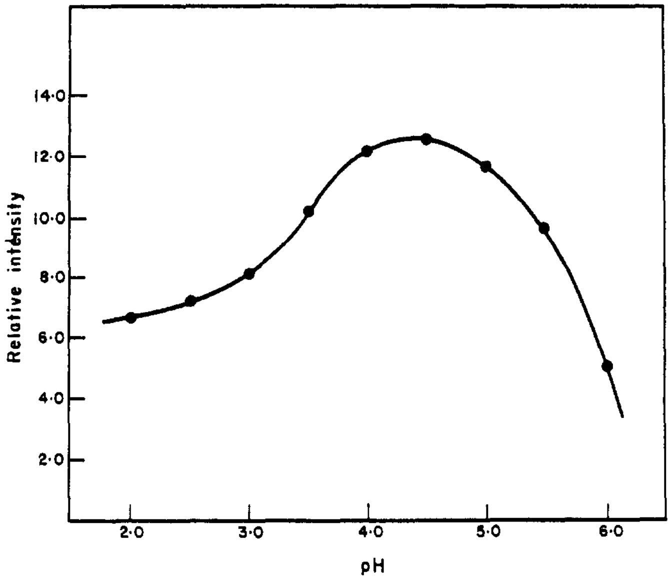

Fig. 2. Effect of pH on the fluorescence intensity of the Alamine 336 complex of Eosine Yellowish in 80% toluene–20% hexanol.
Amine concentration 0·7 μg/ml, citric acid–sodium citrate buffer solutions.

At low pH values the amine is protonated and will not extract completely while at pH values greater than 5, ionization of eosin occurs, with back-extraction into the aqueous phase. A pH of 4·0 was chosen for our method.

Alternative extraction procedure

As an alternative to the procedure outlined it was also possible to use Eosine Yellowish as an aqueous solution and extract this with the recommended solvent at the required pH. When a solution buffered to pH 4·0 is used the dye extract is colourless. The blanks so obtained were, however, considerably higher than those obtained by using the recommended method.

Study of interferences

The recommended method, with a single extraction, was applied to the determination of 2·5 μg of Alamine 336 in the presence of 100 ppm of the following ions: Fe^{3+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, Co^{2+} U(VI) and V(V), as shown in Table 2. No serious interferences were observed. Chloride and nitrate in large excess significantly decreased the fluorescence intensity, as did large amounts of most cations. In all cases where interferences were observed these could be removed by back-washing the first organic extract with a pH-4·0 buffer solution.

Table 2. Interferences in the single-extraction fluorimetric determination of 2·50 μg of Alamine 336 in 80% toluene–hexanol

Ion added	Amount, *mg*	Alamine 336 found, *μg*	Relative error, %
—	—	2·50	0
Fe^{3+}	1	2·71	+8
Fe^{3+}	10	2·13	−15
Ca^{2+}	1	2·60	+4
Mg^{2+}	1	2·65	+5
Zn^{2+}	1	2·51	0
Pb^{2+}	1	2·68	+7
Ni^{2+}	1	2·50	0
Cu^{2+}	1	2·43	−4
Co^{2+}	1	2·50	0
U(VI)	1	2·82	+12
V(V)	1	2·56	+3
PO_4^{3-}	100	2·50	0*
Cl^-	4000	0·63	−74
Cl^-	4000	2·39	−4*
NO_3^-	100	0·70	−72
NO_3^-	100	2·40	−5
SO_4^{2-}	100	2·50	0 }*
Sea-water	10000	2·58	+3

* Extract back-washed with pH-4·0 solution.

No interference was observed when amine solutions equilibrated with kerosene or nonanol were used, these components being likely companions of Alamine 336 in uranium processing raffinates.

It should be stressed that paper tissues and filter papers contain components which fluoresce readily with eosin and therefore should not come in contact with pipettes or other glassware used in the determination, otherwise serious errors may result. All glassware is best cleaned by washing with acetone and air-drying.

Reproducibility of the method

The limit of detection of the method was calculated as 2·83S_b where S_b is the standard deviation of the blank. From the measurement of eight 50-ml blank samples, a mean blank fluorescence intensity of 1·63 units was obtained with a standard deviation of 0·03. This gave a limit of detection of 0·2 μg of amine in a 50-ml sample or 4 ppM.

The relative standard deviation of eight measurements on samples containing 50 ppM of Alamine 336 was 5·1% when a 50-ml aqueous phase volume was used and 3·8% when this volume was only 10 ml.

It should be noted that these figures refer to results obtained on a Farrand spectrofluorimeter. For a less sophisticated instrument the limit of detection could be as much as an order of magnitude higher.

Applications

In addition to the measurement of Alamine 336, the method was tested with Aliquat 336, a long-chain secondary amine, and a long-chain primary amine. In each case it was possible to determine the amine by the fluorimetric method. In the case of the quaternary ammonium salt, the fluorescence intensity of the eosin complex was almost twice that for the same weight of tertiary amine. The intensity of the complex for both the secondary and primary amines was somewhat smaller than that for Alamine 336.

The method was applied to the determination of Alamine 336 in a synthetic raffinate mixture.[2] In all cases, the results were in agreement within the experimental errors of the methods. Table 2 shows that it is also possible to apply the fluorimetric method successfully to the determination of amines in sea-water.

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Zusammenfassung—Ein Verfahren zur Bestimmung langkettiger quartärer Ammoniumsalze, tertiärer und sekundärer Amine in Wasser oderwäßrigen Raffinaten wird angegeben. Es beruht auf ihrer Extraktion und fluorimetrischen Bestim mung als Aminsalze mit Bromeosin in Toluol: Hexanol 4:1. Wenn der Proben-Extrakt einer Gegenstrom-Wäsche unterworfen wurde, störten Metallionen, Chlorid, Nitrat oder Phosphat nicht. Das Verfahren erlaubt die Bestimmung langkettiger tertiärer Amine bis mindestens 4 ppM.

Résumé—On présente une méthode pour le dosage de sels d'ammonium quaternaires à longue chaîne, d'amines tertiaires et d'amines secondaires dans l'eau ou les raffinats aqueux, basée sur leur extraction et lour dosage fluorimétrique à l'état de sels d'amines avec l'éosine en toluène-hexanol (4:1) comme solvant. On n'a pas obtenu d'interférences d'ions métalliques ou d'ions chlorure, nitrate ou phosphate quand une méthode de lavage en retour a été appliquée à l'extrait d'échantillon. La méthode permet le dosage d'amines tertiaires à longue chaîne jusqu'à des teneurs aussi faibles que 4 p.p.M.

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CALCULATION OF STABILITY CONSTANTS FROM PHOTOMETRIC DATA

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Summary—A method originally designed for the determination of stability constants by using a wedge colorimeter has been adapted to normal photometric measuring techniques. The calculations are simple and the method is especially suitable for use when the absorptivities of the absorbing species are unavailable because these species cannot be obtained alone in solution. Results of some determinations are given.

An excellent review of the existing methods for the photometric determination of stability constants has been given by Ramette[1] who distinguishes between four different experimental situations depending upon what absorptivities can be directly determined. These are (if it is assumed that only the ligand and the complex absorb radiation) as follows.

1. The absorptivities of both the ligand and the complex can be directly determined.
2. The absorptivity of the complex can be determined directly, the absorptivity of the ligand is unavailable.
3. The absorptivity of the ligand can be measured directly, the absorptivity of the complex is unavailable.
4. Neither of the absorptivities can be determined directly. (This can be the case if, because of some other reaction—for instance involving an equilibrium with hydrogen ions—the absorbing species cannot be obtained alone in solution.)

The first three cases are simple to solve, the first algebraically and the others by straight line extrapolation techniques yielding the stability constant as the slope and the unknown absorptivity as the intercept of the line with one of the axes.

For solving the fourth case, Ramette recommends an iterative technique by which the value of the absorptivity of the ligand is adjusted until a straight line can be fitted to the experimental data. This can easily be done with the aid of an electronic computer. To the analyst who may only occasionally be interested in determining a stability constant, the computer technique may seem unnecessarily involved. As shown by Sacconi,[2] however, it is possible to use a wedge colorimeter to determine stability constants even in the case when neither the ligand nor the complex can be obtained alone in solution. In this work, Sacconi's approach has been adapted to normal photometric measuring techniques and the stability constant is computed from three absorbance measurements. For the sake of completeness,

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equations have been derived both for what Sacconi calls "single incomplete colour change" (corresponding to cases 2 and 3 above) and for the "double incomplete colour change" case.

The absorptivity of L is known, the absorptivity of ML is not

Consider a reaction between a non-absorbing metal ion M and a coloured reagent L leading to the formation of a coloured complex species ML. (The signs of charge are omitted for simplicity and Ringbom's notation[3] is used in this work.)

The stability constant is denoted by K_{ML}.

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad K_{ML} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{1}$$

If the total analytical concentrations of M and L are denoted by C_M and C_L, respectively, we can then write

$$C_M = [\mathrm{M}] + [\mathrm{ML}] \tag{2}$$

$$C_L = [\mathrm{L}] + [\mathrm{ML}] \tag{3}$$

If the Lambert-Beer-Bouguer law holds, then

$$A_L = a_L b C_L \tag{4}$$

for a solution containing L as the only absorbing species. A_L is the absorbance, a_L the absorptivity of species L and b the thickness of the solution layer in the light path. For a solution n containing a mixture of L and ML the additivity of absorbances gives (a_{ML} being the absorptivity of ML)

$$\begin{aligned} A_n &= a_L b[\mathrm{L}]_n + a_{ML} b[\mathrm{ML}]_n \\ &= a_L b(C_L - [\mathrm{ML}]_n) + a_{ML} b[\mathrm{ML}]_n \\ &= A_L\left(1 + \left(\frac{a_{ML}}{a_L} - 1\right) y_n\right) \end{aligned} \tag{5}$$

where $y_n = [\mathrm{ML}]_n / C_L \leqslant 1$. For two different solutions ($n = \mathrm{I}$ and $n = \mathrm{II}$) having the same C_L but different [ML] : [L] ratios:

$$\frac{[\mathrm{ML}]_{\mathrm{I}}}{[\mathrm{L}]_{\mathrm{I}}} = \frac{y_{\mathrm{I}}}{1 - y_{\mathrm{I}}} \qquad \text{and} \qquad \frac{[\mathrm{ML}]_{\mathrm{II}}}{[\mathrm{L}]_{\mathrm{II}}} = \frac{y_{\mathrm{II}}}{1 - y_{\mathrm{II}}} \tag{6}$$

We can now write

$$\frac{[\mathrm{ML}]_{\mathrm{I}}}{[\mathrm{ML}]_{\mathrm{II}}} = \frac{y_{\mathrm{I}}}{y_{\mathrm{II}}} = \frac{A_{\mathrm{I}} - A_L}{A_{\mathrm{II}} - A_L} = r. \tag{7}$$

The photometer can be adjusted to read zero for the solution containing only L at concentration C_L. Then the differences $A_{\mathrm{I}} - A_L$ and $A_{\mathrm{II}} - A_L$ can be read directly for solutions I and II. The concentration ratios from equation (6) are substituted into equation (1) and give

$$K_{ML} = \frac{1}{[\mathrm{M}]_{\mathrm{I}}} \cdot \frac{y_{\mathrm{I}}}{1 - y_{\mathrm{I}}} = \frac{1}{[\mathrm{M}]_{\mathrm{II}}} \cdot \frac{y_{\mathrm{II}}}{1 - y_{\mathrm{II}}} \tag{8}$$

Considering that $y_I = ry_{II}$ we now get

$$y_I = \frac{r-q}{1-q} \qquad \text{where} \quad q = \frac{[M]_I}{[M]_{II}} \tag{9}$$

and, finally, insertion of equation (9) into equation (8) yields

$$K_{ML} = \frac{1}{[M]_I} \cdot \frac{(r-q)}{(1-r)} \tag{10}$$

Equation (10) is very convenient for use especially when it is possible to measure [M] directly, *e.g.*, when studying the dissociation of acids and bases. The total concentrations may then be unknown. When [M] cannot be measured directly, $(C_M)_n - [ML]_n$ may be substituted for $[M]_n$ in equation (8). The following system of equations with three unknowns will result:

$$K_{ML} \cdot C_L = \frac{y_I}{(1-y_I)(Q_I - y_I)} = \frac{y_{II}}{(1-y_{II})(Q_{II} - y_{II})} \tag{11}$$

$$y_I = ry_{II}, \qquad Q_I = (C_M)_I/C_L \qquad \text{and} \qquad Q_{II} = (C_M)_2/C_L \tag{12}$$

By eliminating K_{ML} and y_I and solving for y_{II} we have (the positive root is disregarded since $0 < y < 1$).

$$y_{II} = \frac{\sqrt{r}(Q_I - Q_{II})(\pm)\sqrt{r(Q_I - Q_{II})^2 - 4(r-1)(Q_I - rQ_{II})}}{2(r-1)\sqrt{r}} \tag{13}$$

When y_{II} has been calculated, K_{ML} is easily obtained from equation (11).

The absorptivity of ML is known, the absorptivity of L is not

An equation analogous to (11) is derived for the case when a_{ML} but not a_L can be measured directly:

$$K_{ML} = \frac{1}{[M]_I} \cdot \frac{(1-r')}{(r'-q')} \qquad \text{where} \quad r' = \frac{A_I - A_{ML}}{A_{II} - A_{ML}} \quad \text{and} \quad q' = \frac{[M]_{II}}{[M]_I} \tag{14}$$

Neither the absorptivity of L nor that of ML is known

A similar technique can be developed also for the case where neither the absorptivity of L nor that of ML can be measured directly. Three solutions are then used. C_L is the same in all three but C_M is varied so that $[M]_I > [M]_{III} > [M]_{II}$ or $[M]_I < [M]_{III} < [M]_{II}$. Consequently, it should be possible to mix solutions I and II in such proportions that the resulting mixture has the same composition as solution III. It can be shown that the condition that must be fulfilled is

$$y_I r'' + y_{II}(1 - r'') = y_{III} \tag{15}$$

where $y_n = [ML]_n/C_L$ as before and $r'' = (A_{III} - A_{II})/(A_I - A_{II})$.

Provided that $[M]_n$ can be measured, the unknown quantities K_{ML} and y_I, y_{II}, y_{III} are interrelated by the following three equations in addition to equation (15).

$$K_{ML} = \frac{1}{[M]_I} \cdot \frac{y_I}{(1-y_I)} = \frac{1}{[M]_{II}} \cdot \frac{y_{II}}{(1-y_{II})} = \frac{1}{[M]_{III}} \cdot \frac{y_{III}}{(1-y_{III})} \tag{16}$$

The system is solved by substituting x_n for $y_n/(1 - y_n)$ and eliminating x_n, yielding

$$K_{\mathrm{ML}} = \frac{1}{[\mathrm{M}]_{\mathrm{II}}} \cdot \frac{r''(q_{\mathrm{I}} - 1) - (q_{\mathrm{II}} - 1)'}{q_{\mathrm{I}}(q_{\mathrm{II}} - 1) - r''q_{\mathrm{II}}(q_{\mathrm{I}} - 1)} \tag{17}$$

where $q_{\mathrm{I}} = \frac{[\mathrm{M}]_{\mathrm{I}}}{[\mathrm{M}]_{\mathrm{II}}}$ and $q_{\mathrm{II}} = \frac{[\mathrm{M}]_{\mathrm{III}}}{[\mathrm{M}]_{\mathrm{II}}}$.

In view of the increasing number of ion-selective electrodes becoming available to the analyst, there should be many cases where equation (17) can be used to advantage, particularly as no exact knowledge of the total concentration of the ligand is required provided that the same concentration is used in all three solutions.

It should be borne in mind, however, that some other means must be used to ascertain that the complexation takes place stepwise. Isosbestic points in photometry often prove useful in this respect.

EXAMPLES OF THE USE OF THE EQUATIONS

Equation (17) has been used to determine the stability constant of the reaction

$$\mathrm{H} + \mathrm{L} \rightleftharpoons \mathrm{HL}$$

L denoting the anion of alizarin complexan.[4] In this case, the usual methods of calculation are laborious to use, since the magnitude of the stability constant is 10^{12} and HL will react further with hydrogen ions to form $\mathrm{H_2L}$ ($\log K_{\mathrm{H_2L}}^{\mathrm{H}} = 10$). The course of the calculations is clear from Table 1. The ionic strength was 0·1 and the measurements were made in aqueous solution and in a mixture of 80% water and 20% dioxan. The value of the stability constant was also determined by potentiometry with the glass electrode in 0·1*M* potassium chloride. The agreement between the values obtained by photometry and potentiometry, $10^{11 \cdot 98}$ and

Table 1. Calculation of the stability constant of the reaction $\mathrm{H} + \mathrm{L} \rightleftharpoons \mathrm{HL}$, L denoting the anion of Alizarin Fluorine Blue. The ionic strength was 0·1 and the total concentration of alizarin complexan was $6 \cdot 00 \times 10^{-5}M$. The temperature was 23°C and the pH values were adjusted by means of glycine buffers

$\mathrm{pH_I}$	$\mathrm{pH_{II}}$	$\mathrm{pH_{III}}$	q_{I}	q_{II}	$A_{\mathrm{I}} - A_{\mathrm{II}}$	$A_{\mathrm{III}} - A_{\mathrm{II}}$	r''	$\log K_{\mathrm{HL}}^{\mathrm{H}}$
In aqueous solution								
12·96	11·91	12·09	0·0891	0·661	0·512	0·119	0·233	11·97
12·96	11·91	12·33	0·0891	0·380	0·512	0·268	0·523	11·97
12·96	11·91	12·55	0·0891	0·229	0·512	0·375	0·733	12·00
12·96	11·91	12·74	0·0891	0·148	0·512	0·451	0·881	11·98
							Mean value	11·98 ± 0·02
In 20% dioxan–80% water								
13·00	12·00	12·40	0·100	0·398	0·320	0·155	0·484	12·18
13·00	12·00	12·60	0·100	0·251	0·320	0·230	0·719	12·14
12·80	12·00	12·40	0·158	0·398	0·289	0·155	0·537	12·25
12·80	12·00	12·60	0·158	0·251	0·289	0·230	0·790	12·20
							Mean value	12·19 ± 0·04

$10^{11\cdot 8}$, respectively, is fair and the difference probably due to the uncertainty of glass-electrode measurements at high alkalinity.

The stability constant of the reaction

$$H + HX \rightleftharpoons H_2X$$

(H_2X denoting alizarin-3-sulphonic acid) has been determined by using equation (10). Table 2 shows the results. Sacconi[2] gives the value $10^{5\cdot 54}$.

Table 2. Determination of the stability constant K^{H}_{H2X} of $H + HX \rightleftharpoons H_2X$ (H_2X = alizarin-3-sulphonic acid). The measurements were made at ionic strength 0·1, temperature 23°C and total concentration of the dye $1{\cdot}2 \times 10^{-4}M$. The pH values were adjusted by means of acetate buffer solutions and the absorbances were measured at 520 nm against a solution of HX at pH = 7·7

pH_1	pH_2	$A_I - A_{HX}$	$A_{II} - A_{HX}$	r	q	$\log K^{H}_{H2X}$
4·29	5·52	0·448	0·242	1·852	17·00	5·54
4·29	5·30	0·448	0·299	1·498	10·23	5·55
4·29	5·00	0·448	0·366	1·224	5·128	5·53
4·29	4·69	0·448	0·416	1·079	2·512	5·55
4·69	5·30	0·416	0·299	1·888	4·070	5·54
5·00	5·52	0·366	0·242	1·513	3·310	5·53
						$\log K^{H}_{H2X} = 5{\cdot}53 \pm 0{\cdot}01$

Equation (13) has been used to determine the stability constant of the reaction

$$AlHL + Al \rightleftharpoons Al_2L + H$$

L again denoting alizarin complexan. The results will be discussed in a subsequent paper.[5]

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Zusammenfassung—Ein ursprünglich zur Bestimmung von Stabilitätskonstanten mit Hilfe eines Keilphotometers entwickeltes Verfahren wurde auf normale photometrische Meßmethoden umgestellt. Die Berechnungen sind einfach und das Verfahren ist dann besonders geeignet, wenn die Extinktionskoeffizienten der absorbierenden Spezies nicht zugänglich sind, weil diese Spezies in Lösung nicht allein erhalten werden können. Es werden die Ergebnisse einiger Bestimmungen angegeben.

Résumé—Une méthode conçue à l'origine pour la détermination des constantes de stabilité en utilisant un colorimètre à coins a été adaptée à des techniques de mesure photométrique normales. Les calculs sont simples et la méthode est particulièrement appropriée à l'emploi quand les capacités d'absorption de l'espèce absorbante ne sont pas connues parce que ces espèces ne peuvent être obtenues seules en solution. On donne les résultats de quelques déterminations.

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PHOTOMETRIC DETERMINATION OF ALUMINIUM WITH ALIZARIN FLUORINE BLUE

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Summary—In order to decide whether Alizarin Fluorine Blue (alizarin complexan, 3-aminomethylalizarin-*N*,*N*-diacetic acid) is a suitable reagent for the spectrophotometric determination of aluminium, values of the stability constants for some reactions of this reagent with aluminium(III) and iron(III) have been determined spectrophotometrically in a medium containing 20% dioxan and 80% water at ionic strength 0·1. The values of the constants that were determined are $\log K^{\mathrm{Al}}_{\mathrm{AlHL}} = 14{\cdot}3$, $\log K^{2\mathrm{Al}}_{\mathrm{Al_2L}} = 25{\cdot}3$ and $\log K^{\mathrm{Fe}}_{\mathrm{FeHL}} = 19{\cdot}6$. These results were employed in the design of a method for the spectrophotometric determination of aluminium in the presence of iron and titanium. The Sandell sensitivity is 0·01 μg/cm^2 and the coefficient of variation for 34 determinations was 0·9%.

In an earlier paper,[1] the acid stability constants of Alizarin Fluorine Blue (alizarin complexan, 3-aminomethylalizarin-*N*,*N*-diacetic acid) were discussed. This paper reports the results of a study of the complexation properties of this reagent with aluminium and ferric ions. The reagent has been used to determine aluminium photometrically in the presence of iron and some results will be given.

THE COMPLEXATION BETWEEN ALIZARIN COMPLEXAN AND Al(III) AND Fe(III)

Leonard and West[2] studied the metal chelates of alizarin complexan and concluded that 1 : 1 chelates are formed by the hexaco-ordinate metal ions. Thorium, being octaco-ordinate, was shown to form a chelate consisting of two thorium ions and one ion of the ligand. The reaction between the hexaco-ordinate metal ions and the reagent may be written in the general form

$$\mathrm{M}^{n+} + \mathrm{HL}^{3-} \rightleftharpoons \mathrm{MHL}^{(n-3)+}$$

It is seen that the chelates of both Al(III) and Fe(III) are uncharged. They are thus expected to be insoluble or only slightly soluble in water. Experiments verified this expectation. However, it was found that the chelates were soluble in a medium containing 20% dioxan and 80% water and this medium was chosen for further experimental work. The main advantage of such a medium is that stability constants that were determined in aqueous solution can, for most analytical purposes, be used without any corrections. Moreover, if the dissociation constants of the acid are known in water and in water–dioxan mixture, a correction may be applied to the stability constants of the metal complexes, according to Irving and Rossotti.[3]

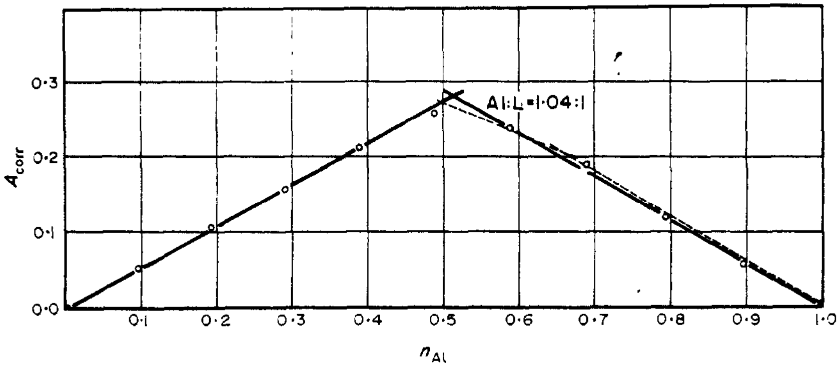

Fig. 1. Continuous variations plot of the system aluminium–Alizarin Fluorine Blue in a medium of 40% dioxan and 60% water at pH 5·4 (n_{Al} denotes the mole fraction of aluminium ions).

Figure 1 shows a Job's plot for the Al(III)–Alizarin Fluorine Blue system, recorded at 500 nm in 40% dioxan and 60% water, $\log[H^+]$ being $-5{\cdot}4$. It is seen that Al(III) forms both a 1 : 1 and a 2 : 1 complex with the reagent, and this is verified in Fig. 2, showing the absorption spectra of solutions having constant contents of the reagent but increasing contents of the metal ion.

There is an isosbestic point at 558 nm in Fig. 2, but as the aluminium content of the solution exceeds the content of alizarin complexan, the absorptivity curves no longer pass through it. This indicates that a new species is being formed in the solution. It also demonstrates that the complexation takes place stepwise. Since the new peak in the spectrum has its maximum at a wavelength that lies close to the wavelength of the fully deprotonated

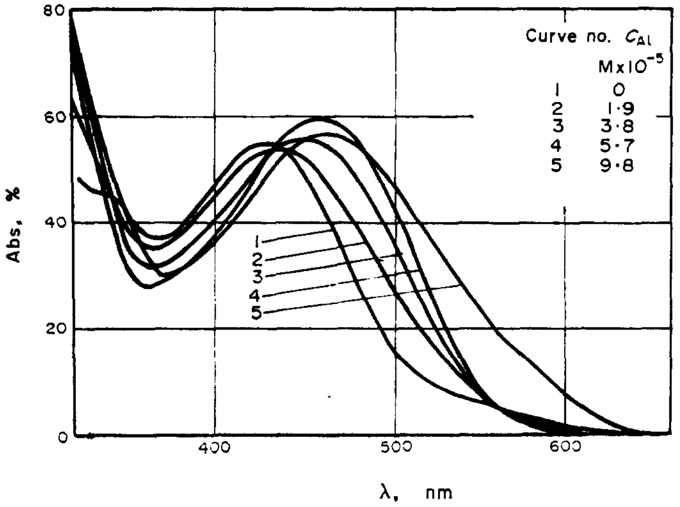

Fig. 2. Absorption spectra of a $6{\cdot}24 \times 10^{-5} M$ solution of alizarin complexan containing various amounts of aluminium ion at pH 4·1 in a medium of 20% dioxan and 80% water.

ligand, it seems not unreasonable to assume that a second aluminium ion is bound to the oxygen atom of the hydroxy group in position 2 (releasing the proton) and to the adjacent anthraquinone oxygen atom:

$$\mathrm{Al} + \mathrm{AlHL} \rightleftharpoons \mathrm{Al_2L} + \mathrm{H}$$

(The signs of charge are omitted for convenience.)

In the spectra of the iron(III)–alizarin complexan system, no isosbestic point can be found at or near 560 nm. However, as can be seen from Fig. 3, there are absorption peaks at 480 nm and close to 600 nm. It may thus be concluded that the same two types of complex are formed with iron(III) as with aluminium ions. However, the formation of these complexes is simultaneous, not stepwise as was the case with Al(III).

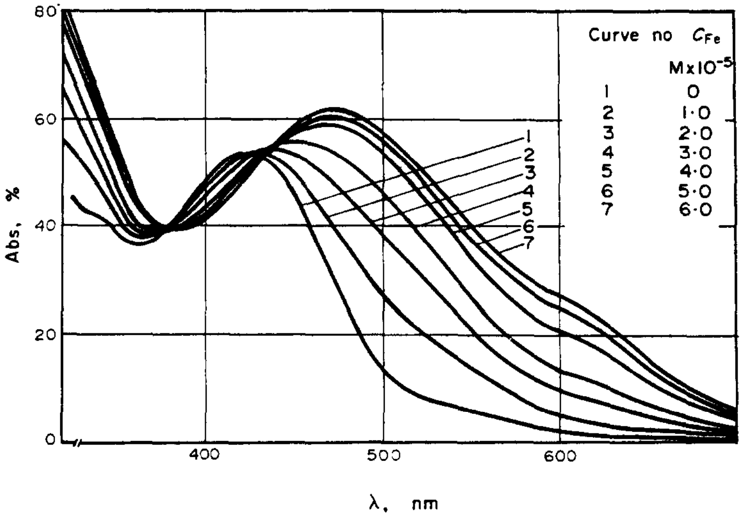

Fig. 3. Absorption spectra of a $6{\cdot}00 \times 10^{-5}M$ solution of alizarin complexan containing varying amounts of ferric ion at pH 4·1 in 20% aqueous dioxan.

Determination of the stability constants

The principal aim of this investigation being to determine whether alizarin complexan could be a suitable reagent for the photometric determination of aluminium in solutions containing ferric iron, a knowledge of the magnitude of the constants is enough. The constants may also be conditional[4] in the sense that if they are valid in the range of concentrations normally encountered in photometric analysis, this will suffice, and therefore no elaborate study of what species there are present in the solution has been conducted. The reader should be aware of the fact that for example in more concentrated solutions, it may well be that binuclear species predominate over the mononuclear ones.

The stability constants of the aluminium complexes of alizarin complexan were determined photometrically. The medium was 20% aqueous dioxan and the ionic strength was kept constant at 0·1 by addition of the calculated amount of formate buffer. The equilibrium was approached from both sides in order to ascertain that the measurements were really made at equilibrium.

The complexation of Al(III) with Alizarin Fluorine Blue being stepwise, only the first complex will be found in a solution containing no excess of aluminium ions. The absorptivities of both MHL and HL may therefore be determined and the value of the conditional stability constant calculated[4] from

$$K' = \frac{1}{[\mathrm{M}]} \cdot \frac{A - A_{\mathrm{HL}}}{A_{\mathrm{MHL}} - A} \tag{1}$$

Table 1 shows the results. In further work, $\log K = 14{\cdot}3$ was used for the reaction Al + HL = AlHL. In order to lower the conditional stability constant of the complex between aluminium and Alizarin Fluorine Blue to a suitable magnitude, EDTA was used as an auxiliary complexing agent. This technique has been described earlier by Schwarzenbach and Freitag[5] and by Fronaeus.[6]

Table 1. Calculation of the stability constant for the reaction $\mathrm{Al} + \mathrm{HL} \rightleftharpoons \mathrm{AlHL}$. The ionic strength was adjusted to 0·1 by adding formate buffer solution. The total concentration of alizarin complexan was $6{\cdot}00 \times 10^{-5} M$ and the temperature 23°C

pH	C_{Al}, M	C_{EDTA}, M	A_{480}	$\log K'$	$\log \alpha_{\mathrm{Al}}$	$\log \alpha_{\mathrm{HL}}$	$\log K$	$\frac{[\mathrm{AlHL}]}{[\mathrm{Al}']}$
4·10	0	$1{\cdot}00 \times 10^{-3}$	$0{\cdot}104 = A_{\mathrm{HL}}$					
4·10	$7{\cdot}61 \times 10^{-4}$	"	0·160	2·61	4·1	7·61	14·31	0·302
4·10	"	"	0·161					
4·09	$8{\cdot}76 \times 10^{-4}$	"	0·199	2·88	3·9	7·61	14·39	0·653
4·09	"	"	0·200					
4·11	$1{\cdot}90 \times 10^{-3}$	$2{\cdot}00 \times 10^{-3}$	0·258	2·99	3·8	7·60	14·38	1·81
4·11	"	"	0·257					
4·10	10^{-4}	0	$0{\cdot}340 = A_{\mathrm{AlHL}}$					
4·13	0	$1{\cdot}00 \times 10^{-3}$	$0{\cdot}108 = A_{\mathrm{HL}}$					
4·13	$2{\cdot}12 \times 10^{-4}$	"	0·123	2·51	4·4	7·55	14·46	0·069
4·13	$4{\cdot}18 \times 10^{-4}$	"	0·132	2·45	4·3	7·55	14·30	0·120
4·12	$8{\cdot}18 \times 10^{-4}$	"	0·182	2·76	3·8	7·57	14·13	0·465
4·13	10^{-4}	0	$0{\cdot}341 = A_{\mathrm{AlHL}}$					
4·42	0	$1{\cdot}00 \times 10^{-3}$	$0{\cdot}112 = A_{\mathrm{HL}}$					
4·41	$7{\cdot}61 \times 10^{-4}$	"	0·144	2·36	4·9	7·0	14·3	0·172
4·42	"	"	0·144					
4·42	$1{\cdot}90 \times 10^{-4}$	$2{\cdot}00 \times 10^{-3}$	0·1844	2·42	4·6	7·0	14·1	0·498
4·41	"	"	0·1842					
4·41	10^{-4}	0	$0{\cdot}3298 = A_{\mathrm{AlHL}}$					

The 2 : 1 complex formed by aluminium with alizarin complexan is weak. At the pH in question, there is also risk that aluminium may precipitate as the hydroxide if a large excess of aluminium ions is added to the solution. It is thus not possible to measure the absorptivity of the complex. In this work, the value of the stability constant K for the reaction

$$\mathrm{Al} + \mathrm{AlHL} \rightleftharpoons \mathrm{Al_2L} + \mathrm{H}$$

was determined by using equation (14), in ref. 7. The determination was made at the isosbestic wavelength, 560 nm, since this made it easy to determine the absorptivity of AlHL. Even in this case, the medium was 20% aqueous dioxan. The results are shown in Table 2.

There is a definite trend towards lower values of the constant as r'' decreases in Table 2. Probably some other species are also formed in the solution, but the effect being so small

Table 2. Calculation of the stability constant K for the reaction $AlHL + Al \rightleftharpoons Al_2L + H$ at ionic strength 0·1, temperature 23°C and total concentration of alizarin complexan $6{\cdot}24 \times 10^{-5}M$

C_{MI} $10^{-4}M$	C_{MII} $10^{-4}M$	Q_I	Q_{II}	$A_I - A_{AlHL}$	$A_{II} - A_{AlHL}$	r''	y_{II}	log K
19·6	4·89	31·41	7·837	0·347	0·170	2·041	0·327	−1·09
"	9·79	"	15·69	"	0·265	1·311	0·534	−1·02
46·8	4·89	75·00	7·837	0·491	0·170	2·892	0·275	−1·19
"	9·79	"	15·69	"	0·265	1·855	0·421	−1·22
"	19·6	"	31·41	"	0·347	1·416	0·495	−1·39
							Mean value	−1·18

as to be negligible for analytical purposes, it was not studied further. For the formation of the 2 : 1 complex log $K^{2Al}_{Al_2L} = 25{\cdot}3$ was calculated from $K^{2Al}_{Al_2L} = K \,.\, K^{Al}_{AlHL} \,.\, K^{H}_{HL}$. The value of K^{H}_{HL} was taken from ref. 7. (Ringbom's notation[4] is used throughout.)

In order to facilitate judging of the possibilities for masking Fe(III), a very rough value of the stability constant of the iron complex of alizarin complexan was needed. As the 2 : 1 and 1 : 1 complexes of iron with the reagent are formed simultaneously, the technique that was used for the aluminium complexes could not be used for iron(III). As, however, only the order of magnitude was needed, the stability constant of the first complex was calculated by using equation (1) and measurements made at 480 nm in 20% aqueous dioxan. In an actual photometric determination the coloured reagent is always added in excess, whereby the effect of formation of Fe_2L is minimized.

In this case the auxiliary complexing agent was NTA (nitrilotriacetic acid), as EDTA forms complexes with ferric ions that are too strong to allow alizarin complexan to compete. The results are shown in Table 3. In further calculations, the value log $K^{Fe}_{FeHL} = 19{\cdot}6$ was used.

Table 3. Calculation of the stability constant for the reaction $Fe(III) + HL \rightleftharpoons FeHL$. The ionic strength was adjusted to 0·1 with formate buffer. The total concentration of alizarin complexan was $6{\cdot}00 \times 10^{-5}M$ and the temperature was 23°C

pH	C_{Fe} $10^{-4}M$	C_{NTA} $10^{-2}M$	A_{480}	log $K^{Fe'HL'}_{FeHL}$	log α_{Fe}	log α_{HL}	log K^{Fe}_{FeHL}
4·00	—	1 drop	$0{\cdot}107 = A_{HL}$				
4·01	4·00	1·00	0·180	2·98	8·9	7·8	19·7
4·00	8·00	1·00	0·213	2·91	8·9	7·8	19·6
4·01	16·00	1·00	0·250	2·87	8·85	7·8	19·5
4·00	0·602	—	$0{\cdot}380 = A_{FeHL}$				

Alizarin complexan as a photometric reagent for the determination of Al(*III*) *in the presence of* Fe(*III*) *and* Ti(*IV*)

Most of the reagents currently used for determining aluminium photometrically are either lake-forming or else several complexes are formed simultaneously even though the reagent is added in excess. Reagents of the former type require strict control of all experimental conditions including time elapsed before measuring the absorbances. The latter type does not give linear calibration plots and many of the reagents are unstable in aqueous solution.

The principal advantages of alizarin complexan as a reagent for the determination of aluminium are the solubility of the complex in 20% aqueous dioxan and the stability of solutions of the reagent and of the complex. When the reagent is added in excess only a 1 : 1 complex is formed and the calibration curves can be expected to be linear.

Knowledge of the stability constants offers valuable aid in deciding optimum conditions for a photometric determination. Table 4 lists the constants necessary for calculating the values in Table 5. First it must be said that the pH interval that may be used is rather narrow. The reagent will precipitate at pH values below about 4. If the solution is made more alkaline than about pH 5, there is risk that aluminium hydroxide may precipitate, or that the reactions may be slow, owing to the formation of polynuclear hydroxy complexes.

Table 4. Stability constants of alizarin complexan and its complexes with Al(III) and Fe(III) at ionic strength 0·1

Reaction	Constant	In aqueous solution	In 20% aqueous dioxan solution
$H + L = HL$	$\log K^{H}_{HL}$	11·98	12·19
$H + HL = H_2L$	$\log K^{H}_{H_2L}$	10·07	10·18
$H + H_2L = H_3L$	$\log K^{H}_{H_3L}$	5·56	5·63
$H + H_3L = H_4L$	$\log K^{H}_{H_4L}$	2·49	
$Al + HL = AlHL$	$\log K^{Al}_{AlHL}$		14·3
$2Al + L = Al_2L$	$\log K^{2Al}_{Al_2L}$		25·3
$Fe(III) + HL = FeHL$	$\log K^{Fe}_{FeHL}$		19·6

On the other hand, in this pH interval only the 1 : 1 complex will be formed. The situation is clarified by Table 5. The values of all the stability constants were determined in 20% aqueous dioxan.[8] The concentration of the excess of the reagent was assumed to be $10^{-3}M$. The course of the calculation has been described previously.[9] It is seen that Fe(III) will interfere with the determination of Al(III). However, the aluminium chelate is strong enough to permit its use for the determination of Al(III).

Table 5

pH	$\log \alpha_{HL(H)}$	$\log \alpha_{Al}$	log[AlHL]/[Al′]	$\log \alpha_{Fe}$	log[FeHL]/[Fe′]
4	7·8	0·0	3·5	1·8	7·0
5	5·9	0·4	5·0	3·7	6·6

In Fig. 4, the absorption curves of H_3L, H_2L and AlHL are shown. The dissociation of H_3L into H_2L and H takes place at pH 5·6. Variations of pH will thus have an appreciable effect on the absorbances in the pH range 4–5, if the absorbances are not measured at the isosbestic wavelength, 455 nm. The sensitivity has its greatest value at 480 nm, but what is lost in sensitivity if the measurements are made at 455 nm is gained in reproducibility. The molar absorptivities at some wavelengths are given in the figure. It is seen that the absorptivity of the reagent at 455 nm, though appreciable, is small enough to permit adjustment of the absorbance scale of most instruments to read zero with a solution of the reagent in the light path.

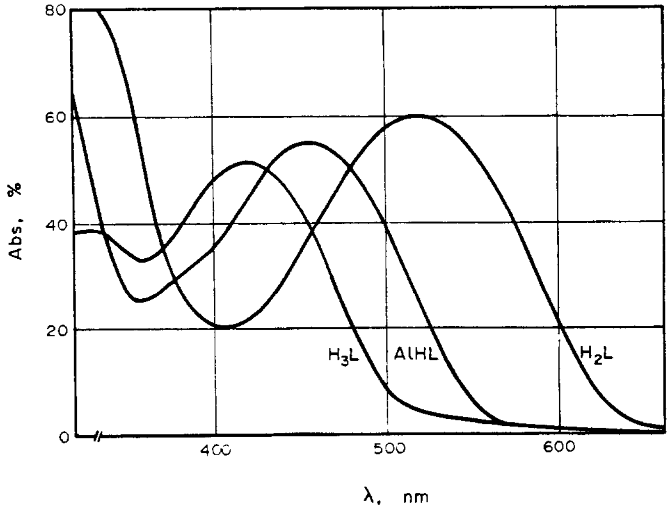

Fig. 4. Absorption spectra of some species of alizarin complexan. The curves for AlHL and H_3L were recorded at pH = 4·1, the curve for H_2L at pH = 7·4.

Interference of iron

Two different approaches can be used to avoid interference of Fe(III). One is masking, probably best carried out by first reducing the iron to iron(II). Possible masking agents are some mercapto-acids, *e.g.*, thioglycollic acid and dithiocarbaminoacetic acid,[10] but the iron complexes of the masking agents should not absorb light at 455 nm.

The other approach implies masking aluminium instead of iron. In practice, the absorbance difference is measured between a solution containing sample and reagent and one containing the same amount of sample and reagent but where aluminium has been masked by some suitable masking agent. If this procedure is chosen, it is possible to determine both aluminium and iron(III) with the same reagent.

If the first approach is chosen, the masking and reduction may be done in acidic solution and no interference from precipitated hydrous ferric oxide is to be expected. However, practical tests carried out with thioglycollic acid indicated that some aluminium is also complexed by this reagent. The second approach was therefore tested.

It is possible to mask aluminium with fluoride ions without influencing the complexation of iron(III) by alizarin complexan unduly. All stability constants that are needed for an estimate of the situation are known.[1,4] By assuming a $10^{-2\cdot7}M$ excess of fluoride ions, we get $\alpha_{Al(F)} = 10^{7\cdot3}$ and $\alpha_{Fe(F)} = 10^{4\cdot1}$. A simple calculation gives, for $[L'] = 10^{-4}M$ and pH = 4·0,

$$\frac{[AlHL]}{[Al']} = 10^{-4\cdot6} \quad \text{and} \quad \frac{[FeHL]}{[Fe']} = 10^{3\cdot5}.$$

This means that aluminium will be completely masked by fluoride whereas practically none of the ferric ions will have reacted with the fluoride ions. A fluoride ion excess of up to $10^{-2}M$ is permissible.

Interference of titanium

According to Leonard and West,[5] the complexes formed by alizarin complexan with Al(III), Ti(III) and Ti(IV) are not decomposed by a moderate excess of EDTA at pH 4·3.

Of these ions, Al(III) forms the weakest complex with EDTA. The complex that is formed by the reagent with either of the titanium ions is consequently stronger than the aluminium complex, and since the fluoride complexes formed by titanium(IV) are weaker than the corresponding aluminium complexes, it is to be expected that titanium is not masked by fluoride ions. Practical tests confirmed this assumption. Aluminium can thus be determined in the indicated manner and the determination will not be disturbed by any titanium present in the solution.

Recommended procedure (iron present)

Take 20 ml of the sample solution [which should contain 1–12 mg/l. of Al(III) and Fe(III) up to 5 mg/l.] and adjust the pH to 2. Add 20 ml of a $5 \times 10^{-4}M$ solution of alizarin complexan, 20 ml of dioxan and 10 ml of a formic acid–sodium formate buffer to make the final pH 4·1–4·3. Heat at 70° in a Teflon beaker for an hour, cool and make up to 100 ml in a volumetric flask. The ionic strength should be controlled by adding a neutral salt if required. Treat another 20 ml of the sample in the same way but add 10 ml of a 0·02*M* solution of sodium fluoride before adding the dioxan. Use this solution to adjust the absorbance scale to zero at 455 nm and read the absorbance of the first solution on that scale. Once developed, the colours remain stable over several weeks.

Perform the calibration in the same way, by reading the absorbance difference between a solution containing fluoride and one containing no fluoride, both having the same (known) contents of aluminium ions.

RESULTS AND DISCUSSION

Beer's law is obeyed up to an aluminium concentration of $10^{-4}M$. Table 6 lists the results of some analyses. It is seen that the accuracy of the method is good. The coefficient of variation for 34 determinations was 0·9%.

Table 6. Results of some determinations of aluminium with alizarin complexan

Al, *mg*			Al, *mg*		
Taken	Found	Fe(III), *mg*	Taken	Found	Fe(III), *mg*
12·8	12·8	—	38·5	38·5	—
12·8	12·75	—	38·5	38·3	28·0
21·6	21·8	—	43·0	43·0	—
25·6	25·5	28·0	43·0	42·8	—
25·6	25·2	—	51·4	51·3	28·0
29·7	29·9	—	67·5	67·0	—
30·9	30·7	—	96·1	95·6	—

The results show that aluminium may be determined photometrically with good accuracy and precision by the proposed method. A sufficiently strong complex is formed in the pH range 4–5 and the formation of other species may be neglected in this range. Neither the reagent solutions nor the solutions containing the complexes with aluminium or ferric ions decompose with time. However, the reaction between the aluminium ions and the reagent being slow, it is necessary to heat the solutions before measuring the absorbances. If ferric ions are present, the solutions should be handled with care in order to prevent precipitation of ferric hydroxide.

Ordinarily, charged species are soluble in water. This means that if for instance a sulphonic acid group could be incorporated in the alizarin complexan molecule, the 1 : 1 complexes with Al(III) and Fe(III) would be water-soluble, thus obviating the addition of dioxan. However, the incorporation of a sulphur atom in the molecule would be likely to affect the stability of the reagent adversely. On the other hand, addition of only 20% of dioxan is enough to keep the complexes in solution and, as is demonstrated in this paper, it is possible to use equilibrium data with very slight modifications (or none) when designing analytical methods—even when the solvent is not pure water.

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Zusammenfassung—Um zu entscheiden, ob Alizarinfluorinblau (Alizarinkomplexan, 3-Aminomethylalizarin-N,N-diessigsäure) als Reagens zur spektrophotometrischen Bestimmung von Aluminium geeignet ist, wurden die Werte der Stabilitätskonstanten einiger Reaktionen dieses Reagens mit Aluminium(III) und Eisen(III) spektrophotometrisch in einem Medium aus 20% Dioxan und 80% Wasser bei einer Ionenstärke von 0,1 bestimmt. Die Werte der ermittelten Konstanten sind log $K^{\mathrm{Al}}_{\mathrm{AlHL}} = 14{,}3$, log $K^{2\mathrm{Al}}_{\mathrm{Al_2L}} = 25{,}3$ und log $K^{\mathrm{Fe}}_{\mathrm{FeHL}} = 19{\cdot}6$. Diese Ergebnisse wurden beim Entwurf einer Methode zur spektrophotometrischen Bestimmung von Aluminium in Gegenwart von Eisen und Titan benutzt. Die Empfindlichkeit nach Sandell beträgt 0,01 μg/cm^2 und der Variationskoeffizient bei 34 Bestimmungen betrug 0,9%.

Résumé—Afin de décider si le Bleu d'Alizarine Fluor (alizarine complexan, acide 3-aminométhylalizarine-N,N-diacétique) est un agent convenable pour le dosage spectrophotométrique de l'aluminium, les valeurs des constantes de stabilité pour quelques réactions de ce réactif avec l'aluminium (III) et le fer (III) ont été déterminées spectrophotométriquement dans un milieu contenant 20% de dioxane et 80% d'eau à une force ionique de 0,1. Les valeurs des constantes qui ont été déterminées sont log $K^{\mathrm{Al}}_{\mathrm{AlHL}} = 14{,}3$, log $K^{2\mathrm{Al}}_{\mathrm{Al_2L}} = 25{,}3$ et log $K^{\mathrm{Fe}}_{\mathrm{FeHL}} = 19{,}6$. Ces résultats ont été employés dans l'étude d'une méthode pour le dosage spectrophotométrique de l'aluminium en la présence de fer et de titane. La sensibilité de Sandell est 0,01 μg/cm^2 et le coefficient de variation pour 34 déterminations a été 0,9%.

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CALCULATION OF CHEMICAL EQUILIBRIUM CONCENTRATIONS OF COMPLEXING LIGANDS AND METALS

A FLEXIBLE COMPUTER PROGRAMME TAKING ACCOUNT OF UNCERTAINTY IN FORMATION CONSTANT VALUES*

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Summary—Metal complexes often act as substrates in enzymic reactions. Because their concentrations cannot be measured directly, they must be calculated from the formation constants and the total concentrations of the different metal and ligand species. An iteration algorithm devised by Sayce has been used to formulate a FORTRAN (ICT 1900) programme, which meets the following requirements. (1) The programme may be made to calculate the total concentrations for the parent species if the *free* concentration of any metal or ligand species is known, or to calculate the free concentrations of all species for which the total concentrations are known. This feature of the programme is useful for calculation of the total amounts which must be put into a solution in order to achieve prescribed free concentrations. (2) To allow for the uncertainty in the formation constants of the complex species the programme permits the input values of the formation constants to be varied automatically and the resulting variation of the calculated concentrations to be evaluated.

Consider a solution which contains given total molar concentrations of metals 1, 2, ... M, and ligands 1, 2, ... L, and assume the pH to have been measured. The metals, ligands, H^+ and OH^- may form complex species, each of which may be described uniquely by the number of metal, ligand, H^+ and OH^- ions contained in it. At chemical equilibrium and given ionic strength,

$$\mathrm{CK}(k) = \mathrm{BK}(k) \cdot \mathrm{CH}^{\mathrm{NH}(k)} \cdot \prod_{m=1}^{\mathrm{M}} \mathrm{CM}(m)^{\mathrm{NM}(m,\,k)} \cdot \prod_{l=1}^{\mathrm{L}} \mathrm{CL}(l)^{\mathrm{NL}(l,\,k)} \tag{1}$$

where

$\mathrm{CK}(k)$ = concentration of the kth complex species
$\mathrm{BK}(k)$ = cumulative formation constant
CH = concentration of H^+
$\mathrm{NH}(k)$ = number of H^+ ions contained in the kth complex species [$\mathrm{NH}(k) < 0$ means that the kth species contains $-\mathrm{NH}(k)$ OH^- ions]
$\mathrm{CM}(m)$ = free concentration of mth metal ion species
$\mathrm{NM}(m, k)$ = number of ions of the mth metal contained in the kth complex species
$\mathrm{CL}(l)$ = free concentration of the lth ligand species
$\mathrm{NL}(l, k)$ = number of particles of the lth ligand contained in the kth complex species

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* Part of this paper (without the information on programme structure) was reported at the "VI. Internationales Berliner Symposium über Struktur und Funktion der Erythrozyten," Berlin, G.D.R., August 1970.

Here, the term "complex species" is used in a generalized manner, so as to include protonated ligands and metal hydroxo-complexes.

The concentrations of the complex species, CK, can be calculated easily according to equation (1) from BK, CH, CM and CL. By summing the products NM(m, k) · CK(k) for all k values, and adding CM(m), the total concentration CTM(m) of the mth metal ion is obtained. The total ligand concentration CTL(l) may be calculated similarly. If the free concentrations are to be calculated from given total concentrations, as is usually the case, a system of (M + L) non-linear equations giving CTM(1), ..., CTM(M), CTL(1), ..., CTL(L) as functions of the free concentrations has to be solved for the (M + L) unknown free concentrations.

Computer programmes capable of solving this problem have been published by various authors, *e.g.*, Perrin and Sayce,[1] and Sillén *et al.*[5] The algorithm devised by Sayce, has proved satisfactory in our programme for the largest system so far treated, with 3 metals, 22 ligands, and 93 complex species. Sillén's more complicated programme[5] permits the treatment of solid phases and the use of the mass-balance equation for the proton (Sayce's very simple algorithm needs the pH to be given, and his programme does not consider solid phases), but these features are not necessary for the biochemical application in question. The algorithm of Sayce has been incorporated into a main programme which had to meet the following requirements.

(1) In theoretical studies the question often arises as to how the concentration of one free or complex species depends on the free rather than on the total concentration of another given species. Thus, the programme should permit the free concentrations to be given (and the total concentrations to be calculated) for any subgroup of metals and ligands.

(2) Often it is desired to repeat the calculation of free and complex species with only a few parameters altered (*e.g.*, a single total concentration increased). In such cases, it should not be necessary to read in all input parameters anew.

(3) The cumulative formation constants available are usually subject to varying degrees of uncertainty. Therefore, the programme should be able to vary the constants within their given limits and to calculate the deviations of free and complex concentrations produced thereby. Because for given total concentrations the free and complex concentrations are non-linear functions of the complex formation constants, their partial derivatives may change their sign. If they do not change sign, the largest and smallest possible free and complex concentrations occur at the BK limits. If, however, the partial derivatives *do* change in sign, maxima and minima of the free and complex concentrations may occur between the BK limits as well as at them, and it is more complicated to find them. The task of deciding of whether or not this is the case and of determining the absolute extrema has not been solved by our programme. Instead, different estimates of the variation of free and complex concentrations are made, as described later.

In the second part of the paper, a description of the programme is given. An application is presented in the third section. The block scheme of the programme, giving detailed information about programme structure, is presented in an appendix. Copies of the ICT 1900 FORTRAN programme are available on request (to a limited extent).

DESCRIPTION OF THE PROGRAMME

Basic parts

(1) Data input. This part has been subdivided according to the different types of data (see appendix).

(2) Single calculation of equilibrium concentrations and print-out of results.

(3) Calculation of equilibrium concentrations with medium values of formation constants and print-out of results, followed by calculation of concentration differences produced by variation of formation constants. Let C_0 be a calculated free metal, free ligand or complex concentration (using the medium value for each formation constant). Let C_i be the concentration value which is obtained if the ith formation constant is altered in a prescribed manner ($i = 1, 2, \ldots$, KV, where KV = number of formation constants to be varied). Then the differences $C_i - C_0$ (i = 1–KV) are calculated and printed for any of the above-mentioned concentrations. Additionally, from the relationship

$$\Delta^2 = \sum_{i=1}^{\mathrm{KV}} (C_i - C_0)^2$$

Δ is determined, which gives an estimate of the expected overall uncertainty of C.

(4) Instead of the differences $C_i - C_0$, partial derivatives are determined for the calculated concentrations with respect to the logarithms of the formation constants, by solving the corresponding system of linear equations. The quantities D^2 and D (see appendix, item 38) are calculated by using the linear terms of the Taylor series, giving the concentrations as functions of the formation constants.

(5) Special values are assigned to the formation constants, which may be expected to produce large or small values of calculated concentrations. This part of the programme makes use of the results of parts (3) or (4). To produce a large value of a concentration C, the maximum value is given to the formation constant BK(k) if C is increased by increasing BK(k), and *vice versa* for producing small C. As long as partial derivatives $\partial C/\partial \mathrm{BK}(k)$ do not change sign, this approach should yield the absolute maxima and minima of the concentrations within the BK-limits given.

However, such changes of sign are possible and therefore the calculated concentrations are not necessarily identical with the absolute extrema.

On the other hand, because this method requires only constancy of sign of the partial derivatives, it describes the variability of concentrations within a larger range of BK values than does estimation of variability with the aid of the partial derivatives (which requires constancy of the derivatives themselves). It may be used for computing minimum ranges of the concentrations.

Transferring control to the different parts of the programme via *punched card input*

In each of the above-mentioned parts of the programme, the last statement causes a new punched card (later referred to as a steering-card) to be read in, which bears an integer number I1. By aid of I1 the computer learns which part of the programme it has to go to.

It is clear that such a flexible programme organization permits the programme to be adapted to quite different sequences of readings and calculations by simply arranging the punched cards in the appropriate order.

Repeating a calculation with only a few parameters altered is greatly facilitated in this way, because only those few parameters are read in by the computer, leaving all others unaltered.

EXAMPLE OF A BIOLOGICAL APPLICATION

In the human erythrocyte the most important constituents are ATP, 2,3-DPG, magnesium, potassium and sodium ions, and the 16 possible complex species formed from them. For biochemical purposes it is of interest to know not only their total concentrations, but also

Table 1. Logarithms of cumulative formation constants, referring to concentrations.

Complex species	log (BK)
1. HDPG	8·21
2. H_2DPG	14·84
3. H_3DPG	18·36
4. KDPG	1·93
5. HKDPG	9·16
6. NaDPG	1·93
7. HNaDPG	9·19
8. MgDPG	3·87
9. HMgDPG	10·92
10. Mg_2DPG	6·12
11. MgATP	4·96
12. HMgATP	9·80
13. KATP	1·15
14. NaATP	1·18
15. HATP	6·95
16. H_2ATP	10·88

the free concentrations, and the concentrations of the complex species. Values for the constants have been taken from O'Sullivan and Perrin[2] and from the references quoted by them, together with new results of Achilles *et al.*[3] These constants are presented in Table 1.

The results of the equilibrium calculations are shown in Table 2. Total concentrations of metals and ligands as found in human erythrocytes have been chosen (the values are given in column 1; they coincide exactly with those selected by Achilles *et al.*[3]). $P_H = 7.2$

From the equilibrium concentrations presented in column 2, the importance of the potassium complexes with 2,3-DPG and the magnesium complex with ATP becomes quite clear (*cf.* Achilles *et al.*[3]). For each single concentration value, the variation range due to the uncertainty of the association constants has been estimated according to basic part (5), allowing each association constant to be multiplied by 1·25 or 0·8 (corresponding roughly to ±0·1 pK units). Whereas the importance of magnesium and potassium complex-formation with ATP and 2,3-DPG respectively is not removed by varying the constants, the single values are found to be altered remarkably (*cf.* columns 3a and 3b). Thus, in comparing biochemical model properties with observational results, the possibility that special features of the model are sensitive to changes within the uncertainty ranges of the complex formation constants should be taken into account.

Column 4 of Table 2 gives some insight into the dependence of the calculated concentrations on formation constants. For each concentration *C*, the two complex formation constants causing (by their variation) the greatest alteration of *C* are given. The concentration of free 2,3-DPG depends most strongly on the formation constants of the complexes HKDPG and KDPG (numbers 5 and 4); these are the two DPG-complexes with the highest concentrations (*cf.* column 2). The concentration of free ATP is most strongly influenced by the formation constants of the complexes MgATP and MgDPG. Because ATP is bound nearly exclusively by formation of MgATP, the MgDPG complex influences the free ATP via Mg more strongly than the other ATP complexes do. For the free magnesium ion concentration, we find the formation constants of MgDPG and HMgDPG. Increasing the MgATP formation constant produces a smaller decrease in free magnesium concentration,

Table 2. Results of different equilibrium calculations

1 Species (tot. concn.) m*M*	2 Concn. (med. formation constants) m*M*	3a Concn. min. m*M*	3b max. m*M*	4 Most important differences m*M*	
DPG (7·2)	0·154	0·123	0·192	5; −9·67E−3	4; −9·07E−3
ATP (2·0)	0·0390	0·0253	0·0612	11; −6·85E−3	8; 2·63E−3
Mg (3·5)	0·520	0·388	0·674	8; −0·0353	9; −0·0255
K (130·0)	126·5	125·8	127·2	1; 0·195	5; −0·192
Na (20·0)	19·4	19·2	19·6	7; −0·0642	6; −0·0560
1. HDPG	1·57	1·10	2·16	1; 0·280	5; −0·0990
2. H_2DPG	0·424	0·278	0·638	2; 0·0974	5; −0·0266
3. H_3DPG	8·86E−5	5·66E−5	13·8E−5	3; 2·21E−5	5; −5·56E−6
4. KDPG	1·66	1·17	2·26	4; 0·289	5; −0·107
5. HKDPG	1·78	1·26	2·40	5; 0·301	4; −0·107
6. NaDPG	0·255	0·166	0·387	6; 0·0597	5; −0·0156
7. HNaDPG	0·292	0·191	0·442	7; 0·0679	5; −0·0179
8. MgDPG	0·593	0·423	0·806	8; 0·0919	9; −0·0326
9. HMgDPG	0·420	0·288	0·597	9; 0·0761	8; −0·0319
10. Mg_2DPG	0·0548	0·0309	0·0887	10; 0·0118	8; −7·60E−3
11. MgATP	1·85	1·74	1·91	11; 0·0265	13; −0·0146
12. HMgATP	8·07E−3	5·09E−3	12·7E−3	12; 2·01E−3	11; −1·52E−3
13. KATP	0·0697	0·0369	0·131	13; 0·0159	11; −0·0122
14. NaATP	11·5E−3	5·97E−3	22·3E−3	14; 2·83E−6	11; −2·02E−6
15. HATP	2·19E−2	0·0114	0·0424	15; 5·34E−3	11; −3·85E−3
16. H_2ATP	11·8E−6	6·11E−6	23·1E−6	16; 2·95E−6	11; −2·07E−6

Note: $a\mathrm{E} - b$ means $a \cdot 10^{-b}$

Column 1: free and complex species considered. For metals and ligands, total concentrations (m*M*) are given in parentheses. Column 2: concentrations as calculated from total concentrations and cumulative complex formation constants (*cf.* Table 1). Columns 3a and 3b: each complex formation constant was allowed to be multiplied by either 1·25 or 0·8, the factors being chosen so as to minimize or maximize respectively the concentration of each species mentioned in column 1. Thus for each species another combination of values for the cumulative formation constants had to be used (*cf.* part (5) of basic programme parts). Column 4: in each line, "*i*;*c j*;*d*" means: the concentration as given in column 2 is incremented by *c* or *d*, if the formation constant of the *i*th (or *j*th) complex species is multiplied by 1·25; multiplying another formation constant by the same factor leads to a *smaller* increment than *d*.

because ATP is nearly saturated by magnesium and the concentration of bound substrate (MgATP) depends only weakly on the formation constant within the saturation range.

In the case of potassium, its large total concentration causes the free potassium concentration to be nearly independent of the choice of formation constants (*cf.* columns 3a and 3b). Increasing the formation constant of HDPG decreases the concentrations of KDPG and HKDPG and thus produces more free potassium. Increasing the constant for KDPG or HKDPG increases one complex at the expense of the other, but in total more potassium than before is bound and thus the free potassium concentration decreases.

As to the complex species, each complex concentration depends most strongly upon the formation constant for that complex. Secondarily, many ATP-complexes depend on the formation constant of MgATP (which exerts the strongest influence on free ATP concentration) and many DPG-complex concentrations depend on the formation constant of HKDPG (which exerts the strongest influence on free DPG concentration).

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APPENDIX

Block scheme of the programme

1 Read in deck of punched cards, the last card of which bears the word "ENDKARTE" in its columns nos. 1–8, and write a picture of each card on magnetic tape. Thereafter release card-reader from the programme (this is for machines permitting multi-programming), and rewind magnetic tape.

2 Read in picture of a punched card from magnetic tape. If this picture by its structure turns out to be a picture of a steering-card*, go to 2b, if not, go to 2a.

2a Print appropriate message and finish actual job.

2b According to the integer number I1* carried by the steering-card, go to the I1th item of the following list

3, 4, 5, 6, 7, 8, 9, 10, 11, 12,
13, 14, 15, 16, 17, 20, 21, 22, 23, 24,
25, 26, 27, 39, 28, 29, 30, 31, 38, 18, 19

(*e.g.*, a steering-card with I1 = 29 causes the computer to go to item 38 (see below), *i.e.* to calculate partial derivatives; whereas I1 = 24 would correspond to item 39, that is to finish the actual job. Thus, in each punched card deck the last steering-card has I1 = 24; it is followed immediately by a card with the word 'ENDKARTE').

3 Read from magnetic tape (hereafter abbreviated as m.t.) two card pictures containing an arbitrary text; write this text, time, and date; go to 2.

4 Read from m.t., and write EPS and ITLIM (in calculating free concentrations by iteration, the improvement of the free concentrations is ceased, if the calculated total concentrations coincide with their known values within relative errors of EPS, or if the number of improvements done exceeds ITLIM); go to 2.

5 Read from m.t. and write the integer numbers KEY 1, KEY 2, KEY 3 (the values of which are needed at items 31, 32, 35, 36 and 37); go to 2.

6 Read from m.t. and write the numbers of metals, ligands, and complex species (MM, ML, MK), the numbers MI and LI (for metals nos. 1–MI, total concentrations are known, whereas for metals from MI + 1 to MM, the free concentrations are known, and *vice versa* for ligands), and KV (for complex species nos. 1–KV, the formation constants are varied automatically by the programme, see below); go to 2.

7 (This item is of minor importance and is therefore not explained here)

8–10 Read from m.t. and write the names of complex species, metals, and ligands respectively; go to 2.

11 Read from m.t. and write NH(k), NM(m, k), NL(l, k), $k = 1, \ldots,$ MK; $m = 1, \ldots,$ MM; $l = 1, \ldots,$ ML; go to 2.

12 (This item is of minor importance and is therefore not explained here)

13 Read from m.t. and write $-\log[H^+]$ and $-\log([H^+]\cdot[OH^-])$; go to 2.

14–17 Read from m.t. and write given values for total metal, free metal, total ligand, and free ligand concentrations respectively; go to 2.

18 and 19 (These items are of minor importance and are therefore not explained here)

20 Read from m.t. and write decadic logarithms of the cumulative formation constants; go to 2.

21 Calculate cumulative formation constants BK(k), $k = 1, \ldots,$ MK, according to the NH sign convention (*cf.* introductory section of paper) from the data read in at items 11, 13, and 20; go to 2.

22 Read from m.t. VA, the amount of relative variation of cumulative formation constants; go to 2.

23 Write VA; calculate maximum values $BK(k)\cdot(1 + VA)$ and minimum values $BK(k)/(1 + VA)$ for cumulative formation constants nos. 1–KV; go to 2.

24 Read from m.t. and write individual maximum and minimum logarithms of cumulative formation constants nos. 1–KV; go to 2.

25 Calculate individual maximum and minimum values of cumulative formation constants nos. 1–KV according to the NH sign convention from the data read in at items 11, 13, and 24; go to 2.

26 and 27 (These items are of minor importance and are not explained here)

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* *Cf.* section on transfer of control *via* punched card input.

28 Look for so-called sub-complexes. A combination of metabolites $A_a \ldots Z_z$ is said to be a sub-complex, if these metabolites do appear in an arbitrary complex species exclusively as multiples of this combination (*e.g.*, if the complex species present are A_2, ABC_2, AD, DB_2C_4, DE, then BC_2 is a sub-complex). If a sub-complex $A_a \ldots Z_z$ is present, and the equilibrium free concentrations of A–Z are much smaller than the total ones, then the calculated equilibrium concentrations are to be looked at with caution and may need improvement.* This case, however, occurred very seldom in our studies. Thus no improvement has been provided as yet. After printing an appropriate message; go to 2.

29 and 30 (These items are of minor importance and are not explained here)

31 If KEY 1 = 1, assign starting values for subsequent iterative improvement to free metal and ligand concentrations; go to 32. If KEY 1 = 2, go immediately to 32.

32 If KEY 3 = 1, 2, 3, 4 or 5, go to 33, 34, 35, 36 or 37 respectively.

33 Calculate free and complex equilibrium concentrations and print results; go to 2.

34 Replace each cumulative formation constant by its medium value. Calculate equilibrium free and complex concentrations and print results. Go to 2. (This branch of the programme is used, if after variation of formation constants a further calculation with medium values of formation constants but, *e.g.*, altered total concentrations is wanted.)

35 Perform computations according to basic part (3) in order to calculate differences of free and complex concentrations caused by variation of each formation constant the no. of which lies within 1... KV. The alteration of each formation constant is done by assigning to it its maximum value (which has been calculated at item 23 or 25). After each equilibrium calculation, print out calculated concentrations, if KEY 2 = 1, and omit printing, if KEY 2 = 2. After varying the last formation constant, print list of concentration differences ΔC as caused by variation of formation constants BK(k) (one difference for each calculated concentration, and each varied formation constant). Calculate and print out Δ [see basic part (3)] for each calculated free metal, free ligand, and complex concentration.

36 and 37 Perform computations according to basic part (5) in order to estimate ranges of calculated free concentrations (36) or complex concentrations (37) due to variation of cumulative formation constants nos. 1... KV.

(These calculations require the calculations at item 35 or item 38 to have been done.) Print out calculated concentrations for each combination of formation constants if KEY 2 = 1, and omit printing if KEY 2 = 2. At any case print list of ranges for all calculated free or complex concentrations. Then go to 2.

38 Compute partial derivatives $\partial C/\partial \log \mathrm{BK}(k)$ of the calculated free and complex concentrations C with respect to the logarithms of the formation constants $\log \mathrm{BK}(k)$ by solving the corresponding system of linear equations (this calculation requires the calculations at item 33 or 34 to have been done). Compute for each calculated free and complex concentration C

$$D^2 = \sum_{k=1}^{\mathrm{KV}} [\partial C/\partial \mathrm{BK}(k) \cdot \Delta \mathrm{BK}(k)]^2$$

with ΔBK = maximum minus medium value of BK (*cf.* items 21–25). Calculate D as well, D giving an estimation for the expected overall uncertainty of C due to the uncertainty of the formation constants. Then go to 2.

39 Write "Job done," time and date. Finish actual job.

Zusammenfassung—Metallkomplexe treten oft als Substrate in enzymatischen Reaktionen auf. Da ihre Konzentrationen nicht direkt gemessen werden können, müssen sie aus den Bildungskonstanten und den Gesamtkonzentrationen der verschiedenen Metall- und Ligandenspezies berechnet werden. Ein von Sayce erstellter Iterations-Algorithmus wurde dazu verwendet, ein Fortran-(ICT 1900) Programm zu formulieren, das folgende Anforderungen erfüllt: 1) Mit dem Programm kann man die Gesamtkonzentrationen der Ausgangsspezies berechnen, wenn die Konzentrationen aller *freien* Metall- und Ligandenspezies bekannt sind, oder die Konzentrationen aller freien Spezies zu berechnen, von denen die Gesamtkonzentration bekannt ist. Diese Eigenschaft des Programms ist dann von Nutzen, wenn man die Gesamtmengen berechnen will, die man in eine Lösung einsetzen muß, um vorgeschriebene Konzentrationen an freien Spezies zu erhalten. 2) Um die Unsicherheit der Bildungskonstanten der Komplexe zu berücksichtigen, erlaubt das Programm, die eingespeisten Werte der Bildungskonstanten automatisch zu variieren und die sich ergebende Änderung der berechneten Konzentrationen zu ermitteln.

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* This situation may also arise if complex species containing metabolites A–Z in a proportion different from that of the sub-complex $A_a \ldots Z_z$ are present, but with negligible concentrations (*cf.* G. Anderegg[4]).

Résumé—Les complexes métalliques agissent souvent comme substrats dans des réactions enzymatiques. Parce que leurs concentrations ne peuvent être mesurées directement, elles doivent être calculées à partir des constantes de formation et des çoncentrations totales de différentes espèces de métaux et coordinats. Un algorithme itératif établi par Sayce a été utilisé pour formuler un programme FORTRAN (ICT 1900), qui répond aux exigences suivantes. (1) Le programme peut être fait pour calculer les concentrations totales pour les espèces apparentées si la concentration *libre* de n'importe quelle espèce de métal ou de coordinat est connue ou pour calculer les concentrations libres de toutes les espèces pour lesquelles les concentrations totales sont connues. Cette caractéristique du programme est utile pour le calcul des quantités totales qui doivent être introduites dans une solution afin d'obtenir les concentrations libres prescrites. (2) Pour tenir compte de l'incertitude dans les constantes de formation de l'espèce complexe le programme permet de faire varier automatiquement les valeurs d'entrée des constantes de formation et d'évaluer la variation résultante des concentrations calculées.

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INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF THIOCYANATE BY EXTRACTION AS BISTHIOCYANATOBISQUINOLINEMERCURY(II) COMPLEX AND ITS LIGAND SUBSTITUTION REACTION WITH DITHIZONE

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Summary—Thiocyanate forms with mercury(II) in the presence of quinoline a mixed-ligand mercury(II) complex, bisthiocyanatobisquinolinemercury(II), and is extracted into chloroform. This mixed-ligand complex is treated with dithizone and forms the bisdithizonatomercury(II) complex. Maximum and constant absorbance of the dithizone complex is obtained when thiocyanate is extracted at pH 5·1–6·5, and Beer's law is obeyed at 498 nm, where the difference in absorbance between the dithizone complex and dithizone is largest. Chloride, bromide, iodide, cyanide and large amounts of ammonium and copper(II) ions interfere.

It is known that some metal ions from mixed-ligand complexes, which are often extractable into an organic solvent. Mercury(II) easily forms mixed ligand complexes with chloride or bromide as charged ligand and with heterocyclic nitrogen bases, such as pyridine or isoquinoline, as adduct ligand.[1,2] These mixed-ligand complexes can undergo a ligand substitution reaction with reagents such as dithizone in the organic phase, and such reactions have been applied successfully for the indirect spectrophotometric determination of chloride[1] and bromide.[2] These methods have high sensitivity and suffer from only a few interferences.[1,2]

The present investigation applies the same principle to the determination of thiocyanate

EXPERIMENTAL

Reagent solutions

Thiocyanate solution, 1·00 mg/ml. Prepared by dissolving recrystallized sodium thiocyanate in water, and standardized by titration with mercury(II).[3]

Mercury(II) solution, 1·15 × $10^{-3}M$. Prepared by dissolving mercury(II) nitrate in water and acidifying with a small amount of nitric acid to prevent hydrolysis.

Quinoline solution, 5·00% v/v. Prepared by dissolving quinoline (distilled under reduced pressure) in methanol.

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Dithizone solution, 0·015%. Purified dithizone[4] was dissolved in chloroform. This solution was prepared freshly every week.

Buffer solutions, 0·2*M* acetic acid–0·2*M* sodium acetate.

All the reagents were of analytical-reagent grade and it was ascertained that they contained no halide and pseudohalide ions. Water distilled twice in glassware was used throughout.

General procedure

To a solution containing <60 μg of thiocyanate add 2·00 ml each of the mercury(II) and quinoline solutions, adjust to about pH 5·7 with the buffer, and make up to 20 ml with water. Equilibrate the solution with 10·0 ml of chloroform by shaking for 1 min. Separate the chloroform phase and remove water from it with small amounts of anhydrous sodium sulphate. To 5·00 ml of this chloroform solution add 1·0 ml of the dithizone solution, dilute to 10·0 ml with chloroform and measure the absorbance at 498 nm against a dithizone blank solution prepared by diluting 1·0 ml of the dithizone solution to 10·0 ml with chloroform.

RESULTS AND DISCUSSION

Preliminary experiments showed that when thiocyanate, mercury(II) and quinoline in aqueous medium were shaken with chloroform and the chloroform phase treated with dithizone, the mercury(II) dithizonate complex was produced. This indicates that the initially extracted complex reacts with dithizone in the chloroform solution. Figure 1 shows the absorption spectra obtained after the extracted complex has been reacted with (I) a

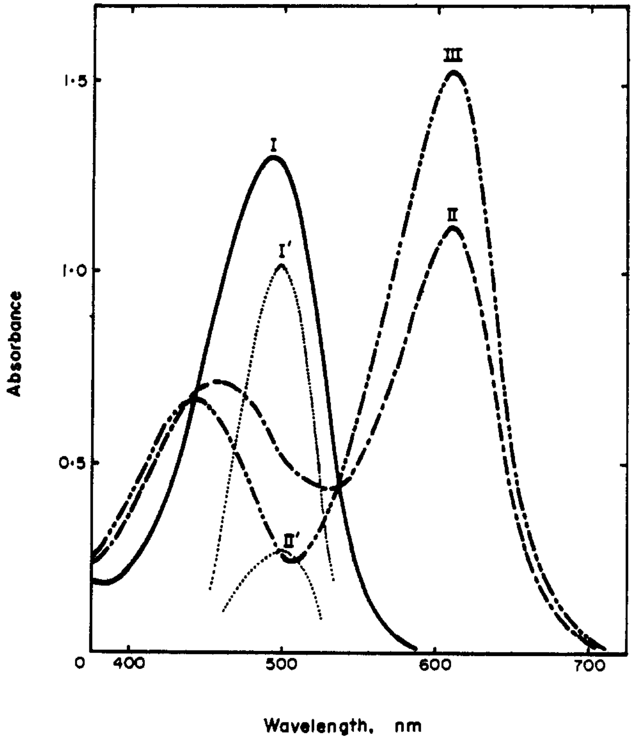

Fig. 1. Absorption spectra of dithizone and its mercury(II) complex.
I, II: Mercury(II) dithizonate complex obtained by the reaction of dithizone with the mixed-ligand complex in chloroform. III: Dithizone. Initial amount of thiocyanate: I: 8·61 μmole (550 μg), II: 0·861 μmole (50 μg), pH of the aqueous phase: 5·5, mercury(II): 2·30 μmole, quinoline: 0·844 mmole. I′, II′: Spectral difference between I, II and III, respectively.

deficiency of dithizone and (II) an excess of dithozine. The spectra relative to that of dithizone (III) are also shown (I′ and II′) and demonstrate that $\lambda_{\max}$ of the spectral difference is not affected by the amount of mercury(II) dithizonate produced.

Effect of pH

Variation of the pH of the aqueous phase between 3·5 and 8·5 showed that extraction was maximal at pH 5·1–6·5. Quinoline forms a protanated species ($\mathrm{p}K_a$ = 4·94)[5] and the decrease in extraction with increasing acidity might be partly due to protonation of the quinoline. The decrease in extraction above pH 6·5 might be due to dissociation of the mixed-ligand complex in the aqueous phase to form hydrolysis products of mercury(II) [log $K_{\mathrm{HgOH}}^{\mathrm{OH}}$ = 10·3, log $K_{\mathrm{Hg(OH)_2}}^{2\mathrm{OH}}$ = 21·7 (μ = 0·5)].[6] A pH of about 5·7 was chosen (acetic acid–sodium acetate buffer).

Effect of mercury(II) concentration

Figure 2 shows that extraction of the mixed-ligand complex increases rapidly to a maximum with increasing amount of mercury(II) and then declines again to a constant value. The maximum corresponds to $[\mathrm{Hg}^{2+}] > 2[\mathrm{SCN}^-]$. Closer inspection reveals that the absorbance is not a linear function of the amount of mercury(II), the deviation increasing with the amount of mercury(II) in the aqueous phase. It is well known that thiocyanate serves as a linear bidentate ligand and that mono- and bisthiocyanatomercury(II) complexes are more easily formed than the higher thiocyanate complexes [log $K_{\mathrm{Hg(SCN)_2}}^{2\mathrm{SCN}}$ = 16·1, log $K_{\mathrm{Hg(SCN)_3}}^{\mathrm{SCN}}$ = 2·9, log $K_{\mathrm{Hg(SCN)_4}}^{\mathrm{SCN}}$ = 1·9 (μ = 1·0)].[7] This can be interpreted as follows. When the mercury(II) is less than equivalent to the thiocyanate, bisthiocyanatomercury(II) is

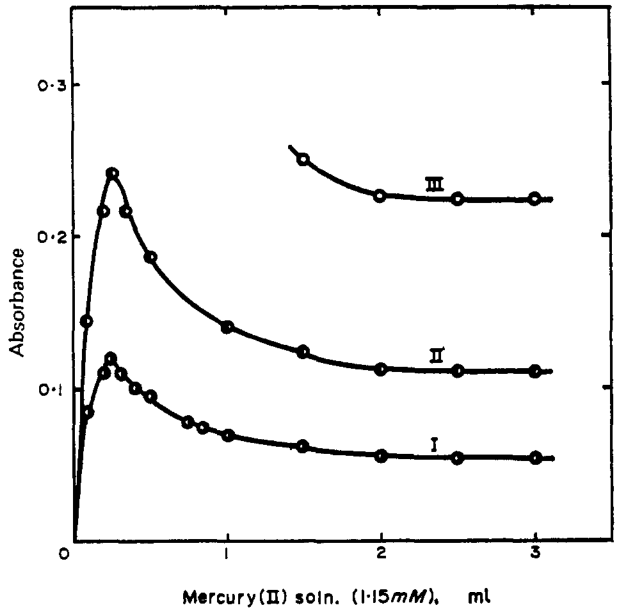

Fig. 2. Relation between amount of mercury(II) and absorbance.
λ: 498 nm. pH of the aqueous phase: 5.5. Amount of thiocyanate: I: 10 μg, II: 20 μg, III: 40 μg.

principally formed and its mixed-ligand complex with quinoline is easily extracted into chloroform. When the amount of mercury(II) is increased, monothiocyanatomercury(II), a charged species, is also formed and is not extracted, so less mercury(II) dithizonate is produced in the exchange reaction and there is departure from linearity of the calibration curve. Monothiocyanatomercury(II) and perhaps thiocyanate-bridged bismercury(II) complex species might be present in the aqueous phase when mercury(II) is added in large excess over thiocyanate. Addition of 2·0 ml of the mercury(II) solution, which reduces the sensitivity but gives good reproducibility, was chosen for analytical purposes.

Effect of amount of quinoline

Extraction of the mixed-ligand complex increases first gradually and then almost linearly with increasing amount of quinoline in the aqueous phase. A large and excessive amount of quinoline is needed for the formation and distribution into chloroform of the mixed-ligand complex, implying that the adduct formation constants might not be so large as the formation constants of the mercury(II)–thiocyanate complexes. The non-linearity at low quinoline concentrations might be due to the formation of a less completely extractable mixed-ligand complex with a lower quinoline content. It is necessary therefore always to add the same amount of quinoline to the initial aqueous phase to obtain reproducible analytical results.

Effect of dithizone concentration

As little as 0·4 ml of the dithizone solution (0·015%) was sufficient for complete ligand substitution. The molar absorptivity of the mercury(II)–dithizone complex was the same whether the complex was obtained from mercury(II) and dithizone or from the substitution reaction, so it is not a mixed complex.

Influence of the phase-volume ratio

The volume of the chloroform phase was kept constant at 10·0 ml and that of the aqueous phase was varied between 15 and 40 ml. Curve I in Fig. 3 shows the results for a constant *amount* of quinoline in the aqueous phase before extraction and curve II those for a constant *concentration* of quinoline in the aqueous phase before extraction. The results imply that the quinoline concentration in the chloroform phase plays an important role. In any case it is necessary to adjust the volume ratio to a fixed value for analytical work and 10·0 ml of chloroform and 20·0 ml of aqueous solution were chosen. Tests with methanol and no quinoline showed that quinoline *is* involved in the extraction, and not the methanol.

Degree of extraction of the mixed-ligand complex

From a calibration curve constructed by using a solution of definite concentration of mercury(II) thiocyanate in chloroform containing quinoline and dithizone solution, it was concluded that 37% of the total thiocyanate present in the initial aqueous phase was extracted as the mixed-ligand complex.

Other factors affecting the extraction

The rate of extraction was found to be rapid, as little as 0·5 min being necessary to attain equilibrium. When the mixed-ligand extract was allowed to stand for various periods before the exchange reaction, no change in absorbance occurred if the standing period was <30 min.

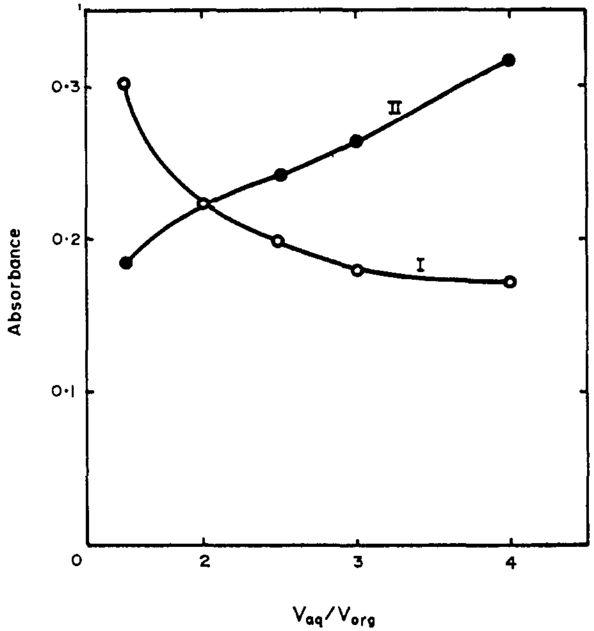

Fig. 3. Relation between volume ratio (V_{aq}/V_{org}) and absorbance.
λ: 498 nm. Amount of thiocyanate: 40 μg. pH of the aqueous phase: 5.5. I: Constant *amount* of quinoline in the initial aqueous phase. II: Constant quinoline *concentration* in the initial aqueous phase.

The degree of extraction decreased with increase in temperature between 15·5 and 31·5°, but the change due to temperature variations of less than $\pm 1°$ was within experimental error. The working temperature should therefore be within 1° of that used when constructing the calibration curve.

Distribution and ligand-substitution reaction

The ratio of mercury(II) to thiocyanate in the mixed-ligand complex was determined by the method of continuous variations at constant concentration of quinoline. Figure 4 shows that the complex extracted is of the form $Hg(SCN)_2Q_m$, where Q is quinoline, though other species may exist in the aqueous phase. The distribution equilibrium of the mixed-ligand complex is represented as follows:

$$Hg^{2+} + 2SCN^- + mQ \rightleftharpoons Hg(SCN)_2\,Q_{m(org)}$$

$$K_{eq} = \frac{[Hg(SCN)_2\,Q_m]_{org}}{[Hg^{2+}][SCN^-]^2[Q]^m} \qquad (1)$$

If a single species is extracted and does not dissociate, polymerize or add further quinoline in the organic phase, the amount of $Hg(SCN)_2\,Q_m$ in the organic phase can be expressed in terms of the amounts of the components in the aqueous phase:

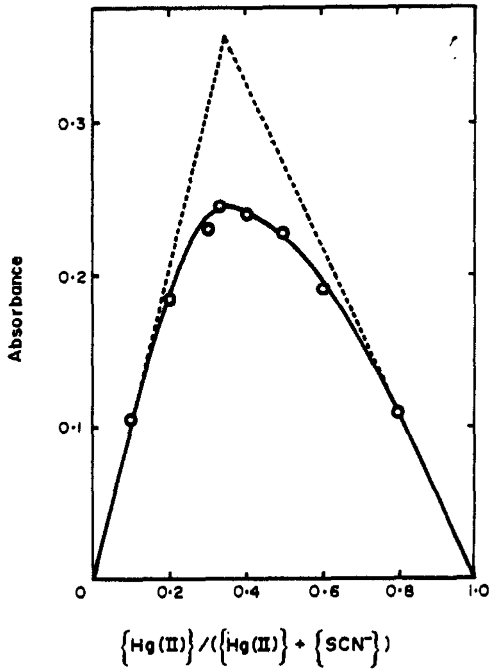

Fig. 4. Composition of the complex: co-ordination ratio of mercury(II) to thiocyanate. Total amounts of mercury(II) and thiocyanate: 0·633 μmole. Amount of quinoline: 0·844 mmole. λ: 498 nm. pH of the aqueous phase: 5.5.

$$\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} = P_{\mathrm{C}}\,\beta_{2m}\,V_{\mathrm{aq}}^{-(m+3)}\,V_{\mathrm{org}}\{\mathrm{Hg}^{2+}\}\{\mathrm{SCN}^-\}^2\{\mathrm{Q}\}^m \tag{2}$$

where V_{org} is the volume of organic phase, V_{aq} that of the aqueous phase, and

$$\beta_{2_m} = \frac{[\mathrm{Hg(SCN)_2\,Q}_m]}{[\mathrm{Hg}^{2+}[\mathrm{SCN}^-]^2[\mathrm{Q}]^m} \tag{3}$$

$$P_{\mathrm{C}} = \frac{[\mathrm{Hg(SCN)_2\,Q}_m]_{\mathrm{org}}}{[\mathrm{Hg(SCN)_2\,Q}_m]} \tag{4}$$

$$K_{\mathrm{a}} = \frac{[\mathrm{Q}][\mathrm{H}^+]}{[\mathrm{QH}^+]} \tag{5}$$

$$P_L = \frac{[\mathrm{Q}]_{\mathrm{org}}}{[\mathrm{Q}]} \tag{6}$$

$$C_{\mathrm{Hg}} = \sum_1^m \sum_1^q \{\mathrm{Hg(SCN)}_q\,\mathrm{Q}_m{}^{(2-q)+}\} + \sum_0^p \{\mathrm{Hg(SCN)}_p{}^{(2-p)+}\{ + \sum_1^n \{\mathrm{HgQ}_n{}^{2+}\}_- \\ + \{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} \tag{7}$$

$$C_{\mathrm{Q}} = \{\mathrm{QH}^+\} + \{\mathrm{Q}\} + \sum_1^m \sum_1^q m\{\mathrm{Hg(SCN)}_q\,\mathrm{Q}_m{}^{(2-q)+}\} + \sum_1^n n\{\mathrm{HgQ}_n{}^{2+}\}$$

$$+\, m\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} + \{\mathrm{Q}\}_{\mathrm{org}} \tag{8}$$

$$\begin{aligned} C_{\mathrm{SCN}} &= \{\mathrm{SCN^-}\} + \sum_1^m \sum_1^q q\{\mathrm{Hg(SCN)}_q\,\mathrm{Q}_m{}^{(2-q)+}\} + \sum_1^p p\{\mathrm{Hg(SCN)}_p{}^{(2-p)+}\} \\ &\quad + 2\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} \end{aligned} \tag{9}$$

where C is the total amount of species indicated by subscript, and $\{\}$ represents the amount of an individual species.

When $C_{\mathrm{SCN}} > 2C_{\mathrm{Hg}}$, to a first approximation only the bisthiocyanatomercury(II) mixed-ligand complex will be formed, because the formation constants of the mercury(II)–thiocyanate complexes are[7] $\log \beta_2 = 16{\cdot}1$, $\log \beta_3 = 19{\cdot}0$, $\log \beta_4 = 20{\cdot}9$; the formation constants of mercury(II)–quinoline complexes have not yet been reported, but they likely to be much smaller than these. In any case, if the total amount of quinoline is constant and a large excess relative to a constant amount of mercury(II), it will constitute a constant interference that can be allowed for in the calibration curves, so any such complexes can be omitted in what follows. Equations (7), (8), and (9) can then be further simplified as follows:

$$\begin{aligned} C_{\mathrm{Hg}} &= \{\mathrm{Hg(SCN)_2}\} + \{\mathrm{Hg(SCN)_2\,Q}_m\} + \{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} \\ &= \{\mathrm{Hg^{2+}}\}\{\mathrm{SCN^-}\}^2\,\beta_{20}V_{\mathrm{aq}}{}^{-2} + (1 + V_{\mathrm{aq}}P_{\mathrm{C}}{}^{-1}V_{\mathrm{org}}{}^{-1})\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} \end{aligned} \tag{7'}$$

$$C_{\mathrm{Q}} = \{\mathrm{QH^+}\} + \{\mathrm{Q}\} + \{\mathrm{Q}\}_{\mathrm{org}} \tag{8'}$$

$$\begin{aligned} C_{\mathrm{SCN}} &= \{\mathrm{SCN^-}\} + 2\{\mathrm{Hg(SCN)_2}\} + 2\{\mathrm{Hg(SCN)_2\,Q}_m\} + 2\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}} \\ &= \{\mathrm{SCN^-}\} + 2C_{\mathrm{Hg}} \end{aligned} \tag{9'}$$

From equations (7′), (8′) and (9′), $\{\mathrm{Hg^{2+}}\}$, $\{\mathrm{SCN^-}\}$, and $\{\mathrm{Q}\}$ can be expressed in terms of $\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}$ as follows:

$$\{\mathrm{Hg^{2+}}\} = \frac{C_{\mathrm{Hg}} - (1 + V_{\mathrm{aq}}P_{\mathrm{C}}{}^{-1}V_{\mathrm{org}}{}^{-1})\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}}{(C_{\mathrm{SCN}} - 2C_{\mathrm{Hg}})^2\,\beta_{20}V_{\mathrm{aq}}{}^{-2}} \tag{10}$$

$$\{\mathrm{SCN^-}\} = C_{\mathrm{SCN}} - 2C_{\mathrm{Hg}} \tag{11}$$

$$\{\mathrm{Q}\} = C_{\mathrm{Q}}/(1 + [\mathrm{H^+}]K_{\mathrm{a}}{}^{-1} + P_{\mathrm{L}}\,V_{\mathrm{org}}\,V_{\mathrm{aq}}{}^{-1}) \tag{12}$$

The relation between $\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}$ and C_{Q} is obtained from equations (2), (10), (11), and (12):

$$\begin{aligned} \frac{1}{\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}} &= \frac{1 + V_{\mathrm{aq}}\,P_{\mathrm{C}}{}^{-1}\,V_{\mathrm{org}}{}^{-1}}{C_{\mathrm{Hg}}} \\ &\quad + \frac{(1 + [\mathrm{H^+}]K_{\mathrm{a}}{}^{-1} + P_{\mathrm{L}}\,V_{\mathrm{org}}\,V_{\mathrm{aq}}{}^{-1})^m\,\beta_{20}\,V_{\mathrm{aq}}{}^{m+1}}{P_{\mathrm{C}}\,\beta_{2m}\,V_{\mathrm{org}}\,C_{\mathrm{Hg}}} \cdot C_{\mathrm{Q}}{}^{-m} \end{aligned} \tag{13}$$

Equation (13) implies that for constant values of C_{Hg}, C_{SCN}, V_{aq}, V_{org}, and pH and if $C_{\mathrm{Q}} \gg C_{\mathrm{Hg}}$ there is a linear relation between $\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}{}^{-1}$ and $C_{\mathrm{Q}}{}^{-m}$ for a particular value of m. Figure 5 shows the relation between $\{\mathrm{Hg(SCN)_2\,Q}_m\}_{\mathrm{org}}{}^{-1}$ and $C_{\mathrm{Q}}{}^{-m}$ for $m = 1$ and 2 for pH = 5·8, $C_{\mathrm{Hg}} = 0{\cdot}115$ μmole, $C_{\mathrm{SCN}} = 0{\cdot}862$ μmole, $V_{\mathrm{aq}} = 20{\cdot}0$ ml, $V_{\mathrm{org}} = 10{\cdot}0$ ml and $C_{\mathrm{Q}} = 0{\cdot}317$–$1{\cdot}27$ mmole (plots for $m > 2$ are non-linear). Figure 5 shows that $m = 2$.

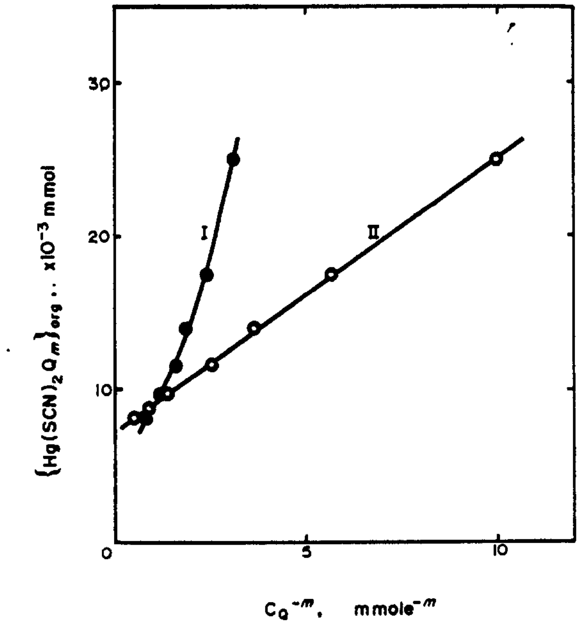

Fig. 5. Composition of the complex: relation between $\{Hg(SCN)_2Q_m\}_{org}^{-1}$ and C_Q^{-m}. V_{aq}/V_{org}: 2(V_{org}: 10·0 ml). pH of the aqueous phase: 5.8. C_Q: 0·317–1·27 mmole. I: $m = 1$, II: $m = 2$.

The ligand substitution reaction in chloroform was studied by the methods of continuous variations (Fig. 6, curve I) and slope ratio. Curve II in Fig. 6 gives comparative results obtained in the absence of quinoline. The ligand substitution reaction of the mercury(II) complex with dithizone proceeds with one mole of dithizone for $Hg(SCN)_2$ and with two moles of dithizone for $Hg(SCN)_2Q_2$. Ligand substitution reaction of the mixed-ligand complex is therefore promoted by the quinoline, which forms with the liberated proton and thiocyanate a molecular complex of the type QHSCN as a reaction product. The ligand substitution reaction should be represented as follows:

$$Hg(SCN)_2Q_{2(org)} + 2H_2Dz_{(org)} \rightleftharpoons Hg(HDz)_{2(org)} + 2QHSCN_{(org)}$$

The slope-ratio method confirmed this result. Beer's law was found to be obeyed at 498 nm.

Interferences

Aluminium, barium, beryllium, cadmium, calcium, chromium(III), cobalt(II), iron(III), magnesium, manganese(II), nickel, lead, strontium, vanadium(IV), zinc, zirconium, flouride, phosphate and silicate, in amounts up to 100 μg, did not interfere in the determination of 40 μg of thiocyanate, within a relative error of 1 %. Alkali metal salts, such as potassium nitrate, sodium acetate, sulphate, perchlorate and borate showed no interferences in amounts up to 10 mg. Ammonium ion showed no interference when less than about 400 μg was present but large amounts (10 mg) gave negative errors owing to competing formation of mixed-ligand complexes of bisthiocyanatomercury(II) with ammonia instead of quinoline.

Less than 10 μg of copper(II) had no influence on the determination, but larger amounts gave a positive error (Table 1) owing to the formation of a mixed-ligand copper(II) complex

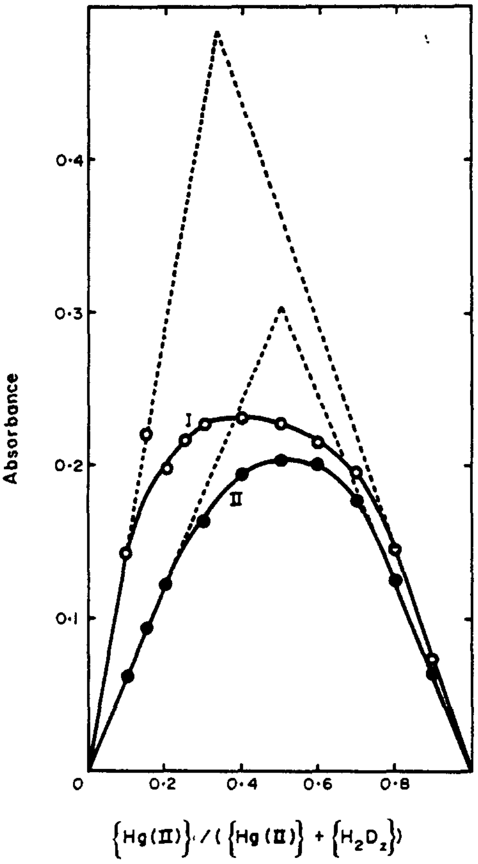

Fig. 6. Reaction ratio of mercury(II) in the mixed-ligand complex to dithizone. Total amount of mercury(II) and dithizone: 0·400 μmole. λ: 498 nm. I: In the presence of quinoline. II: In the absence of quinoline.

Table 1. Interferences

Ion	Amount added, *μg*	Thiocyanate added, *μg*	Thiocyanate found *μg*	Relative error, %
Cl^-	10	0	25·0	+125
	10	20	40·4	+102
Br^-	10	0	23·2	+116
	10	20	37·2	+86
I^-	10	0	107	+535
	10	20	123	+515
CN^-	20	0	14·4	+72
	20	20	21·5	+7·4
Cu(II)	10	40	40·2	+0·5
	100	40	50·4	+26

of thiocyanate and quinoline (greenish-yellow), which was extracted into chloroform and gave a ligand substitution reaction with dithizone. Large amounts of copper(II) and ammonium ions must therefore be absent.

Table 1 shows that influence of halides and pseudohalides on the determination. As expected from the earlier work,[1,2] chloride, bromide, iodide or cyanide interfere, and must be removed before the procedure is applied.

Comparison with an existing method.

Table 2 shows that the method is as satisfactory as the iron (III) method[8] for determination of small amounts of thiocyanate.

Table 2. Comparison of analytical results for thiocyanate by two methods

Thiocyanate taken, μg	Thiocyanate found, μg	
	Present method	Iron(III) method[8]
20·0	21·2	20·9
20·0	19·3	20·5
20·0	19·8	21·3
20·0	20·6	19·7
	Av. 20·3	Av. 20·6
50·0	49·6	50·3
50·0	50·3	50·2
50·0	50·7	50·6
50·0	50·4	49·8
50·0	49·3	50·9
	Av. 50·3	Av. 50·4

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Zusammenfassung—Thiocyanat bildet mit Quecksilber(II) in Gegenwart von Chinolin einen gemischten Komplex, Bisthiocyanatobischinolinquecksilber(II); dieser läßt sich in Chloroform extrahieren. Der Komplex wird mit Dithizon behandelt und bildet Bisdithizonatoquecksilber(II) Die maximale und konstante Extinktion des Dithizonkomplexes erreicht man, wenn das Thiocyanat bei pH 5,1–6,5 extrahiert wird; das Beersche Gesetz gilt bei 498 nm, wo der Extinktionsunterschied zwischen dem Dithizonkomplex und Dithizon am größten ist. Chlorid, Bromid, Jodid, Cyanid und große Mengen Ammonium und Kupfer(II) stören.

Résumé—Le thiocyanate forme avec le mercure (II) en la présence de quinoléine un complexe coordinat mixte-mercure (II), le bisthiocyanatobisquinoléine-mercure (II), et est extrait en chloroforme. Ce complexe coordinat mixte est traité par la dithizone et forme le complexe bis dithizonato-mercure (II). L'absorbance maximale et constante de complexe de la dithizone est obtenue quand le thiocyanate est extrait à pH 5, 1–6, 5 et la loi de Beer est suivie à 498 nm, où la différence d'absorbance entre le complexe de la dithizone et la dithizone est la plus grande. Les chlorure, bromure, iodure, cyanure et de grandes quantités d'ions ammonium et cuivre (II) interfèrent.

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INTERPRETATION OF MASS SPECTRA

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Summary—A computer programme is described which calculates the mass numbers and the relative intensities of each of the lines in the cluster formed in a mass spectrometer from a single type of fragment ion which contains one or more polyisotopic elements. Many elements such as B, C, S, Cl and Br possess more than one naturally occurring isotope, and the relative abundances of the various isotopes are known. A whole series of possible fragment ions may be calculated quite readily, and the results, which are printed numerically and in the form of a histogram, facilitate the interpretation of mass spectra. Trial data, a FORTRAN listing of the programme, and a sample of the output are given. The programme requires approximately 17K of fast core, and should be implemented without difficulty on any computer with a FORTRAN IV compiler.

When an ion is produced in a mass spectrometer, a single peak is produced in the recorded spectrum, at a point corresponding to the mass to charge (m/e) ratio of the ion. Should one or more atoms in the ion be polyisotopic, then instead of a single peak the recorded spectrum will show a cluster of peaks at different values of m/e. The relative intensity and m/e value of each individual peak in the cluster can be calculated from the relative abundance of the various isotopes of the constituent elements, and the probability of every possible arrangement of isotopes.

Such calculations are extremely tedious, particularly if the ion contains many atoms, or if the atoms have several isotopes. Further, with an unknown spectrum it is usually necessary to calculate for a whole series of possible fragment ions, to allow the correct identification of all the observed peaks.

A computer programme has been written in FORTRAN IV to calculate the mass numbers which are possible for a given fragment ion, and the probability or relative intensity of each peak in the spectrum from the atomic constitution of the fragment ion and the naturally occurring abundances of the isotopes of the constituent elements. The programme has been used to compute the clusters of peaks for boron subhalides and mixed boron subhalides as well as organometallic compounds. The results are printed out in numerical form, and as a histogram similar to the trace from a mass spectrometer, thus allowing easy and rapid identification of spectra (Fig. 1).

COMPUTER REQUIREMENTS

The programme requires approximately 17K of fast core on an ICL 1904A computer. All input is from cards, and all output is on the line-printer, which must have a minimum of 120 print positions.

```
B6CL3

NUMBER OF ATOMS OF TYPE B   =  6
NUMBER OF ATOMS OF TYPE CL  =  3

WEIGHT OF MONO-ISOTOPIC ATOMS (TO BE ADDED ON) =  0.0000

MASS NO. PROBABILITY


 165.      0.00

 166.      0.06

 167.      0.64  *

 168.      3.49  ***

 169.     11.04  ***********

 170.     20.27  ********************

 171.     21.82  **********************

 172.     17.64  ******************

 173.     14.53  ***************

 174.      5.52  ******

 175.      4.01  ****

 176.      0.59  *

 177.      0.40

    SUM  100.00%
```

Fig. 1. A sample of the computer output produced for one fragment, showing the various mass numbers which are possible, and the probability of each mass number displayed numerically and as a histogram. Note that the sum of the probabilities should be 100%, and is printed as a check that the calculation is correct. (If it differs by more than can be explained by rounding errors, there is some error such as some isotopes not being included, or too many mass numbers being possible.)

The time taken to perform various calculations on this computer are given in Table 1. (The times given are the amount of central processor time used, and do not include the time taken for input of data or output of results.)

PROGRAMME LIMITS

The statistics and the number of permutations and the amount of core storage available necessitate certain limitations on the number of isotopes of each element which may be handled. For small fragment ions containing 1–3 atoms of one type of element, up to 9 isotopes may be included. If 4 atoms of one element are present then up to 6 isotopes may be included in the calculations, and if 5 or more atoms of one element are

Table 1. Time taken for various calculations

Calculation	Time, *sec*
calculating 91 fragments ranging from $B_{13}Br_{13}$ to BBr	51
calculating 120 fragments from B_9Cl_8Br and B_9ClBr_8 to B_2ClBr	60
calculating 1 fragment $B_{25}Cl_{25}$	4
calculating 1 fragment $B_{50}Cl_{50}$	24
calculating 1 fragment $B_{75}Cl_{75}$	72
calculating 1 fragment $B_{100}Cl_{100}$	162
calculating 1 fragment $B_{125}Cl_{125}$	326
calculating 1 fragment $B_{150}Cl_{150}$	533
calculating 1 fragment $B_{175}Cl_{175}$	787
calculating 1 fragment $B_{200}Cl_{200}$	1075

present in the fragment ion 2 isotopes are considered. If more isotopes are included in the input data than can be handled for the fragment ion specified, then a suitable warning message is printed.

The programme is set to handle up to 300 different *m/e* values from each fragment ion. If more *m/e* values are generated a warning is printed and the excess is ignored. Up to 5 different polyisotopic elements and any number of monoisotopic elements may be present in the ion. The latter contribute only to the *m/e* value, and do not affect the intensity of the various peaks in the spectrum.

There is virtually no practical calculation limit on the number of atoms which may be present in a fragment ion, other than the time taken and the fact that only the first 300 mass numbers produced are stored by the computer.

To avoid producing numbers too large for the computer to store, the percentage abundances of the elements are divided by 100 immediately after they are read in, and the result multiplied by 100 before printing. In calculating the probability of any particular combination of isotopes, a method is used which avoids calculating factorials of numbers which would become too large. No problems have been encountered over the magnitude of numbers, using 24 bits for integers and 48 bits for real numbers.

The programme is written for ICL 1900 series computers which allow free format, literal format and mixed mode arithmetic. Other computers may not have these facilities available. Free format is used on cards 40 and 59, and may be eliminated by changing F0·0 to F8·4. Literal format is used in printing messages, and the characters inside the quotation marks should be written in H format on cards 29, 30, 31, 42, 49, 63, 73, 75, 76, 95, 98, 159, 160, 193, 194, 230, 250, 251, 279, 300, 306, 309 and 310.

INPUT DATA

1. TITLE CARD FORMAT(20A4)
   columns 1–80 any title—usually the name or formula of the fragment ion, punched anywhere on the card.
2. MASS OF MONOISOTOPIC ATOMS FORMAT(F0·0)
   columns 1–80 punch the sum of the mass numbers of all the atoms present which have no isotope. Note that the decimal point must be punched. Punch anywhere on the card.
3. NUMBER OF TYPES OF POLYISOTOPIC ELEMENTS FORMAT(I1)
   column 1 punch the number of elements present in the fragment ion which have isotopes.

4. ATOM CARD FORMAT(A4,3X,I3,8X,I2)
   columns 1–4 element symbol, e.g. B or Cl
   columns 8–10 number of atoms of this element present in the fragment (punch right justified, no decimal point).
   columns 19–20 number of isotopes of this element. (punch right justified, no decimal point).
5. ISOTOPE CARD FORMAT(2F0·0)
   Punch the mass number of one isotope, and its percentage abundance, anywhere on the card providing that the decimal point is punched in both numbers, and at least one blank is left between the two numbers.

   One card of this type must be included for each isotope present.

   Cards should be arranged:
   Atom card for atom type A
   Isotope card(s) for atom type A
   Atom card for atom type B
   Isotope card(s) for atom type B
   and so on
6. END OF PROBLEM CARD FORMAT(I1)
   Punch 0, 1 or 2 in column one on the card.

   A 2 on this card indicates the end of all data, and causes the programme to stop.

   A 0 causes the programme to return to the beginning, and read in a new set of data cards 1–6 as listed above. This is used when a second problem which is totally different from the first is to be calculated in the same run.

   A 1 causes the programme to read a shortened set of data, which is useful if a series of different fragment ions is being calculated which are permutations on the number of atoms present, though all the fragments contain the same elements. The shortened set of data comprises:
   1. TITLE CARD (as before)
   2. WEIGHT OF MONOISOTOPIC ATOMS (as before)
   3. SHORTENED ATOM CARD FORMAT(A4,3X,I3)
      columns 1–4 element symbol
      columns 8–10 number of atoms of this element present in the fragment ion. (punch right justified, no decimal point.)
      punch one of these cards for each element specified originally for the first fragment.
   4. END OF PROBLEM CARD (as before).

Acknowledgements—I wish to express my thanks to Dr. A. G. Massey for suggesting the problem, and for his constant interest, to Mr. B. Negus for numerical and statistical advice, and to the staff of the Loughborough University of Technology Computer Centre for their help.

APPENDIX

TRIAL DATA

```
FRAGMENT∧B2CLBR
0·0
3
B∧∧∧∧∧∧∧2∧∧∧∧∧∧∧∧∧2
10·0∧19·78
11·0∧80·22
CL∧∧∧∧∧∧∧1∧∧∧∧∧∧∧∧∧2
35·0∧75·40
37·0∧24·60
BR∧∧∧∧∧∧∧1∧∧∧∧∧∧∧∧∧2
79·0∧50·54
81·0∧49·46
1
FRAGMENT∧B3CL2BR
0·0
B∧∧∧∧∧∧∧3
CL∧∧∧∧∧∧2
BR∧∧∧∧∧∧∧1
2
```

```
      MASTER MASS SPECTRA
C
C     PROGRAM TO CALCULATE THE INTENSITIES OF MASS-SPECTRA LINES
C     - CAUSED BY THE PRESENCE OF ISOTOPES
C     WRITTEN IN FORTRAN IV FOR AN ICL 1904A COMPUTER
C     COMPILES IN 16832 WORDS WITH #XFAT MK 4C COMPILER IN TRACE 1 MODE
C     J.D.LEE LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY
C
C     ARRAYS SET FOR 5 TYPES OF ATOM, EACH WITH UP TO 9 ISOTOPES
C     THIS VEKSION HANDLES UP TO 300 MASS NUMBERS PER FRAGMENT
C     AND ANY NUMBER OF FRAGMENTS
C     IF 1, 2, OR 3 ATOMS OF ONE TYPE ARE PRESENT IN A FRAGMENT THEN -
C     - UP TO 9 ISOTOPES OF THAT ATOM MAY BE PRESENT
C     IF 4 ATOMS OF ONE TYPE ARE PRESENT ONLY THE FIRST 6 ISOTOPES -
C     - ARE CONSIDERED, ANY OTHERS BEING IGNORED
C     IF 5 OR MORE ATOMS OF ONE TYPE ARE PRESENT IN A FRAGMENT THEN
C     - ONLY THE FIRST 2 ISOTOPES ARE USED IN THE CALCULATIONS.
C
      DIMENSIUN NAIM(5),NI(9),AW(5,9),PA(5,9),A(5,504),B(5,504)
      DIMENSION IR(5),LG(5),IATOM(5),NAME(20)
      COMMON TM(300),TP(300),TQ(300)
C
      NC=0
      JK=0
      IPAGE=1
C
C     WRITF PAGE HEADING
      WRITE (2,1) IPAGE
    1 FORMAT (1H1,'PROGRAM TO CALCULATE THE INTENSITIES OF MASS-SPECTRA
     1LINES FROM THE ABUNDANCE OF THE ISOTOPES',19X,'PAGE',I4,31(3H===),
     2//)
      IPAGE=IPAGE+1
C
C     READ TITLE (NAME OR FORMULA OF FRAGMENT)
    2 READ (1,3) (NAME(I),I=1,20)
    3 FORMAT (20A4)
C
C     READ THE WEIGHT OF ALL THE MONO-ISOTOPIC ATOMS
      READ (1,4) W
    4 FORMAT (F0.0)
      WRITE (2,5) W
    5 FORMAT (1H0,'WEIGHT OF MONO-ISOTOPIC ATOMS (TO BE ADDED ON) =',F8.
     14)
C
C     READ THE NUMBER OF TYPES OF ATOM NTA
      READ (1,6) NTA
    6 FORMAT (I1)
      WRITE (2,7) NTA
    7 FORMAT (1H0,'NUMBER OF TYPES OF ATOM = ',I1)
      IF (NTA.GT.5) GO TO 86
C
C     READ THE ATOM NAME, NO. OF ATOMS IN MOLECULE & NO. OF ISOTOPES
C     -AND PERCENTAGE ABUNDANCES.
```

```
      DO 9 I=1,NTA
      READ (1,8) IATOM(I),NAIM(I),NI(I)
    8 FORMAT (A4,3X,I3,8X,I2)
      IF (NI(I).GT.9) GO TO 88
    9 READ (1,10) (AW(I,J),PA(I,J),J=1,NI(I))
   10 FORMAT (2F0.0)
C
C     PRINT ATOM NAME, NO. OF ISOTOPES AND THEIR MASS NO. AND ABUNDANCE
      WRITE (2,11)
   11 FORMAT (1H0,'ATOM',2X,'MASS NO.',2X,'ABUNDANCE')
      DO 18 I=1,NTA
      WRITE (2,12) IATOM(I)
   12 FORMAT (1H0,A4)
      WRITE (2,13) (AW(I,J),PA(I,J),J=1,NI(I))
   13 FORMAT (1H+,9X,F4.0,4X,F7.4,/(1H ,9X,F4.0,4X,F7.4))
      SUM=0.0
      DO 14 J=1,NI(I)
   14 SUM=SUM+PA(I,J)
      WRITE (2,15) SUM
   15 FORMAT (1H ,10X,'SUM = ',F8.4)
      IF (ABS(SUM-100.0).GT.0.000001) WRITE (2,16)
   16 FORMAT (1H+,26X,'*** SUM OF ABUNDANCES NOT 100% - TOO MANY ISOTOPE
     1S OR SOME MISSING? ***')
      DO 17 J=1,NI(I)
   17 PA(I,J)=PA(I,J)/100.0
   18 CONTINUE
C
C     SET UNUSED PARTS OF ARRAYS TO ZERO
      IF (NTA.EQ.5) GO TO 20
      DO 19 I=NTA+1,5
   19 NI(I)=0
   20 CONTINUE
      DO 21 I=1,5
      IF (NI(I).EQ.9) GO TO 22
      IJK=NI(I)+1
      DO 21 J=IJK,9
      AW(I,J)=0.
   21 PA(I,J)=0.
C
C     WRITE TITLE (NAME OR FORMULA OF FRAGMENT)
   22 WRITE (2,23) (NAME(I),I=1,20),IPAGE
   23 FORMAT (1H1,20A4,32X,'PAGE',I4,/)
      IPAGE=IPAGE+1
      WRITE (2,24) (IATOM(I),NAIM(I),I=1,NTA)
   24 FORMAT (1H ,'NUMBER OF ATOMS OF TYPE ',A4,'=',I3)
      WRITE (2,5) W
      IF (NTA.EQ.5) GO TO 26
      DO 25 I=NTA+1,5
   25 NAIM(I)=0
C
C     BEGINNING OF LOOP TO CALC. MASS NO. & PROBABIL. FOR EACH TYPE
C     OF ATOM. . . . . . . . . . . . . . . . . . . . . . . . . . .
   26 DO 59 I=1,NTA
      IF (NAIM(I).GT.4) GO TO 54
      NN=NAIM(I)+1
      GO TO (57,27,29,34,38), NN
C
C     ENTER IF FRAGMENT CONTAINS ONLY 1 ATOM OF THIS KIND
C     (UP TO 9 ISOTOPES MAY BE PRESENT).
   27 DO 28 J=1,NI(I)
      A(I,J)=PA(I,J)
   28 B(I,J)=AW(I,J)
      LG(I)=NI(I)
      GO TO 58
C
C     ENTER IF FRAGMENT CONTAINS TWO ATOMS OF THIS KIND
C     (UP TO 9 ISOTOPES MAY BE PRESENT).
   29 MT=0
      DO 33 J=1,NI(I)
```

```
      DO 33 K=J,NI(I)
      MT=MT+1
      IF (J-K) 30,31,30
   30 A(I,MT)=2.*PA(I,J)*PA(I,K)
      GO TO 32
   31 A(I,MT)=PA(I,J)**2
   32 B(I,MT)=AW(I,J)+AW(I,K)
   33 CONTINUE
      LG(I)=MT
      GO TO 58
C
C     ENTER IF FRAGMENT CONTAINS THREE ATOMS OF THIS KIND
C     (UP TO 9 ISOTOPES MAY BE PRESENT).
   34 MT=0
      DO 37 J=1,NI(I)
      DO 37 K=J,NI(I)
      DO 37 L=K,NI(I)
      MT=MT+1
      PMULT=1.0
      IF (J.EQ.K.AND.K.EQ.L) GO TO 36
      IF (J.NE.K.AND.J.NE.L.AND.K.NE.L) GO TO 35
      PMULT=3.0
      GO TO 36
   35 PMULT=6.0
      GO TO 36
   36 A(I,MT)=PMULT*PA(I,J)*PA(I,K)*PA(I,L)
   37 B(I,MT)=AW(I,J)+AW(I,K)+AW(I,L)
      LG(I)=MT
      GO TO 58
C
C     ENTER IF FRAGMENT CONTAINS 4 ATOMS OF THIS KIND
C     (ONLY THE FIRST 6 ISOTOPES ARE CALCULATED, ANY OTHERS ARE IGNORED)
   38 MT=0
      NISOT=NI(I)
      IF (NISOT.LE.6) GO TO 40
      WRITE (2,39) NI(I),IATOM(I)
   39 FORMAT (1H0,'*** ONLY THE FIRST 6 OUT OF THE ',I1,' ISOTOPES OF AT
     1OM TYPE ',A4,' HAVE BEEN INCLUDED IN THE CALCULATIONS ***')
      NISOT=6
   40 CONTINUE
      DO 53 J=1,NISOT
      DO 53 K=J,NISOT
      DO 53 L=K,NISOT
      DO 53 M=L,NISOT
      MT=MT+1
      IF (J-K) 44,41,44
   41 IF (J-L) 43,42,43
   42 IF (J-M) 48,47,48
   43 IF (L-M) 50,49,50
   44 IF (K-L) 46,45,46
   45 IF (K-M) 50,48,50
   46 IF (L-M) 51,50,51
   47 PMULT=1.0
      GO TO 52
   48 PMULT=4.0
      GO TO 52
   49 PMULT=6.0
      GO TO 52
   50 PMULT=12.0
      GO TO 52
   51 PMULT=24.0
   52 A(I,MT)=PMULT*PA(I,J)*PA(I,K)*PA(I,L)*PA(I,M)
   53 B(I,MT)=AW(I,J)+AW(I,K)+AW(I,L)+AW(I,M)
      LG(I)=MT
      GO TO 58
C
C     ENTER IF THERE ARE MORE THAN 4 ATOMS OF THIS TYPE IN FRAGMENT
C     (IN THIS CASE ONLY THE FIRST TWO ISOTOPES ARE CONSIDERED).
   54 M=NAIM(I)
      IF (NI(I).GT.2) WRITE (2,55) NI(I),IATOM(I)
```

```
   55 FORMAT (1H0,'*** ONLY THE FIRST 2 OUT OF THE ',I1,' ISOTOPES OF AT
     1OM TYPE ',A4,' HAVE BEEN INCLUDED IN THE CALCULATIONS. ***')
      AMULT=1.0
      DO 56 J=2,M
      AMULT=AMULT/FLOAT(J-1)*(M-J+2)
      A(I,J)=AMULT*PA(I,1)**(M-J+1)*PA(I,2)**(J-1)
   56 B(I,J)=(M-J+1)*AW(I,1)+(J-1)*AW(I,2)
      A(I,M+1)=PA(I,2)**M
      B(I,M+1)=AW(I,2)*M
      LG(I)=M+1
      A(I,1)=PA(I,1)**M
      B(I,1)=M*AW(I,1)
      GO TO 58
C
   57 LG(I)=1
      A(I,1)=1.
      B(I,1)=0.
   58 CONTINUE
   59 CONTINUE
C
C     END OF LOOP FOR EACH TYPE OF ATOM. . . . . . . . . . . . . . . . .
C
C     SET ARRAYS TO ZERO
      DO 60 I=1,300
      TP(I)=0.
      TQ(I)=0.
   60 CONTINUE
C
C     CALCULATE TOTAL NO. OF PERMUTATIONS FROM NO. OF PERMUTATIONS
C     -FOR EACH ATOM
      IP=1
      DO 61 I=1,NTA
      IP=IP*LG(I)
   61 IR(I)=1
C
C     WRITE HEADINGS FOR MASS NUMBERS AND PROBABILITY
      WRITE (2,62)
   62 FORMAT (1H0,'MASS NO. PROBABILITY',/)
      IMESS=0
      DO 74 I=1,IP
      P=1.
      Q=0.
       DO 65 J=1,NTA
       IF (IR(J)-LG(J)) 64,64,63
    63 IR(J)=1
       IR(J+1)=IR(J+1)+1
    64 P=P*A(J,IR(J))
       Q=Q+B(J,IR(J))
    65 CONTINUE
       P=P*100.
       DO 67 L=1,300
       IF (TQ(L)-0.000001) 71,66,66
    66 IF (ABS(Q-TQ(L))-0.000001) 72,67,67
    67 CONTINUE
       IF (L-301) 71,68,74
    68 IF (IMESS) 74,69,74
    69 WRITE (2,70)
    70 FORMAT (1H0,'MORE THAN 300 MASS NUMBERS ARE POSSIBLE FOR THIS FRAG
      1MENT - THOSE OVER 300 IGNORED')
       IMESS=1
       GO TO 74
    71 TP(L)=P
       TQ(L)=Q
       GO TO 73
    72 TP(L)=TP(L)+P
    73 IR(1)=IR(1)+1
    74 CONTINUE
C
C      CALL SUBROUTINE TO SORT THE VARIOUS MASS NUMBERS INTO
```

```
C     -ASCENDING ORDER BEFORE THEY ARE PRINTED
      CALL SORT
C
C     ADD THE MASS OF ANY ATOMS WHICH HAVE NO ISOTOPES TO THE COMPUTED
C     MASS NUMBERS, AND CALCULATE THE SUM OF ALL THE PROBABILITIES FOR
C     THIS FRAGMENT.
      S=0.
      DO 77 I=1,300
      IF (TQ(I)-0.000001) 78,75,75
   75 TM(I)=TQ(I)+W
      IF (TP(I)-0.005) 77,76,76
   76 S=S+TP(I)
   77 CONTINUE
C
C     CALL SUBROUTINE TO PRINT OUT RESULTS FOR FRAGMENT CONSIDERED
   78 CALL PRINT
      WRITE (2,79) S
   79 FORMAT (1H0,3X,'SUM',2X,F6.2,'%')
      NC=NC+1
C
C     DECIDE WHETHER TO  TERMINATE JOB, OR TO READ IN A NEW SET OF DATA
      READ (1,6) JK
C     IF JK=0, PROGRAM READS IN COMPLETE NEW SET OF DATA
C     IF JK=1, PROGRAM READS IN SHORT SET OF DATA
C     IF JK=2,  END OF DATA - TERMINATE JOB
      IF (JK-1) 84,82,80
   80 WRITE (2,81) NC
   81 FORMAT (1H1,'NUMBER OF PROBLEMS COMPUTED = ',I5,/1H0,'JOB COMPLETE
     1D SUCCESSFULLY')
      GO TO 90
C
C     READ IN SHORT SET OF DATA FOR NEXT FRAGMENT
   82 READ (1,3) (NAME(I),I=1,20)
      READ (1,4) W
      READ (1,83) (IATOM(I),NAIM(I),I=1,NTA)
   83 FORMAT (A4,3X,I3)
      GO TO 22
   84 WRITE (2,85) IPAGE
   85 FORMAT (1H1,'NEW SET OF DATA',97X,'PAGE',I4,/)
      IPAGE=IPAGE+1
      GO TO 2
C
C     REPORT ERROR
   86 WRITE (2,87)
   87 FORMAT (1H0,'JOB TERMINATED - MORE THAN 5 TYPES OF ATOM')
      GO TO 90
   88 WRITE (2,89) IATOM(I),NI(I)
   89 FORMAT (1H0,'JOB TERMINATED - NUMBER OF ISOTOPES FOR ATOM ',A4,'IS
     1',I4,' WHICH EXCEEDS THE MAXIMUM OF 9.')
C
C     TERMINATE JOB
   90 CONTINUE
      STOP
      END
      SUBROUTINE SORT
C
C     SUBROUTINE TO SORT THE MASS NUMBERS INTO ASCENDING ORDER
      COMMON TM(300),TP(300),TQ(300)
C
      N=0
      DO 1 I=1,300
      IF (TQ(I)-0.000001) 2,1,1
    1 N=N+1
    2 N=N-1
      J=1
      K=0
    3 IF (TQ(J+1)-TQ(J)) 4,5,5
    4 B=TQ(J)
      TQ(J)=TQ(J+1)
      TQ(J+1)=B
```

```
      B=TP(J)
      TP(J)=TP(J+1)
      TP(J+1)=B
      K=K+1
    5 IF (J-N) 6,7,6
    6 J=J+1
      GO TO 3
    7 IF (K) 8,9,8
    8 IF (N-1) 2,9,2
    9 RETURN
      END
      SUBROUTINE PRINT
C
C     SUBROUTINE TO PRINT THE PROBABILITY OF THE VARIOUS MASS-NUMBERS
C     - PRESENT AS A HISTOGRAM ON THE LINEPRINTER
      DIMENSION B(13),STAR(8)
      COMMON TM(300),TP(300),TQ(300)
      DATA STAR/8H*       ,8H**      ,8H***     ,8H****    ,8H*****   ,8
     1H******  ,8H******* ,8H********/
      DATA STAR8/8H********/,BLANK8/8H        
C
      DO 12 I=1,300
      IF (TQ(I)-0.000001) 13,1,1
    1 K=TP(I)/8
      L=(TP(I)+0.5)-(8*K)
      IF (K) 2,4,2
    2 DO 3 J=1,K
    3 B(J)=STAR8
    4 IF (L) 5,6,5
    5 B(K+1)=STAR(L)
      GO TO 7
    6 B(K+1)=BLANK8
    7 IF (K-12) 8,10,8
    8 DO 9 J=K+2,13
    9 B(J)=BLANK8
C
C     WRITE MASS NO., PROBABILITY AND ONE LINE OF HISTOGRAM
   10 WRITE (2,11) TM(I),TP(I),(B(J),J=1,13)
   11 FORMAT (1H0,F5.0,F9.2,2X,13A8)
   12 CONTINUE
   13 RETURN
      END
```

Zusammenfassung—Es wird ein Computerprogramm beschrieben, das Massenzahl und relative Intensität jeder Linie in der Liniengruppe berechnet, die im Massenspektrometer bei einem einzigen Typ von Fragmention auftritt, wenn dieses ein oder mehrere Elemente enthält, die aus verschiedenen Isotopen zusammengesetzt sind. Viele Elemente, wie B, C, S, Cl und Br enthalten mehr als ein natürlich vorkommendes Isotop, und die relative Häufigkeit der einzelnen Isotope ist bekannt. Man kann ganz leicht eine ganze Serie möglicher Fragmentionen berechnen; die Ergebnisse, die numerisch und in Form eines Strichdiagramms ausgegeben werden, erleichtern die Deutung von Massenspektren. Probedaten, eine Fortran-Auflistung des Programms und eine Probe der Ausgabe werden wiedergegeben. Das Programm benötigt einen schnellen Kernspeicher von etwa 17 K und sollte auf jedem beliebigen Rechner mit Fortran IV-Kompilierer ohne Schwierigkeit ausgeführt werden können.

Résumé—On décrit un programme de calculatrice qui calcule les nombres de masse et les intensités relatives de chacune des raies dans l'amas de pics formé dans un spectromètre de masse à partir d'un seul type de fragment ionique qui contient un ou plusieurs éléments polyisotopiques. De nombreux éléments tels que B, C, S, Cl et Br possèdent plus d'un isotope naturel, et les abondances relatives des divers isotopes sont connues. On peut calculer tout à fait aisément une série complète de fragments ioniques possibles et les résultats, qui sont imprimés numériquement et sous forme d'un histogramme, facilitent l'interprétation de spectres de masse. On fournit des données d'essai, un classement Fortran du programme et un échantillon de la production. Le programme nécessite approximativement 17K de partie centrale solide et devrait être réalisé sans difficulté sur n'importe quelle calculatrice avec un compilateur Fortran IV.

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SHORT COMMUNICATIONS

INDIRECT COMPLEXOMETRIC DETERMINATION OF CHROMATE

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A saturated solution of the brownish-red silver chromate at 25° is about $10^{-4}M$ ($K_s = 1{\cdot}1 \times 10^{-12}$),[1] and this property is utilized in the method described here. The chromate ion is precipitated as Ag_2CrO_4 by adding a saturated solution of silver nitrate to a neutral or slightly alkaline solution containing the chromate ion, then the precipitate is filtered off, washed, and dissolved in an ammoniacal solution of potassium tetracyanonickelate as proposed by Flaschka for silver halides,[2] whereby silver displaces nickel in the complex

$$Ag_2CrO_4 + K_2[Ni(CN)_4] \longrightarrow K_2[Ag_2(CN)_4] + Ni^{2+} + CrO_4^{2-}$$

and the freed nickel can be titrated with EDTA. The chromate content is given by the volume of EDTA used.

The method is accurate and a determination of chromate takes less than an hour. Chromium in minerals can also be determined by this method following extraction of this element by means of an alkaline fusion. Chromium-containing alloys are dissolved by means of an acid attack and the chromium converted into chromate by appropriate procedures. The same principle can be used for the determination of any anion that gives an insoluble silver salt that is soluble in potassium cyanide solution.

EXPERIMENTAL

It is absolutely necessary that reductants and any ion that forms a precipitate with silver that will dissolve in potassium cyanide should be absent from the chromate solution.

Reagents

Saturated silver nitrate solution. Stir 30 g of silver nitrate with 100 ml of cold water and decant the clear solution.

Murexide indicator. Murexide : sodium chloride mixture (1 : 100).[3]

Potassium tetracyanonickelate solution. Titrate a measured portion of 0·2*M* nickel sulphate, after addition of ammonia, with 1*M* potassium cyanide until the indicator (Murexide) changes from yellow to purple. Repeat the titration and average the results. Mix the amounts of the two solutions needed to give $K_2Ni(CN)_4$, add some ammonia, and dilute with water to a tetracyanonickelate concentration of about 0·1*M*. The resulting solution, if sufficiently alkaline, is stable for some months.[4]

EDTA 0·1M.

Procedure

Add dropwise, preferably in a dark corner of the laboratory, a slight excess of silver nitrate solution to an aliquot of the chromate solution made neutral or slightly alkaline with dilute nitric acid or sodium hydroxide solution. Check by the addition of further drops of silver nitrate solution that precipitation is complete. Stir well, allow the precipitate to settle, and check again for completeness of precipitation.

Filter off the precipitate on a 25-ml sintered-glass filter, wash it three or four times with cold water, and transfer the filter and precipitate into a beaker containing sufficient potassium tetracyanonickelate to cover the filter completely. Heat gently while stirring, till all the precipitate has dissolved. Remove the filter carefully from the beaker and rinse it well with water, collecting the washings in the beaker.

Titrate the nickel displaced by silver with 0·1*M* EDTA, using Murexide as indicator. The end-point is indicated by the colour change from yellow-orange to purple.

From

$$Ag_2CrO_4 + K_2[Ni(CN)_4] \longrightarrow 2K[Ag(CN)_2] + Ni^{2+} + CrO_4^{2-}$$

1 ml of 0·1*M* EDTA is equivalent to 11·60 mg of chromate.

RESULTS AND REMARKS

The procedure gives satisfactory results with an error less than 1%. The only cations that interfere are those that give competitive chromate precipitates under the conditions used. Typical results are given in Table 1.

Table 1

CrO_4^{2-} taken *mg*	CrO_4^{2-} found *mg*	Difference *mg*	%
100·0	99·8	−0·2	−0·2
75·0	75·2	+0·2	+0·4
50·0	50·1	+0·1	+0·2
25·0	24·9	−0·1	−0·4
20·0	20·1	+0·1	+0·5
15·0	14·9	−0·1	−0·6
10·0	10·2	+0·2	+2·0

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Summary—Chromate is determined indirectly, by precipitation as silver chromate, dissolution of the precipitate in potassium tetracyanonickelate, and titration of the liberated nickel with EDTA, with Murexide as indicator.

Zusammenfassung—Chromat wird indirekt durch Fällung als Silberchromat bestimmt. Der Niederschlag wird in Kaliumtetracyanonickelat gelöst und das freigesetzte Nickel mit EDTA und Murexid als Indikator titriert.

Résumé—On dose le chromate indirectement, par précipitation à l'état de chromate d'argent, dissolution du précipité dans le tétracyanonickelate de potassium, et titrage du nickel libéré à l'EDTA, avec la Murexide comme indicateur.

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INDIRECT FLAME-PHOTOMETRIC DETERMINATION OF SILICON

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The extensive literature on the determination of silicon is evidence of the importance attached to the determination of this element, and also of the need for a reliable method. In this paper a new method is proposed, using an indirect flame-photometric determination in which the silicon is precipitated as potassium hexafluorosilicate and the potassium in the precipitate is then determined by flame-photometry. Kordon,[1] Sajó[2] and others [3–6] have used potassium hexafluorosilicate as the basis of a volumetric method for silicon,

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75·0	75·2	+0·2	+0·4
50·0	50·1	+0·1	+0·2
25·0	24·9	−0·1	−0·4
20·0	20·1	+0·1	+0·5
15·0	14·9	−0·1	−0·6
10·0	10·2	+0·2	+2·0

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EXPERIMENTAL

Choice of potassium-ion concentration

Equal portions of potassium hexafluorosilicate (100 mg) each containing 12·65 mg of silicon, were dissolved in 10 ml of hydrochloric acid (1 + 1), and the silicon was precipitated after addition of hydrofluoric acid in the presence of different concentrations of potassium nitrate. The results are given in Table 1. Recovery was found to be complete for potassium concentrations above 20 g/l. and a value of 30 g/l. was chosen for the final procedure.

Removal of the excess of potassium ions from the precipitate

Washing with pure water was inadmissible because of the significant solubility of the precipitate. The use of chilled water was little better. Non-aqueous solvents which did not dissolve the precipitate did not remove the surplus potassium either. For these reasons some mixed aqueous/organic solvents were tried, using methanol, ethanol or acetone, and water.

Table 1. Effect of potassium concentration on the recovery of silicon

Potassium con. *g/l*	Potassium : silicon ratio, *w/w*	Silicon found, *mg**
5	20 : 1	7·8
10	40 : 1	10·6
12·5	50 : 1	11·0
15·0	60 : 1	11·5
16·2	65 : 1	11·8
18·8	75 : 1	12·1
20	80 : 1	12·7
30	120 : 1	12·8
40	160 : 1	12·7
50	200 : 1	12·8
60	240 : 1	12·8

* Amount taken = 12·65 mg. Silicon in the precipitate was determined by Sajó's method.[2] In the first two cases three determinations were made, and in all others, six.

The precipitate was washed several times with 5-ml portions of mixed solvent, and was then dissolved in 5 ml of hydrochloric acid (s.g. 1·19) and hot water, and the solution diluted to 100 ml. The potassium was determined by flame photometry. The results indicated that all three solvents were equally suitable when diluted with water in the ratios 2 : 1 and 3 : 1 (water : solvent). For convenience, ethanol was chosen. The effect of repeated washings was studied on 100-mg portions of potassium hexafluorosilicate precipitate, using 5-ml portions of 2 : 1 and 3 : 1 water–ethanol mixtures. After being washed, the residual precipitate was in each case dissolved and the silicon content determined indirectly from the amount of potassium found. The results are presented in Table 2.

Table 2. Recovery of silicon (12·65 mg taken) as a function of the number of washes

	Si found, *mg*								
No. of 5-ml washes	3	4	5	6	8	10	12	15	20
Water–ethanol 2 : 1	15·9	14·5	13·0	12·7	12·7	12·6	12·5	11·7	10·8
Water–ethanol 3 : 1	14·9	13·0	12·7	12·4	12·2	11·7	10·4	—	—

As a more sensitive measure of the effect of repeated washings the potassium present in the individual wash portions was checked. The results are shown in Fig. 1. The constant residual potassium concentration represents the solubility of the precipitate. For the 3 : 1 mixture this concentration is about 50 μg/ml, and remains constant after 4 or 5 washes. For the 2 : 1 mixture the residual concentration of about 20 μg/ml is reached after 9 or 10 washes. On the basis of these data the loss of silicon due to partial dissolution of the precipitate can be calculated. It is clear that insufficient washing will lead to high results, and excessive washing to slightly low values. The 100 μg of potassium in 5 ml of 2 : 1 mixed solvent corresponds to about 35 μg of silicon. The following conclusions may be drawn concerning the washing step. The precipitate should be washed a further 2 or 3 times over and above the minimum number of washes indicated in these experiments, and the 2 : 1 water–ethanol mixed solvent is to be preferred, as the losses due to excessive washing are less than for the 3 : 1 mixture.

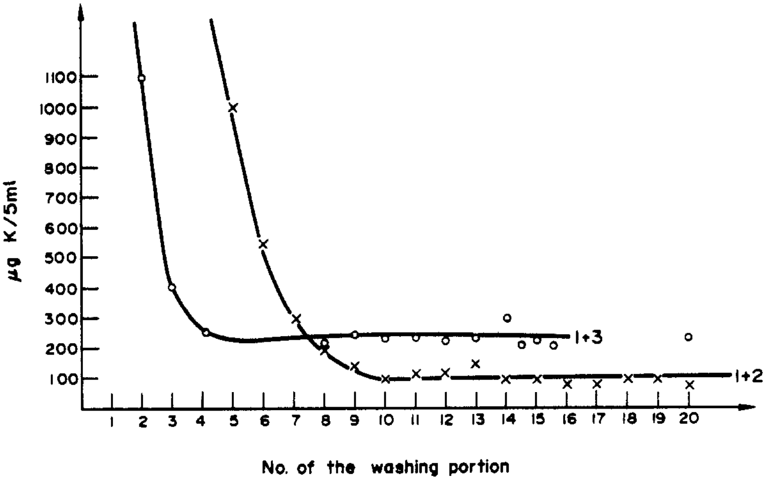

Fig. 1. Potassium content of successive 5-ml portions of wash-liquid, for 2 : 1 water–ethanol (×) and 3 : 1 water–ethanol (○) mixtures.

Procedure

The sample is dissolved in 30 ml of a 1 : 1 : 1 mixture of hydrochloric acid (s.g. 1·19), nitric acid (s.g. 1·49) and hydrofluoric acid (s.g. 1·40), and 20 ml of a 20% solution of potassium nitrate are added slowly, with stirring, over a period of about 3 min. The potassium hexafluorosilicate (K_2SiF_6) precipitate is filtered off by suction on a thin layer (*ca.* 2 mm) of filter paper pulp on a Büchner funnel, and is washed 9 or 10 times with 5-ml portions of 2 : 1 water–ethanol mixed solvent. The precipitate and pulp are then transferred into a beaker containing 20–30 ml of boiling water and 5 ml of hydrochloric acid (s.g. 1·19). The resulting

Table 3. Determination of silicon in ores and alloys

Sample	Silicon found, % gravimetric	Silicon found, % flame-photometric	Number of detns.	Standard deviation, % Si
Iron ore	5·78	5·74	9	0·03
Manganese ore	11·7$_8$	11·8	9	0·06
Iron concentrate	12·8$_4$	12·8		
Blast furnace slag	40·15	40·2		
Steel	0·99	1·02	9	0·014
Fe–Mn alloy	3·52	3·55		
Si–Mn alloy	6·04	6·00		
Si–Mn alloy	14·62	14·8		

solution is filtered and diluted, after cooling, to 100 ml. The potassium concentration is determined by flame-photometry using a propane or butane flame, and the silicon content of the sample calculated accordingly. A determination can be made in about 30 min.

Results

Silicon contents in the range 1–15% in ores and alloys have been determined satisfactorily with this method. In a number of cases the results have been compared with those obtained by a gravimetric determination (as SiO_2 precipitated from hydrochloric acid solution). In all cases the determinations were carried out at least in triplicate. A statistical evaluation of the results is included in Table 3.

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Summary—An indirect flame-photometric method for the determination of silicon in terms of the potassium in precipitated K_2SiF_6 has been developed. Optimum conditions have been found for the precipitation and the washing of the precipitate with aqueous ethanol. Satisfactory results have been obtained for silicon contents $>1\%$ in ores and alloys.

Zusammenfassung—Eine indirekte flammenphotometrische Methode zur Bestimmung von Silicium wurde entwickelt. Dabei wird das Kalium in ausgefälltem K_2SiF_6 bestimmt. Die optimalen Bedingungen für die Fällung und das Auswaschen des Niederschlags mit wäßrigem Äthanol wurden ermittelt. Für Siliciumgehalte unter 1% in Erzen und Legierungen wurden zufriedenstellende Ergebnisse erhalten.

Résumé—On a élaboré une méthode photométrique de flamme indirecte pour le dosage du silicium par rapport au potassium dans K_2SiF_6 précipité. On a trouvé des conditions optimales pour la précipitation et le lavage du précipité par l'éthanol aqueux. On a obtenu des résultats satisfaisants pour des teneurs en silicium $>1\%$ dans les minerais et alliages.

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TALANTA REVIEW*

AUTOMATED WET CHEMICAL ANALYSERS AND THEIR APPLICATIONS

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Summary—A review is presented of automated analysis, including instrumentation and applications.

The trend towards mechanization in analytical chemistry was initially characterized by the development and increasing use of instruments in which the measurement of a physical or physico-chemical parameter replaced the manipulative processes of classical analysis. Subsequently, the need for a greater rate of analytical throughput was met by automating both the instrumental methods and the various techniques used in classical wet chemistry, such as sampling, dilution, reagent addition, titration, phase separation and measurement. A further development which has already reached an advanced stage, involves the use of computers for data processing, report writing and ultimately for control of the various analytical parameters.

In this review of automatic analysers, it is proposed to restrict the field to those types of instrument which may be programmed to perform a variety of determinations with analytically acceptable accuracy and precision with minimum intervention by the analyst between the receipt of the sample and the reporting of the result. The emphasis will therefore be on automated wet chemistry. Instrumental techniques such as automated chromatography and spectrometry are more appropriately considered in reviews of the particular chromatographic, spectrophotometric or other techniques since they basically involve the addition of an automatic sample-handling facility to an existing technique restricted to a range of materials with a specific property such as volatility, adsorptive power or spectral absorptivity.

A wide variety of continuous monitors for on-stream analysis is available. Only those instruments which meet the criteria of wet chemistry and analytical versatility will be referred to. A number of instruments will be mentioned which have been custom-built for a particular analysis and which are not generally commercially available.

The applications of automatic analysers will be dealt with under a number of headings which represent a somewhat subjective choice but also reflect the most frequent uses to which such devices have been put.

Previous reviews have tended to emphasize the instrumental aspects of automated analysis. The well-known text by Siggia[1] devoted one chapter to equipment and in this he covered several automatic titrators and colorimeters. This book appeared two years after the

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* For reprints of this Review, see Publisher's announcement near end of this issue.

commercial development of the continuous-flow type analyser by Skeggs,[2] the Technicon "AutoAnalyzer". This unit has made the largest single contribution to the technology and applications of automatic analysers up to the present time.

At a 1959 Symposium on Automatic Chemical Analysis,[3] thirty papers were presented of which more than half involved the use of the Technicon "AutoAnalyzer". The symposium also illustrated the fact that clinical chemists were largely responsible for the early development and utilization of automated techniques. It was noted[4] that lack of specificity of existing methods and problems of sample-handling often made successful industrial uses more difficult to achieve. However, at two subsequent symposia[5,6] on the subject of "Automation in Industrial Pharmaceutical Process and Quality Control" a variety of methods and devices was presented, some representing adaptations of existing manual procedures and some consisting of entirely new techniques.

Many extensive reviews have been published on automated instruments and methods in specialized areas, such as pharmaceuticals,[7] clinical chemistry,[8–13] the petroleum industry[14,15] and water analysis.[16,17] The annual *Analytical Chemistry* Reviews do not incorporate automated wet chemistry as a separate heading but many of the subjects in both the Fundamental and Application sections contain specific references to automation. Some reviews have appeared in which automated classical chemistry is discussed together with other instrumental techniques.[18–22]

The general philosophy and methodology of automation in analytical chemistry has been discussed by a number of authors.[8,23–30] Malissa[23] considered the physical aspects of mechanization, the chemistry and physics of instrumentation and the cybernetics of the measurement and output of results. Examples of open, closed and computer-controlled systems were given. To enable the concepts to be communicated more readily, a symbolic sign language was developed,[24] which was subsequently extended for use with high-level computer languages.[25] A group of German, Austrian and Swiss workers is formulating a set of definitions for the various concepts in analytical automation (see *Talanta*, 1973, **20**, 811).

INSTRUMENTATION

A recent report[31] predicts that the market for automated wet chemistry instruments will achieve an annual growth rate in excess of 15% for the period between 1970 and 1980 compared with an average growth rate of 9% per year for all laboratory analytical instruments (excluding computers). This indicates that a list of manufacturers and models at any one time is rapidly outdated since changes are frequent. Furthermore, availability, price and service vary considerably between countries. It is more meaningful to discuss types of instruments and illustrate these with reported applications. Some publications comparing commercially available analysers should be mentioned, however.[10–12,32–34]

The classification of automated wet chemical instruments which is most commonly used and which will be followed here is based on the method of transporting samples and reagents, *i.e.*, continuous-flow or batchwise processing. A new type of fast parallel-flow analyser and some automatic titrators will also be discussed. The many special-purpose instruments which have been reported and which may not readily fit these categories will be mentioned under the appropriate applications.

Continuous-flow instruments

The widespread use of the Technicon "AutoAnalyzer" testifies to the versatility of the continuous-flow system. It is assumed that the reader is familiar with the principle of operation and the range of modules which is available. A general description has been given by

Siggia[1] and others.[2,7] Originally developed for clinical use, Technicon equipment is now finding an increasing number of industrial applications. The original single-channel instrument with colorimeter read-out has been supplemented by later models and analytical systems with two, three, six and twelve channels. Also, versatile accessories have been developed, a continuous digestor for temperatures above 100°, a solid sampler, a microdistillation unit, a tape filter and alternative measurement facilities such as a spectrophotometer or a flame photometer. A variety of integrated systems for multiple determinations in clinical and environmental chemistry will be mentioned under the relevant applications.

Regular Technicon Symposia have been held since 1964 and the proceedings have been published in book form. At these symposia a considerable number of applications and new instrumental developments have been reported. It is considered more useful for the purpose of this review to concentrate on publications in the general analytical literature. An excellent bibliography[35] containing 1825 references up to November 1967 has been published by Technicon. However, approximately half of the papers cited originate from Technicon Symposia.

The dialyser has proved to be one of the most useful accessories, particularly in the analysis of biological materials, to effect separations between the analyte and other diffusable materials and macromolecules such as proteins which may interfere with the colorimetric measurement. The original application of the dialyser for urea nitrogen determination[2,36] has been followed by others which will be referred to below.

The need for a rapid and automatic Kjeldahl determination led to the development of a continuous digestor[37] in which heating for a few minutes at a temperature of 400° or higher replaces the prolonged boiling required in the manual procedure. The versatility and validity of the automated technique were demonstrated in later publications.[38,39] Other workers[40] have noted that the recovery of nitrogen when compared with the manual Kjeldahl method varies with the type of compound and could be as low as 70%. Uhl *et al.*,[41] however, using standard compounds, found that the automated procedure frequently produced a better accuracy at a relative standard deviation of 2–3% for both methods. The continuous digestor has also been used for distillation[42] and evaporation of an organic solvent.[43]

A solid-sampling device[44] was specifically developed for pharmaceutical quality control of tablets. The commercial unit manufactured by Technicon is also able to handle preweighed samples of powders. The large number of applications of the solid sampler which have been reported were reviewed by Kuzel *et al.*[7]

Liquid–liquid extraction is one of the most important unit operations in clinical as well as general analytical chemistry, and consequently many workers have attempted to devise automated techniques. Because of the extent of mechanization of continuous-flow systems it is possible to achieve an acceptable precision under conditions of incomplete or non-equilibrium extractions. Two major problems have been attack on the tubing by organic solvents and insufficient mixing of the phases. Although various grades of acid- and solvent-resistant tubing are now available, special precautions must be taken. A displacement technique in which water is pumped into a vessel containing the immiscible solvent was first presented by Taylor and Marsh.[45,46] The same technique was applied by Roudebush[47] in the determination of an antibiotic by an absorbance measurement at 283 nm on a chloroform extract. Thus the possibility of ultraviolet-absorbing materials being leached from the pump tubing is eliminated. Mixing of two phases is usually allowed to take place by passing the air-segmented mixture through glass coils of varying lengths. To increase extraction efficiency coils filled with glass beads,[47] or long spirals[48] have been used. However, they suffer from a large dead volume, resulting in greater sample interaction and loss of precision. An interesting modification was used by Carter and Nickless.[49] Each of four mixing coils in series was shaken mechanically with an amplitude of approximately 1 cm. The degree of extraction increased with the speed of vibration. At 45 Hz, extraction was essentially complete without a significant increase in diffusion. For the determination of barbiturate in serum a double extraction has been used in which a small magnetically-stirred vessel[50] of 5 ml capacity replaced the conventional mixing coil. A magnetic stirrer has also been incorporated in a flowing stream to smooth the recorded response.[51]

Other techniques reported for phase separations include filtration and distillation, both of which are more difficult to automate than extraction in a continuous-flow system. A filter has been used in tablet assays[52] to clarify solutions before measurement on a spectrophotometer. A heated in-line gas filter was constructed by Knowles and Hodgkinson[53] to remove aerosols from an air stream containing carbon dioxide, which formed part of an enzymatic method for the determination of oxalic acid in serum. A modified Technicon microdistillation unit was used by Friestad *et al.*[54] for the colorimetric determination of phenols. A more elaborate unit was described by Keay and Menage[55,56] for the determination of ammonium ion and nitrate in soil extracts.

It will be evident from the examples above that many authors have devised modifications or additions to standard Technicon "AutoAnalyzer" modules to solve a specific analytical problem. The usefulness of such modifications is often enhanced by other workers adapting them to different applications. A lot of effort has been spent on developing alternative read-out modules replacing the standard colourimeter. Examples of new detectors are ultraviolet and visible spectrophotometers, spectrofluorimeters, atomic absorption, flame emission, potentiometric and coulometric devices, including polarographic cells and flow-through liquid scintillation counters. A series of papers by Růžička *et al.*[57–62] demonstrated the feasibility of performing substoichiometric analysis in a continuous system by a radioactive isotope-dilution technique. Mercury[58] could be determined down to 5×10^{-8} g by the addition of a labelled standard and zinc dithizonate followed by extraction with carbon tetrachloride, phase separation and counting of gamma-ray emission from the organic phase. Subsequently,[59] phase separation was found to be not necessary and a solvent displacement technique was used to avoid problems with adsorption of the zinc dithizonate reagent on the pump tubing. An increased reliability was obtained with a two-detector method.[61]

Not all of the modifications and special techniques reported in the literature will be commented on in detail. In Table 1 an attempt has been made to list these references under a number of broad headings. All have in common that at least one standard Technicon "AutoAnalyzer" component has been used.

The limitations of the continuous-flow method are illustrated by the number of papers on techniques to correct errors arising from sample interaction and instrument drift. The use of a continuously flowing air-segmented stream of sample and reagents causes problems of mixing and carry-over which adversely affect the precision and accuracy of automated determinations in comparison with the corresponding manual procedure. Thiers and Oglesby[191] were the first of many workers to examine the effect of instrumental parameters such as sample volume and sampling rate. They considered the errors in six determinations of clinical interest: sodium, potassium, chloride, carbon dioxide, urea and glucose. The sample interaction was quantified and found to vary from 1% (for glucose) to 10% (for carbon dioxide). They also demonstrated that errors can arise from differences in volumes

Table 1. References to accessories, modifications or special techniques for use with the Technicon "AutoAnalyzer"

Sampling devices	
solid sampler (standard type)	43,44,52,87,88,90,91,93,104,117,131,186
solid sampler (bead and chain)	65
dual sampling	72
suspension sampler	94
micro sampler	97
pneumatic sampler	69
plastic sample covers	80
anodic sample dissolution	77
timing and programming	67,79,144,147
modified sampler	73,80,96
modified fraction collector	92,118
Phase separations	
continuous filter	43,51,52,87,88,91,95,111,131,134,151,166,186
special purpose filters	53,90
distillation units	54–56,82,99,109,136,137,151,154,184
solvent displacement technique	45–49,59,86,121,176
shaking and magnetic stirring	49–51
improved separators	86,132,133
Detection devices	
ultraviolet–visible spectrophotometer	43,47,50–52,84–88,91,94,129,131,155,188
multichannel photometer	74,75
repetitive scanning	87
infrared spectrophotometer	135,165,186
flame photometer	63–65,124,125,138,174
atomic-absorption spectrophotometer	68,70,120,124,125,167–170
fluorometer	66,72,100,113–116,131,149,158–164,173,176,179,181
luminescence	157
scintillation counter	57–62,110
thermometric	76
coulometric and polarographic	140,141,153
potentiometric	89,145
testing device	142
Coulter counter	182
Miscellaneous	
continuous digestor	37–43,82,102,103,106,108,109,117,123,126,139,156,175,183
chromatographic column	74,75,78,84,130,150,181
reductor column	81
ion-exchange column	131,134
thin-layer chromatography	71
ultraviolet irradiation and photolysis	66,94,184
modified flow cells	85,119,127,128,152
multicomponent determination	70,74,75,80,89,102,105,107,112,131,164,166,170–173,178,182,189
ultrasonic bath	51
special mixing device	131
medical isotope production	98
batchwise incubation	92
interference testing	143
modified flow system	148
chart reading device	177
fragile incubation coil	180
gas absorber	184
countercurrent dialysis	185
air-rinsing technique	187

of samples placed in the sample cups. A redesigned sampler[80] in which the aspirator tube moved more rapidly in and out of the sample cups was shown to decrease the variability from this cause. A similar modification was used by Kuzel[96] and a subsequent model of the Technicon Sampler incorporated these changes.

Two approaches may be used to minimize sample interaction. One is to change the sampling parameters until the desired precision is obtained. It has been shown[192,193] that interaction can be significantly reduced by increasing the time of sample pick-up and the ratio of sampling to washing periods. However, a larger volume of sample is required and sample peaks may become difficult to read when the valleys between them become less pronounced. It can be demonstrated that the frequent objective of producing sharp peaks with deep valleys is directly opposed to obtaining optimum precision and minimum interaction. Short-term fluctuations due to electronic noise, mechanical problems, bubbles in the optical path or insufficient sample are less likely to be detected under conditions producing sharp sample peaks.

The other and more frequently used procedure involves the application of an appropriate correction factor.[191,194–197] This factor depends on the concentration of the preceding sample, the sample and wash timing and the type of analysis being performed. The improvement in precision resulting from this correction has been up to twofold.[191] Several authors[195–197] have applied the correction by means of a computer programme which generally performs several other functions, including drift correction, curve fitting, converting peak height into concentration and reporting in an appropriate format. The nature of the correction factor is derived from studies of the kinetic parameters in continuous-flow analysis.[198–202] Similar conclusions were reached by Thiers *et al.*[192] and Walker *et al.*[198] from a consideration of the " lag time ", the effect of overlapping rise and fall curves and the steady-state conditions. These parameters are incorporated in the exponential correction equation for carry-over. An empirical equation was presented by Stickler *et al.*[199] and applied to four clinical determinations of varying degrees of complexity. It was shown that application of the correction would allow a twofold increase in the assay rate without deterioration of the reproducibility. In two recent papers, Begg[201,202] derived a linear model in which the leakage between successive slugs of solution depended only on the slug-volume and distance travelled, and a non-linear model in which the leakage rate also varied (linearly) with concentration. By comparison of experimentally found rise curves with calculated concentration distributions it was found that the linear model holds for the simple systems examined. Walker[203] showed that sampling rates up to 180/hr became possible by applying an exponential correction to the sloping sections of the recorder trace and generating a new curve. The calculations involved become practical only if a computer is used. No information was supplied on the precision obtainable at the higher sampling rate.

It has been recognized that sample interaction is in part a result of the debubbling process which occurs just before the flowing stream enters the colourimeter cell. Habig *et al.*[204] have devised a system in which the air-segmentation is retained but the recorder is inactivated when an air-bubble is in the cell, as detected by a conductivity measurement. The bubble-gating system requires careful control over the regularity of the bubble pattern, a flow-through cell of reduced volume, and increased flow-rate. The authors consider these factors mitigate against its routine use. An interesting application arises when more than one measurement is to be made on the one stream as in kinetic analysis.

Variations in the sample time have been shown[192] to affect sample interaction and therefore precision in continuous-flow analysis. Friedman[79] has shown that such variations can be caused by large tolerances in the mechanical specifications of sampling cams. Jansen *et al.*[147] designed a new instrument around a sampling system which is based on volume rather than time. This was achieved by a pair of platinum electrodes inserted in the sample line, which activate the sample-changing mechanism when the passage of an air-bubble is detected. An improvement in the relative standard deviation from 2·0 to 1·2% was claimed for the determination of urea.

Faithfull[205] has recently shown that a " warm-up " time as long as 40 min may be required in order to stabilize the tubing in the peristaltic pump. Histograms of the results of nitrogen and potassium determinations demonstrated that a normal distribution and acceptably low standard deviation could be obtained after an equilibrium period which was considerably longer than the time required to stabilize the flame photometer or other measuring modules.

A scheme has been recommended[206] for the evaluation of automatic analysers. It includes specifications for the measurement of accuracy, precision, cross-contamination, overall performance and running costs. Although the scheme is designed for clinical and biochemical analysis it should be equally useful in other fields. An assessment of the precision of five clinical determinations on the Technicon "AutoAnalyzer" has been made.[207] An unconscious bias introduced in the manual reading of "AutoAnalyzer" charts has been discussed by Corns and Corns.[208]

Only relatively few continuous-flow analysers of other makes are available. The Italian-made Carlo Erba instrument also utilizes a peristaltic pump for transport of samples, standards and reagents. However, it does not use air-segmentation and appears to have only a limited number of accessories. Blaedel and Olsen[126] have reviewed (in 1963) several commercially available continuous single-purpose analysers principally used for water analysis.

The continuous flow of reagent and samples by a combination of gravity and a peristaltic-pump feed was used by Blaedel and Hicks[209] in an instrument for enzyme assay and the measurement of enzyme-catalysed reactions. To decrease the response time and prevent laminar flow the reagent line is mechanically pulsed at a frequency of 5 Hz and an amplitude which may be varied to optimize the response. Up to thirty determinations per hour may be performed. The instrument as described is only partly automated since sample change-over is performed manually.

A different type of continuous analyser has been described by Natelson[97] and has been the subject of several patent applications[210–213] assigned to Scientific Industries Inc. The instrument is claimed to be especially suitable for clinical analysis. It consists of a tape to which samples are applied from capillaries. This tape is brought into contact with another containing a reagent capable of producing a colour. The spots are then read densitometrically. The system is limited to simple chemistries and does not appear to be used to any great extent.

Automatic titrations are commonly discontinuous operations. One continuous device has been described by Pauschmann[214] in which a stream of sample to which an indicator has been added flows through a transparent channel containing a series of narrow holes. A titrant solution is pumped into the sample stream through these holes. The sample concentration can be obtained from the distance at which the indicator undergoes a change of colour. Various modifications of this principle are discussed, including alternative methods of end-point detection, such as a change in pH, temperature, conductivity and absorption of light. A similar system of flowing sample and titrant streams was patented,[215] but the titrant was delivered by a variable-speed pump. The speed of the pump was servo-controlled by the difference between an electrode signal and a preset potential indicating the endpoint. The desired concentration is then obtained from the generator which feeds the variable-speed motor.

A large number of special purpose instruments is now commercially available for continuous monitoring or on-line analysis of liquid and gaseous process streams. Many of these devices are purely instrumental rather than wet chemical and are capable of achieving a precision which may be sufficient for their intended purpose but which would usually be unacceptable for general analytical work. However, some involve the transfer of reagent solutions and are adaptable to the measurement of several parameters. Simpson[216,217] has described the types of analysers available for the continuous monitoring of gaseous pollutants. He has indicated the limitations on selectivity and sensitivity of wet chemical techniques for some of the common gases of interest in pollution control. McWilliam[218] has provided a listing of 41 specific and non-specific techniques, mostly continuous, for on-line analysis in the chemical and petroleum industries. He has also reviewed the factors to be considered in the justification of purchasing or developing an automated system. Lörinc[219] has presented a review of automatic instruments suitable for the analysis of flowing streams. Some special problems arising in the sampling of aqueous process streams have been discussed by Babcock[220] and a guide to the selection, installation and operation of air monitoring equipment has been given by Elfers.[221]

Discrete-sample processers

The essential feature of discrete-sample analysers is the fact that samples are processed and conveyed in individual containers from the initial sampling up to and sometimes including the final read-out stage. Such instruments are also referred to as discontinuous, repetitive or batch analysers. The techniques used more closely approximate those in conventional wet chemistry and as a result a manual procedure is usually more readily converted into an automated version. However, the problems involved in automating phase-separation techniques (distillation, filtration, extraction) on a discrete basis are probably responsible for the greater popularity of continuous-flow methods.

There are some distinct advantages in discrete-sample processing. Since each step in the procedure is independent, trouble-shooting is greatly facilitated. Individual samples retain their identification without ambiguity, and interaction or cross-contamination may readily be eliminated. An inherently greater sensitivity may be expected because the measurement in the static system requires less solution than in a flowing system. In general, the consumption of samples and reagents is considerably less. One might also expect an easier adaptation of alternative read-out techniques. However, this is not borne out by published work in this area.

The distinction between continuous and discontinuous processing is not always clear, since each uses some features of the other. Sample presentation in a continuous system is usually performed on a discrete basis by means of a turntable with individual containers. On the other hand, the measurement stage of a discrete-type instrument generally involves the transfer of the reaction mixture into the flow-through cell of a colourimeter or spectrophotometer.

It is known that many commercial instruments have been produced from time to time and an even larger number of special purpose analysers have been constructed. In spite of this, relatively few publications have appeared in which such instruments have been evaluated or compared with manual or continuous techniques. A large proportion of the papers published has in fact been written by those involved in the building and development of analysers rather than by the users.

Kuzel, Roudebush and Stevenson[7] have reviewed the literature on automated techniques in pharmaceutical analysis up to July 1968. Their paper covers a number of batch analysers from the very simple automated colourimeters to the very elaborate systems capable of 3000 determinations per hour, with data-processing facilities. Therefore, mainly the more recent work will be reviewed here.

Many of the commercial and special instruments have been designed for clinical analysis.[10,34] Five instruments of British manufacture have been reviewed by Rose.[12] Trotman[222] has described an apparatus consisting of a sample turntable and four syringe-dispensers for the reagents in the Wassermann test. Sampling is performed manually and the test result is assessed visually. An instrument was developed by Westlake *et al.*[223] in which each sample is accompanied by an IBM card containing the relevant information. Sampling and reagent dispensing is performed by pipettes and syringes at a rate of 120 samples per hour. Carry-over in the colorimeter cell is about 2% and after correction for this the relative standard deviation for aqueous glucose standards varies from 0.2 to 0.7%. The photometer signal and the information on the card are simultaneously processed by a computer. Three analysers performing seven different tests with varying degrees of automation are linked to the central data-logging system.

A relatively new instrument, the "Autolab," made by A. B. Lars Ljungberg & Co., Sweden, has been described by Aberg.[224] It is modular in construction and comprises sampling and reagent units, an incubator and a colorimeter with digital display or print-out. Samples are transported in tubes held in chain holders of unlimited length. Carry-over is minimized by the application of wash-water followed by suction to the outside of the sampling probe. A suction device for the removal of gases has been described by Hulthe *et al.*[225] Again, the "Autolab" is principally designed for clinical analysis. It can handle 240 samples per hour and reproducibilities between 1.0 and 3.8% have been claimed for a variety of determinations.

An apparatus for enzyme assay was constructed by Cove[226] from a Unicam SP800 spectrophotometer with a cell-changer and programme-controller. Eight Hook and Tucker diluter units were used to dispense the sample enzyme with and without the substrate materials in four sample and four reference cells respectively. The sequence of operations was controlled by a Londex Rotaset Program Timer at an analysis rate of 48 assays per hour. It was claimed that the reproducibility of 10% was accounted for by dispensing inaccuracies. Enzyme analysis was also performed with a Unicam AC60 system.[227] This instrument also consists of a chain of tubes which passes a number of reagent stations before the solution is finally transferred to a spectrophotometer. A coefficient of variation of 2.7% was claimed for eleven determinations on each of two serum samples and excellent agreement between the automated and manual methods was demonstrated. Several specially built automatic stopped-flow instruments have been described for kinetic determinations, utilizing motor-driven syringes[228] and valves or pneumatically-actuated components.[229] The latter system was shown to produce faster mixing and reduced dead time. Approximately 1000 phosphate determinations per hour could be handled at relative standard deviations of 1–3%.

Potentiometric measurements by selective ion-sensitive electrodes have been automated on a discontinuous basis. A system for the determination of pH of soil was presented by Baker[230] in which containers move on an endless belt. Addition of water, stirring, pH-measurement and rinsing are performed automatically at a rate of 100 samples per hour. A more elaborate device for the determination of sodium, potassium, chloride and pH in blood was constructed by Dahms.[231] The system incorporates a peristaltic pump, a pneumatic timer, a rotary valve and specially made glass capillary flow-through electrodes for the alkali metals and pH. A pH-meter with an automatic probe-selector is connected through a data-transfer system to a card punch for data logging. Each cycle of measurements requires 65 sec and calibration is performed after each tenth sample. The speed of analysis is limited by the electrode response. This parameter and its effect on the precision of automated measurements with selective ion-sensitive electrodes has been discussed by Malissa and Jellinek.[232]

Solvent extractions have been automated by several workers[233–236] and applied to the determination of detergents[233,234] and an oil-additive.[234] A typical discrete system consists of commercially available syringe-dispensers and a beaded coil, followed by a phase-separator and a flow-through cell in a spectrophotometer. Later, a continuous-flow method was developed[235] which could extract trace amounts with equal efficiency and greater versatility. Two different systems based on the timed flow of reagents through precision-bore tubing and a centrifugal separator were described by Trowell.[236]

An apparatus for the automated determination of mercury was constructed by Lindstedt and Skare.[237–239] It consists of a peristaltic pump for the batchwise addition of reagents to predigested samples and transfer to a tower for scrubbing with nitrogen. The gas, containing the mercury vapour, is then passed through a flow-through gas cell in a spectrophotometer.

An elaborate instrument for the evaluation of antibiotics and vitamins has been constructed by Kuzel and Kavanagh.[240,241] It is based on a turbidimetric determination on an incubated sample to which a nutrient broth has been added. The equipment comprises a sampling and reagent module, an incubator and a measurement module. Data can be printed out or processed by an on-line computer.

Table 2 lists the majority of currently available automatic analysers utilizing discontinuous processing. Some instruments used exclusively for clinical applications have been included for comparative purposes. Where general use is indicated the instrument has frequently been designed for clinical laboratories but has sufficient versatility to be programmed for a variety of determinations. A filtration, or in biochemical terms a deproteinization step, is of importance in many clinical methods and several of the instruments shown in the table have this capability. One model, the " Mecolab," combines the advantages of automation with the versatility of batch processing. Samples are treated in groups of fifteen on each module (dilution, centrifugation, measurement) for 3-min periods. Transfer from one module to another is performed manually. An automatic microcentrifuge is available on one instrument, the Quickfit 617 Automatic Analyser, but no information is available on its performance.

Fast parallel analysers

A new approach towards high-speed automated analysis was taken at the Oak Ridge National Laboratory by Anderson with the development of a fast analyser based on the transfer of samples and reagents by centrifugal force.[267–277] The prototype of this instrument was given the name of GeMSAEC (General Medical Sciences, Atomic Energy Commission). It employs a "Teflon" rotor containing cavities to hold samples and reagents. By spinning at speeds of about 1200 rev/min the solutions are mixed and transferred into a

Table 2. Commercially available discrete analysers

Manufacturer, instrument and country	Uses(1)	Detection system(2)	Presentation of results(3)	Max. No. of samples/hr	References
AB Lars Ljungberg, Autolab, Sweden	C,G	CO	DD,DP	240	224,225
AGA Corporation, AutoChemist, Sweden	C	CO	DD,DP,CM	135	242
Amer. Instr. Co., Assayomat, U.S.A.	P	SP	R		243
Amer. Opt. Instr. Co., Robot Chemist, U.S.A.	C,G,P	SP	DD,DP	120	244–248
Baird & Tatlock, Analmatic Clinical System, U.K.	C	CO,FP	DP	300	12
Bausch & Lomb, Automatic Sample Processor, U.S.A.	G	CO,SP	DD,DP	300	
Beckman, Discrete Sample Analyzer, DSA–560, U.S.A.	C,G	CO	R,DD,DP,TY	160	34,249,250
Du Pont, Automatic Clinical Analyzer, U.S.A.	C	CO	DP	100	34,251,252
Electro-Nucleonics GeMSAEC Systems, U.S.A.	C	CO,SP	R,OD,TY,CM	300	253,254
Gilford, Automatic Enzyme Analyzer, Model 3400, U.S.A.	C	SP	DP		
Griffin & George, Bioanalyst, U.K.	C,G	CO(4)	DP	120	12
Hycel Inc., Mark X, U.S.A.	C	CO	R	400	255
Joyce Loebl, Mecolab, U.K.	G	CO	R,DP	240	12
Lab-Line, Clinomak, Mark II, U.S.A.	C		R	300	34
LKB, Ultrolab System, Sweden	C,G	CO(5)	DD,DP	400	256
Perkin–Elmer, C4 Automatic Analyzer, U.S.A.	C,G	SP	R,DP	120	34,257–259
Quickfit & Quartz, 617 Automatic Analyser, U.K.	C,G	CO(6)	DP	100	12
Radiometer, ATS1 Autopipetting Titration System, Denmark	G	P	DP		
Unicam, AC60 Chemical Processing Unit, U.K.	G	SP	R,DD,DP	120	34,227 260–264
Union Carbide, Centrifichem, U.S.A.	C	CO	DP	600	34,265
Vickers, Multi-channel 300,	C	CO,SP,FP	DP,TY,CM	300	12,34,266

(1) C: clinical, G: general, P: pharmaceutical.

(2) CO: colourimetric, SP: spectrophotometric, FP: flame photometric, P: potentiometric.

(3) R: recorder, DD: digital display, DP: digital print-out, OD: oscillographic display, TY: typewriter, CM: computer.

(4) EEL model 171 Automatic Colorimeter.

(5) LKB Calculating Absorptiometer or LKB Reaction Rate Analyser.

(6) EEL model 171 Automatic Colorimeter or Joyce Loebl Auto-Colourimeter.

set of fifteen or more cuvettes arranged radially around the rotor. The cuvettes spin past the stationary beam of light of a photometer. The absorbances of all samples are displayed simultaneously as a series of peaks on the screen of an oscilloscope. Analysis is therefore parallel rather than sequential.

Volumetric measurement of samples[267] and phase separations[274] are also accomplished by centrifugation and the appropriate choice of transfer disc and sequence of rotation.

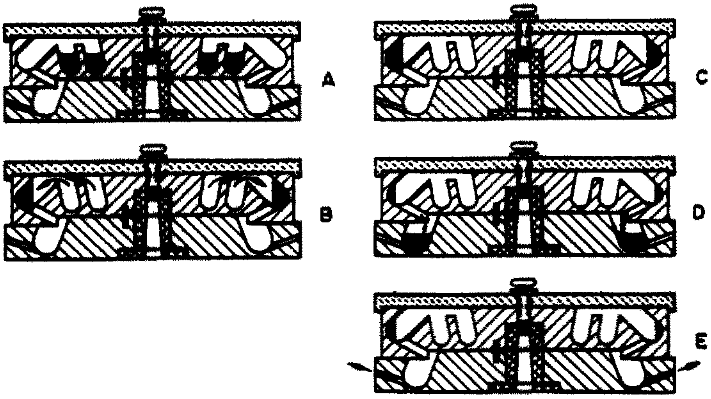

Fig. 1. Operating sequence of the rotor for the separation of precipitates (GeMSAEC Fast Analyser).
In (A), the sample and precipitating reagent are placed in the upper wells and remain unmixed at rest. During rotation (B) the two solutions mix, precipitation occurs, and the precipitate is centrifuged against the wall (C). During deceleration, the supernatant liquid is decanted into the lower holding chamber (D), and the precipitate is left in the upper sedimentation chamber. On reacceleration (E), the supernatant liquid is transferred centrifugally into a cuvette or into a plastic measuring chamber. (Reproduced by permission of the copyright holders from N. G. Anderson, *Anal. Biochem.*, 1969, 31, 272.)

Figure 1 illustrates the procedure for the removal of a precipitate.[268] The major advantage of such a system is that the total time for one analysis is the same as for 15 or more determinations regardless of the complexity. Turn-round time for one set of samples may be as little as a minute. It is obvious that analytical data produced at this speed are ideally suited for computer processing

Hatcher and Anderson[271] have compared the results of the determination of serum protein on the GeMSAEC system with the results obtained by the Kjeldahl method and by the Technicon "AutoAnalyzer". Levels of precision were comparable but the GeMSAEC system proved slightly more accurate, was faster and required considerably less sample and reagents. Up to thirty different clinical analyses were claimed by Hatcher[275] to have been automated, but few details were provided. He also introduced a new concept of absorbance measurement involving a common source and detector and various bundles of optical fibres for the simultaneous display of the signal from a number of probes.

Burtis *et al.*[276] have described the development of a 42-place fast analyser and have presented results for a number of chemical and enzymatic analyses. Determinations for ten blood constituents were performed with relative standard deviations mostly less than 2%. Although only 2 min were required to obtain 40 results, the actual time taken from the start of reagent preparation of the final washing of the absorption cells ranged from 16 to 20 min per transfer disc. This corresponds to 120–160 samples per hour and the authors claim that this could be increased by replacing the manual sample and reagent loading with an automated procedure. More recently a miniature fast analyser was described.[277]

Three commercial versions[278] of the system were first announced in 1970. Two of these, by Electro-Nucleonics and Union Carbide, have been included in Table 2. Little information is available on the performance of these instruments under routine laboratory conditions. Maclin[253] has discussed the theoretical basis of kinetic enzyme determinations with the

Electro-Nucleonics GeMSAEC instrument and the effect of changing the variable parameters on the precision which may be expected. Tiffany *et al.*[254] obtained relative standard determinations of 2·2–4·8% on some clinical analyses. The programming of a minicomputer for use with this system was described by Kelly and Jansen.[279]

The Union Carbide system, known as "Centrifichem", utilizes a 30-cuvette rotor. Its performance on the determination of serum creatinine was presented by Fabiny and Ertingshausen.[263] Relative standard deviations from 3 to 7% were obtained by a method which involved two sets of absorbance readings, taken 20 and 80 sec respectively after starting the rotor.

It would seem that fast parallel analysers have considerable potential in general analytical chemistry, particularly for those applications in which a fast result is required on a relatively small number of samples. Obviously, many technical improvements are required before the more complex procedures may be handled by this system. A variety of rotors could be made for different types of analyses and one could visualize such rotors being automatically preloaded with the appropriate reagents so that the user need only introduce the samples. One factor which will prevent the widespread use of the commercial versions is the high cost, at present around $20,000 excluding the computer.

Automatic titrators

Titrimetric procedures have been automated[280] for many years to various extents. This is presumably due to the repetitive and therefore tedious nature of the operations involved in carrying out a titration. Automatic titrators have been based on one of two principles. In one type, a reagent is added at a controlled rate and the variable measured (electrode potential, absorbance, *etc.*) is continuously monitored and displayed as a function of the volume of titrant. Thus the full titration curve is displayed from which the equivalence point is obtained and the calculation made. In the other type, addition of titrant is automatically stopped at the equivalence point, generally because a preset potential has been reached, and the equivalence volume may then be read from the titrant-dispensing mechanism. In both instances sample presentation, pretreatment, emptying and washing of the titration vessel, resetting of the instrument and calculation of the result has to be performed manually for each analysis. In an on-stream automatic titrator, such as the "Titromatic Analyzer" described in Squirrell's book,[280] most of these functions are automated. However, such instruments require considerable maintenance and results are subject to errors when electrode potentials tend to drift or when the inflection at the equivalence point becomes less pronounced.

One system for automatic titrations was recently described by Johansson.[281,282] It utilizes the graphical method of Gran for the calculation of the equivalence point. The titrant is added in equal increments and the electrode potential obtained after each addition. The sample is taken by an automatic syringe and reagents or diluents may be added before the titration. Sample carry-over is minimized by a water rinse between samples. The precision of the delivery is better than ±0·1%. Electrode potentials are measured and printed out at a preset interval after each addition. Relative standard deviations for the titration of a strong and a weak acid with sodium hydroxide were 0·3 and 0·4% respectively at an analysis rate of 30 samples per hour. The desirability of computer calculation was mentioned but not discussed in any detail.

A semi-automatic computer-based system for titrations was described by Jagner.[283] It comprises a series of motor-driven syringes and also uses Gran's method for the determination of the equivalence point. The emphasis in this instrument is on high precision. Jagner claims that weighing of samples is inherently more precise than volumetric measurement. Since weighing has not been satisfactorily automated, samples are weighed and presented manually. The electrode potential is measured with a digital voltmeter which is interfaced to a "Teletype" paper-tape punch. A scanner enables the progress of up to 45 titrations to be followed simultaneously. The data on punched tape are processed by the computer in an off-line mode although on-line data-logging and calculations are also possible. The system was used by Jagner and Årén[284] for the potentiometric determination of total halides in sea-water. Graphical evaluation was compared with computer calculations. The latter method produced a better precision (0·02 %). In a subsequent paper by Anfält and Jagner[285] a fully computer-controlled system was described.

Both of the Swedish groups of workers mentioned above base their determination of the equivalence point on the extrapolation method described by Gran.[286] Extensions of these equations have been developed[287,288] for titrations involving weak acids or bases. The precision and accuracy obtainable from various methods of equivalence-point determination has been recently reviewed by Anfält and Jagner.[289] It was shown that a modified Gran procedure was superior to any other method. However, the calculations involved are of a certain complexity so that a computer becomes almost an essential component of the system. Several approaches to the computation of titration curves have been described.[290–293] Both the principle of Gran's method[294–296] and the advantages of computer evaluation[297] have been receiving renewed interest recently and further developments in their utilization in automated analysis can be confidently predicted.

An automatic titrator with thermometric sensing has been described by Guillot.[298] Sample and reagent are measured by pneumatically operated syringes into a cell equipped with a thermistor and stirrer. Determinations by neutralization, redox and complexation reactions were performed with a precision of about 1 %. Mueller and Burke[299] have constructed a computer-controlled reagent-addition system incorporating a syringe microburette and a spectrophotometer. An acid–base titration with photometric end-point detection provided an accuracy and precision of better than 0·5 %. A novel method of digitizing the titrant delivery in an automatic titration apparatus has been developed by Hieftje and Mandarano.[300] Uniform droplets of the titrant are produced and counted. The rate of delivery may be varied near the end-point. The system is suited for the production of derivative titration curves. A simpler drop-counting mechanism was described by Olsen and Foreback[301] for the partial automation of spectrophotometric titrations. Several other titrators with fully automatic sample-changing facility have been described[302–304] and one commercial unit has been included in Table 2.

APPLICATIONS

The uses to which automatic analysers are now being put cover every field of analytical chemistry. The unique requirements of clinical laboratories, *i.e.*, a large number of determinations for a small number of sample constituents with a relatively wide tolerance on accuracy and precision, together with the introduction of the Technicon "AutoAnalyzer", were initially responsible for the widespread application in this field. Subsequent improvements in instrumentation and development of a greater variety of methods resulted in automatic analysers being used also in other areas, particularly in pharmaceutical quality control, agricultural chemistry and food analysis. More recently, the demand for more data in environmental studies has led to a greater use of automated techniques in this field.

The literature on applications has by now grown so voluminous that a comprehensive coverage is difficult to achieve and becomes rapidly outdated. In this review particular emphasis will be given to those types of applications which have not been dealt with elsewhere.

Clinical chemistry

Methods and techniques in clinical chemistry are periodically reviewed[305,306] in the Applications Section of *Analytical Chemistry* Reviews, including a section on automation. There is therefore no need to provide a detailed catalogue of applications here. The needs, both satisfied and unsatisfied, of automated clinical laboratories have been discussed by Gambino.[9] The trend to multi-component methods and instruments has been reviewed by Laessig[10] with particular reference to the costs of large-scale health-screening programmes. The economics of laboratory automation have also been analysed in a recent book.[11] Several other reviews have appeared on automation in clinical chemistry.[12,34,307–310]

A system for performing eight different determinations sequentially was first described by Skeggs and Hochstrasser.[311] Precalibrated recorder charts serve as the analysis report. A parallel multichannel analyser was constructed by Thiers *et al.*[80] from standard Technicon components, including seven colourimeters, one flame photometer and one fluorometer. Technicon eventually developed the SMA 12-30, a sequential multiple analyser capable of determining 12 components on each sample at the rate of 30 samples per hour. Evaluations of this instrument have been made by Broughton *et al.*[312] and Hoffmeister and Junge.[313,314] The latter workers studied the effect of storage time and temperature on the stability of serum samples and improved the reliability of the system by a new method of control and standardization. A subsequent model, the SMA 12–60, was evaluated by Finley *et al.*[315] In spite of some excellent results reported, Laessig[10] still considers that in general less accurate data are produced by multichannel systems than by the older single- and dual-channel analysers. A computer-based system with 12 test channels assembled from standard Technicon components has been described by Abernethy *et al.*[197,316] The use of an off-line computer was shown by Flynn[317] to increase the speed of presentation with a reduction in the frequency and magnitude of laboratory errors.

Some of the techniques developed especially for clinical work could have a wider application, but by being published in specialist journals escape general attention. An automated method for the determination of protein-bound iodine has been described by Knapp and Spitzy.[318] They combine a continuously operating ashing oven with an "AutoAnalyzer" for iodide. An automated procedure for iodine at low concentrations in biological materials was evaluated and compared with a neutron-activation method.[319] Both methods were found to have comparable precision and accuracy.

Blood-cell counting has been automated by interfacing a standard "Coulter Counter" with an "AutoAnalyzer" which also performs haemoglobin determinations.[182] Cell sedimentation in the samples is prevented by magnetic stirring. The Technicon method for glucose determination has been the subject of a lot of attention mainly because of its lack of specificity. Edwards and Freier[320] have determined the extent to which disaccharides and other reducing substances dialyse across the membrane. They also determined the effect of temperature and analysis rate on the dialysis efficiency of glucose and found that interaction between samples was up to 4·7%. Hinton and Norris[321] found that the presence of sucrose affected the performance of continuous-flow systems for protein determination. A twofold increase in cross-contamination occurred when the sample was 1·8M in sucrose.

Elimination of the dialysis step to simplify the simultaneous microdetermination of urea and glucose in serum was reported by Caron *et al.*[322] The reliability of the *o*-toluidine method for blood-sugar determination was found by Sommer and Herbinger[323] to depend critically on the concentration and speed of analysis. Sudduth *et al.*[324] compared this method with a ferricyanide and a specific enzymatic procedure. The *o*-toluidine method produced the best accuracy and a relative standard deviation of 1·2%. Other hexoses were found to interfere. A modified enzymatic procedure for glucose in blood was described by van der Silk *et al.*[325] Hornby *et al.*[326] have reported a novel method for glucose in which glucose oxidase is chemically attached to the inner surface of a polystyrene coil in a continuous-flow system.

Electrolytes of clinical interest include sodium, potassium, calcium, magnesium, iron, certain other metals and halides. A procedure for serum sodium and potassium determination, utilizing a Technicon sampler, an on-line diluter and a flame photometer, has been presented by Pennacchia *et al.*[174] The simultaneous determination of sodium, potassium and chloride has been performed by Haeckel[258] on a Perkin–Elmer C4 analyser. The usable range for potassium was limited and other halide ions interfered. A simplified system for the two alkali metals with carbon dioxide and urea has been described by Kind *et al.*[327] Calcium and magnesium determinations in serum and other biological materials have been performed by atomic-absorption spectrophotometry.[162,163] Lott and Herman[328] have shown that the presence of proteins can be a source of error by increasing the rate of dialysis of calcium and magnesium ions.

Colorimetric procedures have been used for iron and iron-binding capacity in serum, with continuous-flow systems.[329,330] The simultaneous determination of copper and iron has been described by Kattermann and Koehring.[171] Fluoride in urine has been determined by Hargreaves *et al.*[154] with a lanthanum–alizarin complexone reagent after a distillation. Chloride and carbon dioxide in plasma have been simultaneously determined with the "AutoAnalyzer".[172] A turbidimetric method for sulphate determination was automated by Dieu.[187] Coating of the flow-cell with barium sulphate was prevented by an air-rinse between samples.

Deuterium oxide in water and biological fluids was determined[165] by coupling an infrared spectrophotometer to an "AutoAnalyzer". Concentrations between 0·1 and 1% D_2O could be determined with a relative standard deviation of 1–4%. Knowles and Hodgkinson[53] described an enzymatic method for the determination of oxalic acid in serum. The specific enzyme decarboxylates oxalic acid to produce carbon dioxide which is then determined colorimetrically. A heated gas filter is used to remove any aerosol from the gas phase. The metabolic activity of collagen has been assessed by the determination of hydroxyproline in plasma and urine by an "AutoAnalyzer" procedure.[331] In the concentration range of 2·5–15 μg/ml, the relative standard deviation was 2·6% and excellent agreement was obtained with an isotope-dilution method. Grant and Hall[332] have reviewed automated methods for steroid analysis.

An interesting application of a continuous-flow dialysis technique has been reported by Stein.[333] The binding of dialysable compounds to macromolecules was studied by a dynamic method utilizing an "AutoAnalyzer". The information was obtained faster than by the conventional equilibrium procedures.

The procedures of clinical interest which may be performed on parallel fast analysers (GeMSAEC) have already been referred to.

Pharmaceutical chemistry

Two symposia[5,6] and a review[7] with 293 references have dealt with the use of automated techniques in pharmaceutical analysis up to 1968. Some of the special requirements of pharmaceutical quality control include the need to determine one or more active components in a single determination, the ability to handle solid samples such as tablets, and the use of turbidimetric procedures for biological assays.

The construction and operation of an automatic dispensing analyser for the assay of individual tablets has been described by Beyer and Smith[334]. It incorporates a Technicon pump and continuous filter. The simultaneous determination of several components in single tablets has been described recently by Urbányi and O'Connell.[131] Reserpine, hydralazine hydrochloride and hydrochlorothiazide were assayed respectively by fluorometric, colorimetric and ultraviolet spectrophotometric measurements. Murfin[166] has reported "AutoAnalyzer" methods for the determination of two or three components of commercial analgesic tablet formulations. Urbányi and Lim[186] used an infrared spectrophotometer coupled to an "AutoAnalyzer" with solid sampler to determine methylphenidate hydrochloride in tablets after extraction. Although the method is not specific and less precise than the official procedure, it is adequate for uniformity testing. A similar technique has been employed by Ryan *et al.*[135] for the determination of meprobamate. A dual extraction procedure for tablet assay has been described by Ahuja *et al.*[43] Single tablets of chloral betaine have been assayed by Bryant *et al.*[335] after double dialysis.

A variety of amine drugs has been analysed by Robertson *et al.*[336] by the acid dye technique. Bromothymol Blue at pH 6 is used for all polar, primary and quaternary amines while Bromocresol Purple at pH 2 is the indicator for non-polar compounds. The determination of phenylephrine hydrochloride has been automated by Lane.[132] This method has been the subject of a collaborative study[133] showing a maximum coefficient of variation of 4·5%. Cyclohexylamine in cyclamates has been determined by Berry and Crossland[337] at concentrations as low as 5 ppm, using a colorimetric "AutoAnalyzer" method. Multivitamin preparations have been analysed by Cavalli and Rurali,[338] Geller *et al.*[339] and Bryant *et al.*[340]

Penicillin determination by a colorimetric "AutoAnalyzer" method has been described recently by Holm.[189] A high degree of sensitivity, accuracy and precision is claimed. The assay of a variety of commercial penicillin preparations has been reported by Mills.[260] An automated apparatus for the turbidimetric determination of antibiotics has been constructed by Kuzel and Kavanagh.[240,241] The calculation of potencies may be performed by computer.[341] More recently a similar apparatus has been built by Rippere and Arret[342] from commercially available components. Several other procedures for automated microbiological analysis have been described.[343–345]

Some additional recent papers have been included in Table 3 under a number of broad headings.

Agricultural and food chemistry

The use of a Technicon "AutoAnalyzer" for chemical analysis in agricultural research has been discussed by Skokan.[356] The determination of total nitrogen in fertilizers has been automated by Gehrke *et al.*[139] This involves the manual reduction of all nitrogen compounds to ammonia followed by automated digestion and reaction with hypochlorite and alkaline phenol. In a later paper[183] the reduction step was also automated. Potassium in

Table 3. References to automated pharmaceutical analyses

amphetamines	336
antibiotics (colourimetric)	189,260,353
antibiotics (turbidimetric)	240,241,341–345
barbiturates	50
chloral betaine	335
codeine	336
cyclamates	337
digitoxin	350,351
enzymes	226,261
ephedrines	132,133,336
hydralazine hydrochloride	131
meprobamate	135
methylphenidate hydrochloride	186
paracetamol	166
phenacetin	166
phenmetrazine	43,336
reserpine	131,348,349,354
reviews	5–7,346
steroids	352
tablets	43,131,186,334,339,350
vitamins	338–340,347,355

fertilizers has been determined by automated flame photometry and the results of a collaborative study were presented by Hambleton.[138,357] The determination of manganese in fertilizers containing trace elements has been described by Holz.[358] Phosphorus has been determined in rock,[359] fertilizers[360] and superphosphoric acid.[361]

One of the earliest non-clinical applications of the Technicon "AutoAnalyzer" was the determination of zinc and other trace metals in soil extracts by Stanton and McDonald.[121,122] The simultaneous analysis of soils for calcium, potassium, magnesium and phosphorus has been performed by Lacy.[124] The first two elements are determined by flame photometry, magnesium by atomic absorption and phosphorus by the molybdenum blue method. Up to 40 samples per hour may be handled. In a study of American soils similar procedures have been followed by Flannery and Markus,[362] using different extractants. It was noted that low calcium values were obtained in the presence of sulphate. Automated methods for the determination of nitrogen in soil extracts have been developed by Keay and Menage[55,56] and Henriksen and Selmer-Olsen.[81] The latter reduce nitrate to nitrite by passing the solution through a coppered cadmium reductor-column interfaced with an "AutoAnalyzer" manifold. Nitrite is then determined colorimetrically with sulphanilic acid and 1-naphthylethylenediamine dihydrochloride. The exchange capacity of a large number of African soil samples has been determined by Burdin *et al.*[363] The results from the automated method were slightly higher than from the manual distillation procedure. The determination of pH of soils has been automated by Baker.[230] Up to 100 samples per hour can be measured with automatic temperature compensation, magnetic stirring, washing of electrodes and rinsing of containers. A high degree of correlation with manual pH determination was found. Varley and Baker[67] have described an electronic timer to increase the speed of analysis of plant and soil samples.

Plant tissues and extracts have been analysed for a variety of elements. Boron has been determined by Willis,[364] using quinalizarin, and by Basson *et al.*[365] with the condensation product of salicylaldehyde and H-acid. Nitrogen in plant tissue has been determined by the indophenol method after manual[125,366] or automatic[123] digestion. An acid digestion has also been performed on plant extracts for fluoride determination.[42] Hydrofluoric acid is distilled in the digestor helix and collected in lanthanum–alizarin complexone reagent for colourimetric estimation. Plant growth has been studied by automated starch determination[367] on the "AutoAnalyzer", by means of the blue colour obtained with iodine. Good precision and recovery were also obtained in the estimation of starch in tobacco leaves.[368]

The automation of sugar analysis has been discussed by de Boos,[369] including a number of physical measurement and data-processing techniques. Floridi[130] has developed a method for the separation of mono-, di- and trisaccharides by ion-exchange chromatography followed by a colorimetric determination on an "AutoAnalyzer". A continuous method for the measurement of periodate uptake in oxidized sugars by determination of iodate has been described by Barker *et al.*[370] Sawyer and Dixon have developed an automated procedure for the determination of the " original gravity of beer, " involving analysis for reducing sugars[371] and alcohol.[136] A special distillation unit was developed for use with an "AutoAnalyzer". A system for peak detection and data processing has also been given.[372] A review of electrometric methods including the determination of sugars in beer has been made by Sawyer and Foreman.[145]

Table 4 provides a summary of the applications in agricultural and food analysis.

Environmental chemistry

This field is inherently very large, particularly when one includes the automated determination of naturally occurring substances as well as those which have been introduced by man into the environment. Frequently, the concentration range of interest is considerably lower than in other types of applications. As legislative control over the type and concentration of wastes being discharged into the environment is becoming more prevalent, the use of automated techniques is expected to increase. Many single-purpose monitors are available but these are generally based on instrumental rather than wet chemical principles and will therefore not be dealt with here.

Automated methods are reviewed annually[385,386] with the emphasis on inorganic constituents in waters and waste waters. In the Applications Section of *Analytical Chemistry* Reviews a part of the review on water analysis is usually devoted to automated techniques.[387] The instrumentation for water analysis has been discussed by Sprenger,[16] and King[388] has listed some methods for use with the Technicon "AutoAnalyzer". An elaborate instrument for the determination of oxygen-demand, phenol, cyanide, oil and turbidity in environmental water and industrial discharges has been presented by Sunahara *et al.*[389] It is a discrete system in which most of the parameters are determined by wet chemical means. An evaluation of the Technicon CSM-12 for the continuous determination of twelve water-quality parameters has been made by O'Brien and Olsen.[390] They found poor agreement with manual procedures and experienced a number of mechanical difficulties. Hey and Harkness[391] have discussed some of the problems involved in automating existing methods for the analysis of sewage and effluents. They divide waste water determinations broadly into three categories: organic matter, nitrogenous substances and miscellaneous inorganic elements and ions. Stack[392] has reviewed the water-quality surveillance programmes used by the Environmental Protection Agency, geologists and industry generally. He emphasizes the need for "real-time" analytical information. A system for data collection from automatic water-pollution monitoring stations has been described by Manczak.[393] The use of

Table 4. References to automated analysis in agricultural and food chemistry

Review	356
Fertilizers:	
nitrogen	139,183
phosphorus	359–361
potassium	138,357
trace metals	358
Soils:	
exchange capacity	363
herbicides	383
K, Ca, Mg, P	124,362
nitrogen	55,56,67,81,366
pH	230
trace metals	121,122
Plants, foods, beverages:	
alcohol	136,376
animal feeds	353,355
beer	136,137,145,371,372,376
boron	364,365
coffee beans	377
enzymes	256,377,384
fluoride	42
fruit juice	347
grain, flour	41,375,380
K, Ca, Mg	125,373
meat	381,382
nitrogen	41,123,125,175,366,374,375,380,381
pesticides	109,378,379,384
phosphorus	123,125,373,382
starch	367,368
sugars	130,145,369–372
tobacco	367,368
vitamins	347,355

selective ion-electrodes in the monitoring of water-treatment processes for a variety of added chemicals has been discussed by Rivers and Schweitzer.[394]

A guide to the selection of methods and equipment for automatic air-monitoring has been given by Elfers.[221] A brief description of the Technicon CSM6 Air Monitor has appeared[395] and Zaleiko[396] has presented a general review of colorimetric procedures for use on the Technicon "AutoAnalyzer" in air-pollution measurement programmes.

The tedious nature of the manual determination of chemical oxygen demand (C.O.D.) in waters, coupled with the importance of such data, has produced a variety of automated techniques. The principle of oxidation with potassium dichromate has been used by Hey *et al.*[397] using a specially built apparatus, and by Haines and Anselm[398] on a Technicon "AutoAnalyzer". The reaction time has been shortened from several hours under reflux to approximately 10 min by heating to 150°. Hey *et al.* designed their system around commercial syringe-dispensers because of attack by concentrated sulphuric acid on the peristaltic-pump tubing. Some of the auxiliary equipment for this instrument has been described by Phillips.[399,400] A method for organically bound carbon, involving a silver-catalysed oxidation by persulphate, has been automated by Popp and Engelhardt.[401] Recently, Fleet *et al.*[141] have used a novel system based on a Technicon "AutoAnalyzer" with potassium dichromate or permanganate as the oxidant. The excess of oxidant is reacted with hydrogen

Table 5. References to automated analysis in environmental chemistry

air monitoring	48,216,217,221,395,396
boron	225,402
chloride	403
C.O.D.	141,397–401,404
cyanide	184,405
detergents	153,233,235
effluents	153,388,389,391,402,405
fluoride	406,407
mercury	60,68,120,237–239
metals	48,101,152
nitrogen	81,82,108,408–411
pesticides	109
phenols	54
reviews	17,385–387,392
sea-water	225,408–410,412
sulphate	134
sulphide	99,412,413
water monitoring	16,385,386,389,390,392–394,407

peroxide and the oxygen produced is measured coulometrically by a porous catalytic silver electrode. Satisfactory agreement is obtained for a number of organic compounds with the standard manual procedure and with theoretical C.O.D. values. A summary of these and some additional references is presented in Table 5.

Miscellaneous applications

The increasing use of automated techniques in general and industrial analysis is shown by the number of recent papers which do not fall into any of the categories used so far. One area in which considerable development is occurring at the present time is that of reaction-rate techniques in analytical chemistry. Such methods frequently have advantages of sensitivity and selectivity and are becoming of practical significance with the introduction and improvement of automated instrumentation. Reviews on the use of enzymes and kinetic aspects have generally incorporated a section on automated techniques[414,415] and the use of computers.[416] A detailed discussion here is not warranted because a number of review papers have appeared recently.[417–420]

The automation of the analysis of heterogeneous and bulk materials such as rocks and alloys is limited by the difficulty in obtaining a representative sample without manual intervention. An anodic dissolution technique has been described[77] for the determination of phosphorus in copper in which the manual operation is reduced to inserting the sample into an electrolytic cell. It is doubtful whether such a technique would be generally suitable for alloys. Steel samples[421,422] are usually brought into solution in the conventional manner so that the time-saving achieved by automating the colourimetric measurement is minimal. However, Atherton *et al.*[423] have found that rock analysis can be done three times as fast by automated methods as by manual methods, without any loss in precision.

Corrosion problems have been studied by the automatic determination of trace metals in water[424] and chloride in industrial liquors.[425] Sebborn[426] has applied automated techniques for metals in the range up to 10 ppm in several hundred chemicals used in the photographic industry. Fleet *et al.*[140] have described a method for the determination of sodium hypochlorite in bleaching solutions. It is based on a Technicon "AutoAnalyzer" and uses a

Table 6. Miscellaneous applications of automated techniques

aluminium	427,428
amino-acids	100,146
bleaching agents	140
boron	429
carbohydrates	100,107
chloride	425
corrosion studies	424,425
formaldehyde	100
geological materials	129,421,423
kinetic methods	155,209,250,414–420
metals, alloys	77,421,422,428,429
molybdenum	129
petroleum products	15,234
phosphates	78,107,431–434
silicon	421
thorium	435
trace metals	424,426,431
uranium	151,436,437
urea	430

hydrogen peroxide reagent and a coulometric oxygen sensor consisting of a porous catalytic silver electrode. The same procedure may be used for hydrogen peroxide determinations with a potassium periodate reagent.

These and other applications are summarized in Table 6. Recently, a standard format has been recommended[438] for the publication of automated analytical methods. The format provides for description of apparatus, analytical principles involved, calibration and performance checks, maintenance of the system and experimental procedure.

COMPUTERS

No review on automated analysis would be complete without some reference being made to the use of digital computers. The type and volume of data produced by automatic analysers are ideally suited to computer processing, particularly if the calculations include the application of corrections for sample interaction and instrument drift. There are three basic modes in which computers are utilized. In the first, the instrument signal is recorded on chart paper, punched tape or in any other suitable form and the computer calculations are performed later. This method is generally referred to as "off-line" or "batch-processing." It is generally the most economical technique and is suitable for automatic analysers where the rate of data production is relatively slow when compared with chromatographs or scanning spectrophotometers. In the second method, the computer acquires and processes the data from the analyser as they are being generated. Since this "on-line method" may be an inefficient use of computer capability, time-shared systems are frequently used in which the output from several instruments is processed by a common computer. In the third mode, which may be on a "stand-alone" or time-shared basis, the computer controls all of the operations of the automatic analyser as well as carrying out data processing. Such a system has inherent advantages and is desirable whenever the analytical information is used for automatic control of a plant or a process. During the discussion of instrumentation and applications, examples of the three methods have been mentioned. Many of the modern instruments, including the specially built automatic titrators, produce data in a format such that a computer is either an integral component of the system or a desirable accessory.

A detailed review of the literature is not necessary since a number of comprehensive review papers have appeared in the last few years. Childs *et al.*[439,440] have surveyed the applications of computers in analytical chemistry with emphasis on spectroscopic, electroanalytical and chromatographic techniques and the calculations of ionic equilibria and kinetic parameters. No references were given to automatic wet chemical analysers. Frazer[441] discusses digital control computers and specifically mentions a commercially available 24-channel discrete-sample analyser which incorporates a computer. More recently, Perone[442] has reviewed computer applications in the chemistry laboratory, including a discussion of the historical development and possible future applications. Useful sections on computers may also be found in the review by Kuzel *et al.*[7] and in the Technicon Bibliography.[35] General criteria for on-line computerization of analytical instruments have been described.[443,444]

A growth rate of 18% per annum has been predicted[31] in the use of computers with analytical instruments and by 1980, 30% of all such instruments capable of being computerized will be. Economic considerations in the installation of on-line computers with time sharing have been discussed by Munson and Schneider.[445,446] They have approached the subject from the position of both laboratory personnel and laboratory management. Clinical applications account for the majority of publications on computerized automatic analysers. A system in which up to twelve test channels from six standard "AutoAnalyzers" are coupled to a PDP8/S computer has been described by Abernethy *et al.*[197,316,447] The analytical signal is obtained from retransmitting slidewires on the recorders. The programme functions include peak detection, data smoothing, drift correction, third-order polynomial curve-fitting, correction for specimen interaction and collation and print-out of results. The computer has a memory core of 8K and a 32K disc file is used for programme storage. Several other clinical systems have been described[448,449] and Whitby[450] has reviewed the suitability of on-line and off-line methods for large and small hospital laboratories. An off-line system has been described[451] incorporating a peak-reading device for use with a data terminal to a remote computer. It has also been shown[452] how a relatively inexpensive programmable calculator can be used for calculations of concentrations from absorbance values.

Four different methods for calculating concentrations from "AutoAnalyzer" results were compared by Torud.[453] Two involved computer programmes of differing complexities, one used a programmable calculator and one method was largely manual, using a transparent chart-reading device. It was shown that the corrections for drift in baseline and standards which the computer programmes apply resulted in a slight but significant improvement in both accuracy and precision. Keay[454] has discussed the application of a computer in the automated analysis of soils. The equipment required to interface the colourimeter of the analyser to either a paper-tape punch or a computer is described.

A recent paper by Mueller and Burke[299] describes a reagent-addition system and spectrophotometer under closed-loop control by a Hewlett–Packard computer. A photometric titration is performed in which the titrant addition rate is varied by programme control to meet the requirements of the solution being titrated. Some of the other computerized automatic titrators[281–285,300] have already been mentioned. A miniature on-line digital computer has been developed by Parker and Pardue[455] in which several programmes for various applications are stored. The system incorporates a numerical data display and has been used for the kinetic analysis of organic and inorganic compounds.

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Résumé—On présente une revue de l'analyse automatisée, comprenant l'instrumentation et les applications.

Zusammenfassung—Es wird eine Übersicht über die automatisierte Analyse gegeben, einschließlich instrumenteller Ausrüstung und Anwendungen.

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PRECIPITATION OF MAGNESIUM AMMONIUM PHOSPHATE FROM HOMOGENEOUS SOLUTION BY MEANS OF HYDROLYSIS OF *p*-NITROPHENYLPHOSPHATE WITH AN ALKALINE PHOSPHATASE

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Summary—In the precipitation of magnesium ammonium phosphate from homogeneous solution, phosphate ions were generated by means of hydrolysis of *p*-nitrophenylphosphate with an alkaline phosphatase. Conditions for the gravimetric determination of magnesium ion as magnesium ammonium phosphate hexahydrate were investigated.

Precipitation from homogeneous solution (PFHS) is a useful technique in gravimetric analysis, and hydrolysis of urea with urease has been applied to the precipitation of some metal-chelate compounds[1–4]. The application of the catalytic action of enzymes for generating precipitants *in situ* has also been investigated.

Although, up to the present, the pyrophosphate and 8-hydroxyquinoline methods have been utilized for the gravimetric determination of magnesium[5,6], both have some troublesome problems. However, gravimetric determination of magnesium as magnesium ammonium phosphate can be done simply and satisfactorily by means of PFHS, applying hydrolysis of *p*-nitrophenylphosphate with an alkaline phosphatase in weakly alkaline solution. Conditions for the determination have been investigated and the effect of Cu(II), Zn(II), Ni(II) and Co(II) tested.

EXPERIMENTAL

Reagents

Magnesium solution, 1 mg/ml. Prepared by dissolving magnesium sulphate in water, and standardized with EDTA solution which had been standardized with metallic zinc (99·999% pure), Eriochrome Black T being used as indicator.

Sodium p*-nitrophenylphosphate solution* (NPP), 0·8*M*. Further diluted with water as required.

Alkaline phosphatase, 0·1% (*w*/*v*) *aqueous solution*. Prepared from calf-intestine alkaline phosphatase (activity: 1·2 units/mg, Miles-Seravac (Pty) Ltd.) and kept in the refrigerator before use.

Buffer solution, pH 9·5. Equal volumes of 5*M* ammonia and ammonium chloride solutions.

Wash-solution. A 1 : 1 : 5 : 3 mixture of 0·1*M* disodium hydrogen phosphate, conc. ammonia solution, ethanol and water.

All chemicals used were analytical-reagent grade.

Procedure

Transfer 10 ml of a sample solution containing less than 20 mg of magnesium into a 100-ml beaker. Add 5 ml of buffer solution (pH 9·5), 3 ml of 0·8 *M* *p*-nitrophenylphosphate (*i.e.*, equivalent to 3 times the amount of phosphate needed for 20 mg of magnesium) and 3 ml of 0·1 % alkaline phosphatase solution, and dilute to 50 ml with water. Keep the beaker containing the solution at 30° for 8 hr, filter off the precipitate and wash it with 50 ml of wash-solution, dry it at 50° for 7 hr, and weigh as $MgNH_4PO_4 \cdot 6H_2O$.

RESULTS AND DISCUSSION

Activity of alkaline phosphatase

The activity of an enzyme, in general, depends on temperature, hydrogen ion concentration of the solution, kinds of metal ion present, its history, *etc.* The optimum pH and temperature had to be established for *p*-nitrophenylphosphate to be hydrolysed smoothly with alkaline phosphatase.

pH. Ammonia–ammonium chloride buffer solutions of pH 7–11 were prepared. Then 1 ml of $10^{-3}M$ *p*-nitrophenylphosphate, 1 ml of 0·01 % alkaline phosphatase solution, and 10 ml of water were added to 10 ml of each buffer solution and the mixtures were kept at 30° for 1 hr. Five ml of each solution were transferred into separate 50-ml volumetric flasks containing *ca.* 40 ml of saturated sodium carbonate solution (to stop the reaction). The solutions were diluted to 50 ml with the sodium carbonate solution, and the absorbances were measured at 400 nm.

As shown in Fig. 1, the phosphatase has optimal efficiency at around pH 9·5. The result agrees with the literature[7] value and the pH value is also suitable for precipitation of magnesium as $MgNH_4PO_4 \cdot 6H_2O$.[6]

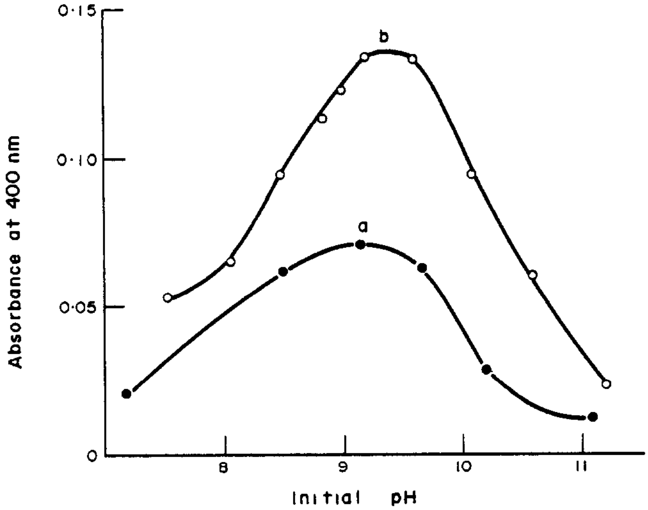

Fig. 1. Effect of buffer solution on activity of the enzyme.

Buffer soln.	$10^{-3}M$ NPP	0·01 % Enzyme	H_2O
a: 10 ml	1 ml	1 ml	10 ml
b: 10 ml	1 ml	2 ml	9 ml

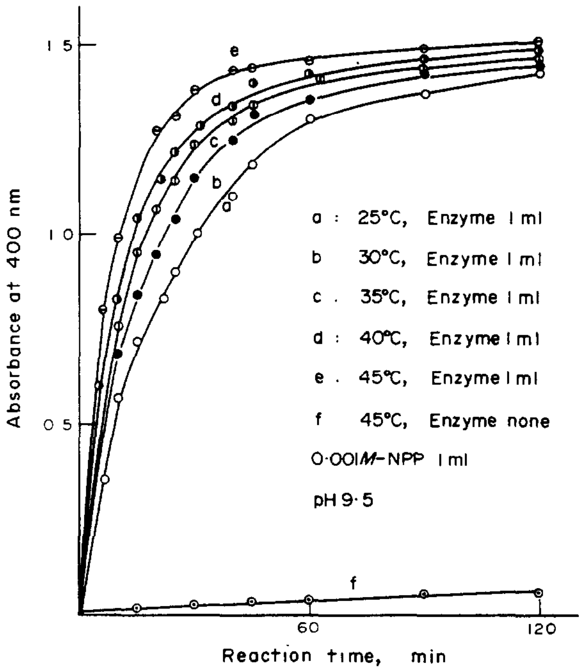

Fig. 2. Hydrolysis of NPP

Temperature. In experiments at 25–45°, efficiency of the enzyme increased with temperature. However, as shown in Fig. 2, the hydrolysis is 60–70% complete in about 2 hr, irrespective of temperature.

To find the optimum conditions for the PFHS, the effects of the amount of enzyme, buffer action, amount of precipitant *etc.* were examined.

Effect of amount of enzyme

The rate of hydrolysis of the *p*-nitrophenylphosphate depends on the amount of enzyme. The effect of hydrolysis rate on precipitation of magnesium ammonium phosphate was studied under the following experimental conditions: Mg(II) 10 mg, pH 9·5, 0·4*M* *p*-nitrophenylphosphate 3 ml, alkaline phosphatase 0·25–3·0 mg, reaction temperature 30°. At equal intervals, the solution was filtered and the concentration of magnesium in the filtrate was determined by atomic-absorption spectrometry. Results are shown in Fig. 3.

The rate of hydrolysis can be controlled easily by changing the phosphatase concentration, if other experimental conditions are kept constant. To precipitate quantitatively 10 mg of magnesium the following conditions are recommended: 3 ml of 0·4*M* *p*-nitrophenylphosphate, 3 mg of alkaline phosphatase, 8 hr standing at 30°. Use of higher temperatures tends to give wool-like precipitates.

Effect of buffer

Table 1 shows the results which were obtained for 9·74 mg of magnesium when 0·5–6·0 ml of the pH 9·5 buffer solution were used. Satisfactory results can be obtained by addition of more than 2 ml of the buffer solution, but 5 ml were used in the further experiments.

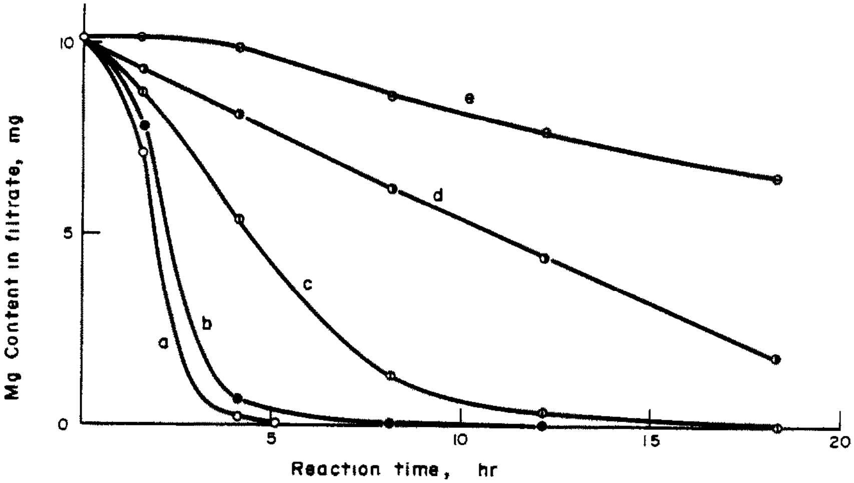

Fig. 3. Effect of amounts of enzyme
Amounts of enzyme (mg).
a: 3·0, *b*: 2·0, *c*: 1·0, *d*: 0·5, *e*: 0·25.

Effect of precipitant

p-Nitrophenylphosphate was chosen as the reagent, because it hydrolyses stoichiometrically to phosphate and *p*-nitrophenol, and the hydrolysis can be stopped easily by pouring the solution into saturated sodium carbonate solution. The degree of the hydrolysis can be easily estimated by absorbance measurements.

As shown in Table 2, satisfactory results are obtained when at least 100% excess of reagent is added.

Wash-solution

It has been recommended in general to add alcohol to the wash-solution in the magnesium determination, because magnesium ammonium phosphate is relatively soluble. Three wash-solutions were prepared: *A* ($5M\mathrm{NH_3} : 5M\mathrm{NH_4Cl} : 0{\cdot}1M\mathrm{Na_2HPO_4} = 1:1:1$), *B* (solution *A*: $\mathrm{C_2H_5OH} = 4:1$), and *C* ($0{\cdot}1M$ $\mathrm{Na_2HPO_4}$: conc. $\mathrm{NH_3}$: $\mathrm{C_2H_5OH}$: $\mathrm{H_2O} = 1:1:5:3$).

When precipitates of magnesium ammonium phosphate (10·11 mg of Mg) were washed with 100 ml of each solution, losses of magnesium were 0·01, 0·01, and 0·003 mg, for *A*, *B*

Table 1. Effect of buffer

Buffer solution added, *ml*	Final pH	Mg found, *mg*	Difference *mg*
0·5	8·7	9·54	−0·20
1·0	9·0	9·65	−0·09
2·0	9·3	9·70	−0·04
3·0	9·4	9·70	−0·04
5·0	9·5	9·72	−0·02
6·0	9·5	9.70	−0·04

(Mg 9·74 mg, initial pH 9·5, 0·4*M* NPP 3 ml, enzyme 3 ml)

Table 2. Effect of precipitant

0·4*M* NPP added, *ml*	Mg Taken, *mg*	Mg Found, *mg*	Difference *mg*
0·4	9·74	2·83	−6·91
0·8	9·74	5·38	−4·36
1·0*	9·74	7·34	−2·40
2·0	9·74	9·69	−0·05
3·0	9·74	9·73	−0·01
4·0	9·74	9·77	+0·03
6·0	9·74	9·73	−0·01
10·0	9·74	9·75	+0·01

* Equivalent to Mg.
(Buffer solution 5 ml, pH 9·5, enzyme 3 ml).

and *C* respectively. With 50 ml of *C*, the loss of magnesium was 0·0025 mg. Less than 50 ml of wash-solution did not give sufficient washing and the precipitates were coloured a little yellow by adsorption of *p*-nitrophenol. It is best to wash the precipitates with more than 50 ml of *C*, to reduce loss of magnesium.

Drying of precipitates

Although $MgNH_4PO_4 \cdot 6H_2O$ is not preferred as the weighing form in the conventional method, the possibility of using it was studied. It was difficult to obtain constant weight as $MgNH_4PO_4 \cdot H_2O$ by drying the precipitate at 80° and negative errors were obtained when the precipitate was dried at 65° to yield $MgNH_4PO_4 \cdot 6H_2O$. When, however, precipitates were dried at 50° for more than 5 hr, the weight of $MgNH_4PO_4 \cdot 6H_2O$ agreed satisfactorily with the theoretical value for 10 mg of magnesium. If the amount of precipitate is less or more than that for 10 mg of magnesium, the drying time should be changed; for instance, 3 hr at 50° for 5 mg and more than 7 hr for 20 mg of magnesium.

Determination of magnesium

By means of the proposed procedure 5–20 mg of magnesium were determined satisfactorily as shown in Table 3. The magnesium content of the filtrates was determined by atomic-absorption spectrometry and was below 0·01 mg.

The dried precipitates were dissolved in 0·1*M* hydrochloric acid and Mg^{2+}, NH_4^+ and PO_4^{3-} determined by the usual methods.[5] The results (Table 4) agree well with the cal-

Table 3. Determination of magnesium

No. of expts.	Mg Taken, *mg*	Mg Found, *mg*	Standard deviation, *mg*	Random error %
5	4·87	4·86	0·02	
10	9·74	9·77	0·02	0·1–0·6
3	10·11	10·09	0·02	
5	19·48	19·53	0·01	

Table 4. Composition of precipitate

	Theoretical value for $MgNH_4PO_4 \cdot 6H_2O$, %	Experimental value, %
Mg^{2+}	9·9$_1$	9·9 ± 0·3
NH_4^+	7·3$_5$	7·6 ± 0·2
PO_4^{3-}	38·7	40 ± 1
H_2O	44·0	43 ± 1

culated values for $MgNH_4PO_4 \cdot 6H_2O$. The water contents were calculated by difference and the value agreed with the result obtained by means of a differential scanning calorimeter.

Although the accuracy and precision of the PFHS method were almost as good as those of the conventional method, the PFHS method gave much lower co-precipitation of Cu(II), Zn(II), Ni(II) and Co(II). Results are shown in Table 5.

Table 5. Effect of some diverse ions

		PFHS method		Conventional method	
Ions added, *mg*	Mg taken, *mg*	Mg found, *mg*	Error %	Mg found, *mg*	Error %
Cu 10	9·74	9·71	0·3	9·79	0·5
Zn 10	9·74	9·79	0·5	10·60	8·8
Ni 10	9·74	11·14	14·4	13·11	34·6
Co 10	9·74	13·73	40·9	16·86	73·1

As shown in Table 5, the presence of the same weights of copper and zinc as of magnesium may be tolerable for the determination of magnesium. When only nickel is present, and no magnesium, no precipitate is formed, but nickel co-precipitates when magnesium is also present. Part of the cobalt precipitates simultaneously with the magnesium. These two species should be removed before the determination of magnesium.

Ferric iron and aluminium give precipitates with *p*-nitrophenylphosphate itself, and alkaline earth metals are precipitated as phosphates.

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Zusammenfassung—Bei der Fällung von Magnesiumammoniumphosphat aus homogener Lösung wurden Phosphationen durch Hydrolyse von *p*-Nitrophenylphosphat mit einer alkalischen Phosphatase erzeugt. Es wurden die Bedingungen zur gravimetrischen Bestimmung des Magnesiumions als Magnesiumammoniumphosphat-Hexahydrat untersucht.

Résumé—Dans la précipitation du phosphate ammoniaco-magnésien d'une solution homogène, les ions phosphate ont été produits au moyen de l'hydrolyse du phosphate de *p*-nitrophényle par une phosphatase alcaline. On a étudié les conditions du dosage gravimétrique de l'ion magnésium à l'état de phosphate de magnésium et d'ammonium hexahydraté.

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TETRACYANOETHYLENE π-COMPLEX CHEMISTRY

INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF DIELS-ALDER-ACTIVE 1,3-DIENES

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Summary—An indirect spectrophotometric method, based on the rapid Diels-Alder reaction between cisoid 1,3-dienes and tetracyanoethylene (TCNE) and the destruction of an aromatic–TCNE π-complex, was developed to determine eleven 1,3-dienes in the 0·05–1·00 × $10^{-3}M$ range. These dienes were: cyclopentadiene; 1,3-cyclohexadiene; *trans*-1,3-pentadiene; 2,4-dimethyl-1,3-pentadiene; *trans*-2-methyl-1,3-pentadiene; 2-methyl-1,3-butadiene; 9-methylanthracene; 9,10-dimethylanthracene; 1,6-diphenyl-1,3,5-hexatriene; 2,3-dimethyl-1,3-butadiene; and 1,4-diphenyl-1,3-butadiene. Three 1,3-dienes were determined in the 0·05–1 × $10^{-4}M$ range: cyclopentadiene, *trans*-2-methyl-1,3-pentadiene, and anthracene. The limit of detection for cyclopentadiene in carbon tetrachloride solutions is 0·11 μg/ml. Fourteen 1,3-dienes were found to form stable π-complexes and could not be determined by the proposed method. For these 1,3-dienes, the spectra of some of the complexes are reported; in addition, relative equilibrium constants for the π-complexes of 2,5-dimethyl-2,4-hexadiene, *cis*-1,3-pentadiene, 4-methyl-1,3-pentadiene, and 1,3-cyclo-octadiene were estimated. An explanation of the transient colour in the 1,3-diene–TCNE Diels-Alder reaction is suggested.

The Diels-Alder reaction of a 1,3-diene and a dienophile to form a cyclohexene derivative is a major synthetic organic reaction. However, the literature does not contain any reports of the use of this reaction for the trace analysis of a series of 1,3-dienes, though isolated examples have been found.[1–4] With the synthesis of tetracyanoethylene (TCNE) in 1957,[5] a new extremely electrophilic dienophile (and π-acid) became available for use in Diels-Alder reactions. The great reactivity of this dienophile with 1,3-dienes was first cited by Middleton *et al.*[6] and later by Stewart.[7] In 1961, Schenk and Ozolins[4] demonstrated the utility of this rapid Diels-Alder reaction by the indirect determination of anthracene in trace quantities.

Small amounts of certain 1,3-dienes have also been determined by a diazo reaction,[8] by formation of coloured fulvenes,[9] by spectrophotometry,[10] gas chromatography,[11] mass spectrometry,[12, 13] coupled gas chromatography/mass spectrometry,[14] and coupled coulometry/spectrophotometry.[15]

In this paper a simple method with the utilization of relatively inexpensive instrumentation is described. The basis of the method is the formation of a coloured aromatic-TCNE π-complex and measurement of the decrease in absorbance of the π-complex in the presence of a Diels-Alder-reactive 1,3-diene. The decrease is usually proportional to the concentration of 1,3-diene present although the reaction is not exactly stoichiometric. The formation

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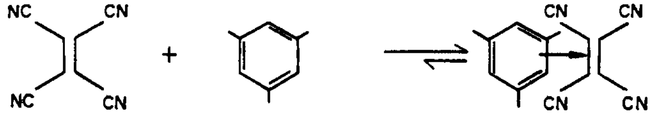
of the yellow mesitylene-TCNE π-complex from colourless reactants illustrates the utility of these complexes



The equilibrium constant, K_π, for this reaction is defined by

$$K_\pi = \frac{[\text{mesitylene-TCNE complex}]}{[\text{mesitylene}]\,[\text{TCNE}]} \qquad (1)$$

Unfortunately, the equilibrium constants reported in the literature for TCNE (see the K_N values in Table 1) are defined by means of a mole-fraction term (footnote, Table 1). The K_π constant is defined entirely in terms of molarities so that the values of K_π are somewhat smaller than those of K_N. In methylene chloride, $K_\pi = K_N/16$.

To design an optimum method, the optimum aromatic hydrocarbon (π-base) must be selected to form a π-complex with TCNE. Some of the parameters involved are listed in Table 1 for various aromatic hydrocarbons. The choice of the optimum aromatic hydrocarbon is determined by its availability in quantity, its purity, its K_π value and the molar absorptivity of its TCNE complex, ε. After substitution of absorbance for concentration of the π-complex in equation (1) and adjustment for the mole fraction of the π-base, the rearranged Benesi-Hildebrand equation[16] giving the relationship between the initial molarity of the π-acid, C^0_{acid}, and the absorbance A, ε, and K_π is:

$$C^0_{\text{acid}} = A\left[\frac{1}{K_\pi \cdot \varepsilon \cdot C^0_{\text{base}}} + \frac{1}{\varepsilon}\right] \qquad (2)$$

where C^0_{base} is the initial molarity of the π-base.

After selection of a given aromatic hydrocarbon for evaluation, equation (2) can be used to calculate the *initial* molarity, C^0_{acid}, of TCNE needed. (This is the molarity of TCNE present before it reacts with the 1,3-diene.) In choosing an arbitrary value for A in equation (2), it is important to select a *large* value. This is because the absorbance will *decrease* after TCNE reacts with the 1,3-diene to be determined. To achieve a large A, a large excess of aromatic hydrocarbon is needed because the complexes of TCNE are rather weak. A value of 1·0*M* for C^0_{base} was arbitrarily chosen to achieve a value of 0·50 for A.

Table 1. Constants for some TCNE π-complexes in CH_2Cl_2 solvent[17]

π-Donor	K_N*	ε, *l. mole*$^{-1}$. *cm*$^{-1}$	$\lambda_{\max}$, *nm*
Naphthalene	11·7	$1{\cdot}24 \times 10^3$	550
Mesitylene	17·3	$3{\cdot}12 \times 10^3$	461
Durene	54·2	$2{\cdot}08 \times 10^3$	480
o-Xylene	6·97	$3{\cdot}86 \times 10^3$	430
Pyridine	12·0	$1{\cdot}05 \times 10^4$	422
Hexamethylbenzene	263	$4{\cdot}39 \times 10^3$	545
Benzene	2·00	$3{\cdot}57 \times 10^3$	384

* $K_N = \dfrac{[\text{Aromatic–TCNE complex}]}{[\text{TCNE}]\,(\text{Aromatic})}$, where (Aromatic) is the mole fraction of the aromatic hydrocarbon

Sample calculations for both the pyridine-TCNE and mesitylene-TCNE π-complexes will now be discussed. For pyridine-TCNE, the K_N value in Table 1 corresponds to a value of 0·75 for K_π. For this complex then, in methylene chloride solvent,

$$C^0_{TCNE} = 0{\cdot}50[1{\cdot}27 \times 10^{-4} + 0{\cdot}95 \times 10^{-4}] = 1{\cdot}1 \times 10^{-4}M$$

This implies that the upper limit of 1,3-diene that can be measured in methylene chloride solvent is about $1 \times 10^{-4}M$; the lower limit should be about 1% of this or $1 \times 10^{-6}M$.

For mesitylene–TCNE, the K_N value in Table 1 corresponds to a value of 1·1 for K_π. For this complex in the same solvent,

$$C^0_{TCNE} = 0{\cdot}50[2{\cdot}9 \times 10^{-4} + 3{\cdot}2 \times 10^{-4}] = 3{\cdot}0 \times 10^{-4}M$$

This implies that the upper limit of 1,3-diene that can be measured in methylene chloride solvent is almost $3 \times 10^{-4}M$; the lower limit should be about 1% of this or $3 \times 10^{-6}M$.

Pyridine is thus a better choice than mesitylene for forming a π-complex to measure the lowest concentration of 1,3-dienes. Initial work involved the use of this π-complex; however, it was found that precipitates formed when 1,3-dienes were added. Hence most of the experimental work was done with mesitylene (and naphthalene). To compensate for the lower stability of the mesitylene–TCNE complex chloroform and/or carbon tetrachloride were substituted for the methylene chloride solvent. In these solvents K_π is appreciably larger than it is in methylene chloride. The effect of this substitution is to lower the calibration curve range for mesitylene–TCNE to a range close to that of pyridine–TCNE in methylene chloride.

EXPERIMENTAL

Reagents

Standard 0·0500*M TCNE.* Dissolve 0·6406 g of doubly sublimed TCNE in 100 ml of reagent grade methylene chloride and store in the dark. (This solution appears to be stable for about two months.)

Standard 1·50M naphthalene. Weigh 192·3 g of reagent-grade naphthalene into a 1-l. volumetric flask and dissolve it in about 750 ml of reagent-grade carbon tetrachloride or chloroform. (The dissolution of naphthalene is endothermic and slow.) Make the final dilution with the same solvent after the solution has attained room temperature (about one day).

Standard $2{\cdot}5 \times 10^{-3}M$ 1,3-*diene solutions.* Weigh exactly 0·62 mmole of the 1,3-diene (reagent-grade or doubly distilled and checked for purity) into a flask, cover the flask with aluminium foil, and add 250 ml of reagent-grade carbon tetrachloride or chloroform to dissolve the diene. Store in the dark since photodecomposition may occur with some solutions. Because cyclopentadiene polymerizes very quickly at room temperature, store the pure cyclopentadiene at " dry ice "–acetone temperatures and use prepared solutions within a couple of hours. Prepare other standard 1,3-diene solutions by making the appropriate dilution.

Apparatus

Spectrophotometric measurements were made in round and square 1·1 cm cells on the Spectronic 20, and square 1·00 cm cells on the Beckman DB-G and Cary 14 spectrophotometers. For purity checks, a Carle gas chromatograph and Abbe refractometer with temperature bath were used.

Weighing of mg quantities of volatile 1,3-*dienes.* Place about 4 ml of solvent in a 5–6 ml capacity ampoule. Over the top of the solvent-containing ampoule place and squeeze a rubber pipette-bulb which will fit a Pasteur disposable pipette. Weigh the ampoule. Introduce small amounts of 1,3-diene into the ampoule by means of a 2-ml syringe equipped with a small hypodermic needle and filled with the pure diene. Weigh the ampoule with the diene added. Take off the rubber bulb and immediately transfer the contents of the ampoule to an appropriate volumetric flask. Rinse out the ampoule three times with solvent. Dilute the sample of diene as quickly as possible and store in the dark if necessary.

Calibration plot for 1,3-*dienes in the* $0{\cdot}5$–$1{\cdot}0 \times 10^{-3}M$ *range*

By pipette transfer 1 ml of 0·05*M* TCNE into a 50-ml volumetric flask, and add 1–20 ml of $2{\cdot}5 \times 10^{-3}M$ 1,3-diene solution, washing down the sides of the flask with 1–2 ml of solvent. Allow to react in the dark for the time specified in Table 2. After the reaction is essentially complete, add 20 ml of 1·50*M* naphthalene

Table 2. Reaction times for 1,3-diene–TCNE reactions

1,3-Diene	Reaction times 0·05–1 × $10^{-3}M$	 0·05–1 × $10^{-4}M$
Cyclopentadiene	5 min	12 hr
trans-2-Methyl-1,3-pentadiene	0·5 hr	24 hr
2,4-Dimethyl-1,3-pentadiene	1 hr	—
2,3-Dimethyl-1,3-butadiene	2 hr	—
1,3-Cyclohexadiene	8 hr	—
2-Methyl-1,3-butadiene	2 days	—
1,4-Diphenyl-1,3-butadiene	24 hr	—
1,6-Diphenylhexatriene	2 days	—
Anthracene	0·33 hr	24 hr
9-Methylanthracene	10 min	—
9,10-Dimethylanthracene	10 min	—
trans-1,3-Pentadiene	24 hr	—

solution by pipette and dilute to the mark. Prepare a reagent blank by the addition of the same quantities of TCNE and naphthalene to a 50-ml volumetric flask, and dilute to the mark with the same solvent as above. Read the absorbance or transmittance of each solution at 550 nm. Plot absorbance *vs.* concentration to prepare the indirect calibration plot.

To utilize the more accurate Reilley-Hildebrand[18] method for indirect spectrophotometric measurements, set the transmittance to 100% at 550 nm for the diene solution and read the transmittance of the reagent blank. Repeat this procedure for each solution and setting transmittance to 100% for each diene solution. (For a double-beam spectrophotometer, place the diene solution in the reference beam and the reagent blank in the sample beam.) A plot of absorbance *vs.* concentration of 1,3-diene yields a typical calibration plot.

Table 3. Stability of complexes of TCNE with 1,3-dienes

1,3-Diene	Initial colour (λ_{max}, *nm*)	Time for disappearance of colour, *min*	Estimated K_x
cis-1,3-Pentadiene	Yellow-orange (480)	∞ (stable)	0·74
trans-1,3-Pentadiene	Yellow-orange (490)	>5	—
4-Methyl-1,3-pentadiene	Violet (535)	∞ (stable)	1·5
trans-2-Methyl-1,3-pentadiene	Reddish violet	0 (fast reaction)	—
2,4-Dimethyl-1,3-pentadiene	Bluish violet	0 (fast reaction)	—
2,5-Dimethyl-2,4-hexadiene	Blue (645)	∞ (stable)	9·7
cis, trans-1,3-Hexadiene	Orange (485)	>5	—
2,3-Dimethyl-1,3-butadiene	Orange	0 (fast reaction)	—
2-Methyl-1,3-butadiene	Yellow-orange (455)	>5	—
1,3-Cyclo-octadiene	Reddish orange (490)	∞ (stable)	0·54
Anthracene	Green	>5	—
9-Methylanthracene	Yellow	0 (fast reaction)	—
9-Anthraldehyde	Green	∞ (stable)	—
9,10-Dimethylanthracene	Green(?)	0 (fast reaction)	—
1,2,5,6-Dibenzanthracene	Blue	∞ (stable)	—
Benz[*a*]anthracene	Light violet	60	—
Calciferol	Yellow	∞ (stable)	
1,4-Diphenyl-1,3-butadiene	Bluish green	15–20	
1,3-Cyclohexadiene	Violet	>5	
1,6-Diphenylhexatriene	Green to yellow	15–20	
Cyclopentadiene	Not observable		
1,2,3,4-Tetraphenyl-1,3-cyclopentadiene	Yellow	∞ (stable)	
Furan	Orange (445–50)	∞ (stable)	0·35
2-Methylfuran	Red (510)	∞ (stable)	
2,5-Dimethylfuran	Blue (575)	∞ (stable)	

Calibration plot of 1,3-*dienes in the* 0·5–1·0 × $10^{-4}M$ *range*

Transfer 2 ml of 2·5 × $10^{-3}M$ TCNE into a 50-ml volumetric flask and wash down the sides of the flask with 1–2 ml of solvent. Allow reaction to occur for the time specified in Table 2. Then add 5 ml of pure mesitylene and make the final dilution. Prepare a reagent blank by the additon of 5 mmole of TCNE and 5 ml of mesitylene to a 50-ml volumetric flask and dilution to the mark with the same solvent as above.Read the transmittance or absorbance of each solution at 460 nm (Table 2), or use the Reilley-Hildebrand method at 460 nm.

Estimation of K_N and ε values for some 1,3-*dienes*

Weigh a 10-ml volumetric flask and stopper. With a syringe place about 1 mmole of 1,3-diene in the flask and weigh again. Add (by pipette) 10 ml of 0·50–0·025*M* TCNE to the flask and weigh. As soon as possible, measure the absorbance of the solution at λ_{max} for the 1,3-diene π-complex with TCNE (Table 3), against reagent-grade methylene chloride as reference.

RESULTS AND DISCUSSION

Effect of solution variables

Concentration of 1,3-*dienes.* With both the indirect and Reilley-Hildebrand methods, it was found that the spectrophotometric measurement of reactions of cyclopentadiene, 1,3-cyclohexadiene, 9-methylanthracene, 9,10-dimethylanthracene, 1,6-diphenyl-1,3,5-hexatriene, 1,4-diphenyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and 2,4-dimethyl-1,3-pentadiene generates essentially straight line plots in the 0·05–1·00 × $10^{-3}M$ range while cyclopentadiene, anthracene, and *trans*-2-methyl-1,3-pentadiene give straight line plots in the 0·05–1·00 × $10^{-4}M$ range. Although these Diels-Alder reactions are not exactly stoichiometric, differences in the calibration plots are slight, but a calibration plot should be prepared for each 1,3-diene to be determined.

The plots for isoprene and piperylene (*trans*-1,3-pentadiene) were found to deviate from linearity as shown in Figs. 1 and 2. The usefulness of these methods in the vicinity of 1·00 × $10^{-3}M$ concentrations of 1,3-diene is limited by the curvature of the line. It may be that these two 1,3-dienes polymerize faster than the others and that the rate of polymerization is close to the rate of Diels-Alder reaction with TCNE. On the other hand, at higher 1,3-diene concentrations, the strength of the π-complex between TCNE and the transoid conformation of the 1,3-diene may hinder the formation of the cisoid conformation (this conformation is necessary for a Diels-Alder reaction) of the 1,3-diene. This point is discussed

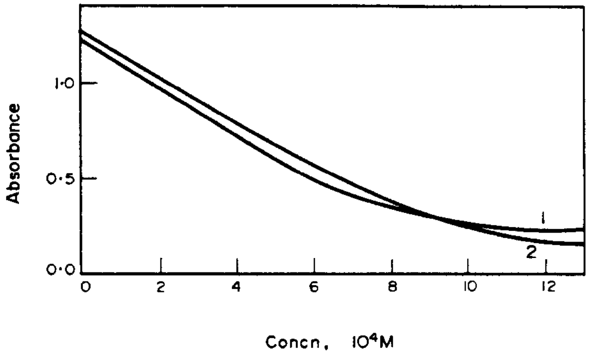


Fig. 1. Deviations in the indirect spectrophotometric plots of 1,3-dienes (Spectronic 20).
(1) Isoprene.
(2) *trans*-1,3-pentadiene.

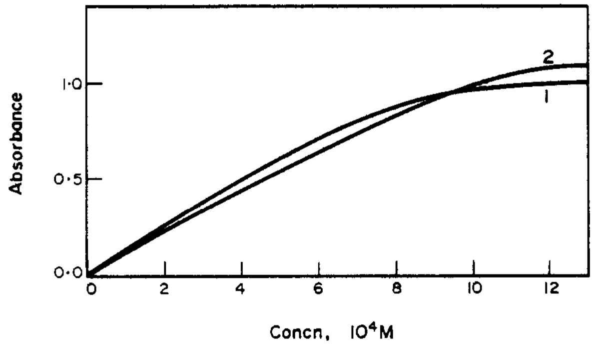


Fig. 2. Deviations in the Reilley-Hildebrand plots for 1,3-dienes (Spectronic 20).
(1) Isoprene.
(2) *trans*-1,3-Pentadiene.

in the section on the nature of 1,3-diene–TCNE π-complexes. Probably each of these effects contributes to the abnormally high deviations at higher concentrations of 1,3-dienes.

The following compounds were not amenable to this method of analysis: calciferol; 1,3-cyclo-octadiene; 9-anthraldehyde; 4-methyl-1,3-pentadiene; 2,5-dimethyl-2,4-hexadiene; *cis*-1,3-pentadiene; benz[*a*]anthracene; 1,2,5,6-dibenzanthracene; 1,2,3,4-tetraphenyl-1,3-cyclopentadiene; furan; 2-methylfuran; and 2,5-dimethylfuran. Most of these compounds form stable complexes with TCNE (Table 3); however, benz[*a*]anthracene and calciferol do undergo very slow reactions with TCNE. Probably *trans*-1,3-hexadiene could be determined in the 0·05–1·00 × $10^{-3}M$ range by the method since a preliminary test on the *cis*, *trans* mixture of 1,3-hexadiene indicated that its reaction time is slightly faster than that of the piperylene. No separation for the mixture was found; therefore, no calibration plot was prepared. In addition, the determination of 9-methylanthracene and 9,10-dimethylanthracene appears to be feasible in the 0·05–1·00 × $10^{-4}M$ range, according to the reaction times; however, no results were collected for these two aromatic dienes.

Solvent effect. As is indicated in Table 4, change of solvent drastically affects the absorbance; therefore, the calibration plots should be prepared with the samples and standards in comparable solvent systems.

Stability of solutions. The stability of the naphthalene–TCNE solutions is excellent, the absorbance varying by no more than 0·006 units over some hours. Except for slight fading, the mesitylene–TCNE solutions are also stable for long periods of time. A precision study of ten solutions for the 5·0 × $10^{-5}M$ *trans*-2-methyl-1,3-pentadiene system gave absorbance values of 0·164 ± 0·002 (indirect) and 0·141 ± 0·002 (Reilley-Hildebrand). The Reilley Hildebrand absorbance measurements were taken one day after the indirect measurements were taken. This indicates any fading is consistent throughout the set of solutions.

Table 4. Effect of solvent on diene reagent blank

Solvent	Absorbance, 550 *nm* (Spectronic 20)	Absorbance, 550 *nm* (Cary 14)
CCl_4	1·28	1·078
$CHCl_3$	0·85	0·730
CH_2Cl_2	0·50	0·432

Table 5. Effect of concentrations of naphthalene on absorbance of the naphthalene–TCNE complex

Concentration of naphthalene, M	Absorbance of blank*	Absorbance of sample†	Difference in absorbance, ΔA
0·75	1·109	0·642	0·467
0·69	1·120	0·590	0·530
0·60	1·075	0·567	0·508
0·51	1·009	0·522	0·487
0·45	0·950	0·520	0·430

* The blank was prepared by the addition of 1 ml of 0·050M TCNE and the appropriate volume of 1·50M naphthalene to a 50-ml flask and diluting to the mark with CCl_4. All readings were taken on the Cary 14 spectrophotometer.

† The sample was prepared in the same manner as the blank except for the addition of 10 ml of $2·5 \times 10^{-3}M$ cyclopentadiene before dilution.

Concentration of naphthalene and mesitylene. Schenk and Ozolins[4] showed that the naphthalene–TCNE reagent was suitable for the indirect spectrophotometric determination of anthracene. Hence essentially the same reagent was used for the 1,3-diene determinations in the $0·05–1·00 \times 10^{-3}M$ 1,3-diene concentration range. Table 5 indicates that the 0·60M naphthalene–TCNE reagent gives nearly the highest sensitivity. The 0·60M naphthalene concentration was chosen because (*a*) at higher concentrations of naphthalene solvent evaporation is great enough to leave a white powdery film of crystalline naphthalene on the glassware, and (*b*) the absorbance of the reagent blank is approximately in the centre of the minimum error range for a double-beam spectrometer.[19]

Doubly distilled mesitylene gave no better reagent blank values than did Baker White Label mesitylene. Therefore, Baker or other commercially available mesitylene was used for measurements in the $0·05–1·00 \times 10^{-4}M$ range. A study of various concentrations of mesitylene for the reagent blank indicated that 5 ml of mesitylene per 50 ml in carbon tetrachloride gave nearly the optimum absorbance measurement.

Interferences. Schenk and Ozolins delineated the major interference effects of aromatic hydrocarbons in this type of analysis. Experiments have shown that mixtures of 1,3-dienes which react at comparable rates can be analysed by an indirect differential kinetic spectrophotometric method, and that very slow-reacting 1,3-dienes do not significantly interfere with the determination of the faster-reacting 1,3-dienes. This subject will be presented in a subsequent publication.

Order of addition of reagents. To minimize the reaction time, it is important to adopt a specific order of addition of reagents. If the 1,3-diene and TCNE solutions are mixed before the aromatic donor is added, the reaction is found to take only half as long as when the aromatic donor and TCNE are mixed before addition of the 1,3-diene sample.

Instrumental effect. Since the absorption bands of aromatic–TCNE π-complexes are unusually wide, the methods were found to be feasible on all four spectrophotometers utilized. Nevertheless, the band-pass of the instrument is reflected in the absorbance measurements. This is indicated for the Spectronic 20 and the Cary 14 spectrophotometers by the solvent effect study on the naphthalene–TCNE solutions cited previously, and also for the Beckman DB-G and Spectronic 20 spectrophotometers. The following trend was observed:

the larger the bandwidth of the spectrophotometer, the higher the absorbance readings. This study simply indicates that the method is feasible on both narrow and wide bandwidth spectrophotometers.

Precision and reproducibility. With carbon tetrachloride as the solvent, the naphthalene–TCNE reagent blank was found to yield absorbances of 1·03 ± 0·02 and 1·090 ± 0·006 for ten independent solutions measured on the Beckman DB and Cary 14 spectrophotometers, respectively. Precision studies for ten independent solutions of $7 \cdot 50 \times 10^{-4}M$ 9-methylanthracene and $7 \cdot 20 \times 10^{-4}M$ *trans*-2-methyl-1,3-pentadiene solutions in carbon tetrachloride gave absorbances of 0·726 ± 0·004 and 0·664 ± 0·008, respectively (Beckman DB spectrophotometer). Precision measurements on other 1,3-diene systems gave similar results in both ranges for both methods. With the values of precision found for a number of systems, the reproducibility of the calibration plots should be good. This was observed qualitatively since the shapes of the calibration plots did not vary even though the slopes did, especially for slow-reacting dienes when the reaction times were changed. Therefore for optimum results, the reaction times in Table 2 should be used to within about ±10%.

Sensitivity and detection limit. The only meaningful sensitivity for these systems is the quantity $\Delta A/\Delta C$ over the straight-line portion of the calibration plot. This quantity is equivalent to the effective molar absorptivity, ε_{eff}, for a particular aromatic–TCNE complex. For the naphthalene–TCNE solutions with carbon tetrachloride as the solvent, the $\Delta A/\Delta C$ value for most 1,3-diene systems is $1050 \pm 50\ 1 \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ whereas with chloroform as the solvent the sensitivity is significantly lowered to 670 ± 50. With the mesitylene–TCNE system, ε_{eff} is $3 \cdot 20 \pm 0 \cdot 50 \times 10^3$ for the three 1,3-diene systems studied with carbon tetrachloride as the solvent. Practically, the lowest possible detection limit is $2 \cdot 5 \times 10^{-5}M$ for the naphthalene–TCNE system and $2 \cdot 5 \times 10^{-6}M$ for the mesitylene–TCNE system, although measurements were not made at these levels. These concentrations correspond to 1·1 and 0·11 ppm, respectively, for cyclopentadiene in carbon tetrachloride.

Nature of 1,3-*diene–TCNE complexes*

Absorption spectra. Transient colours are observed in the Diels-Alder reactions of 1,3-dienes with TCNE; however, some of the 1,3-dienes do not readily undergo the Diels-Alder reaction but do form relatively stable complexes with TCNE (see Table 3). The spectra of some of these complexes (Fig. 3) show an increased bathochromic shift of about

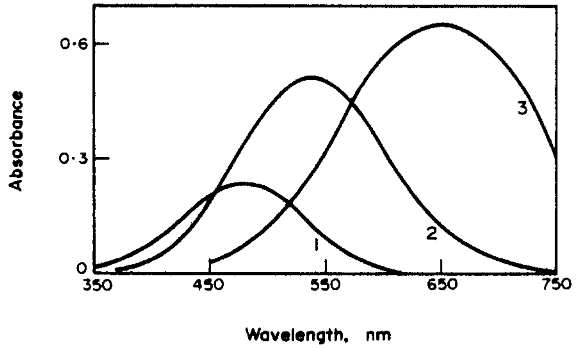


Fig. 3. Spectra of Some 1,3-diene–tetracyanoethylene complexes.
(1) *cis*-1,3-Pentadiene, $10^{-4}M$.
(2) 4-Methyl-1,3-pentadiene, $10^{-4}M$.
(3) 2,5-Dimethyl-2,4-hexadiene, $10^{-4}M$.

60 nm with each additional methyl group or the equivalent, compared to the parent 1,3-diene.

Estimations of K_π and ε values for aliphatic 1,3-dienes. The spectra of the 1,3-diene–TCNE molecular complexes are very similar to those found by Merrified and Phillips[17] for π-complexes of aromatic compounds with TCNE. In order to determine the magnitude of the π-complex formation constant, K_π, a plot of $C^0_{\pi\text{donor}}/A$ *vs.* $1/C^0_{\text{TCNE}}$ was made. The slope of this plot is equal to $1/(K_\pi \cdot \varepsilon)$ and the intercept is equal to the reciprocal of the molar absorptivity of the π-complex.

Usually the Benesi-Hildebrand equation would predict a linear plot of C^0_{TCNE}/A *vs.* $1/N_{\text{donor}}$, where N_{donor} is the mole fraction of the donor. However, when the donor is an aliphatic 1,3-diene, small concentrations of TCNE and an excess of the donor will force an addition reaction of some type to occur, and the result is a marked fading of the π-complex colour. If the TCNE–mesitylene π-complex values for K_π and ε from Table 1 are used as standards, meaningful plots for the TCNE–diene complexes and the mesitylene–TCNE π-complex can be made as shown in Fig. 4. Similar plots were obtained for *cis*-pentadiene,4-methyl-1,3-pentadiene and cyclo-octadiene. The mole-fraction term becomes meaningless in these plots for the system described since the solvent concentration is so large that the only real variable is the concentration of TCNE. Hence it was decided to use just $1/C^0_{\text{TCNE}}$. If the assumption is made that $\varepsilon_{1,3\text{-diene}} \sim \varepsilon_{\text{mesitylene}}$, then the slope of the line is equivalent to the reciprocal of K_π. The molar absorptivity assumption is valid for these crude measurements since ε for the series of benzene and methylated benzene derivatives is about $3{\cdot}20 \times 10^3\ \text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$, and the slopes for the aliphatic 1,3-dienes studied coincide closely with the mesitylene slope in Fig. 4. If the molar absorptivity of the aliphatic 1,3-dienes is smaller than ε for mesitylene, then the K_π values reported here would be increased, not decreased.

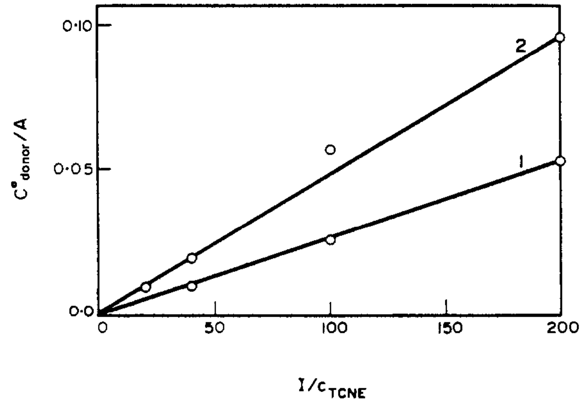
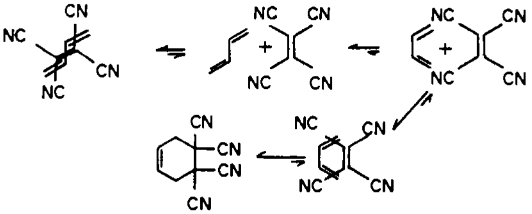


Fig. 4. Comparison of 1,3-diene and mesitylene–TCNE complexes.
(1) Mesitylene.
(2) 2,5-Dimethyl-2,4-hexadiene.

The K_π values for the aliphatic 1,3-dienes listed in Table 3 are not absolute; they indicate only the relationship of one 1,3-diene to another and the similarity of the 1,3-diene–TCNE π-complexes to their aromatic analogues. The K_π values reflect an increase in complex formation with an increase of methyl substituents in the diene. This is similar to the behaviour of aromatic–TCNE systems. The most salient feature of this study is to show that there exist finite K_π values for the 1,3 diene–TCNE systems.

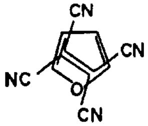
The transient colour in the Diels-Alder reaction. Since the existence of the 1,3-diene–TCNE π-complexes has now been established, the transient colour in the 1,3-diene–TCNE Diels-Alder reaction may be understood by considering the cisoid and transoid conformations of the aliphatic 1,3-dienes:

A cisoid conformation of the 1,3-diene is necessary for the formation of a Diels-Alder reaction adduct;[21] however, if a transoid conformation of the aliphatic 1,3-diene is formed, no Diels-Alder adduct is observed. For aliphatic 1,3-dienes with free rotation around the middle single bond, the transoid conformation exists in much larger concentrations than the cisoid conformation.[22] This leads to the conclusion that if the 1,3-diene is in the cisoid conformation, as for 2-methyl-1,3-pentadiene, the observed transient π-complex assists the rate of reaction. However, if the 1,3-diene is in the transoid conformation, the Diels-Alder reaction is inhibited since the π-complex between the 1,3-diene and TCNE has to dissociate and rotation of the aliphatic 1,3-diene to the cisoid conformation has to take place before reaction can occur. The proposed explanation can be pictured as:

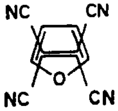


π-Complexes of furan and its derivatives. Since furan is known to undergo a quantitative Diels-Alder reaction with maleic anhydride in about half an hour,[23] and since TCNE is known to react many times more rapidly with 1,3-dienes than does maleic anhydride,[6] it was thought that furan and its derivatives could be determined by the proposed methods. As noted by Ozolins,[24] furan does not react to form the Diels-Alder adduct as rapidly as expected. In fact, when TCNE is mixed with furan, 2-methylfuran, or 2,5-dimethylfuran, stable coloured π-complexes are formed as noted in Table 3. These coloured complexes have still been in existence months after they were prepared; with slow evaporation, crystals of the complexes are formed. No characterization was made of these crystals; however, an addition product or π-complex appears to be formed.

Since cyclopentadiene reacts so rapidly with TCNE and maleic anhydride reacts fairly quickly with furan, it should be reasonable to assume that furan should react rapidly with TCNE. However, the opposite is true. Butler and his associates[23] found that maleic anhydride forms a 1 : 1 π-complex with furan, and the equilibrium constant is about 0·06 as determined by ultraviolet–visible spectrophotometric and nuclear magnetic resonance techniques. Yoshida and Kabayashi[20] found the equilibrium constant for the furan–TCNE complex to be 0·35 with an ε of $2{\cdot}11 \times 10^3\ \mathrm{l \cdot mole^{-1} \cdot cm^{-1}}$ at 445 nm. *A priori,* the TCNE must position itself on the furan and its derivatives in a manner that would not lead immediately to a Diels-Alder adduct. If maximum overlap produces the most stable situation, it appears that the TCNE would position itself over the furan systems in this manner:



rather than the Diels-Alder-active position:



This proposed position would allow the electron-deficient TCNE to share the electron-rich oxygen atom, which might be explained on the basis of resonance and a co-ordinate covalent bond.

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Zusammenfassung—Es wurde eine indirekte spektrophotometrische Methode zur Bestimmung von elf 1,3-Dienen im Konzentrationsbereich 0,05–1,00 · 10^{-3}M entwickelt. Sie beruht auf der raschen Diels–Alder-Reaktion zwischen cisoiden 1,3-Dienen und Tetracyanäthylen (TCNE) und der Zerstörung eines π-Komplexes zwischen einem Aromaten und TCNE. Die Diene waren: Cyclopentadien; 1,3-Cyclohexadien; trans-1,3-Pentadien; 2,4-Dimethyl-1,3-pentadien; trans-2-Methyl-1,3-pentadien; 2-Methyl-1,3-butadien; 9-Methylanthracen; 9,10-Dimethylanthracen; 1,6-Diphenyl-1,3,5-hexatrien; 2,3-Dimethyl-1,3-butadien; 1,4-Diphenyl-1,3-butadien. Drei 1,3-Diene wurden im Bereich 0,05–1 · 10^{-4}M bestimmt: Cyclopentadien, trans-2-Methyl-1,3-pentadien und Anthracen. Die Nachweisgrenze für Cyclopentadien in Tetrachlorkohlenstofflösung beträgt 0,11 μg/ml. Vierzehn 1,3-Diene bilden stabile π-Komplexe und ließen sich nach der vorgeschlagenen Methode nicht bestimmen. Für diese 1,3-Diene werden die Spektren von einigen der π-Komplexe angegeben; dazu wurden die relativen Gleichgewichtskonstanten der π-Komplexe von 2,5-Dimethyl-2,4-hexadien, cis-1,3-Pentadien, 4-Methyl-1,3-pentadien und 1,3-Cyclooctadien abgeschätzt. Es wird eine Erklärung für die vorübergehende Farbe bei der Diels–Alder-Reaktion zwischen 1,3-Dienen und TCNE vorgeschlagen.

Résumé—On a développé une méthode spectrophotométrique indirecte, basée sur la réaction de Diels–Alder rapide entre des 1,3-diènes cisoïdes et le tétracyanéthylène (TCNE) et la destruction d'un complexe π aromatique–TCNE pour doser onze 1,3-diènes dans le domaine 0,05–1,00 × 10^{-3} *M*. Ces diènes sont: cyclopentadiène; 1,3-cyclohexadiène; *trans*-1,3-pentadiène; 2,4-diméthyl 1,3-pentadiène; *trans*-2-méthyl 1,3-pentadiène; 2-méthyl 1,3-butadiène; 9-méthylanthracène; 9,10-diméthylanthracène; 1,6-diphényl 1,3,5-hexatriène; 2,3-diméthyl 1,3-butadiène; et 1,4-diphényl 1,3-butadiène. Trois 1,3-diènes ont été déterminés dans le domaine 0,05–1 × 10^{-4}*M*: cyclopentadiène, *trans*-2-méthyl 1,3-pentadiène, et anthracène. La limite de détection pour le cyclopentadiène dans des solutions en tétrachlorure de carbone est 0,11 μg/ml. On a trouvé quatorze 1,3-diènes formant des complexes π stables et qui ne peuvent pas être déterminés par la méthode proposée. Pour ces 1,3-diènes, on rapporte les spectres de quelques-uns des complexes π; de plus, on a estimé les constantes d'équilibre relatives pour les complexes π des 2,5-diméthyl 2,4-hexadiène, *cis*-1,3-pentadiène, 4-méthyl 1,3-pentadiène et 1,3-cyclooctadiène. On suggère une explication de la couleur fugace dans la réaction de Diels–Alder 1,3-diène–TCNE.

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COULOMETRIC MICRODETERMINATION OF PEROXIDES—I

HYDROGEN PEROXIDE

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Summary—An electroanalytical method, based on controlled-potential coulometry in the iodine-iodide system, has been developed for determination of small amounts of hydrogen peroxide. The sample is added to an electrolyte containing an acid solution of iodide and the iodine, which is produced rapidly, is reduced at a rotating platinum electrode. The number of coulombs consumed in the cell reaction is determined by electronic integration. Samples containing 1 μg–1 mg of hydrogen peroxide were analysed with an accuracy of ±0·2%. The analysis time ranged from 3 to 7 min.

An accurate and precise method for the determination of small amounts of peroxides is now a matter of some importance, especially in the analysis of many industrial products. The present paper describes a coulometric method, based on iodometry, for the determination of hydrogen peroxide. A second paper will describe the determination of organic peroxides.

A number of coulometric determinations of hydrogen peroxide have been described in the literature. Coulometrically generated permanganate has been employed in the titration of 0·7–5·5 mg of hydrogen peroxide with an average error of 0·3–0·4%,[1] and electrogenerated cerium(IV) has been used to titrate samples of 0·7 mg with an error of 2%.[2] A sensitive and precise method, based on a coulometric titration of hydrogen peroxide with electrogenerated hypobromite, has been described by Feldman and Bosshart.[3] The range investigated was 1–100 μeq of peroxide (0·017–1·7 mg) and the mean errors were reported to be less than 0·2%.

The controlled-potential coulometric determination of hydrogen peroxide has been investigated by Harrar.[4] In a supporting electrolyte of 1*M* sulphuric acid, 0·1–2 mg of hydrogen peroxide was determined by oxidation at a platinum gauze at +0·93 V *vs.* SCE. Attention had to be given to the catalytic decomposition of hydrogen peroxide at the platinum electrode.

The iodometric determination is based on the well-established reaction between hydrogen peroxide and iodide in acid solution:

$$H_2O_2 + 2H^+ + 2I^- \rightleftharpoons I_2 + 2H_2O$$

In the presence of a molybdenum catalyst, the reaction is quite rapid. Christian[5] has described a coulometric method where reaction of hydrogen peroxide with iodide is followed by addition of an excess of thiosulphate, the excess then being determined by titration with electrogenerated iodine. By this method samples containing from 0·9 μg to 2·6 mg of peroxide have been analysed with an average error from 0·1 to 4%. Finally, Malmstadt and Pardue[6] used precision null-point potentiometry (PNPP) for determination of the iodine produced. Hydrogen peroxide in the range 3·6–36 μg was determined with an error of not more than 0·05 μg.

In the study reported here, the iodometric determination of hydrogen peroxide by coulometry at controlled potential has been investigated. The electrolyte in the sample compartment of the electrolysis cell consists of a strongly acid solution of iodide. At a rotating platinum electrode all iodine present is reduced at constant potential. When the sample of hydrogen peroxide is added, an equivalent amount of iodine is produced rapidly and immediately reduced at the working electrode. Hydrogen peroxide in the range 0·001–1 mg has been successfully determined by this method. The results obtained have been compared with those obtained by titrimetry. For sample weights >3 μg the accuracy was found to be better than ±0·1%.

EXPERIMENTAL

Electrolysis cell

The electrolysis cell used is shown in Fig. 1. The sample compartment consists of a B45 ground-glass joint provided with a Teflon plug, making a gas-tight cover for the compartment. The Teflon plug has five holes, for reference electrode (A), nitrogen inlet (B), bearing for the working electrode (C), Teflon stopper (D) and sample addition and nitrogen outlet (E). The Teflon stopper is removed for refilling the compartment, the capacity of which is about 15 ml. The connecting chamber, filled with 1*M* sodium perchlorate, is separated from the auxiliary and sample compartments by two Haldenwanger clay filters (F). The pore size of these filters is about the same as that of glass frits of porosity 5 (2 μm), but their resistivity is much lower. The auxiliary compartment consists of a B19 socket fitted with a Teflon plug and electrode holder, and is also filled with 1*M* sodium perchlorate.

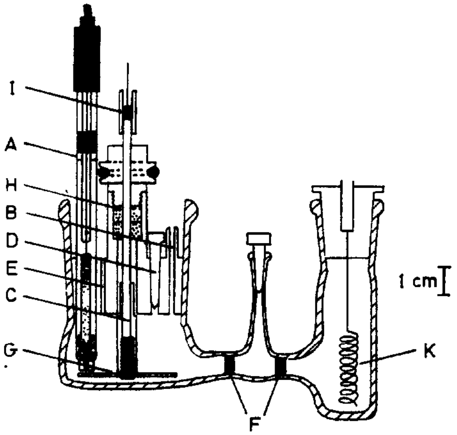

Fig. 1. Electrolysis cell.
A—Reference electrode
B—Nitrogen inlet
C—Electrode axis
D—Teflon stopper
E—Sample addition and nitrogen outlet
F—Haldenwanger clay filters
G—Working electrode
H—Stainless-steel ball-bearings
I—Mercury pool
K—Counter-electrode

Electrodes

The working electrode (G) is a 36-mesh circular platinum gauze, 35 mm dia. fixed to a platinum rod, which is soldered to a stainless-steel rod, fitted with a mercury contact at the top (I). The whole shaft of the electrode is Teflon-covered. The rotational speed of the electrode can be varied stepwise by means of a transmission system and a stirring motor (Radiometer Type M22). The speed most frequently used was about 600 rpm. The reference electrode is a saturated calomel electrode (Radiometer K 401). The counter-electrode (K) consists of a spiral of platinum wire 0·2 mm dia. and about 250 mm long.

Apparatus

The controlled potential system used is illustrated in Fig. 2. The potentiostat is based on an operational amplifier provided with a booster, having a maximum output current of about 500 mA. The number of coulombs consumed in the cell reaction is determined by integration of the current. This is accomplished by means of an integrator, based on a chopper-stabilized operational amplifier and calibrated by application of known voltages for measured time periods. The read-out device is a digital voltmeter, which gives fast and accurate presentation.

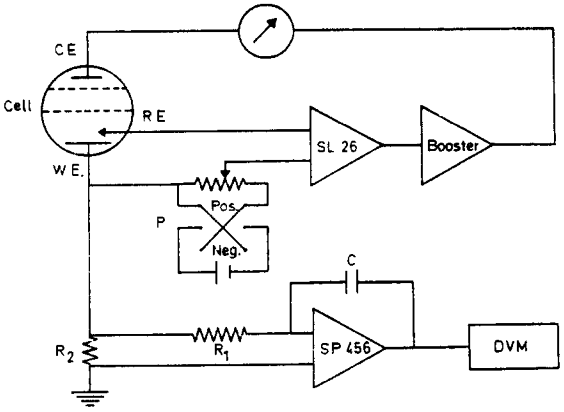

Fig. 2. Electronic circuitry.
W.E. —working electrode
R.E. —reference electrode
C.E. —counter electrode
P—potentiometer
C—capacitor, 10 μF
R_1—resistor, 500 kΩ
R_2—resistor, 10 Ω

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized, freshly distilled water.

Hydrogen peroxide solutions, 125–0·5 mM, were prepared by successive dilutions of 30% unstabilized reagent-grade solution with water.

The arsenic(III) oxide, was 99·99% pure, NBS No. 83c and was dried at 115° for 8 hr.

The nitrogen, purity >99·9%, was passed over copper at 500°.

Procedures

Titrimetric determination. The method for standardization of the permanganate solution is that proposed by Kolthoff, Laitinen and Lingane.[7] About 250 mg of As_2O_3 are dissolved in 10 ml of 6*M* sodium hydroxide, 10 ml of conc. hydrochloric acid are added, and the sample is diluted to 50 ml with water in a calibrated flask; 10 ml are pipetted into a beaker and 15 ml of water added. The reaction is catalysed by the addition of one drop of 2·5m*M* potassium iodate together with 1 g of sodium chloride. The sample is titrated with 0·1*N* potassium permanganate, nitrogen being used for stirring and ferroin as indicator.

The method used for the titrimetric determination of hydrogen peroxide with permanganate is a modification of that proposed by Huckaba and Keyes.[8] Five ml of conc. sulphuric acid are poured into 10 ml of water in a beaker, and cooled. Then 20 ml of 25m*M* hydrogen peroxide are pipetted into the beaker, followed by titration with 0·1*N* permanganate (ferroin as indicator).

Coulometric determination. The working compartment of the electrolysis cell is filled with electrolyte, $1M$ with respect to sodium perchlorate, sodium iodide and hydrochloric acid. The pH of this solution is about zero. Nitrogen is passed through the cell, the platinum electrode is set in motion and all iodine present is reduced, until the current reaches a stable residual value (0·5–5 μA).

After this start-up the following sequence of operations is used for *large samples.*

1. Switch off the reduction current.
2. Reset the integrator and timer.
3. Add the sample and allow 10–30 sec for complete reaction.
4. Reduce the iodine produced.
5. Read the integrator and timer, when the current has reached its residual value.
6. Repeat steps 1–5 but replace sample addition by an equivalent amount of electrolytically generated iodine (blank test).

The actual efficiency of the oxidation–reduction process is calculated (step 6) and the integrator reading (step 5) corrected.

For *small samples* (<100 μg) the pre-reaction time before reduction can be excluded and the procedure is even simpler.

1. Reset the integrator and timer.
2. Add the sample and reduce the iodine produced.
3. Read the integrator and timer, when the current has reached its residual value.

This simplified procedure, avoiding a transient signal at the start of the reduction and involving shorter electrolysis times, eliminates the need for a blank test; the integrator reading is corrected only for the integral of the residual current during the time of analysis.

The integrator reading obtained is converted into μg of hydrogen peroxide as follows:

$$17{\cdot}005 \times \frac{10^6 \cdot A \cdot U_c}{F} = \mu\text{g } H_2O_2$$

where 17·005 = equivalent weight of hydrogen peroxide
A = factor for integrator components (in this case 0·49750 sec/ohm)
F = Faraday constant (96487 C/mole)
U_c = integrator read-out, corrected (V)

Samples ranging from 50 to 250 μl were added from an all-glass micrometer syringe burette (Agla), fixed on a rigid steel stand. By this method sample volumes were accurate to $\pm 0{\cdot}02$ μl. The analysis time varied from 3 to 7 min for the range investigated (1 μg–1mg).

RESULTS AND DISCUSSION

Electrolytes with different compositions were investigated to find the most satisfactory conditions. The pH was varied from about 6 to 0 and the iodide concentration from 0·2 to $1M$. All electrolytes tested contained $1M$ sodium perchlorate as an inert (supporting) electrolyte. The rate of reduction of hydrogen peroxide by iodide is favoured by a high concentration of iodide and a low pH. This was confirmed by the coulometric measurements, where the electrolyte having pH ~ 0 and $[I^-] = 1{\cdot}0M$ was found to be the best, with complete reaction within 30 sec.

In the titrimetric determination of hydrogen peroxide with iodide, the pH of the solution must not be too low, otherwise the following titration with thiosulphate will give erroneous results. The optimum pH is about 3. To increase the rate of reaction, a catalyst, molybdate, has to be added. In the coulometric method, however, the low pH makes the use of a catalyst superfluous; besides, molybdate would cause a serious interference, being reduced at about the same potential as iodine.

The electrolyte was built up stepwise and each step was studied by means of current–voltage measurements. Figure 3 shows the curves for oxidation of water to oxygen in pure inert electrolyte and oxidation of iodide to iodine in working electrolyte at positive potentials. At negative potentials reduction of hydrogen ion to hydrogen takes place. From these

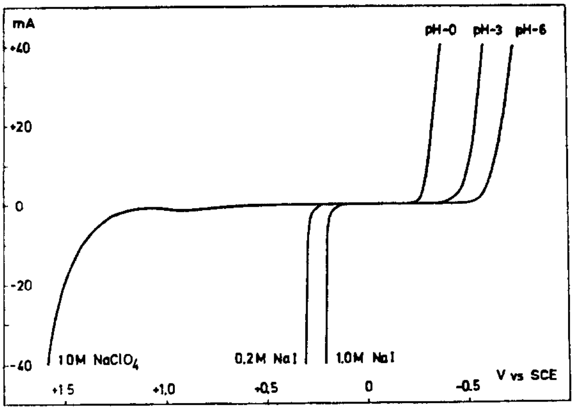

Fig. 3. Current–voltage curves.

curves a working potential of about 0 mV *vs.* SCE was chosen for the reduction step. This was in good agreement with the results obtained by calculation according to the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{ox}]}{[\text{red}]}$$

where E^0, R, T, n and F have their usual meanings,[9] while [ox] and [red] represent the activities of the oxidized and reduced form respectively. A sample of 85 μg of hydrogen peroxide produces 2·5 μmole of I_2. The potential at which the iodine concentration has decreased to 0·01 % of its original value is calculated from

$$E = 0{\cdot}5355 + 0{\cdot}0296 \log \frac{2{\cdot}5 \times 10^{-6} \times 10^{-4}}{15 \times 10^{-3}}$$

$$E = 0{\cdot}305 \text{ V } vs. \text{ NHE} = 0{\cdot}060 \text{ V } vs. \text{ SCE}$$

$E^0(I_3^-/I^-)$ being 0·5355 V *vs.* NHE. That is, for samples in the range 1 μg–1 mg, the reduction potential is calculated to range from 0 to +90 mV *vs.* SCE. Usually, a more negative potential is chosen if possible; in this case, however, the evolution of hydrogen starts at negative potentials. The working potential for reduction was therefore selected to be 0 mV *vs.* SCE in all experiments. For the blank tests the electrolytically generated iodine was produced at +300 mV *vs.* SCE.

During the reduction of an acid solution containing the iodine–iodide couple, two opposite effects have to be considered; loss of iodine from the working compartment due to diffusion through the filters, and production of iodine due to aerial oxidation of iodide. The diffusional loss, which is proportional both to the concentration of iodine and to the pre-reaction time, is minimized by using filters with small pore size. Losses of iodine owing to its volatility can be neglected, if sufficient iodide is present, whereby I_3^- is formed. The rate of aerial oxidation of iodide increases rapidly with increasing acidity and is photochemical in nature. Thus, deaerating the solution with nitrogen has two purposes; it prevents reduction of oxygen (see Fig. 3) and formation of iodine. In extreme cases the solution can also be protected from light. Figure 4 illustrates the efficiency of the redox reaction at two different pH-values. For pH ~0 the efficiency is 100% for oxidation and reduction of about 5 µmole of iodine. For pH ~6 the same amount of iodine is reduced with 99·8% efficiency. The reproducibility is, however, very good: when 2·5000 µmole of iodine were produced by oxidation at pH ~0 the reduction gave 2·5035 ± 0·0004 µmole (95% confidence limits). The nitrogen flow-rate through the cell was 10 ml/min.

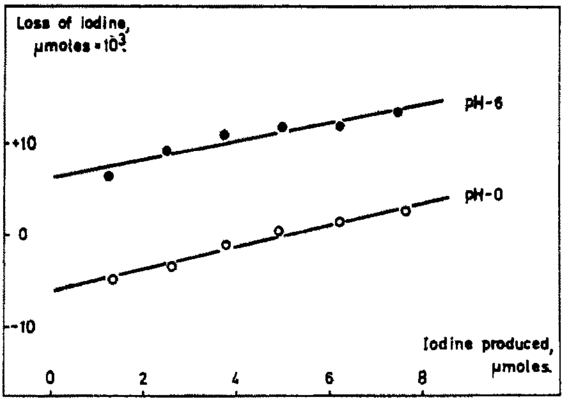

Fig. 4. The loss of iodine from the sample compartment of the cell during reduction as a function of total amount of iodine produced in solutions at two different pH-values.

Injection of a sample containing pure water causes a small amount of iodine to be produced in the cell, because of the dissolved oxygen. This matrix-correction corresponded to about 0·014 µg of hydrogen peroxide per 100 µl of water.

The catalytic decomposition of hydrogen peroxide at a platinum electrode[4] need not be considered in this case, where a halide-containing solution is used. It has been reported[10] that the metal loses its catalytic activity when it cannot be covered by an adsorbed oxide layer, as is the case when it forms complexes with the solution (platinum in hydrochloric acid).

For an electrode reaction carried out at a potential at which the reaction rate is limited by the rate of mass transfer of electroactive species to the electrode, and where convection is maintained in the bulk of the solution, the electrolysis current decays (according to Lingane[11]) as follows:

$$i_t = i_0 \cdot e^{-pt}$$

where i_0 = initial current; i_t = the current at time t; $p = AD/V\delta$; A = electrode area; D = diffusion coefficient; V = solution volume; δ = thickness of the diffusion layer.

The electrolysis time decreases with increasing values of p. Conditions for achieving a high p-value have been chosen: a large electrode area, a small solution volume and effective stirring to decrease δ. The diffusion coefficient D increases with increasing temperature; however, all experiments were performed at 25 ± 1°. By plotting ln i *vs.* t a straight line is obtained from which p and i_0 can be determined. The cell used gave a p-value of 2·1 min^{-1}. The value of i_0 is proportional to the original concentration of electroactive species; for the largest samples of hydrogen peroxide investigated (~1 mg) an i_0-value of 200 mA was observed.

In Table 1 the results for the determination of hydrogen peroxide by the coulometric method (H_2O_2 found) are compared with results obtained by conventional titrations (H_2O_2 calculated). The amount of peroxide added was calculated from the volume and concentration of the solutions used, the concentrations being obtained from titration of the 25 m*M* stock solution and the dilution factors.

Table 1. Coulometric determination of hydrogen peroxide

H_2O_2 calculated		H_2O_2 found	No. of	Error,	Precision (%) at a confidence
µg	*µmole*	*µmole*	determinations	%	limit of 95%
0·85	0·02500	0·02484	6	−0·63	±0·29
1·70	0·05000	0·04971	4	−0·58	±0·35
2·55	0·07500	0·07473	3	−0·36	±0·42
4·25	0·12500	0·12495	9	−0·04	±0·05
8·50	0·2500	0·2498	6	−0·09	±0·17
17·0	0·5000	0·5003	6	+0·06	±0·19
42·5	1·2500	1·2495	5	−0·04	±0·12
85·0	2·500	2·497	9	−0·10	±0·11
213	6·250	6·250	11	±0·00	±0·04
425	12·500	12·503	7	+0·02	±0·05
850	25·000	25·015	3	+0·06	±0·17

A new electrolysis cell, provided with a glass jacket for circulation of water, has been constructed, thus enabling the reaction mixture to be maintained at any desired temperature. This cell has been used for the determination of organic peroxides of different reactivities, as will be described in Part II of this investigation.

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Zusammenfassung—Zur Bestimmung kleiner Mengen Wasserstoffperoxid wurde ein eelektroanalytische Methode entwickelt, die auf Coulometrie bei geregeltem Potential im System Jodid beruht. Die Probe wird zu einem Elektrolyten gegeben, der eine saure Jodidlösung enthält; das rasch gebildete Jod wird an einer rotierenden Platinelektrode reduziert. Die bei der Reaktion in der Zelle verbrauchte Anzahl Coulomb wird durch elektronische Integration bestimmt. Proben, die 1 µg–1 ml Wasserstoffperoxid enthielten, wurden mit einer Genauigkeit von ±0,2% analysiert. Die Analysenzeit beträgt 3–7 min.

Résumé—On a élaboré une méthode électroanalytique, basée sur la coulométrie à potentiel contrôlé dans le système iode-iodure, pour le dosage de petites quantités de peroxyde d'hydrogène. L'échantillon est ajouté à un électrolyte contenant une solution acide d'iodure et l'iode, qui est produit rapidement, est réduit sur une électrode tournante de platine. Le nombre de coulombs consommés dans la réaction dans la cuve est déterminé par intégration électronique. Des échantillons contenant 1 $\mu g - 1$ ml de peroxyde d'hydrogène ont été dosés avec une précision de ±0,2%. Le temps d'analyse est de 3 à 7 mn.

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SELECTRODE—THE UNIVERSAL ION-SELECTIVE ELECTRODE—V

COMPLEX FORMATION STUDIES WITH THE Cu(II) SELECTRODE

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Summary—The Cu(II) Selectrode, calibrated in a series of Cu(II) buffers at various pH levels, has been used for the determination of the stability constants of the Cu(II) complexes of glycine and EGTA at an ionic strength of 0·1. Methods for the calculation of the stability constants of chelate complexes from pH and pM values are presented. The values obtained compare very favourably with those recorded in the literature. For the Cu(II)–EGTA system, for which only a few stability constants have been determined, the following constants were found: $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = 16{\cdot}80$; $\log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} = 5{\cdot}30$; $\log K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}} = 7{\cdot}64$; $\log K_{\mathrm{CuH_2L}}^{\mathrm{H,CuHL}} = 2{\cdot}34$; $\log K_{\mathrm{CuHL}}^{\mathrm{Cu,HL}} = 12{\cdot}56$; and $\log K_{\mathrm{CuH_2L}}^{\mathrm{Cu,H_2L}} = 5{\cdot}97$. Examples of the application of the Cu(II) Selectrode in replacement reactions are illustrated.

The present availability of a large number of ion-sensitive electrodes has focused attention on the use of these sensors in complex-formation studies. Of the various methods for the determination of stability constants of metal chelates, those based on pH measurements have most frequently been used, *i.e.*, as protons are liberated when metal ions replace hydrogen ions in the ligand, the concentration of free ligand can be determined from the change in pH. The method gives good results for complexes of medium stability, but if very stable complexes are formed, the replacement of protons will be so complete that pH measurements cannot yield accurate values of stability constants—as amply reflected in the results accumulated in the literature. This difficulty is largely overcome by applying cation-sensitive electrodes which directly measure metal ion activities. Thus by having immediate access to the measurement of two parameters, pH and pM, the problem of determining equilibrium constants is greatly simplified and more reliable results can be obtained. In addition, the method of direct measurements of metal ion activities may potentially be applicable to a wide range of ionic media, and, *e.g.*, also serve as a means to measure extraction constants (two-phase stability constants).

A survey of the literature from the last few years clearly reveals that ion-sensitive electrodes have indeed found increased applications. It is, however, of inherent importance to determine the dynamic range within which any ion-sensitive electrode has the capacity to yield reliable results. This can only be done by calibrating the electrodes with a series of buffered solutions. This is, of course, the approach which has long been applied for the calibration and testing of pH electrodes. It is therefore rather surprising that it has become common practice—unfortunately also recommended by manufacturers—to standardize and test ion-sensitive electrodes by means of extensively diluted solutions of well-ionized salts.

Even if absolutely pure degassed solutions are prepared, reliable dilutions down to $10^{-10}M$ can never be hoped for, quite apart from the fact that electrode measurements in ultrapure solutions would bear no relation to the use of the electrodes in practical situations.

Intrinsically, the potentials measured with an ion-sensitive electrode, *e.g.*, an M^{n+} sensor, indicate activities and not concentrations. At *constant ionic strength*, however, the ionic activity is directly proportional to the concentration, thus furnishing the basis for an operational p*M*-scale where p*M* is defined by $pM = -\log[M^{n+}]$. In consequence, the true position of the calibration curve for an M^{n+} ion-sensitive electrode may remain virtually unknown, yet *well fixed* for a series of M^{n+} buffer solutions adjusted to constant ionic strength.[1] Furthermore, by use of a constant ionic strength, any variation in the junction potential of the reference electrode is avoided, *i.e.*, this contribution is incorporated in the normal potential of the metal M. In the present paper an ionic strength of $\mu = 0{\cdot}10$ was chosen, as this is the value most commonly applied in the literature. Furthermore, ionic strengths in the range 0·05–0·5 are those most frequently encountered in analysis.

The present complex-formation studies with the Cu(II) Selectrode are therefore aimed at two related tasks: (*a*) to demonstrate the capacity of this electrode, calibrated in a series of Cu(II) buffers at various pH levels, and its use in determinations of complex-formation constants, in particular those for the Cu(II)–EGTA system, for which only a few approximate values are known, and (*b*) to illustrate a few simple methods which may be used for such determinations. In addition to the Cu(II)–EGTA system which gives rise to a 1:1 complex of high stability, the Cu(II)–glycine system was investigated as an example of a system where both 1:1 and 1:2 complexes of medium stability are formed. Finally, the formation constants of EDTA with Ca and Zn ions were determined with the Cu(II) Selectrode in order to illustrate the application of the electrode in replacement reactions.

EXPERIMENTAL

Apparatus

The preparation of the Cu(II) Selectrode has been described previously.[1] The electrode was used together with a saturated calomel reference electrode (Radiometer, type K 401) for measurements of the Cu(II) ion activity in solution; the pH was measured with a Radiometer type G 202B glass electrode against the same reference electrode. The e.m.f. measurements were recorded with a Radiometer PHM52 digital pH meter, and the pH readings were taken with a Radiometer PHM51 pH meter.

Reagents

Analytical-grade chemicals were used throughout. All solutions were prepared with redistilled water.

Calibration of the Cu(II) Selectrode in Cu(II) buffers

The Selectrode was calibrated in Cu(II) buffers which were prepared as described in detail by Hansen *et al.*[1] Three series of Cu(II) buffers were made, the pH being adjusted to 4·75 with acetate buffer in the first series, to *ca.* 9 with borate buffer in the second and in the third to 10 with ammonia buffer. All three series were prepared to contain a total concentration of uncomplexed ligand, [L'], of $10^{-3}M$, the ligand being NTA (nitrilotriacetic acid) or EDTA (ethylenediaminetetra-acetic acid). The buffers covered a pCu range from *ca.* 7 to 19. In the region of pCu = 2–5 it was found that solutions prepared by the normal dilution technique were satisfactory. The ionic strength in *all* buffered and unbuffered solutions was made up to 0·10 by the addition of a calculated amount of potassium nitrate.

The calibration curve of the Cu(II) Selectrode is shown in Fig. 1. In solutions of pCu 2–9 potentials stable within ±0·2 mV were usually obtained after *ca.* 1–2 min. For higher pCu values, times of up to 5 min were usually necessary. All measurements were made at 25°, and potentials are referred to the saturated calomel electrode (SCE).

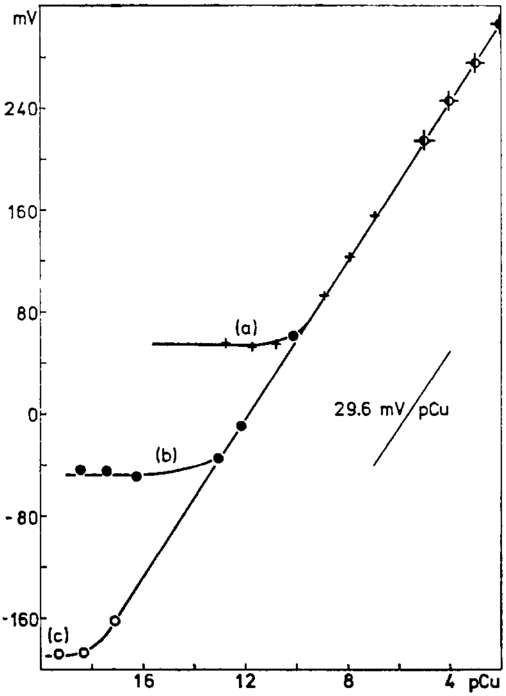

Fig. 1. Calibration curve for the Cu(II) Selectrode at (*a*) pH 4·8 (+); (*b*) pH 9 (●); and (*c*) pH 10 (○). Ionic strength 0·1.

Procedures

The complex-formation studies with Cu(II) ions and glycine or EGTA were carried out by mixing copper(II) nitrate and ligand at various initial ratios and conducting a series of pH and pCu measurements, gradually varying the pH by small additions of potassium hydroxide or nitric acid. The ionic strength was in all cases 0·10, adjusted by addition of the calculated amount of potassium nitrate.

The determinations of the complex-formation constants of EDTA with Ca and Zn ions at $\mu = 0{\cdot}1$ were performed by mixing an aliquot of CuEDTA solution with a solution of the metal nitrate salt. The pH was varied by small additions of potassium hydroxide. While the potentials recorded in the CuEDTA/Zn system were stable within a few minutes at each pH value, up to *ca*. 30 min were necessary in the CuEDTA/Ca system, owing to slow establishment of the equilibrium of this replacement reaction.[2]

The acidity constants of the complexing agents were taken from the literature.[2,3]

DISCUSSION AND RESULTS

The stability constant of the reaction between the metal ion M^{n+} and the ligand L^{m-} leading to the formation of the mononuclear complex $ML_x^{(n-xm)+}$ is defined by the equation:

$$M^{n+} + xL^{m-} \rightleftharpoons ML_x^{(n-xm)+};\ \frac{[ML_x^{(n-xm)+}]}{[M^{n+}][L^{m-}]^x} = K_{ML_x} \qquad (1)$$

where K_{ML_x} is the concentration stability constant at the ionic strength used. By taking logarithms and introducing the concepts of side-reaction coefficients, α, and conditional stability constants, K'_{ML_x}, equation (1) may be rearranged to read[1]:

$$pM = -\log[M] = \log K'_{ML_x} + \log \alpha_M + \log \frac{[L']^x}{[(ML_x)']} \qquad (2)$$

charges being omitted for the sake of clarity, and where

$$K'_{ML_x} = K^{L',M'}_{(ML_x)'} = \frac{\alpha_{ML_x}}{\alpha_M \alpha_L{}^x} \cdot K_{ML_x} \tag{3}$$

Thus, equation (2) may also be written:

$$pM = \log K_{ML_x} + \log \frac{\alpha_{ML_x}}{\alpha_L{}^x} + \log \frac{[L']^x}{[(ML_x)']} \tag{4}$$

or

$$\log K_{ML_x} = pM + x \log \alpha_L - \log \alpha_{ML_x} - \log \frac{[L']^x}{[(ML_x)']} \tag{5}$$

If the only side-reactions occurring in the system are those with H^+ (or OH^-), (5) can be read as:

$$\log K_{ML_x} = pM + x \log \alpha_{L(H)} - \log \alpha_{ML_x(H,OH)} - \log \frac{[L']^x}{[(ML_x)']} \tag{6}$$

where

$$\alpha_{L(H)} = 1 + \sum_{i=1}^{n} [H]^i \beta_i = \sum_{i=0}^{n} [H]^i \beta_i \tag{7}$$

and β_i is the cumulative protonation constant ($\beta_0 = 1$).

If no protonated or hydroxo complexes are formed by ML_x, the term $\log \alpha_{ML_x(H,OH)}$ is zero. The pH range in which this condition is fulfilled may generally be determined as demonstrated by Ringbom and Harju,[4] *i.e.*, the curve of $\log K^{M,xL}_{(ML_x)'}$ plotted as a function of pH will show a minimum in this pH range [see section (*c*) below]. The sum of the other terms of equation (6) will then be equal to $\log K_{ML_x}$:

$$\log K_{ML_x} = pM + x \log \alpha_{L(H)} - \log \frac{[L']^x}{[ML_x]} \tag{8}$$

Thus, K_{ML_x} may be determined by conducting a series of pH and pM measurements on a solution containing known initial concentrations of metal and ligand and varying the pH gradually.

A necessary condition is that equation (1) truly represents the main reaction of the system, that is:

$$\frac{[ML_{x+1}]}{[ML_x]} = [L] K^{L,ML_x}_{ML_{x+1}} \ll 1, \qquad \text{where } [L] = \frac{[L']}{\alpha_{L(H)}}$$

i.e.,

$$K^{L,ML_x}_{ML_{x+1}} \ll \frac{\alpha_{L(H)}}{[L']} \tag{9}$$

Additionally, it is assumed that the dominant side-reaction of the ligand is that with H^+, *i.e.*,

$$\alpha_{L(ML_x)} = 1 + [ML_x] K^{L,ML_x}_{ML_{x+1}} \simeq [ML_x] K^{L,ML_x}_{ML_{x+1}} \ll \alpha_{L(H)} \tag{10}$$

The applicable pH range for the determination of the K_{ML_x} value is therefore restricted to the range where equations (8)–(10) are satisfied simultaneously.

(*a*) $\mathrm{Cu(II)} + \mathrm{L} \rightleftharpoons \mathrm{CuL}$, *where* $\mathrm{L} =$ *glycine*

The pH and pM measurements were performed in a solution containing the metal ions and ligand in an initial concentration ratio of $C_{\mathrm{Cu}}{}^0 : C_{\mathrm{L}}{}^0 = 1:2$. If the complex formation were practically complete, the last term of equation (6) would be zero. If the complexation is not sufficiently complete, the term $[\mathrm{L}']/[(\mathrm{CuL})']$ can be replaced by the value:

$$\frac{[\mathrm{L}']}{[(\mathrm{CuL})']} = \frac{C_{\mathrm{Cu}}{}^0 + [\mathrm{Cu}']}{C_{\mathrm{Cu}}{}^0 - [\mathrm{Cu}']} = \frac{\frac{1}{2}C_{\mathrm{L}}{}^0 + [\mathrm{Cu}']}{\frac{1}{2}C_{\mathrm{L}}{}^0 - [\mathrm{Cu}']} \tag{11}$$

where $[\mathrm{Cu}'] = \alpha_{\mathrm{Cu(OH)}} [\mathrm{Cu}^{2+}]$.

If the pH of the solution is less than approximately 8, $\alpha_{\mathrm{Cu(OH)}} \sim 1$, and (11) reduces to:

$$\frac{[\mathrm{L}']}{[(\mathrm{CuL})']} = \frac{C_{\mathrm{Cu}}{}^0 + [\mathrm{Cu}^{2+}]}{C_{\mathrm{Cu}}{}^0 - [\mathrm{Cu}^{2+}]} = \frac{\frac{1}{2}C_{\mathrm{L}}{}^0 + 10^{-\mathrm{pCu}}}{\frac{1}{2}C_{\mathrm{L}}{}^0 - 10^{-\mathrm{pCu}}} \tag{12}$$

If the pM/pH measurements are performed in the pH range where $\log\alpha_{\mathrm{CuL}} \simeq 0$, equation (6) takes the form:

$$\log K_{\mathrm{ML}} = \mathrm{pCu} + \log\alpha_{\mathrm{L(H)}} - \log \frac{\frac{1}{2}C_{\mathrm{L}}{}^0 + 10^{-\mathrm{pCu}}}{\frac{1}{2}C_{\mathrm{L}}{}^0 - 10^{-\mathrm{pCu}}} \tag{13}$$

Table 1 shows sets of pH and pCu values recorded. The lower pH limit applicable in this case is not imposed because of formation of protonated complexes, but rather because of the limited stability of the CuL complex in acid solutions. The upper pH limit, however, is determined by the two conditions outlined in equations (9) and (10). This will be discussed in section (*b*).

The arithmetic mean value of Table 1 is in good agreement with the values 8·0–8·12 and 8·36 which have been reported[3,5] [at $\mu = 0{\cdot}1$ (potassium nitrate) and at 25°].

Table 1. pH and pCu values for the determination of the stability constant of the 1:1 complex of Cu(II) and glycine. $C_{\mathrm{Cu}}{}^0 = 1{\cdot}0 \times 10^{-4}M$; $C_{\mathrm{L}}{}^0 = 2{\cdot}0 \times 10^{-4}M$, $\mu = 0{\cdot}1$ (potassium nitrate)

pH	$\log\alpha_{\mathrm{L(H)}}$	*E mV*	pCu	$\log\frac{[\mathrm{L}']}{[\mathrm{CuL}]}$ eqn. (12)	$\log K_{\mathrm{CuL}}$ eqn. (13)
5·07	4·63	244·6	4·16	0·74	8·05
5·30	4·40	241·9	4·24	0·57	8·07
5·46	4·24	240·1	4·31	0·47	8·08
5·61	4·09	237·8	4·37	0·40	8·06
5·99	3·71	230·9	4·60	0·22	8·09
6·28	3·42	224·9	4·80	0·14	8·08
Logarithm of arithmetic mean value:					8·07

(*b*) $\mathrm{Cu(II)} + 2\mathrm{L} \rightleftharpoons \mathrm{CuL}_2$, *where* $\mathrm{L} =$ *glycine*

The stability constant for this reaction may in principle be determined by the procedure outlined under section (*a*), *i.e.*, sets of pM and pH values are determined in a solution containing a large excess of the ligand, the pH being varied by addition of potassium hydroxide. If each metal ion does not take up more than two ligand molecules (which in

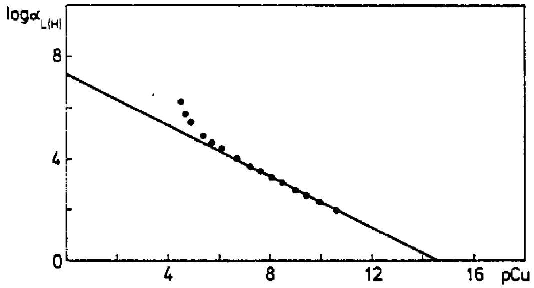

Fig. 2. Determination of the stability constant, K_{CuL_2}, of the mononuclear biligand copper(II)–glycine complex.
$C_{Cu}{}^0 = 5 \times 10^{-5}M$; and $C_L{}^0 = 5 \times 10^{-3}M$; $\mu = 0{\cdot}1$ (potassium nitrate). The y-intercept is 7·30.

this case is justified as it can be shown that $K^{L,CuL_2}_{CuL_3} < 1$) and the complex formed is not very weak, $C_{Cu}{}^0$ can be substituted for $[(CuL_2)']$ and $C_L{}^0 - 2C_{Cu}{}^0$ for $[L']$. The stability constant of the mononuclear biligand complex, K_{CuL_2}, is then given by equation (8) which transforms into:

$$\log K_{CuL_2} = pCu + 2\log\alpha_{L(H)} - \log\frac{(C_L{}^0 - 2C_{Cu}{}^0)^2}{C_{Cu}{}^0} \qquad (14)$$

This equation is applicable, of course, only when $\log\alpha_{CuL_2} \simeq 0$. This condition will, however, likely apply as the formation of mononuclear biligand complexes is generally limited to complexing agents containing few co-ordination centres. Thus, stable basic mononuclear biligand chelates are not common.

Equation (14) may also be rearranged to read:

$$pCu = \log K_{CuL_2} - 2\log\alpha_{L(H)} + \log\frac{(C_L{}^0 - 2C_{Cu}{}^0)^2}{C_{Cu}{}^0} \qquad (15)$$

In the range where $C_{Cu}{}^0 = [(CuL_2)'] = [CuL_2]$, equation (15) predicts that a plot of pCu *vs.* $\log\alpha_{L(H)}$ should give a straight line of slope -2 and a y-intercept equal to $\frac{1}{2}\left(\log K_{CuL_2} + \log\frac{(C_L{}^0 - 2C_{Cu}{}^0)^2}{C_{Cu}{}^0}\right)$.

This graphical relationship is shown in Fig. 2. The y-intercept is 7·30, which for the initial concentrations of $C_L{}^0 = 5 \times 10^{-3}M$ and $C_{Cu}{}^0 = 5 \times 10^{-5}M$ gives $\log K_{CuL_2} = 2 \cdot 7{\cdot}30 - \log 0{\cdot}48 = 14{\cdot}60 + 0{\cdot}32 = 14{\cdot}92$ which is in good agreement with the reported values of 14·9–15·2.[3,5]

When a large excess of ligand is present, the assumption that $[(ML_2)'] \sim C_M{}^0$ is usually justified. If the formation of the biligand complex is incomplete, however, a corrected expression must be used:

$$[(ML_2)'[= C_M{}^0 - [(ML)'] - [M'] \qquad (16)$$

where $[M'] = \alpha_M[M]$ and $[(ML)'] = K_{ML}\frac{\alpha_{ML(H,OH)}}{\alpha_{L(H)}}[M][L']$. $[M]$ is measured, and α_M will usually be equal to $\alpha_{M(OH)}$.

Since the two complex-formation constants for Cu(II) and glycine are $\log K_{\mathrm{CuL}} = 8{\cdot}07$ and $\log K_{\mathrm{CuL_2}} = 14{\cdot}92$, respectively, the stability constant $\log K_{\mathrm{CuL_2}}^{\mathrm{L,CuL}}$ is thus equal to $14{\cdot}92 - 8{\cdot}07 = 6{\cdot}85$ (literature values[3] 6·87–6·91). This constant having been calculated, the pH range within which the K_{CuL} constant may be determined can be derived, as the upper pH limit is imposed by the simultaneous satisfaction of equations (8)–(10).

As $[\mathrm{L}'] \sim 10^{-4}M$, equation (9) yields:

$$K_{\mathrm{CuL_2}}^{\mathrm{L,CuL}} = 10^{6\cdot85} \ll \frac{\alpha_{\mathrm{L(H)}}}{[\mathrm{L}']} = \frac{\alpha_{\mathrm{L(H)}}}{10^{-4}}$$

or

$$\alpha_{\mathrm{L(H)}} \gg 10^{2\cdot85}$$

and equation (10) yields:

$$\alpha_{\mathrm{L(H)}} \gg [\mathrm{ML}]K_{\mathrm{CuL_2}}^{\mathrm{L,CuL}} = 10^{-4} \cdot 10^{6\cdot85} = 10^{2\cdot85}$$

(*i.e.*, the same value since the inital concentrations in this case were chosen in a ratio of $C_{\mathrm{Cu}}{}^0 : C_{\mathrm{L}}{}^0 = 1:2$).

These equations are simultaneously satisfied for pH $\ll 6{\cdot}9$, *i.e.*, the applicable range is in practice pH ~ 5–6.

It is observed that if the last term of equation (13) were constant, the K_{CuL} value could be derived graphically in the same manner as performed under section (*b*), *i.e.*, on the basis of the tangent of slope −1.

(*c*) Cu(II) + L ⇌ CuL, *where* L = EGTA

EGTA [ethyleneglycol bis(2-aminoethylether)tetra-acetic acid] is a sexidentate complexing agent which forms mononuclear monoligand complexes with Cu(II) ions. In addition to the complex CuL, it might be expected that protonated complexes such as CuHL and $\mathrm{CuH_2L}$ can also be formed. A simple and elegant method of graphical evaluation of the stability constants of chelate compounds from pH and pM values has been formulated by Ringbom and Harju.[4] As before, a series of pH and pCu measurements is performed on a solution containing known initial concentrations of Cu(II) and ligand, the pH being gradually varied by addition of either base or acid. The equilibrium constant $K_{\mathrm{CuL}}^{\mathrm{Cu,L}}$ is then given by equation (6), which for $C_{\mathrm{Cu}}{}^0 : C_{\mathrm{L}}{}^0 = 1:2$ and practically complete complex formation is reduced to

$$\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = \mathrm{pCu}_{0\cdot5} + \log \alpha_{\mathrm{L(H)}} - \log \alpha_{\mathrm{CuL(H,OH)}} \qquad (17)$$

or

$$\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}} = \mathrm{pCu}_{0\cdot5} + \log \alpha_{\mathrm{L(H)}} \qquad (18)$$

In Table 2 sets of pH and pCu values are recorded, the pCu values calculated on the basis of the mV readings and the calibration curve. If no protonated (or hydroxo) complexes are formed, the last term of equation (17) is zero and consequently $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = \log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}}$. Thus, if $\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}}$ is plotted as a function of pH, the ordinate of the minimum point of the curve gives directly the value of the stability constant, $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}}$. In Table 2, the values of $\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}}$ are calculated in the fifth column. At low pH values (pH $\leqslant 2$) a correction is necessary since the complex formation cannot be considered complete. This correction is executed according to equation (11). The conditional stability constant as a function of pH is plotted in Fig. 3.

Table 2. pH and pCu values for the determination of the stability constants of the 1:1 complexes of Cu(II) and EGTA. $C_{Cu}{}^{0} = 1{\cdot}0 \times 10^{-3}M$; $C_{L}{}^{0} = 2{\cdot}0 \times 10^{-3}M$; $\mu = 0{\cdot}1$ (potassium nitrate)

pH	*EmV*	pCu	$\log\alpha_{L(H)}$	$\log K^{Cu,L}_{(CuL)'}$	$\log K^{Cu,L}_{(CuL)'}$ (corr.)
1·28	262·5	3·50	18·24	21·74	22·02
1·65	241·2	4·20	16·90	21·10	21·16
2·00	219·3	4·92	15·60	20·52	20·53
2·12	212·4	5·15	15·25	20·40	
2·37	201·1	5·52	14·50	20·02	
2·48	194·6	5·72	14·10	19·82	
2·62	187·2	5·98	13·76	19·74	
2·75	183·1	6·12	13·40	19·52	
2·82	179·5	6·23	13·20	19·43	
3·01	172·8	6·45	12·68	19·13	
3·20	166·5	6·67	12·25	18·92	
3·22	165·8	6·68	12·20	18·88	
3·44	156·6	7·00	11·70	18·70	
3·81	144·2	7·40	10·90	18·30	
4·21	128·8	7·90	10·05	17·95	
4·60	111·8	8·47	9·25	17·72	
4·85	99·4	8·87	8·75	17·62	
5·20	81·6	9·46	8·10	17·56	
5·61	60·0	10·16	7·25	17·41	
5·88	46·8	10·60	6·70	17·30	
6·30	23·0	11·37	5·90	17·27	
9·50	−132·0	16·48	0·32	16·80	
9·98	−137·7	16·65	0·14	16·79	

It is observed that between pH ~ 6·5 (adjusted with potsasium hydroxide) and pH 9·5 (adjusted with ammonia buffer) no points are plotted. This is because within this pH range the copper ion activity becomes so low that the Selectrode is no longer capable of measuring

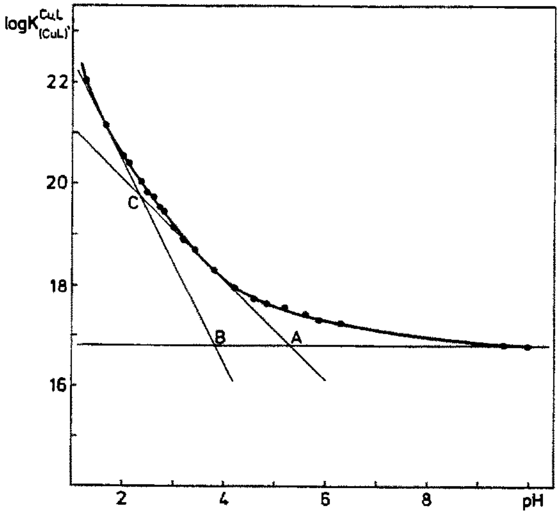

Fig. 3. Log$K^{Cu,L}_{(CuL)'}$ of EGTA calculated from pCu as a function of pH.

it, *i.e.*, pCu is larger than *ca.* 13. Owing to the sensitivity of the Selectrode in ammonia solutions, however, reliable values can be obtained in these media, as verified by the calibration curve.

The curve of Fig. 3 is horizontal above pH 9, with a sharp rise below this value, proving the existence of protonated complexes. No hydroxo complexes, however, are formed (below pH 10). The ordinate at the minimum gives the value of the stability constant, hence $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = 16{\cdot}80$ (literature values[2,6,7] 17–17·8).

The curvature of the plot indicates that complexes with one and two protons are formed. Since the relationship between $\alpha_{\mathrm{CuL(H)}}$ and the two protonation constants, $K_{\mathrm{CuHL}}^{\mathrm{H,CuL}}$ and $K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}}$ is given by:

$$\alpha_{\mathrm{CuL(H)}} = 1 + [\mathrm{H}]K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} + [\mathrm{H}]^2 K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}} \tag{19}$$

it is furthermore possible to read these two constants directly from Fig. 3 without any calculations [*cf* equations (17) and (18)] provided the two values are not too close to each other. If this condition is fulfilled, pH ranges may be chosen where one of the last two terms will be dominant. Thus, for the determination of the constant $\log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}}$, equations (17)–(19) yield:

$$\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log \alpha_{\mathrm{CuL(H)}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log([\mathrm{H}]K_{\mathrm{CuHL}}^{\mathrm{H,CuL}})$$

or

$$\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} - \mathrm{pH} \tag{20}$$

i.e., the tangent of slope −1 to the curve is simply extended to its point of intersection with the horizontal line through the ordinate $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}}$ (point A), yielding $\log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} = 5{\cdot}30$ (literature values[2,8] 4·28–4·4). If two protons are taken up, the last term in (19) will predominate and the slope will be −2 since equations (17)–(19) now give:

$$\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log \alpha_{\mathrm{CuL(H)}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log([\mathrm{H}]^2 K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}})$$

or

$$\log K_{\mathrm{(CuL)'}}^{\mathrm{Cu,L}} = \log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} + \log K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}} - 2\mathrm{pH} \tag{21}$$

This is the case at the extreme left and the constant can be determined in a similar way, *i.e.*, $\log K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}} = 2 \times 3{\cdot}82 = 7{\cdot}64$ (point B). The abscissa of the point of the intersection of the two straight lines (point C) equals 2·34; hence $\log K_{\mathrm{CuH_2L}}^{\mathrm{H,CuHL}} = 2{\cdot}34$. For these two latter constants no values are recorded in the literature.

Based on the determination of these constants, the following stability constants may be calculated:

$$\begin{aligned} K_{\mathrm{CuHL}}^{\mathrm{Cu,HL}} &= K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} \cdot K_{\mathrm{CuL}}^{\mathrm{Cu,L}} \cdot \frac{1}{K_1} \\ &= 12{\cdot}56 \text{ (literature value}^{8}\text{ 12·61)} \end{aligned} \tag{22}$$

where K_1 is the acidity constant ($\log K_1 = 9{\cdot}54$). Also:

$$\begin{aligned} K_{\mathrm{CuH_2L}}^{\mathrm{Cu,H_2L}} &= K_{\mathrm{CuH_2L}}^{\mathrm{2H,CuL}} \cdot K_{\mathrm{CuL}}^{\mathrm{Cu,L}} \cdot \frac{1}{K_1 K_2} \\ &= 5{\cdot}97 \ (\log K_2 = 8{\cdot}93). \end{aligned} \tag{23}$$

No value for this constant is recorded in the literature.

The graphical method based on extrapolated tangents gives correct constants only if the differences between the values of successive protonation constants are sufficiently large. This will generally be the case if the ΔpH between the abscissae of two intersecting points (in this example A and C) is larger than 2 (as the correction then will be less than 0·1 logarithmic unit[4]). The difference in this case is *ca.* 3 so that no corrections were found necessary.

(*d*) *Replacement reactions*

By monitoring a titration with an electrode sensitive to ion M_I, a solution of the cation M_{II} can be titrated with the ligand L by adding a small amount of M_IL as indicator.[1] A necessary prerequisite is that $K'_{M_IL} > K'_{M_{II}L} \gg 1/K'_{HL}$. If it can be assumed that this condition is fulfilled, an electrode such as the Cu(II) Selectrode may equally well be used to determine complex-formation constants on the basis of the replacement reaction:

$$CuL + M_{II} \rightleftharpoons Cu + M_{II}L$$

where the copper(II) ion activity is measured by the Selectrode.

The equilibrium constant of this reaction is:

$$K = \frac{[Cu'][(M_{II}L)']}{[(CuL)'][M_{II}']} = \frac{K'_{M_{II}L}}{K'_{CuL}} = \frac{K_{M_{II}L}}{K_{CuL}} \cdot \frac{\alpha_{M_{II}L}\alpha_{Cu}}{\alpha_{CuL}\alpha_{M_{II}}} \tag{24}$$

If the initial concentrations of the complex and the metal ion are denoted by $[CuL]^0$ and $[M_{II}]^0$, respectively, and if the conditions are selected so that the species do not participate in any side-reactions, the calculation of the constant $K_{M_{II}L}$ is especially simple since:

$$K_{M_{II}L} = K_{CuL} \cdot K = K_{CuL} \frac{[Cu^{2+}]^2}{([CuL]^0 - [Cu^{2+}])([M_{II}]^0 - [Cu^{2+}])} \tag{25}$$

where $[Cu^{2+}]$ is the copper-ion concentration as determined by the Cu(II) Selectrode (*i.e.*, the ionic strength is kept constant and the copper concentration derived on the basis of the calibration curve).

The stability constants of the Ca(II) and Zn(II) complexes with EDTA were determined by this method. To a solution of the metal nitrate a small amount of CuEDTA was added, and the ionic strength was adjusted to 0·1 with potassium nitrate. Corresponding measurements of pCu and pH were made, the pH being varied by small additions of potassium hydroxide or nitric acid. If the conditions for equation (25) are satisfied, a constant potential is recorded over a certain pH range, the width of which depends upon the concentration and nature of the individual species. The copper concentration corresponding to this constant potential was used for the calculation of $K_{M_{II}L}$ according to equation (25).

For the determination of K_{ZnEDTA} ($\mu = 0{\cdot}1$), the following initial concentrations were used: $[Zn^{2+}]^0 = [CuEDTA]^0 = 2{\cdot}5 \times 10^{-3}M$. Between pH 2·6 and 5·2 a constant potential of 256·5 mV was recorded, corresponding to a pCu value of 3·78. Inserted in equation (25) this gives a value of $\log K_{ZnEDTA} = 16{\cdot}50$ (literature value[2] 16·5)

In the case of calcium, concentrations of $[Ca^{2+}]^0 = 0{\cdot}033M$ and $[CuEDTA]^0 = 2{\cdot}5 \times 10^{-3}M$ were used. Between pH 6·5 and 6·9 a constant potential of 166·0 mV was recorded, corresponding to a pCu value of 6·78. From (25) the value $\log K_{CaEDTA} = 10{\cdot}78$ at $\mu = 0{\cdot}1$ was calculated (literature value[2] 10·7).

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Zusammenfassung—Die Kupfer(II)-"Selektrode", die bei verschiedenen pH-Werten in einer Reihe von Cu(II)-Puffern geeicht war, wurde zur Bestimmung der Stabilitätskonstanten der Kupfer(II)-Komplexe von Glycin und EGTA bei einer Ionenstärke von 0,1 verwendet. Es werden Methoden angegeben, um aus pH- und pM-Werten die Stabilitätskonstanten von Chelatkomplexen zu berechnen. Die erhaltenen Werte schneiden beim Vergleich mit den in der Literatur aufgezeichneten sehr gut ab. Im System Cu(II)-EGTA, bei dem nur einige wenige Stabilitätskonstanten bestimmt waren, wurden folgende Konstanten gefunden: $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = 16{,}80$; $\log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} = 5{,}30$; $\log K_{\mathrm{CuH2L}}^{\mathrm{2H,CuL}} = 7{,}64$; $\log K_{\mathrm{CuH2L}}^{\mathrm{H,CuHL}} = 2{,}34$; $\log K_{\mathrm{CuHL}}^{\mathrm{Cu,HL}} = 12{,}56$; $\log K_{\mathrm{CuH2L}}^{\mathrm{H2L}} = 59{,}7$. Beispiele für die Verwendung der Cu(II)-Selektrode bei Verdrängungsreaktionen werden geschildert.

Résumé—On a utilisé la Sélectrode de Cu (II), étalonnée dans une série de tampons Cu (II) à diverses valeurs de pH, pour la détermination des constantes de stabilité des complexes Cu (II) de la glycine et de l'EGTA à une force ionique de 0, 1. On présente les méthodes pour le calcul des constantes de stabilité des complexes chélatés à partir des valeurs de pH et de pM. Les valeurs obtenues sont très favorablement comparables à celles rapportées dans la littérature. Pour le système Cu (II)–EGTA, pour lequel seulement un petit nombre de constantes de stabilité ont été déterminées, on a trouvé les constantes suivantes: $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = 16{,}80$; $\log K_{\mathrm{CuHL}}^{\mathrm{H,Cu,L}} = 5, 30$; $\log K_{\mathrm{CuH2L}}^{\mathrm{2H,CuL}} = 7, 64$; $\log K_{\mathrm{CuH2L}}^{\mathrm{H,CuHL}} = 2, 34$; $\log K_{\mathrm{CuHL}}^{\mathrm{Cu,HL}} = 12{,}56$; et $\log K_{\mathrm{CuH2L}}^{\mathrm{Cu,H2L}} = 5, 97$. Des exemples de l'application de la Sélectrode Cu (II) dans des réactions de remplacement sont présentés.

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TRIEN AND TETREN AS TITRANTS IN POTENTIOMETRY WITH A SILVER INDICATOR ELECTRODE

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Summary—The possibility of application of triethylenetetramine (TRIEN) and tetraethylenepentamine (TETREN) in metal titrations with the silver electrode as indicator was investigated. Copper, cadmium and zinc were determined in the presence of calcium, magnesium, aluminium and iron(III) in the concentration range from 0·02 to 2m*M*. The errors did not exceed 1 %. On a similar basis copper and iron may be successfully determined in their mixtures under carefully controlled conditions. Copper is titrated with TRIEN, and both metals with EDTA at pH 7·5–8·0 in sulphosalicylate medium. The results obtained were in good agreement with those theoretically predicted.

In parallel to the development of new potentiometric sensors, interesting and analytically promising results in titrimetry may be obtained by the use of various complexing titrants. In this respect aliphatic polyamines show advantageous properties and may be used for determination of transition metals in the presence of elements of the main groups, which have lower affinity for nitrogen donors.

Reilley and Sheldon[1] have used triethylenetetramine (TRIEN), and Reilley and Vavoulis[2] have used tetraethylenepentamine (TETREN), as metal titrants, with the mercury indicator electrode. They have shown that calcium, magnesium, aluminium and lanthanum do not interfere in the determination of transition metals.

The selectivity of amines as titrants is connected with the stability constants of the metal complexes, which were investigated by several authors[3–5] (Table 1). The higher stability of the silver complex should favour the use of the silver electrode for monitoring the course of titration, improving the end-point potential jump.[6] The silver indicator electrode has

Table 1. Stability constants of polyamine complexes (Ringbom)[16]

Cation	TRIEN			TETREN	
	log β_1	log β_2	log K^{H}_{MHL}	log β_1	log K^{H}_{MHL}
Ag^+	7·7		8·1	7·4	8·3*
Cd^{2+}	10·75	13·9	6·4	14·0	
Cu^{2+}	20·4		3·6	24·3	5·6
Hg^{2+}	25·26		5·6	27·7	
Zn^{2+}	12·1		5·2	15·4	

* Additional constants for protonated complexes[16] $K^{2H}_{AgH2L} = 10^{15 \cdot 8}$, $K^{3H}_{AgH3L} = 10^{21 \cdot 3}$.

been used several times in EDTA titrations, even for concentration as low as $10^{-5}M$.[7-9] Among other titrants EGTA was claimed as advantageous for calcium titration in the presence of magnesium.[10,11] DTPA was found useful in automatic determination of alkaline earths,[12] and for lead in the presence of aluminium.[13]

In this paper the titration with TRIEN and TETREN of individual metal ions and their mixtures, using the silver indicator electrode, is discussed. The titration curves are considered in terms of the equation previously derived[6] and its validity for these systems is checked.

EXPERIMENTAL

Reagents and apparatus

TRIEN solutions were prepared by dissolving TRIEN sulphate in $0{\cdot}04M$ sodium hydroxide. The reagent was purified according to Reilley and Sheldon[1] and the solutions were standardized potentiometrically, using the mercury indicator electrode and standard copper nitrate solution.

TETREN solutions were prepared similarly by dissolving TETREN sulphate in water, and adding sodium hydroxide till the pH was 7·0. TETREN (Koch Light) was purified according to Reilley and Vavoulis,[2] and the solutions were standardized as for TRIEN.

EDTA and DTPA solutions were prepared as usual and standardized with zinc nitrate solution.

Metal ion solutions were prepared as nitrates and standardized complexometrically with EDTA, using the mercury indicator electrode.

All solutions were prepared from analytically pure reagents and doubly distilled water. The saturated borax solution was prepared from the twice-crystallized reagent.

The silver electrode was prepared as previously described.[9] The reference electrode was a Radiometer saturated calomel electrode K 401.

Procedure

The sample should contain 0·002–0·2 mmole of the metal to be determined, in the form of a salt of which the anion does not react significantly with silver. To the sample in a 250-ml beaker 1 ml of $10^{-4}M$ silver nitrate is added. This makes it necessary to take into account a correction equal to 0·1 μmole of the titrant. For more dilute solutions it is recommended to add the indicator ion in the form of its TRIEN or TETREN complex. To the sample 50 ml of saturated borax solution is added and after dilution to the total volume of about 100 ml the sample is titrated with a $0{\cdot}001$–$0{\cdot}05M$ titrant depending on the concentration of the sample. The end-point is determined graphically from the intersection of the two branches of the asymmetrical titration curve. In the case of the symmetrical titration curve the end-point should be obtained by using the first derivative method or the Gran procedure.

DISCUSSION AND RESULTS

Choice of titration conditions of individual ions

As representative ions, Cu^{2+}, Cd^{2+} and Zn^{2+} were titrated with TRIEN and TETREN. In our previous paper[9] it was found that a borax buffer of pH 9–10 is the most convenient medium for titrations in which the silver indicator electrode is used, because silver forms rather weak complexes with the ligands used.[14] A decrease in the borax concentration improves the potential jump and a half-saturated solution was found the best. Further decrease of the borax concentration significantly influences the rate of potential establishment, and a threefold dilution makes the titration impossible. Nevertheless titration is also possible in unbuffered solution, but seems rather impractical because of instability of the conditions (see Fig. 7).

In all the titrations mentioned the titration curves were asymmetrical. Results correct within ±1 % may be obtained for amounts from 0·0025 to 0·2 mmole in 100 ml (Table 2). The asymmetry of the titration curve is most pronounced in the case of copper, but the end-point can easily be found by extrapolation of the two nearly linear parts of the curve, even for $2 \times 10^{-5}M$ solution. Some titration curves of Zn^{2+} with TETREN are shown in Fig. 1.

Table 2. Polyamine titrations in the absence of interfering ions

Ion determined	Taken, *mmole*	Titrant: TRIEN Found, *mmole*	Titrant: TRIEN Error, %	Titrant: TETREN Found, *mmole*	Titrant: TETREN Error, %
Cd^{2+}	0·1977	0·1981	+0·2	0·1976	−0
		0·2011	+1·2		
	0·0988	0·0986	−0·2	0·0985	−0·3
		0·0987	−0·1		
	0·04940	0·04973	+0·8	0·04920	−0·4
		0·04928	−0·2		
	0·00988			0·00986	−0·2
	0·00494			0·00500	+1·2
Cu^{2+}	0·2066	0·2063	−0·15	0·2065	−0
		0·2059	+0·3		
	0·1033	0·1036	−0·3	0·1026	−0·6
		0·1038	+0·8	0·1034	+0·2
	0·05165	0·05154	−0·2	0·05165	0
		0·05163	0·0		
	0·01033	0·01031	−0·2	0·01045	+1·1
		0·01024	−0·8		
	0·00250	0·002570	+2·9		
		0·002530	+1·1		
Zn^{2+}	0·2002	0·1991	−0·5	0·2000	−0·1
		0·2001	−0·1		
	0·1001	0·1004	+0·3	0·0999	−0·2
	0·05005	0·05009	+0.1	0·05003	0·0
	0·01001			0·00994	−0·7
	0·00500	0·00483	−3·4	0·00503	+0·6
		0·00489	−0·7		
	0·00250	0·00248	−0·8		

Theoretical treatment of experimental data

In determination of a given ion the symmetrical or asymmetrical shape of the titration curve depends on whether the conditional stability constant of the indicator ion complex is greater or smaller than that of the ion determined. For the silver electrode used in our experiments the values of the conditional constants of the silver complex (K'_{AgY}) are rather small (Fig. 2) and do not exceed the values for the Cu^{2+}, Cd^{2+} and Zn^{2+} complexes. Therefore[6] the potential change $\Delta E_{1/2,2}$ obtained in titrations of metals of total concentration C_M is given by the equation:

$$\Delta E_{1/2,2} = \frac{RT}{F} \ln(C_M \cdot K'_{AgY})$$

indicating that it is best to perform titrations with TETREN and TRIEN at pH 9–10. The effect of the conditional constant for the silver complex is clearly seen when titration curves of the same ion but for different titrants (forming silver complexes of different stability) are compared (Fig. 3). The good agreement of experimental and calculated potential changes ($\Delta E_{1/2,2}$) is shown by a linear regression line, which may not be limited to polyamine titrants but also extend to some polyaminopolycarboxylic titrants.

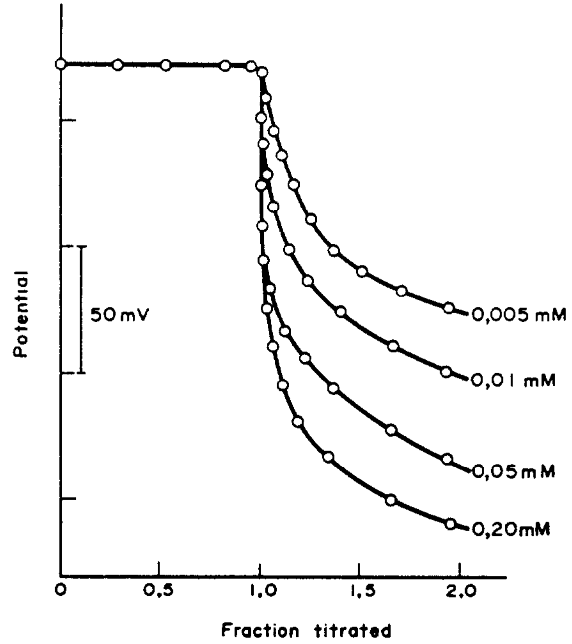

Fig. 1. Titration of zinc in various concentrations with TETREN at pH 9·0 in half-saturated borax medium, $C_{Ag} = 10^{-6}M$, $V = 100$ ml, silver indicator electrode.

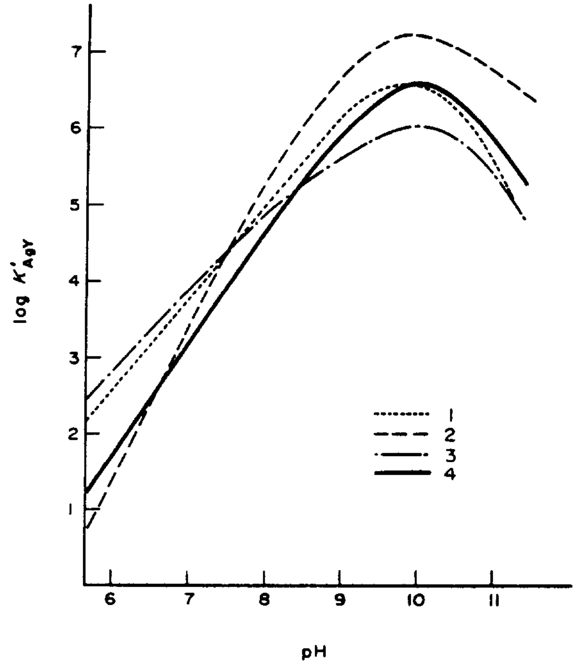

Fig. 2. Change of conditional stability constants of silver complexes with pH. 1—TETREN, 2—DTPA, 3—EDTA, 4—TRIEN.

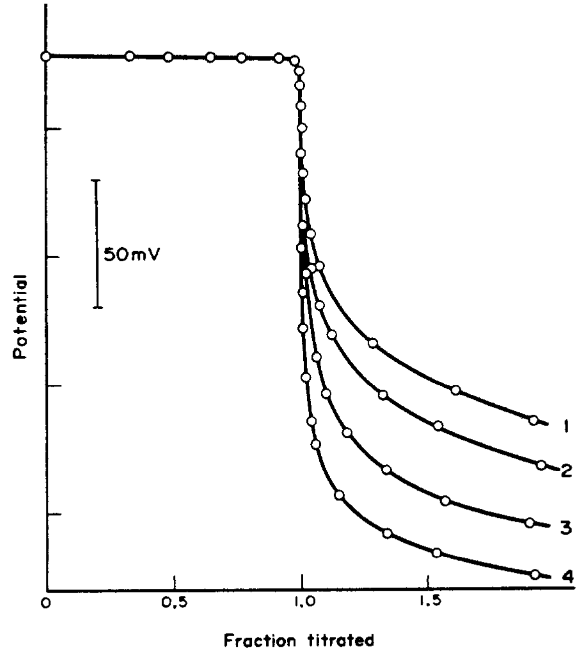

Fig. 3. Titration of 0·1M copper with various titrants: 1—EDTA, 2—TRIEN, 3—TETREN, 4—DPTA. Other conditions as for Fig. 1.

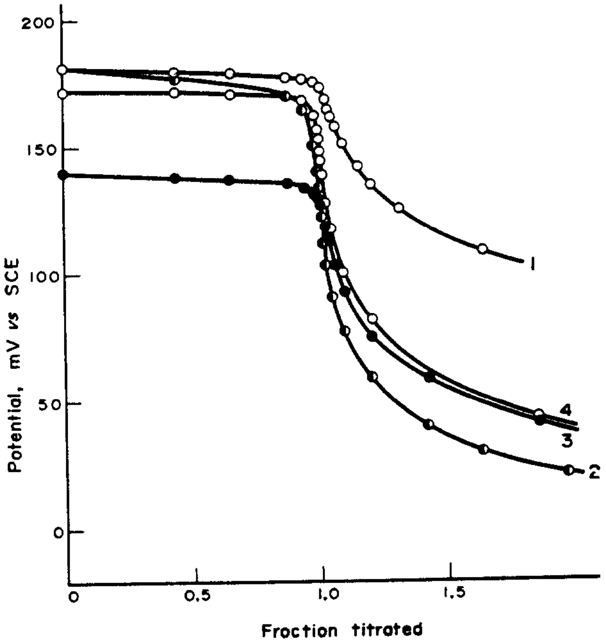

Fig. 4. Titration of 0·1mM cadmium with TRIEN in the presence of interfering ions: *1*—1·0mM Ca^{2+} + 1·0mM Mg^{2+}, pH 8·0; *2*—0·1mM Al^{3+}, pH 9·2; *3*—1·0mM Al^{3+}, 0·05M acetylacetone, pH 8·7; *4*—0·1mM Fe^{3+}, 0·01M sulphosalicylate, pH 9·0. In all titrations: $C_{Ag} = 10^{-6}M$, $V = 100$ ml, half-saturated borax, silver indicator electrode.

Titration of Cu^{2+}, Cd^{2+} and Zn^{2+} in presence of other ions

From theoretical consideration it follows that Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} should not interfere in titration of ions which complex preferentially through nitrogen donors.

TRIEN. Tenfold excess of calcium and magnesium does not interfere in titration of Cu^{2+}, Cd^{2+} or Zn^{2+} at pH 8. The use of higher pH values is rather undesirable because the reaction becomes sluggish, even at pH 8.5. The presence of aluminium in equimolar amounts interferes, except for titration of Cu^{2+}, because the reaction becomes slow. In the case of Cd^{2+} determination, this can be prevented by the use of acetylacetone as a masking agent, but not for Zn^{2+}, which is too strongly complexed by this masking ligand. The presence of iron(III) needs addition of sulphosalicylic acid for masking, which also complexes copper significantly, making the titration curve symmetrical. Some examples of titration curves are given in Fig. 4, and the results in Table 3.

Table 3. TRIEN titrations in the presence of interfering ions

Ion determined	Foreign ions, *mmole*	Masking agent, *M*	pH	Amount of ion determined *mmole* Taken	Found	Error %
Cd^{2+}	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0	0·0968	0·0966	−0·2
	0.1 Al^{3+}	—	9·2		0·0965	−0·3
	0·1 Al^{3+}	—	9·2		0·0966	−0·2
	1·0 Al^{3+}	0·05 acac*	8·7		0·0963	−0·5
	0·1 Fe^{3+}	0·01 sulphosal†	9·0		0·0971	+0·3
Cu^{2+}	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0	0·1033	0·1031	−0·2
	0·1 Al^{3+}	—	9·1		0·1027	−0·5
	0·1 Fe^{3+}	0·01 sulphosal	8·8		0·1030	−0·3
	0·1 Fe^{3+}	0·01 sulphosal	8·8		0·1031	−0·2
Zn^{2+}	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0	0·0994	0·0997	+0·3
	0·1 Al^{3+}	—	9·1		0·0985	−0·9
	0·1 Fe^{3+}	0·01 sulphosal	8·9		0·0992	−0·2

* acac = acetylacetone.
† sulphosal = sulphosalicylic acid.

TETREN. In general the conclusions are similar to those for TRIEN. Some improvement in the rate of Cd^{2+} titration may be observed when succinate is added first, which complexes the interfering elements in a small but sufficient degree. When iron(III) is present sulphosalicylic acid should be used. In Table 4 corresponding results are given. For both titrants the error does not exceed 1% and is <0·5% for 70% of measurements.

Potentiometric titration of Cu^{2+} and Fe^{3+} in mixtures

At pH 8.8 copper may be titrated successfully with TRIEN when comparable amounts of iron(III) are masked with sulphosalicylic acid (Fig. 5). With EDTA as titrant both metals may be titrated when conditions are carefully controlled. At pH 7·5–8·0 and sulphosalicylic acid concentrations from 0·01 to 0·05*M* the yellow iron(III) complex is

Table 4. TETREN titrations in the presence of interfering ions

Ion determined	Foreign ions, *mmole*	Masking agent, *M*	pH	Amount of ion determined, *mmole* Taken	Found	Error, %
Cd^{2+}	1·0 Ca^{2+}	—	10·8	0·0969	0·0965	−0·4
	1·0 Ca^{2+}	0·05 succinate	8·6		0·0977	+0·8
	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	10·0		0·0966	−0·3
	0·1 Al^{3+}	—	9·0		0·0971	+0·2
	1·0 Al^{3+}	0·05 acac	8·6		0·0972	+0·3
	0·1 Fe^{3+}	—	9·0		0·0975	+0·6
	0·1 Fe^{3+}	0·05 sulphosal	8·0		0·0967	−0·2
	0·1 Fe^{3+}	0·004 TEA	9·1		0·0978	+0·9
Cu^{2+}	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0	0·1033	0·1040	+0·7
	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0		0·1042	+0·9
	0·1 Al^{3+}	—	9·1		0·1031	−0·2
	0·1 Fe^{3+}	0·01 sulphosal	8·8		0·1026	−0·7
Zn^{2+}	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	9·0	0·0995	0·0995	0
	1·0 Ca^{2+} + 1·0 Mg^{2+}	—	8·0		0·1007	+1·2
	0·1 Al^{3+}	0·05 acac	9·0		0·1002	+0·7
	0·1 Fe^{3+}	0·01 sulphosal	9·0		0·0992	−0·3

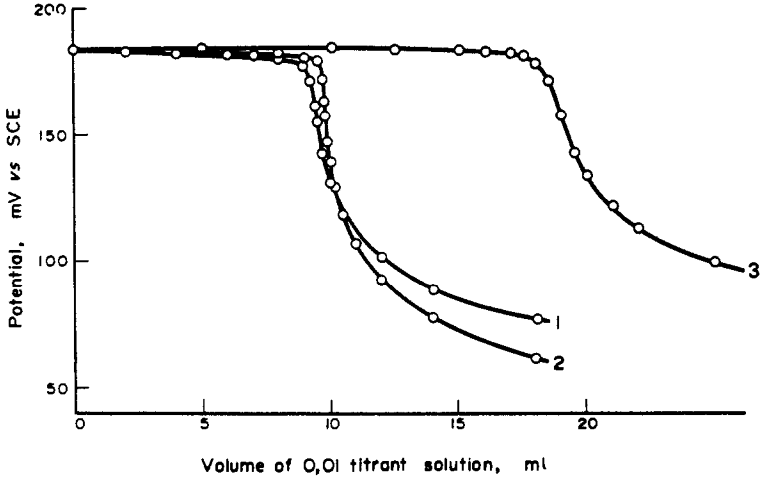

Fig. 5. Titrations of copper and iron(III) using silver indicator electrode. *1*—0·1m*M* Fe^{3+}, 0·01*M* sulphosalicylate, pH 8·0, titrant EDTA; *2*—0·1m*M* Cu^{2+} + 0·1m*M* Fe^{3+}, 0·001*M* sulphosalicylate, pH 8·8, titrant TRIEN; *3*—0·1m*M* Cu^{2+} + 0·1m*M* Fe^{3+}, 0·05*M* sulphosalicylate, pH 8·0, titrant EDTA. In all titrations $C_{Ag} = 10^{-6}M$, half-saturated borax, $V = 100$ ml.

sufficiently stable to prevent formation of the hydroxide but it still reacts quantitatively with the titrant. At pH < 7·5 the potential change at the equivalence point is too small, whereas at pH > 8·0 the formation of hydroxo-complexes significantly inhibits the rate of titration, even at 50–60°. On this basis both ions in mixtures can be titrated, the sum with EDTA as titrant, and TRIEN for copper.

Table 5. Determination of copper and iron in mixtures

Titrant	Taken, *mmole* Cu	Taken, *mmole* Fe	pH	[sulphosalicylate], *M*	Found, *mmole*	Error, %
EDTA		0·1016	8·2	0·01	0·1006 Fe	−1·0
		0·0998	7·0	0·05	0·0999 Fe	+0·1
		0·0998	7·5	0·05	0·0996 Fe	−0·2
		0.0998	8·0	0·05	0·0987 Fe	−1·0
	0·1034	0·1016	8·0	0·05	0·2066 Cu + Fe	+0·8
	0·1034	0·1016	8·0	0·05	0·2060 Cu + Fe	+0·5
TRIEN	0·1033	0·0998	8·8	0·01	0·1030 Cu	−0·3
	0·1033	0·0998	8·8	0·01	0·1031 Cu	−0·2

CONCLUSIONS

The application of the silver indicator electrode in titrations with polyamines offers several advantages compared to methods previously used. TRIEN and especially TETREN give a greater potential change than EDTA, approaching the magnitude of the end-point jump found with DTPA. Compared with the polyaminopolycarboxylic acids as titrants, polyamines permit determination of ions in several mixtures which are difficult to analyse with EDTA as titrant.

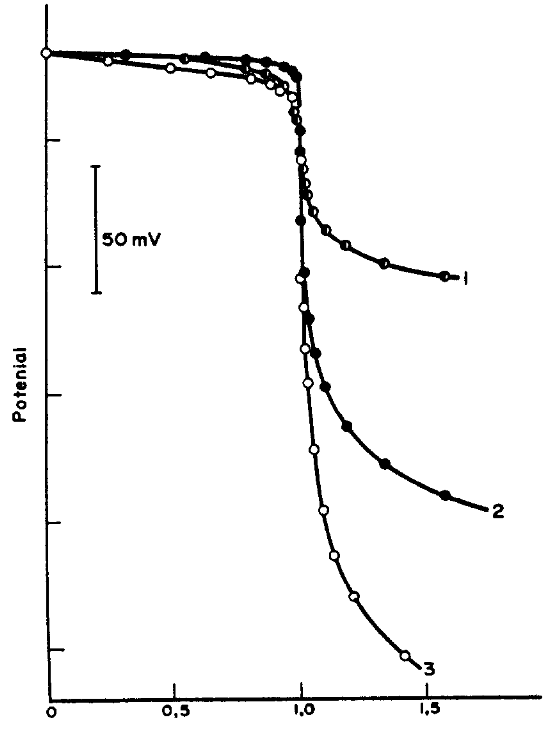

Fig. 6. Titrations with TETREN as titrant, using various indicator electrodes. 1—mercury electrode, pH 4·6, acetate buffer; 2—silver electrode, pH 9·0, half-saturated borax; 3—silver electrode, pH at the end-point 9·1, unbuffered solution. In all titrations $V = 100$ ml.

The replacement of the mercury electrode by the silver electrode bears some advantages. The potential change is in general greater (Fig. 6), improving the precision. The potential readings with the silver electrode are usually more stable,[12], improving the process of titration. The negative potential range is more easily accessible even when the solution is not carefully deaerated. Finally, no undesirable precipitates are formed on the electrode surface, such as those observed on the mercury electrode surface and causing positive errors.[17]

The one drawback of the silver indicator electrode is the difficulty of masking, and application of the procedure to mixtures of ions. In this respect the mercury electrode seems to be superior, but the use of polyamines described in this paper still offers some advantage.

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Zusammenfassung—Die Verwendbarkeit von Triäthylentetramin (TRIEN) und Tetraäthylenpentamin (TETREN) bei Metalltitrationen mit der Silberelektrode als Indikator wurde untersucht. Kupfer, Cadmium und Zink wurden in Gegenwart von Calcium, Magnesium, Aluminium und Eisen(III) im Konzentrationsbereich 0,02 bis 2 mM bestimmt. Die Fehler überstiegen 1% nicht. Auf ähnlicher Grundlage können Kupfer und Eisen in ihren Mischungen unter sorgfältig kontrollierten Bedingungen mit Erfolg bestimmt werden. Kupfer wird mit TRIEN, beide Metalle werden mit EDTA bei pH 7,5–8,0 in Sulfosalicylat-Medium titriert. Die erhaltenen Ergebnisse stimmten mit den theoretisch vorhergesagten gut überein.

Résumé—On a étudié la possibilité d'application de la triéthylènetétramine (TRIEN) et de la tétraéthylènepentamine (TETREN) dans le titrage de métaux avec l'électrode d'argent comme indicateur. On a dosé les cuivre, cadmium et zinc en la présence de calcium, magnésium, aluminium et fer (III) dans le domaine de concentration de 0,02 à 2 m*M*. Les erreurs n'excèdent pas 1 %. Sur une base semblable, on peut déterminer avec succès le cuivre et le fer dans leurs mélanges dans des conditions soigneusement contrôlées. Le cuivre est dosé par le TRIEN, et les deux métaux par l'EDTA à pH 7,5—8,0 en milieu sulfosalicylate. Les résultats obtenus sont en bon accord avec ceux prévus théoriquement.

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SELECTIVE SEPARATION OF URANIUM FROM OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROBROMIC ACID AND HYDROCHLORIC ACID–ACETONE MIXTURES

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Summary—U(VI) can be separated from Ga, Fe(III), Bi, Pb, Cd, Zn, Cu(II) and Au(III) by quantitative elution with 0·50*M* HBr in 86% acetone or with 0·35*M* HBr in 90% acetone from a column of AG50W-X4 cation-exchange resin of 200–400 mesh particle size. U(VI) and many other ions are retained. U(VI) then can be eluted selectively with 0·50*M* HCl in 83% acetone or with 0·35*M* HCl in 85% acetone. Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th and La are quantitatively retained by the column. These elements then can be eluted with 5*M* HNO_3. At the higher acid concentration (0·50*M*) the separation between U(VI) and Li is not satisfactory but is excellent at the lower acid concentration; the U(VI) peak is sharper at the higher acid concentration. Separations are sharp and quantitative, as is demonstrated by results for some synthetic mixtures. Distribution coefficients and elution curves are presented.

The selective separation of uranium from other elements has received considerable attention during the last fifteen years. The widely known anion-exchange procedure in sulphate solution[1] has been made more selective by substituting 0·25*M* sulphuric acid[2] for the acid ammonium sulphate used originally. Some elements such as Zr and Hf, which accompany U(VI) in the sulphate anion-exchange procedure, can be separated by anion-exchange in aqueous hydrochloric acid together with many other elements, according to the distribution coefficients published by Kraus *et al.*[3,4]. Other metals are eluted with 4*M* hydrochloric acid and U(VI) with 1*M* hydrochloric acid, but Fe(III), Mo(VI), W(VI), Ga, In, and Pb are not completely separated from U(VI) by this procedure. Attempts have been made to improve the selectivity of the anion-exchange separation of U(VI) in hydrochloric acid and also in nitric acid by adding water-miscible organic solvents. A comprehensive summary of the available procedures is given by Korkisch.[5] Probably the most selective anion-exchange procedure is that using Dowex 1-X8 resin and hydrochloric acid–methyl glycol mixtures for eluting many species, including Fe(III), while U(VI) is retained and is eluted with 1·0*M* hydrochloric acid.[6,7] Of more than 20 ions investigated, only Pb(II) accompanies U(VI). but the suggested elution volumes for In, Mn(II) and Cu(II) are rather large for the small columns used.[6] Only a limited number of ions can be separated from U(VI) by cation-exchange procedures in aqueous media. The best selectivity is obtained in aqueous sulphuric acid by eluting U(VI) with 0·50*M* acid.[8] A very selective procedure has been described by Korkisch *et al.*[9] who use 0·6*M* nitric acid in 90% tetrahydrofuran for the elution of Au(III), Mo(VI), V(V) and the platinum metals. U(VI) is then eluted with the same reagent, while many other elements are strongly retained by the column. Only Bi has been claimed to accompany U(VI) in this procedure, but the distribution coefficient for U(VI) (40) is rather high and comparatively large elution volumes are required.

During a systematic study of cation-exchange distribution in hydrobromic acid–acetone mixtures it was observed that at fairly high acetone concentrations U(VI) is adsorbed more strongly from hydrobromic acid–acetone mixtures than from the corresponding hydrochloric–acetone mixtures. This fact has been utilized for a very selective separation of U(VI) from other ions. In the first step a large number of ions, including Cu(II), which is eluted together with U(VI) in hydrochloric acid–acetone, and also Pb and Bi, are eluted with hydrobromic acid–acetone, while U(VI) is retained. In the second step U(VI) is eluted selectively from the same column with hydrochloric acid–acetone, while many other ions are retained. This is a simple single-column procedure in which additional selectivity is obtained by changing from one selectivity sequence to another. Korkisch *et al.*[10] have studied the cation–hydrobromic acid–organic solvent mixtures (including acetone) and have suggested 0·9*M* hydrobromic acid in 90% aqueous acetone for separation of U(VI) from Fe(III), but no quantitative separations appear to have been done.

EXPERIMENTAL

Reagents and apparatus

The resins used were the AG50W-X8 and AG50W-X4 sulphonated polystyrene cation-exchangers marketed by BioRad Laboratories of Richmond, California. Resin of 100–200 mesh particle size was used for determination of distribution coefficients and of 200–400 mesh for column work. The resin used for column work was stirred in a beaker with 0·01*M* nitric acid containing 50% acetone (v/v) and the slurry transferred into the column with the same reagent. Borosilicate glass tubes of about 20 mm bore with fused-in glass sinters of No. 2 porosity and a burette tap at the bottom, and a B19 ground-glass joint at the top, were used as columns. All chemicals used were of analytical-reagent grade purity.

Atomic-absorption measurements were carried out on a Perkin–Elmer 303 instrument and for spectrophotometric determinations a Zeiss PMQII spectrophotometer was used.

RESULTS

Distribution coefficients with -X8 resin

An inspection of known distribution coefficients with AG50W-X8 resin in hydrochloric acid–acetone[11] and hydrobromic acid–acetone[12] mixtures seemed to indicate that good separations with large separation factors could be obtained in 0·5*M* acids. This acid concentration also ensures reasonably fast elution of larger amounts of the ions. Graphs of distribution coefficients in 0·5*M* acids against acetone concentration were then plotted for the various ions in order to find the most favourable acetone concentrations. From these graphs it was decided to elute Cu(II), Zn, Fe(III) and other less strongly adsorbed ions with 0·50*M* hydrobromic acid in 86% acetone, U(VI) being retained. U(VI) is then eluted selectively by 0·50*M* hydrochloric acid in 83% acetone. The relevant distribution coefficients were read from the graphs and are presented in Table 1. The coefficients show that all the ions below Li in the first column can easily be eluted with 0·50*M* hydrobromic acid in 86% acetone. Of the ions retained Li and Na move down the column, but still remain in the upper half. The separation factor between Ga, which has the highest coefficient of the eluted group, and U(IV), is about 75. In the second column of Table 1 distribution coefficients are given for the hydrochloric acid–acetone mixture. These coefficients show that U(VI) can be eluted selectively with a separation factor of larger than 10 from all the remaining elements.

Distribution coefficients with -X4 resin

Because uranium shows some tailing during elution with 0·5*M* hydrochloric acid–acetone mixtures from AG50W-X8 resin[13,14] and tailing often increases when hydrobromic acid is

Table 1. Distribution coefficients of elements with AG50W-X8 resin

Ion	Eluting agent: 0·50*M* HBr in 86 % acetone	Eluting agent: 0·50*M* HCl in 83 % acetone
Th, Zr, Hf R.E., Y, Sc	>10^4	>10^4
Ba	>10^4	precipitated
Sr	8200	3500
Al	4960	1110
Ti(IV)	2960	865
Ca	2880	1570
U(VI)	501	$\boxed{5{\cdot}6}$
Mg	455	386
Ni(II)	406	298
Cs	385	316
Mn(II)	385	177
Co(II)	352	70
Rb	238	378
V(IV)	224	87
K	196	443
Be	158	170
Na	85	195
Li	52	65
Ga	6·7	4·4
Pb(II)	5·5	6·6
Fe(III)	3·5	1·5
Cu(II)	2·3	3·3
Z	1·5	1·4
In	1·4	0·5
Sn(IV)	1·3	0·5
Cd	0·8	0·5
Au(III), Pt(IV), Pd(II) Rh(III), Ir(III), Hg(II) As(III), Sb(III), Tl(III), Bi(III)	<1·0	<1·0
	↓ eluted (Ga to Cd)	↓ eluted with 0.5*M* HBr + 86% acetone (Ga to Bi(III))

used instead of hydrochloric acid the use of a resin with 4 % cross-linkage was investigated. This would lead to improved kinetics and reduced tailing. From general considerations the distribution coefficients of complex-forming elements should not differ too much in the relevant acetone concentration range, because the magnitude of the coefficients in this region should mainly be determined by the complex equilibria in the external solution and less by the resin cross-linkage. Only ions not forming halide complexes, such as alkali, alkaline earth and rare-earth metal ions, could have appreciably lower distribution coefficients with the 4 % cross-linked resin. Figures 1 and 2 show comparative distribution coefficients in 0·5*M* hydrochloric acid in 83 % acetone for Co(III). This metal has the lowest distribution coefficient (other than Li) in the second column of Table 1 and is therefore the most difficult to separate from U(VI). The coefficients for Li and Na are only slightly lower with the 4 % cross-linked resin. In 0·50*M* hydrobromic acid containing 86 % acetone the coefficients of Ga and the elements below Ga in the first column of Table 1 are lower with the

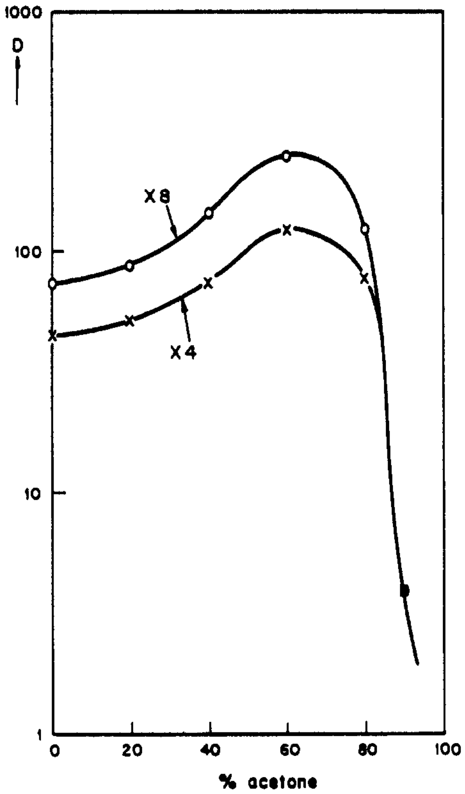

Fig. 1. Distribution coefficients for Co(II) in 0·5*M* HCl with various amounts of acetone. AG50W-X8 and AG50W-X4 resins.

4% resin. Those of Li and Na are slightly lower and the elements above Li that form chloro-complexes should follow the pattern indicated for Co(II) and U(VI) in Figs. 1 and 2. It appears that the coefficients presented in Table 1 can be used with minor adjustments for the predictions of the best conditions for separations with 4% cross-linked resin.

Elution curves

Experimental elution curves for separations of some of the most critical pairs of ions were prepared. About 25 ml of a solution containing about 1 mmole each of Ga, the most strongly adsorbed element in the easily eluted group, and U(VI) in 0·1*M* nitric acid containing 50% acetone were passed through a column of 65 ml (15 g) of AG50W-X4 resin of 200–400 mesh particle size. The column had been equilibrated by passage through it of 50 ml of 0·1*M* nitric acid in 50% acetone and it was 20 cm in length and 2·1 cm dia. The ions were washed onto the column with 0·1*M* nitric acid in 50% acetone and then eluted with 0·50*M* hydrobromic acid in 86% acetone. The flow-rate was kept at 3·0 ± 0·5 ml/min. Fractions 25 ml in volume were taken from the beginning of the elution step by means of an automatic fraction collector and the amounts of the elements in the fractions were determined. Figure 3 shows the elution curve obtained. No uranium could be detected in the first 1000 ml of eluate. Figure 4 shows an elution curve for the Pb–U(VI) pair obtained under the same

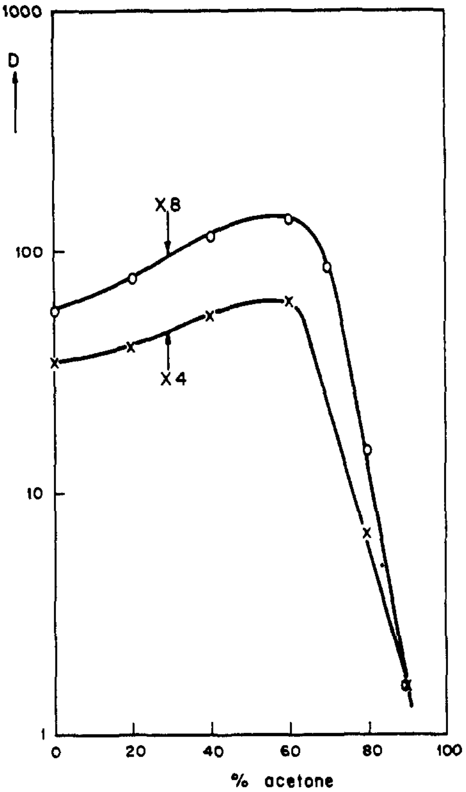

Fig. 2. Distribution coefficients for U(VI) in 0·50*M* HCl with various amounts of acetone. AG50W-X8 and AG50W-X4 resins.

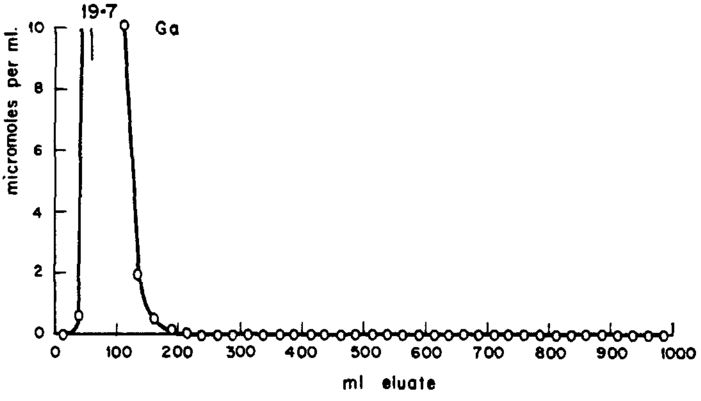

Fig. 3. Elution curve Ga–U(VI) with 0·50*M* HBr in 86% acetone. 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

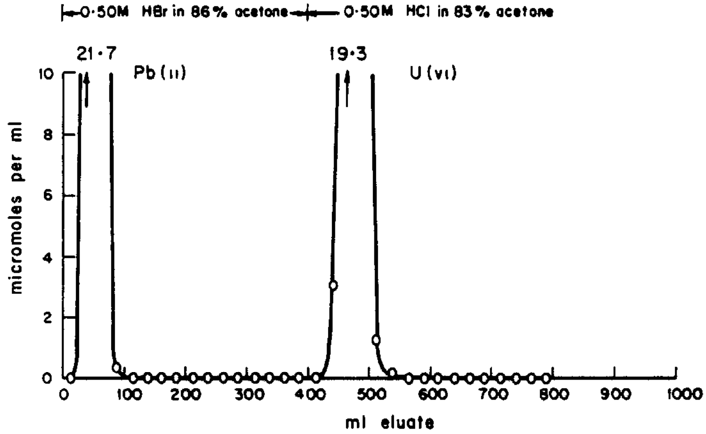

Fig. 4. Elution curve Pb–U(VI). 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

experimental conditions as described above, but the elution with 0·50*M* hydrobromic acid in 86% acetone was stopped after 400 ml had been passed through the column, and U(VI) was then eluted with 0·50*M* hydrochloric acid in 83% acetone.

Figure 5 shows an elution curve for the U(VI)–Co(II) pair, because, excepting lithium, cobalt has in 0·50*M* hydrochloric acid containing 83% acetone the lowest distribution coefficient of the ions retained (Table 1). U(VI) was eluted from the beginning with 0·50*M* hydrochloric acid in 83% acetone and the elution was continued until most of the cobalt had appeared in the eluate.

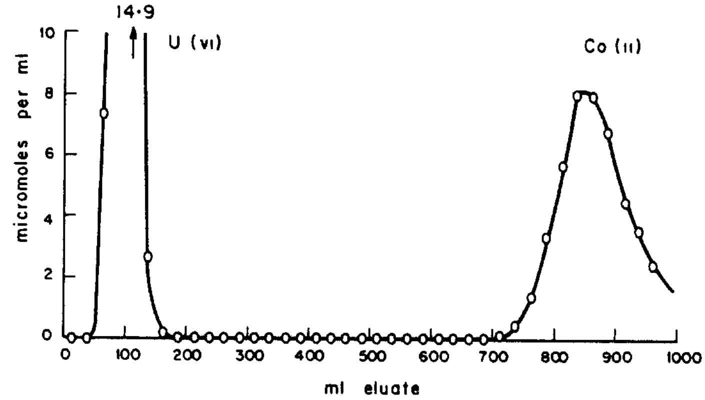

Fig. 5. Elution curve U(VI)–Co(II) with 0·50*M* HCl in 83% acetone. 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

Figure 6 shows an elution curve for Cu(II)–U(VI)–Co(II), simulating an actual analytical situation with U(VI) and one ion of each group present. The elutions of Cu(II) and U(VI) were in this case stopped after 300 ml of the respective eluting agents had been used and Co(II) was finally eluted with 3*M* hydrochloric acid.

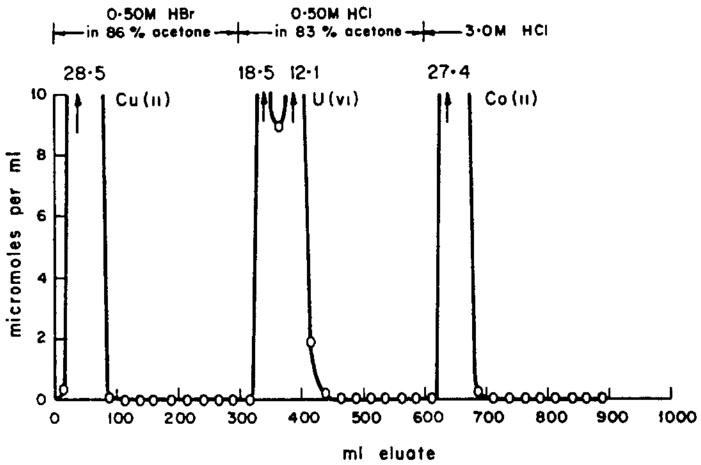

Fig. 6. Elution curve Cu(II)–U(VI)–Co(II). 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

Figure 7 shows a similar elution curve for Bi–U(VI)–Li. This curve was included because Li is the element which in both eluting agents, 0·50*M* hydrobromic acid in 86 % acetone and 0·50*M* hydrochloric acid in 83 % acetone, has the lowest distribution coefficient of the ions retained (Table 1). With 4 % cross-linked resin the distribution coefficients are even lower and the conditions for separation of Li from U(VI) are critical. In this case the medium for loading the ions onto the column was 25 ml of 0·5*M* hydrobromic acid containing 86 % acetone and the adsorption step is included in the elution curve. The figure shows that the separation between U(VI) and Li is not satisfactory for quantitative analysis.

Ions such as Fe(III), Cu(II), Zn, In, Sn(IV), Cd, Au(III), Pt(IV), Pd(II), Rh(III), Ir(III), Hg(II), As(III), Sb(III), Tl(III) and Ge are eluted together with or ahead of Ga while Mn(II),

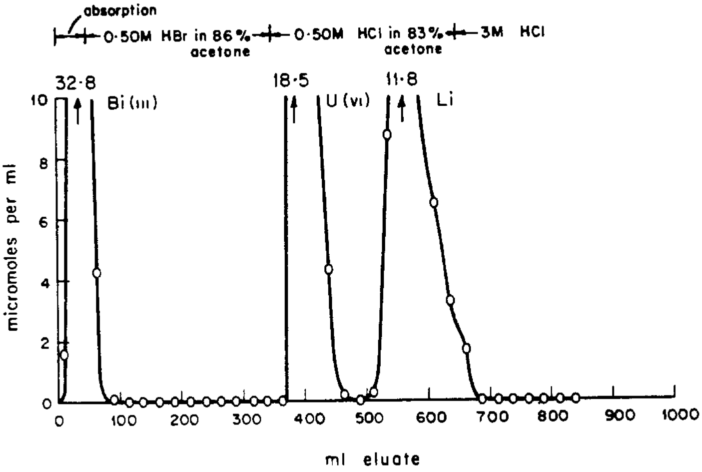

Fig. 7. Elution curve Bi–U(VI)–Li. 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

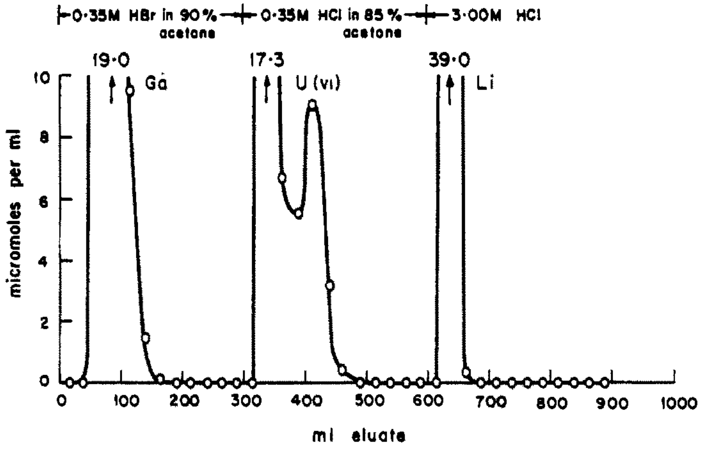

Fig. 8. Elution curve Ga–U(VI)–Li. 65 ml [21 × 2·1 cm] AG50W-X4 resin, 200–400 mesh. Flow-rate 3·0 ± 0·5 ml/min.

V(IV), Ni, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Al, Sc, Y and the lanthanides, Ti, Zr, Hf and Th are retained together with Co(II).

In order to obtain a satisfactory separation from lithium, lower acid and higher acetone concentrations can be employed though the uranium peak will be wider in this case. Figure 8 shows an elution curve for a Ga–U(VI)–Li mixture. The ions were adsorbed from 0·1*M* nitric acid in 50% acetone. Ga was eluted with 0·35*M* hydrobromic acid in 90% acetone, U(VI) with 0·35*M* hydrochloric acid in 85% acetone and lithium with 3·0*M* hydrochloric acid. In this case the separation between U(VI) and Li is quite satisfactory. Co(II), Mn(II) and the other ions retained are eluted later than Li.

Quantitative separations

Amounts of standard solutions of uranium (VI) and one other element is 0·1*M* nitric acid containing 50% acetone were measured out in triplicate, mixed and adsorbed on a column of 65 ml (15 g) of AG50W-X4 resin of 200–400 mesh particle size. The column was 21 cm in length and 2·1 cm in diameter and had been equilibrated with 50 ml of 0·1*M* nitric acid containing 50% acetone. The beakers were rinsed and the ions were washed onto the resin with the same reagent. From mixtures containing Ga, Pb, Fe(III), Cd, Cu(II) and Zn these elements were eluted with 300 ml of 0·50*M* hydrobromic acid in 86% acetone, followed by elution of U(VI) with 300 ml of 0·50*M* hydrochloric acid in 83% acetone. From mixtures containing Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th, and La, the U(VI) was eluted first with 300 ml of 0·50*M* hydrochloric acid in 83% acetone followed by elution of the other elements; 200 ml of 3*M* hydrochloric acid were used for Co(II), Mn(II), Mg and Ti(IV). The solutions of Ti(IV) and the eluting agents contained a few drops of 30% hydrogen peroxide; 300 ml of 3*M* hydrochloric acid were used for Al and Ca and 400 ml of 4*M* hydrochloric acid for La and Zr. Th was eluted with 500 ml of 5*M* nitric acid. Mixtures containing Bi and Au(III) were loaded onto the column in 50 ml of 0·50*M* hydrobromic acid containing 86% acetone and the eluate was collected from the beginning of the adsorption step. The column had been equilibrated with 50 ml of the same reagent, and Bi and Au(III) were eluted in the same way as Ga above, followed by the elution of U(VI) In addition one experiment was carried out in which Ga was eluted with 300 ml of 0·35*M* hydrobromic acid in 90% acetone followed by elution of uranium by 350 ml of 0·35*M* hydrochloric acid in 85% acetone and, furthermore, in another experiment U(VI) was eluted first with 350 ml of 0·35*M* hydrochloric acid in 85% acetone, followed by elution of Co(II) or Li with 200 ml of 3*M* hydrochloric acid. Flow-rates were 3·0 ± 0·5 ml/min throughout.

The eluates were evaporated to dryness on the steam-bath after 150 ml of water had been added to minimize formation of condensation products of acetone. Gallium solutions containing acetone could not be evaporated on the steam-bath because of the volatility of the gallium. An anion-exchange separation of gallium from the acetone, which has been described previously,[15] had to be used. After destruction of residual organic material the amounts of the elements in the eluate fractions were determined. The results are presented in Table 2 and the analytical methods are given in Table 3.

Table 2. Quantitative separation of synthetic mixtures

Taken			Found*	
U(VI) *mg*	Other species	*mg*	U(VI) *mg*	Other species, *mg*
246.1	Co(II)	59·00	246·2 ± 0·2	59·02 ± 0·04
492·2	Co(II)	0·118	492·2 ± 0·4	0·118 ± 0·001
0·246	Co(II)	118·0	0·247 ± 0·003	118·0 ± 0·1
246·1	Pb(II)	206·4	246·1 ± 0·2	206·5 ± 0·2
492·2	Pb(II)	0·206	492·1 ± 0·3	0·205 ± 0·002
0·246	Pb(II)	412·8	0·247 ± 0·003	412·7 ± 0·3
246·1	Ga	74·11	246·0 ± 0·2	74·08 ± 0·08
246·1	Fe(III)	55·63	246·1 ± 0·2	55·65 ± 0·05
246·1	Bi(III)	208·2	246·1 ± 0·3	208·2 ± 0·2
246·1	Cd	112·8	246·2 ± 0·2	112·8 ± 0·1
246·1	Au(III)	196·1	246·1 ± 0·2	196·0 ± 0·2
246·1	Cu(II)	63·81	246·0 ± 0·3	63·78 ± 0·06
246·1	Zn	65·66	246·1 ± 0·2	65·65 ± 0·07
246·1	Mn(II)	55·12	246·2 ± 0·2	55·10 ± 0·04
246·1	Mg	24.48	246·1 ± 0·2	24·47 ± 0·03
246·1	Ca	40·41	246·1 ± 0·2	40·41 ± 0·03
246·1	Ti(IV)	48·11	246·2 ± 0·3	48·13 ± 0·06
246·1	Al	27·08	246·1 ± 0·2	27·09 ± 0·03
246·1	Zr	91·38	246·0 ± 0·2	91·35 ± 0·09
246·1	Th	232·4	246·1 ± 0·2	232·3 ± 0·2
246·1	La	138·1	246·1 ± 0·3	138·1 ± 0·1
†246·1	Li	12·81	246·1 ± 0·2	12·82 ± 0·03
†246·1	Ga	74·11	246·0 ± 0·2	74·09 ± 0·07
†246·1	Co(II)	59·00	246·1 ± 0·02	58·99 ± 0·05

* Mean of triplicate runs with calculated standard deviations.
† Elution with 0·35*M* acid as shown on Fig. 8.

Table 3. Methods of determination

Species	Method
U(VI)	Gravimetrically as U_3O_8 after precipitation with CO_2-free ammonia solution. Spectrophotometrically as PAR-complex at pH 8·0 in the presence of DCTA for small amounts.
Co(II)	Complexometrically with EDTA, Naphthylazoxine-S at pH 6·0 as indicator. Atomic-absorption spectrometry for small amounts.
Pb, Zn	Complexometrically with EDTA, Xylenol Orange (XO) at pH 5·5 as indicator. Atomic-absorption spectrometry for small amounts.
Cu(II)	Complexometrically with EDTA, Methylthymol Blue (MTB) in the presence of 1,10-phenanthroline as indicator.
Cd, Ca, Mn(II)	Complexometrically with EDTA, MTB as indicator.
Bi	Complexometrically with EDTA, XO at pH 1 as indicator.
Al, Ga, Fe(III)	Complexometrically with DCTA. Back-titration with $ZnSO_4$, XO at pH 5·5 as indicator.
Mg	Complexometrically with EDTA, Eriochrome Blue-Black B at pH 10 as indicator.
Ti(IV)	Spectrometrically as H_2O_2 complex at high absorbance.
Zr	Gravimetrically as the oxide after precipitation with ammonia solution.
Th, La	Gravimetrically as the oxides after precipitation of the oxalates from 0·1*M* HCl.
Au(III)	Gravimetrically as the metal.
Li	Gravimetrically as Li_2SO_4.

DISCUSSION

The method described is an excellent example of the application of selectivity differences of an ion in two eluting agents for the development of a selective separation procedure. Because the stabilities of U(VI) complexes with halides decrease rapidly in the order $F^- > Cl^- > Br^-$ and this tendency is enhanced by the presence of acetone, U(VI) is much more strongly adsorbed by cation-exchangers from hydrobromic acid solutions containing acetone than from corresponding hydrochloric acid solutions. Ions such as Cu(II) which have very similar elution behaviour to U(VI) in hydrochloric acid–acetone mixtures[16] can easily be eluted with hydrobromic acid–acetone while uranium is very strongly retained. The separation factor for this pair increases from less than 2 in hydrochloric acid–acetone mixture to more than 250 in hydrobromic acid–acetone. There is more tailing with hydrobromic acid solutions than with hydrochloric acid solutions. A resin of lower cross-linkage would therefore be an advantage. Because distribution coefficients were available only for 8% cross-linked resin (Table 1) it had to be established whether these data could also be applied to 4% cross-linked resins. Figures 1 and 2 indicate that in the relevant acetone concentration region differences in distribution coefficients are relatively small for the two resins and any adjustments needed in the acid or the acetone concentration tend to be small or negligible. The data of Table 1 were therefore used to develop the separation on the kinetically more favourable AG50W-X4 resin of 200–400 mesh. It is shown that Cu(II), Fe(III), Ga, Zn, In, Cd, Au(III) and also Pb and Bi which are not eluted together by the selective procedures of Korkisch[6,9] can be eluted quantitatively with 300 ml of 0·50*M* hydrobromic acid in 86% acetone. When large amounts of Bi are present the sample has to be loaded onto the column in the eluting agent to avoid precipitation. Elution peaks are sharp and show very little tailing. Sn(IV), Pt(IV), Pd(II), Rh(III), Ir(III), Hg(II), As(III), As(V), Sb(III), Tl(III) and Ge have not been investigated quantitatively but should be eluted together with Cu(II) according to their distribution coefficients and elution curves. Mo(VI) and W(VI) can be eluted ahead of all these species with 0·01*M* nitric acid containing 0·05% hydrogen peroxide. Vanadium will accompany them as V(V) and some of the other elements of the group, (which was not quantitatively investigated) will also pass through the column. The 0·01*M* nitric acid will then be followed up with 0·50*M* hydrobromic acid in 86% acetone to elute Cu(II). U(VI) can then be eluted quantitatively with 300 ml of 0·50*M* hydrochloric acid in 83% acetone, Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th and La being retained by the column. Na, K, Rb, Cs, Be, Sr, Ba, Ni, V(IV), Hf, Sc, Y and the other rare-earth ions have not been investigated quantitatively, but should be retained together with Co(II) according to their distribution coefficients and elution curves. All these, including Th, can be eluted with 500 ml of 5*M* nitric acid. The only ion which is not separated satisfactorily is lithium (Fig. 7). Since lithium is present only in trace quantities in most uranium-containing materials and does not interfere in most methods of uranium determination, this is not serious. When a quantitative separation of lithium is required Cu(II), Fe(III) *etc.* can be eluted with 300 ml of 0·35*M* hydrobromic acid in 90% acetone followed by elution of U(VI) with 350 ml of 0·35*M* hydrochloric acid in 85% acetone. This provides a perfect separation from lithium (Fig. 8) but the uranium peak is slightly wider than with the higher acid concentration.

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Zusammenfassung—U(VI) kann von Ga, Fe(III), Bi, Pb, Cd, Zn, Cu(II) und Au(III) getrennt werden durch quantitative Elution mit 0,5 M HBr in 86% Aceton oder mit 0,35 M HBr in 90% Aceton von einer Säule mit AG 50 W-X4 Kationenaustauschharz der Teilchengröße 200–400 mesh. U(VI) und viele andere Ionen werden festgehalten. U(VI) kann dann selektiv mit 0,50 M HCl in 83% Aceton oder mit 0,35 M HCl in 85% Aceton eluiert werden. Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th und La werden quantitativ von der Säule festgehalten. Bei der höheren Säurekonzentration (0,50 M) ist die Trennung zwischen U(VI) und Li nicht zufriedenstellend, bei der niedrigeren Säurekonzentration ist sie ausgezeichnet; dagegen ist der U(VI)-Peak bei der höheren Säurekonzentration schärfer. Die Trennungen sind scharf und quantitativ, wie man an den Ergebnissen bei einigen synthetischen Gemischen sieht. Verteilungskoeffizienten und Elutionskurven werden mitgeteilt.

Résumé—On peut séparer U(VI) de Ga, Fe(III), Bi, Bb, Cd, Zn, Cu(II) et Au(III) par élution quantitative avec HBr 0,50*M* en acétone à 86 % ou avec HBr 0,35*M* en acétone à 90 % à partir d'une colonne de résine échangeuse de cations AG 50W-X4 de dimension de particule 200–400 mailles. U(VI) et de nombreux autres ions sont retenus. U(VI) peut alors être élué sélectivement avec HCl, 0,50*M* en acétone à 83 % ou avec HCl 0,35*M* en acétone à 85 %. Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th et La sont retenus quantitativement par la colonne. A la concentration d'acide la plus élevée (0,50*M*), la séparation entre U(VI) et Li n'est pas satisfaisante, mais elle est excellente à la concentration d'acide la plus faible; le pic de U(VI) est plus accentué à la concentration d'acide la plus élevée. Les séparations sont nettes et quantitatives, ainsi qu'il est démontré par les résultats pour quelequs mélanges synthétiques. On présente les coefficients de partage et les courbes d'élution.

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POLAROGRAPHIC PROCEDURES WITHOUT REMOVAL OF OXYGEN, AND OTHER APPROACHES TO MAKING THE DETERMINATIONS MORE RAPIDLY

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Summary—One disadvantage of conventional d.c. polarography as an analytical method has always been its relative slowness. The possibility of simplifying and speeding up analyses by avoiding the necessity for removal of oxygen is demonstrated under suitable conditions with current-sampled d.c., pulse and a.c. polarography. In particular it is shown that high-frequency phase-selective a.c. polarography gives considerable discrimination against the oxygen electrode process in some aqueous media. Under these conditions, the high-frequency a.c. technique can be combined with the method of short drop-time, fast scan-rate rapid a.c. polarography to provide a most attractive method of routine analysis. Polarographic analysis in non-aqueous media without removal of oxygen is also discussed.

One of the disadvantages of conventional d.c. polarography as an analytical method has always been its relative slowness. Using a dropping mercury electrode, D.M.E., with a natural drop-time of between 2 and 8 sec typically necessitates a period of about 10 min for the recording of a complete current–voltage curve. Times as lengthy as this are necessary because the scan-rate of d.c. potential must be low enough (*e.g.*, 1–2 mV/sec) to enable sufficiently accurate current–voltage curves to be obtained.

One approach permitting the use of much faster scan-rates of d.c. potential is the use of short controlled drop-times as an alternative to natural drop-times. This technique, often referred to as "rapid polarography," has recently been reviewed[1] and it was concluded that the rapid method could be given considerably more attention. The use of short drop-times and fast scan-rates of potential reduces the time needed for the polarography to the 10–60 sec range for routine analysis. This obviously allows considerable time saving.

For systems exhibiting reversible electrode processes, a.c. polarographic techniques offer considerable advantages over d.c. methods[2–6] and the analytical use of the a.c. methods is steadily increasing.[4] The use of short controlled drop-time techniques in so-called rapid a.c. polarography is eminently successful because there is no accompanying loss in precision and no other inherent disadvantage arising from the short drop-times.[1]

Recently, the introduction of phase-sensitive detection in rapid a.c. polarography has been described in detail,[7] and it was suggested that the shorter the drop-time the more ideally the behaviour of the system with respect to phase-sensitive detection and the subsequent discrimination against charging current. Thus at least in theory, the shorter the drop-time the lower the concentration detection limit, and rapid a.c. polarography has a further advantage. In contrast, in d.c. polarography, the shorter the drop-time the less favourable becomes the ratio of charging to faradaic current[7,8] and the concentration limit of detection becomes correspondingly worse.[8] Hence time is saved by rapid d.c. polarography at some slight expense in another direction.

Another time-consuming step that often occurs in polarography is the removal of dissolved oxygen. The oxygen can be removed chemically, but is most frequently displaced with nitrogen, argon or hydrogen.[9] Most reviews and textbooks on the analytical use of polarography stress, with reasons, the need for doing this, and the removal of oxygen has probably become so firmly entrenched in the polarographic literature that for users of the technique it is probably a routine and unquestioned point in the procedure. This assertion is made on the grounds of the paucity of examples in the literature where authors have discussed or shown whether the removal of oxygen is in fact necessary for their particular analytical procedure.

To simplify polarographic procedures, and just as importantly, to decrease the cost, it would be extremely advantageous if the oxygen-removal step could be avoided as often as possible. If this could be achieved and combined with a rapid-scan short drop-time technique, then the speed and simplicity of polarography could be considerably improved.

The purposes of this paper are therefore several. One is the question whether oxygen need be eliminated, and hence to stimulate a critical approach to this question and oppose unthinking acceptance of the idea that oxygen should always be removed. In particular the manner in which use of high-frequency a.c. polarography can often make deoxygenation unnecessary, will be discussed as an example of what can be achieved. In addition, it will be shown that when this approach is combined with short drop-time rapid a.c. polarography, it is possible to perform simple routine polarographic analysis in fractions of a minute. Finally, there is a discussion of situations in which oxygen need not be removed, and a recommendation that authors reporting polarographic analytical methods could usefully indicate how much (if at all) their method suffers from oxygen interference.

EXPERIMENTAL

All chemicals used were of reagent grade purity. All solutions were temperature-controlled at 20·0 ± 0·1° and deoxygenated with argon (where stated) for 15 min before recording of a polarogram.

All polarograms, unless otherwise stated, were recorded with PAR Electrochemistry System Model 170 (Princeton Applied Research Corporation, New Jersey). Controlled drop-times of 5, 2, 1, and 0·5 sec were achieved with PAR Drop Timer Model 172. Controlled drop-times of 0·16, 0·20, 0·24, 0·28, and 0·32 sec were obtained with Metrohm Polarographie Stand E354.

In aqueous media, Ag|AgCl ($5M$ NaCl) was used as the reference electrode and tungsten wire as the third or auxiliary electrode. In acetone media, two identical Ag|AgCl ($0{\cdot}1M$ LiCl; acetone) reference electrodes connected to the test solution *via* a salt-bridge filled with 0·1 M tetraethylammonium perchlorate served as the reference and third electrodes. The supporting electrolyte used was $0{\cdot}1M$ tetraethylammonium perchlorate.

All a.c. measurements, unless otherwise specified, were made with phase-sensitive read-out, either in phase with the applied a.c. voltage or 180° out of phase. Total alternating current measurements were made with Metrohm AC Modulator E393 coupled to Metrohm Polarecord E261.

The pulse and current-sampled d.c. polarographic measurements were made for a 15-msec period near the end of a 1 sec drop-life, using a controlled drop-time technique with "On Line Sync." Further details are given in the text.

RESULTS AND DISCUSSION

Why remove oxygen?

Before proceeding to describe and discuss approaches to avoid the need for removal of oxygen it is essential to consider and understand the polarographic behaviour of oxygen. Many discussions and accounts of why oxygen should be removed are available. However, probably the most informative and precise summary so far available is provided in a recent application note[10] which is produced in part below. It must be stressed, however, that this description and most others are only valid for aqueous solutions. This latter point frequently appears to have been overlooked or ignored because the basis for elimination of oxygen in non-aqueous solvents more often than not appears to have been simply an extrapolation of ideas derived for the aqueous solvent system.

Oxygen is capable of dissolving in aqueous solutions to the extent of forming a one millimolar solution at room temperature and pressure and the polarographic reduction of oxygen complicates the polarographic determination of other electroactive materials.

"Since it can be present in solutions in high concentrations and since it is electroactive, oxygen must be removed from the analyte prior to polarographic analysis."

Problems arise both from the voltammetric behaviour of oxygen itself and from the associated chemical reactions that can take place with oxygen or its reduction products. Oxygen gives two polarographic waves. The first is due to reduction of oxygen to hydrogen peroxide or hydrogen peroxide and hydroxide (depending on the pH):

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \text{ (acid media)}$$

$$E_{1/2} \sim -0{\cdot}05 \text{ V } vs. \text{ SCE}$$

$$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2OH^- \text{ (neutral or alkaline media)}$$

The second involves the reduction of hydrogen peroxide to hydroxide or water:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \text{ (acid media)}$$

$$E_{1/2} = -0{\cdot}5 \text{ V to } -1{\cdot}3 \text{ V } vs. \text{ SCE}$$

$$H_2O_2 + 2e^- \rightleftharpoons 2OH^- \text{ (neutral or alkaline media)}$$

"It is thus evident that two types of complications can arise if oxygen is not removed. The hydrogen peroxide produced from the first reaction can produce invidious effects on other electroactive species present in solution since it can function as both an oxidizing agent and a reducing agent. More significantly, however, pH changes can occur in the vicinity of the dropping mercury electrode due to the electro-reduction of oxygen. The resultant increase in pH in the vicinity of the dropping mercury electrode can precipitate heavy metal ions and thus diminish their diffusion currents. Also, those species (i.e., organics) whose reduction involves hydrogen ions will be adversely affected due to the localized increase in pH at the dropping mercury electrode.

Outgassing prior to polarographic analysis is also necessary to prevent the following reaction:

$$O_2 + 2Hg + 2Cl^- + 2H_2O \rightleftharpoons H_2O_2 + Hg_2Cl_2 + 2OH^-$$

The above non-electrochemical process, which can occur in neutral, unbuffered metal salt solutions containing metallic mercury and dissolved oxygen, require that the latter be removed by rigorous outgassing procedures."

Direct current and pulse polarography without removal of oxygen

If the only interference caused by oxygen were the presence of the oxygen waves themselves, then many polarographic techniques would not require the elimination of oxygen. With modern polarographic instrumentation and techniques it is well known that

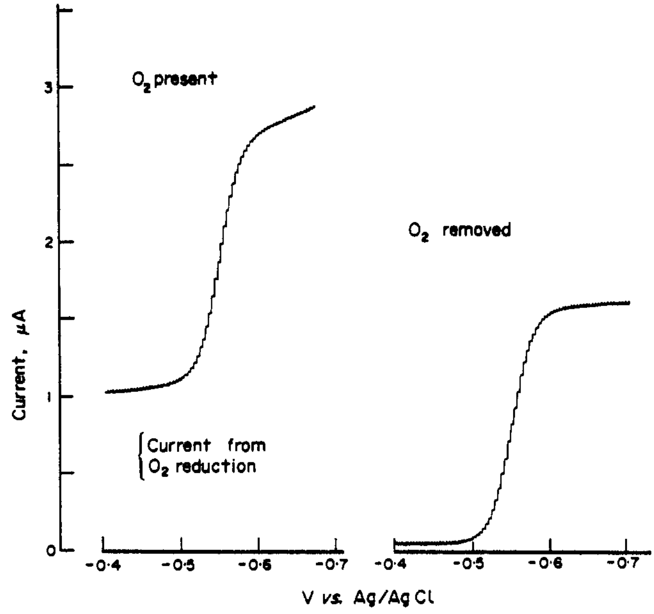

Fig. 1. Tast (current-sampled) d.c. polarography with and without removal of oxygen in acidic media. Concentration of cadmium = $10^{-3}M$. Medium = $0{\cdot}1M$ HCl/$0{\cdot}9M$ $HClO_4$.

simultaneous determination of several species is often possible and under such circumstances oxygen could be simply treated as another electroactive species.

For example, current-sampled d.c. polarography permits the determination of a particular depolarizer in the presence of another more negatively reduced species, where conventional d.c. polarography cannot be readily applied,[11] and oxygen can simply be regarded as a normal case of this type. Figure 1*a* shows the determination of cadmium in an acidic medium by current-sampled d.c. polarography without removal of oxygen. Figure 2*a* shows the same determination by current-sampled derivative d.c. polarography which, as expected, provides significant improvement. Figure 1*b* and 2*b* show the analogous polarograms after removal of oxygen. It can be seen therefore that with this electrolyte, the removal of oxygen is not strictly necessary, although the presence of the oxygen gives rise to large d.c. currents which cause some inconvenience in the measurement, particularly when the concentration of depolarizer to be determined is considerably less than that of the oxygen. Figures 3 and 4 show equivalent polarograms to Figs. 1 and 2 but with a neutral supporting electrolyte. In this instance and with cadmium, the desirability of removing oxygen is most evident as electrochemical interference is readily observed. That is, the wave shape, position and height are all influenced by the presence of oxygen. This is attributable to interaction with hydroxide, the product of the oxygen electrode process in neutral media.[2,12] In concentrated acid media hydrogen peroxide is the only product and presumably this does not interfere. Furthermore in such media the system is effectively buffered against hydroxide and if any hydroxide were produced it would not alter the pH in the vicinity of the DME.

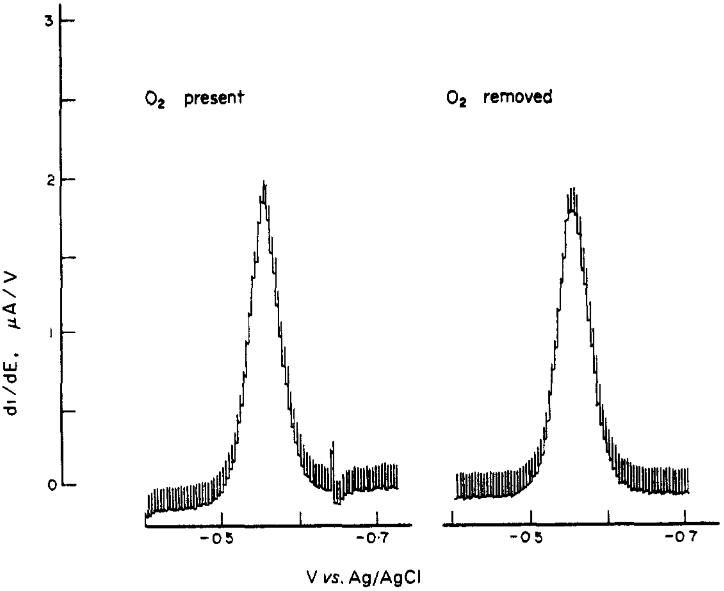

Fig. 2. Derivative Tast (current-sampled) d.c. polarography with and without removal of oxygen in acidic media. Concentration of cadmium $= 10^{-3}M$. Medium $= 0{\cdot}1M$ HCl/$0{\cdot}9M$ $HClO_4$.

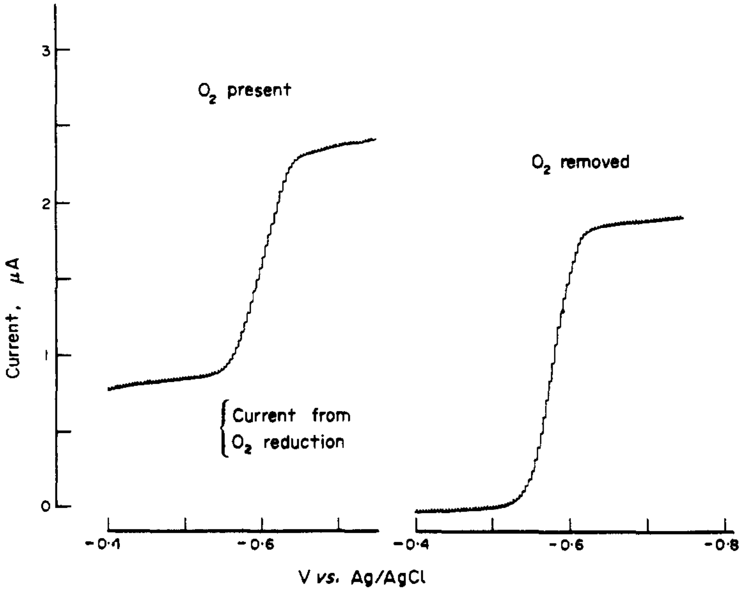

Fig. 3. Tast (current-sampled) d.c. polarography with and without removal of oxygen in "neutral" media. Concentration of cadmium $= 10^{-3}M$. Medium $= 0{\cdot}1M$ KCl.

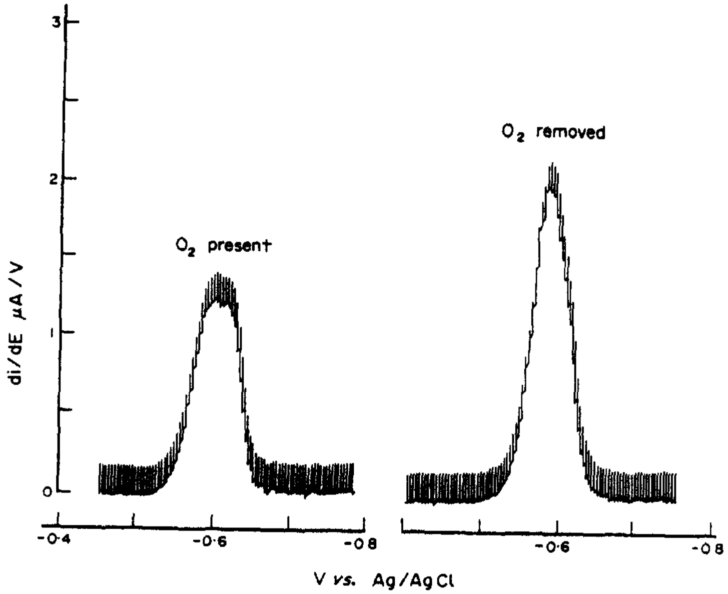

Fig. 4. Derivative (current-sampled) Tast d.c. polarography with and without removal of oxygen in "neutral" media. Concentration of cadmium = $10^{-3}M$. Medium = $0 \cdot 1M$ KCl.

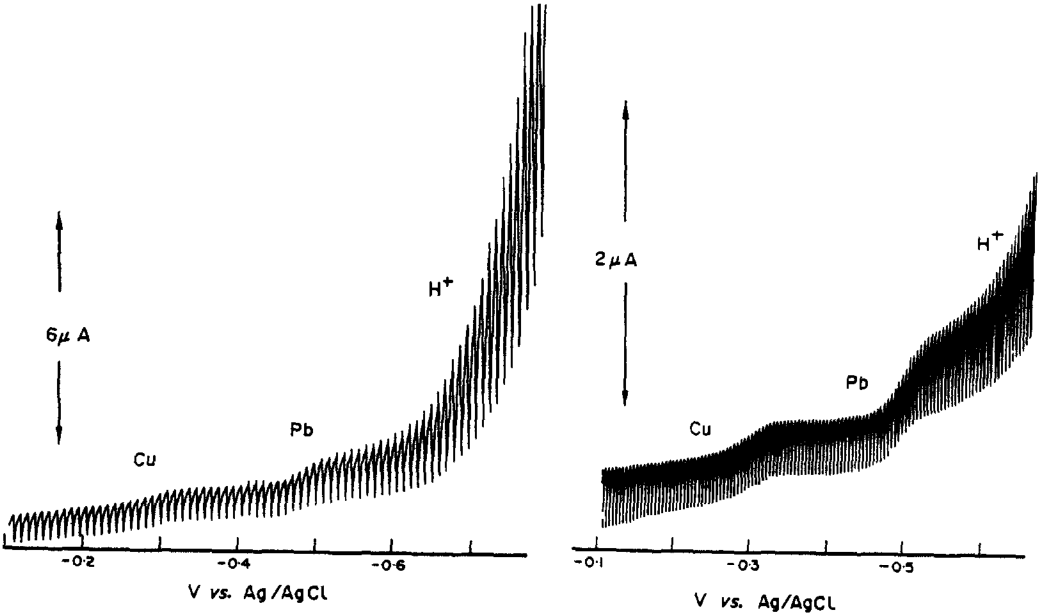

Fig. 5.(*a*) Direct current polarogram of $8 \times 10^{-5}M$ Cu(II) and Pb(II) in $5M$ HCl without removal of oxygen. Controlled drop-time of 1 sec and scan-rate of 5 mV/sec. (*b*) Same as (*a*) but with removal of oxygen and scan-rate of 2 mV/sec.

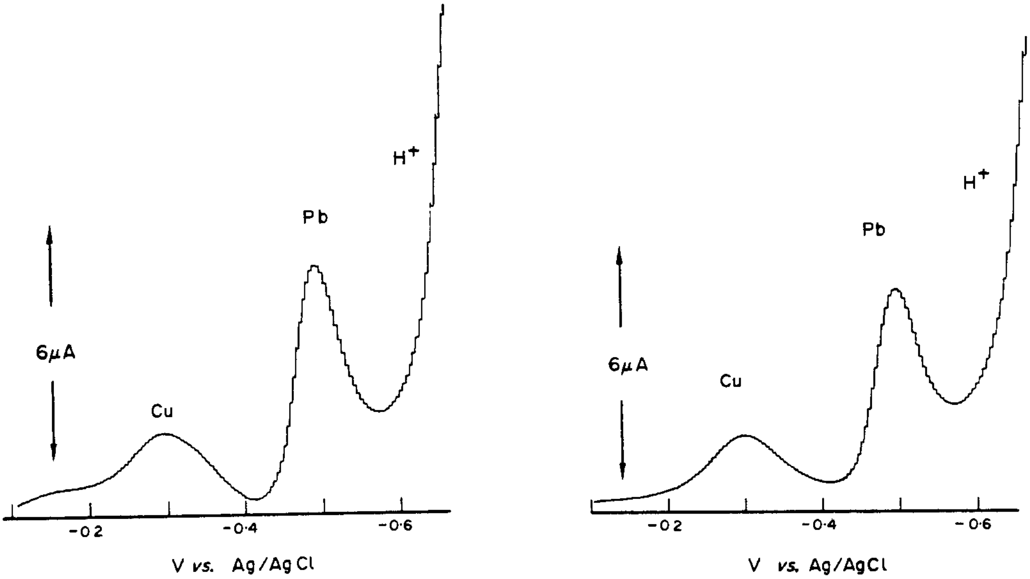

Fig. 6.(*a*) Differential pulse polarogram of $8 \times 10^{-5}M$ Cu(II) and Pb(II) in 5*M* HCl without removal of oxygen. Pulse height of 25 mV. (*b*) Same as (*a*) but with removal of oxygen.

Pulse polarography is particularly sensitive to oxygen and large currents are produced when oxygen is present at its equilibrium concentration. However, this is a current-sampled technique and can be used in the same manner as current-sampled d.c. polarography to avoid removal of oxygen. Pulse polarography can be used in its normal form or in derivative or differential modes, the latter two giving shapes akin to current-sampled, derivative d.c. polarograms, and the normal form giving the shape of a current-sampled d.c. polarogram. Figure 5*a* shows a d.c. polarogram of a solution of Cu(II), Pb(II), Cd(II) and Zn(II) (each $8 \times 10^{-5}M$ in 5*M* hydrochloric acid in the presence of oxygen. The $\mathrm{Cu(I)} + \mathrm{e} \rightleftharpoons \mathrm{Cu}$ and $\mathrm{Pb(II)} + 2\mathrm{e} \rightleftharpoons \mathrm{Pb}$ waves can just be seen, but the $\mathrm{Cd(II)} + 2\mathrm{e} \rightleftharpoons \mathrm{Cd}$ and $\mathrm{Zn(II)} + 2\mathrm{e} \rightleftharpoons \mathrm{Zn}$ electrode processes are masked by the irreversible but catalysed reduction of the hydrogen ion, $2\mathrm{H}^+ + 2\mathrm{e} \rightarrow \mathrm{H}_2$, and by the oxygen or other electrode processes present in this medium. This curve is entirely unsatisfactory for analytical purposes. After removal of oxygen, satisfactory current–voltage curves can be obtained as higher instrument sensitivities can be used, as shown in Fig. 5*b*.

Figures 6*a* and 6*b* show equivalent differential pulse polarograms, both in the presence and absence of oxygen. The copper and lead waves are now almost as well defined even in the presence of oxygen and differential pulse polarography and other pulse polarographic methods can be used without degassing, on suitable systems which do not suffer from electrochemical interference from the presence of oxygen or overlap with the oxygen waves themselves. In the absence of the catalysed hydrogen-ion wave or at lower concentrations of hydrochloric acid, copper, lead and cadmium, for example, can each be determined quantitatively at least down to the 5×10^{-6}–$10^{-5}M$ concentration range in the presence of oxygen by differential pulse polarography.

However, with both d.c. current-sampled and pulse polarographic methods one limitation has been found. For most systems studied it has been found that the lower limit of concentration detection is less favourable in the presence of oxygen. This arises because the concentration of oxygen is high and these techniques are sensitive to its electrode processes. Thus the current due to oxygen becomes extremely important at the lower concentrations of the species being determined and causes difficulties in accurate measurement of the current–voltage curve. That is, current-sampled techniques can often be satisfactorily applied without removal of oxygen but their use is sometimes limited because they do not discriminate against oxygen, in contrast with the high-frequency a.c. techniques to be discussed below.

Alternating current polarography

In the preceding discussion it has been established that d.c. and pulse methods are not as effective as they might be in enabling polarographic analysis to be undertaken in the presence of oxygen, because they do not discriminate severely against the oxygen electrode process. The a.c. polarographic methods, however, are not particularly sensitive to irreversible electrode processes[3] (low current per unit concentration) and in determination of a species exhibiting reversible electrode processes, considerable discrimination can be provided in suitable media. This was the reason why the early literature on a.c. polarography suggested this method could be used without removal of oxygen.[2]

In a more critical account, Bond and Canterford[12] found that for several systems in acid media, the only form of interference encountered was in fact from the alternating current due to the oxygen a.c. electrode process itself. However, in other media, as expected, considerable electrochemical interference was also encountered. This previous work utilized low-frequency natural drop-time a.c. polarography at 50 Hz. In most analytical applications of a.c. polarography the low-frequency spectrum of the usable frequency range is recommended for instrumental and other[3] reasons.

Figure 7 shows the total alternating current for oxygen with a short controlled drop-time of 0·32 sec in 1*M* hydrochloric acid at the low frequency of 50 Hz. The same instrumentation

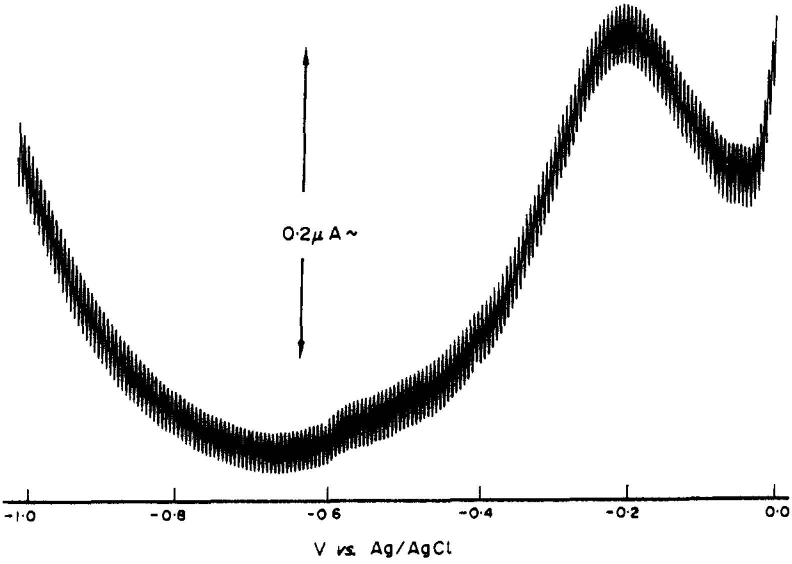

Fig. 7. Rapid low-frequency a.c. polarogram of oxygen in 1*M* HCl. Drop-time of 0·32 sec. Applied alternating potential 10 mV, r.m.s. Frequency 50 Hz. Total alternating current recorded.

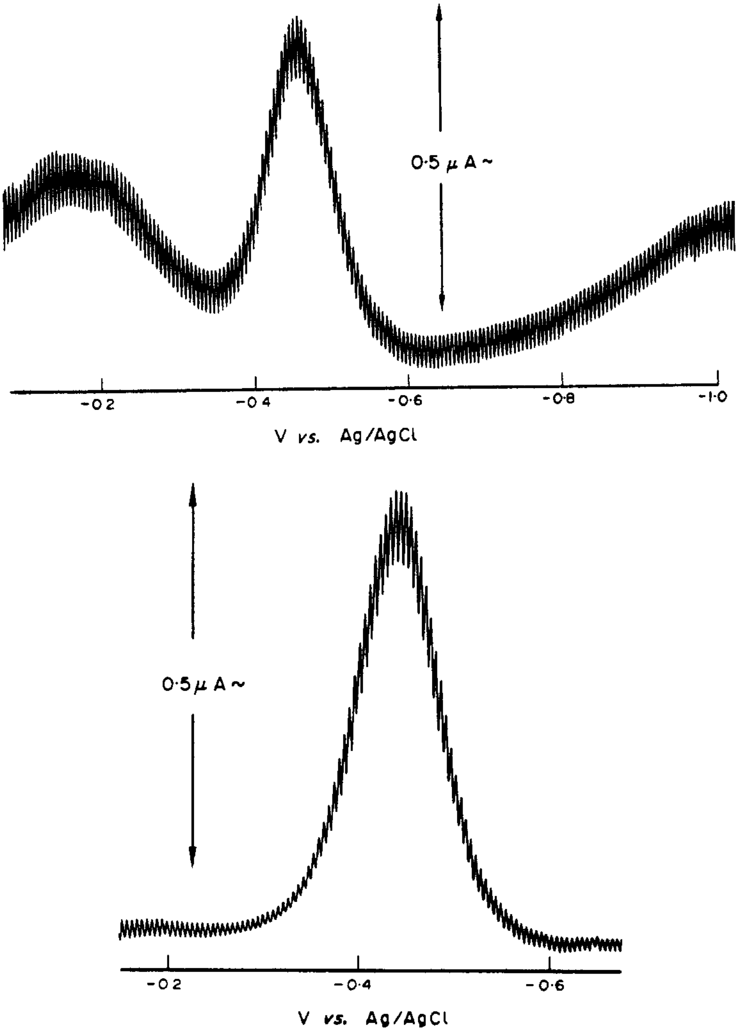

Fig. 8.(*a*) Rapid low-frequency a.c. polarogram of $10^{-4}M$ Tl(I) in $1M$ HCl. (*b*) Same as (*a*) but with removal of oxygen.

Drop-time 0·32 sec. Applied alternating potential 10 mV r.m.s., Frequency 50 Hz. Total alternating current recorded.

as previously[12] was used to record this polarogram except that rapid short drop-time a.c. polarography was used instead of natural drop-time polarography. Figures 8 and 9 show thallium(I) and antimony(III) a.c. polarograms in the presence and absence of oxygen in $1M$ hydrochloric acid. It is readily apparent that an extremely rapid polarographic technique without removal of oxygen can be obtained in suitable electrolytes with the normally used low-frequency range. Furthermore, in accordance with previous findings in the natural drop-time studies[12] the only limitation in such systems is the presence of the oxygen waves themselves. That is, the better the discrimination against oxygen the better will be the method and, as can be shown from the theory below, this can be achieved by the use of higher frequencies than normally used in analytical work, coupled with phase selective detection.

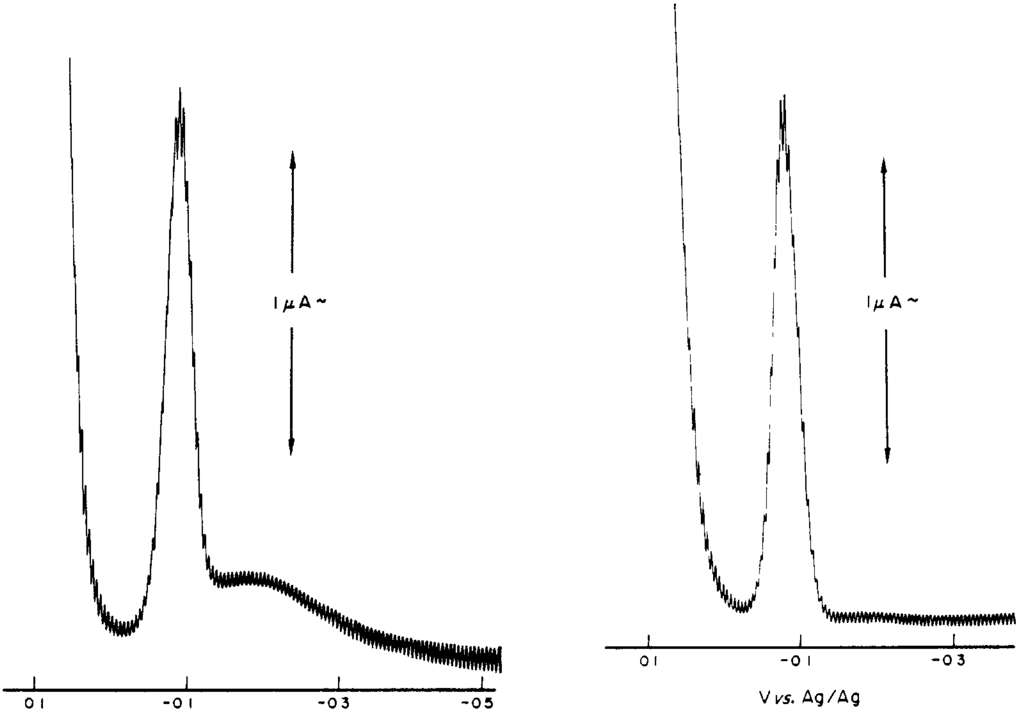

Fig. 9.(*a*) Rapid low-frequency a.c. polarogram of $10^{-4}M$ Sb(III) in $1M$ HCl. (*b*) Same as (*a*) but with removal of oxygen.
Drop-time 0·32 sec. Applied alternating potential 10 mV, r.m.s. Frequency 50 Hz. Total alternating current recorded.

Oxygen is irreversibly reduced at the DME in many media. Examination of the theory for a totally irreversible a.c. electrode process[13] shows that in addition to the current being small, relative to a reversible electrode process, it is independent of frequency. Even if the a.c. electrode process is quasi-reversible, the alternating current will only increase with frequency to a certain value, at which point the current becomes independent of frequency[3,5] and behaves like that for an irreversible electrode process. The exact nature of the oxygen a.c. electrode processes is extremely complex. However, relative to a reversible a.c. electrode process, in both neutral and acidic aqueous media, the current per unit concentration is extremely low and the behaviour is certainly characteristic of a considerable degree of irreversibility.

On the other hand, species being determined by a.c. polarography are usually close to being reversible in behaviour. For such electrode processes the current increases with the square root of frequency ($\omega^{1/2}$). Thus as the frequency of the experimental increases, the current from the species being determined should increase at a rate proportional to $\omega^{1/2}$ and that from oxygen not at all or certainly at a rate much less than $\omega^{1/2}$. From this it follows that the higher the frequency of the a.c. used the better should be the discrimination against oxygen and at very high frequencies it should be possible, at least in principle, to have an analytical method which is equally as good in either the presence or absence of oxygen and the ideal situation should be reached.

However, the use of high-frequency a.c. polarography introduces complications from the instrumental point of view. First, charging-current phenomena become critical and total alternating current measurements are no longer suitable, so that phase-sensitive detection must be used.[3] Secondly, the use of phase-sensitive detection at high frequencies requires that ohmic *iR* losses must be kept to a minimum. The use of a three-electrode potentiostat system is therefore required Finally, to provide a really rapid a.c. technique, in addition to overcoming the need for elimination of oxygen, it would be desirable to couple the short drop-time technique with high-frequency a.c. polarography as mentioned in the introduction.

High-frequency, rapid, phase-sensitive a.c. polarography without degassing

The desirability of using rapid, high-frequency a.c. polarography with three-electrode instrumentation and phase-sensitive detection having been established, the technique was applied to a detailed study of polarography without removal of oxygen.

The electrode processes used for detailed study were $\mathrm{Bi(III)} + 3e \rightleftharpoons \mathrm{Bi}$ and $\mathrm{Cd(II)} + 2e \rightleftharpoons \mathrm{Cd}$, both in $1M$ hydrochloric acid.

It was found with both these systems that in the presence of oxygen and at 1000 Hz, the limit of detection was between 5×10^{-7} and $8 \times 10^{-7}M$. Furthermore, polarograms and the limit of detection were equivalent with or without removal of oxygen and with rapid or natural drop-times. Thus the ideal situation was obtained in this supporting electrolyte, where routine determination of either cadmium or bismuth can be made by using rapid scan-rates and without degassing. The proposed discrimination against the oxygen electrode process is realized and the time needed for the polarography is considerably decreased.

To test the general applicability of the approach many other elements were examined. Table 1 lists those for which the approach was completely successful. Frequencies in the range of 300–1100 Hz were used. Figure 10 shows the a.c. polarogram at 300 Hz of the system used for pulse and d.c. polarography in Figs. 5 and 6, without removal of oxygen. The

Table 1. Some elements which can be determined in aqueous media without removal of oxygen

Element	Electrode process	Supporting electrolyte*
Bi(III)	(III) → (0)	$1M$ HCl
Sb(III)	(III) → (0)	$1M$ HCl
Rh(III)	(III) → (0)	$5M$ HCl
In(III)	(III) → (0)	$1M$ HCl
Cu(II), Cu(I)	(I) → (0)	$1M$ HCl
Cd(II)	(II) → (0)	$1M$ HCl
Pb(II)	(II) → (0)	$1M$ HCl, $1M$ H_2SO_4
Tl(I)	(I) → (0)	$1M$ HCl, $1M$ NaCl
Sn(IV), Sn(II)	(II) → (0)	$5M$ HCl
U(VI)	(VI) → (V)	$1M$ H_2SO_4
Na(I)	Na(I) → (Na(0)	0·1M $(CH_3CH_2)_4NClO_4$
K(I)	K(I) → K(0)	0·1M $(CH_3CH_2)_4NClO_4$
Li(I)	Li(I) → Li(0)	0·1M $(CH_3CH_2)_4NClO_4$
Rb(I)	Rb(I) → Rb(0)	0.1M $(CH_3CH_2)_4NClO_4$
Cs(I)	Cs(I) → Cs(0)	0·1M $(CH_3CH_2)_4NClO_4$
Ba(II)	Ba(II) → Ba(0)	0·1M $(CH_3CH_2)_4NClO_4$

* This does not imply that this is the best electrolyte, but one which has been tried and is known to be suitable.

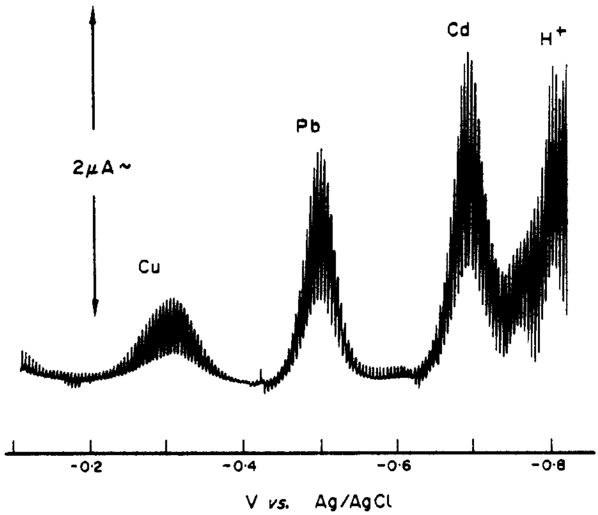

Fig. 10. High frequency a.c. polarogram of $8 \times 10^{-5}M$ Cu(II), Pb(II), and Cd(II) in 5*M* HCl. Drop-time 1 sec. Applied alternating potential 10 mV, peak-to-peak. Frequency 300 Hz. In-phase alternating current recorded.

polarogram after removal of oxygen is identical. It can be noted that in the a.c. polarogram, the $Cd(II) + 2e \rightleftharpoons Cd$ electrode process, which was obscured by the irreversible but catalysed hydrogen electrode process with pulse or d.c. polarography, is clearly seen. The ability of high-frequency a.c. polarography to discriminate against irreversible electrode processes in general is clearly illustrated.

Polarography in non-aqueous solvents without degassing

Discussion of whether deoxygenation is necessary has usually stemmed from results and experience obtained with aqueous media. For non-aqueous solvents it can be suggested that removal of oxygen will certainly not always be required. As an example of this, the acetone system is considered briefly below.

With acetone media one complex oxygen wave is observed. Oxygen is very soluble in acetone, so large d.c., pulse, or a.c. currents, *etc.* are obtained. However, in acetone, with 0·1*M* tetraethylammonium perchlorate for example, the wave does not occur until about −0·7 V *vs.* Ag|AgCl, as shown in Fig. 11. The anodic limit for this supporting electrolyte is about +0·8 V *vs.* Ag|AgCl. Thus there is a 1·5-V span for acetone media over which oxygen is completely electro-inactive. Acetone is a most useful solvent for many organic compounds, as well as inorganic and organometallic compounds, and the author has encountered many examples where these compounds exhibit waves before the oxygen reduction and where the polarographic behaviour is totally unaffected by the presence of oxygen.

CONCLUSIONS

From this work it is concluded that for routine polarographic analysis there are likely to be many situations where the elimination of oxygen is not needed. Certainly routine degassing without consideration of whether it is necessary should not be encouraged. Although there will always be many cases where deoxygenation cannot be avoided, such as when

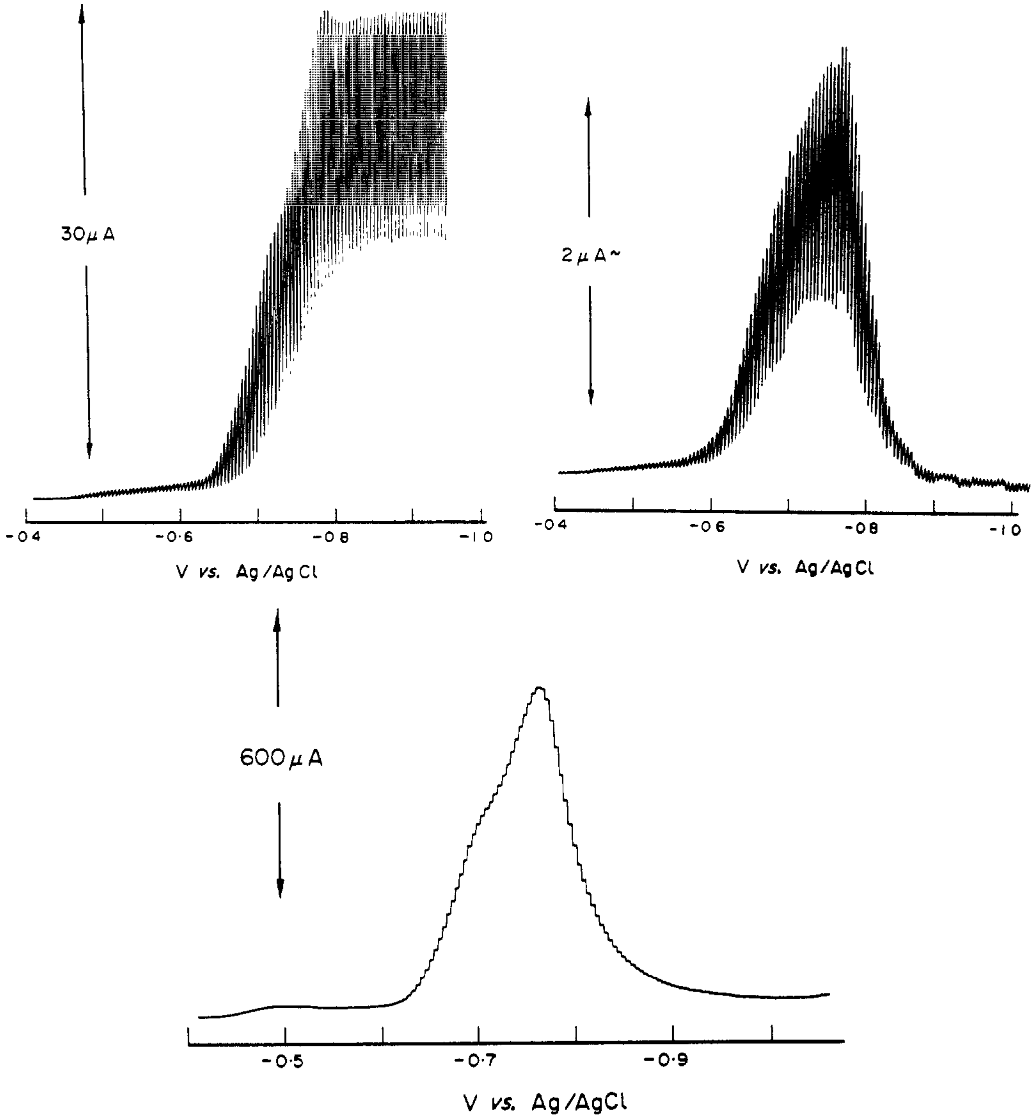

Fig. 11. Oxygen wave in acetone, 0·1*M* tetraethylammonium perchlorate. Controlled drop-time 1 sec. (*a*) Direct current polarogram. (*b*) Alternating current polarogram (applied alternating potential 10 mV peak to peak; frequency 80 Hz; in-phase alternating current measured). (*c*) Differential pulse polarogram (pulse height 25 mV).

oxygen-induced complex chemical reactions occur, the use of high-frequency a.c. polarography as a means of discriminating against the oxygen electrode process appears to have considerable promise in avoiding the necessity for degassing in situations where other polarographic methods might require this. When oxygen can be left in and the short controlled drop-time rapid a.c. technique used, a most convenient and simple form of polarographic analysis, particularly suited to large numbers of samples, is obtained, because the time needed for the polarography is reduced to some tens of seconds.

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Résumé—Un désavantage de la polarographie en courant continu classique comme méthode analytique a toujours été la lenteur. La possibilité de simplification et d'accélération d'analyses en évitant la nécessité d'élimination de l'oxygène est démontrée dans des conditions convenables avec une impulsion de courant continu d'intensité choisie et polarographie en courant alternatif. On montre en particulier que la polarographie en courant alternatif à haute fréquence sélective de phase présente une discrimination considérable vis-à-vis du processus d'oxygène à l'électrode dans quelques milieux aqueux. Dans ces conditions, la technique en courant alternatif à haute fréquence peut être combinée avec la méthode de polarographie en courant alternatif rapide à court temps de goutte et vitesse rapide d'exploration pour donner une méthode d'analyse de routine des plus intéressantes. On discute aussi de l'analyse polarographique en milieux non aqueux sans élimination d'oxygène.

Zusammenfassung—Ein Nachteil der konventionellen Gleichstrompolarographie als analytische Methode war seit jeher ihre Langsamkeit. Es wird gezeigt, daß man unter geeigneten Bedingungen die Analysen dadurch vereinfachen und beschleunigen kann, daß man den Sauerstoff bei der Gleichstrom-Tastpolarographie und bei der Wechselstrom polarographie nicht mehr zu entfernen braucht. Insbesondere wird gezeigt, daß die phasenselektive Hochfrequenz-Wechselstrompolarographie in einigen wäßrigen Medien eine beträchtliche Diskrimination gegenüber dem Elektrodenprozeß des Sauerstoffs liefert. Unter diesen Bedingungen kann die Hochfrequenz-Wechselstrommethode mit der Methode der schnellen Wechselstrompolarographie mit kurzen Tropfzeiten und raschem Scan kombiniert werden; es ergibt sich ein sehr attraktives Verfahren der Routineanalyse. Die polarographische Analyse in nichtwäßrigen Medien ohne Entfernung von Sauerstoff wird ebenfalls erörtert.

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DETERMINATION OF VANADIUM AND MOLYBDENUM BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—A method is described for the determination by atomic-absorption spectrophotometry of vanadium and molybdenum, up to the milligram level, in samples of yellow cake, uranium-bearing minerals and geochemical standards. After attack with acids these two elements are separated from each other and from matrix elements by means of anion-exchange in 6*M* hydrochloric acid on the strongly basic anion-exchange resin Dowex 1, X8 (chloride form). Vanadium is unadsorbed and passes into the effluent while molybdenum is adsorbed on the resin. For the elution of molybdenum a mixed aqueous–organic solvent system consisting of methanol and 6*M* hydrochloric acid (9 : 1 v/v) is used. After evaporation of the 6*M* hydrochloric acid effluent and of the mixed aqueous–organic eluate vanadium and molybdenum are determined by atomic-absorption spectrophotometry. The method was tested by analysing numerous samples with contents ranging from a few ppm to milligram amounts of vanadium and molybdenum. For comparison, the concentrations of these two elements were determined in a large number of samples by spectrophotometric and titrimetric procedures. In all cases very good agreement of results was obtained.

Vanadium is often determined spectrophotometrically in complex materials, *e.g.*, geological samples, because such materials usually contain only small concentrations of vanadium (mainly in the ppm range). The greatest disadvantage of such procedures is that they are not selective and hence less generally applicable than atomic-absorption methods. The latter have been used extensively for the determination of vanadium in a variety of materials, including silicates,[1,2] ores,[3] calcium sulphate minerals,[4] geochemical standards,[5] salt-lake brines,[6,7] lake waters,[8] atmospheric particulate matter,[9] fuel oils and petroleum products,[10–14] metallurgical products,[15–17] titanium tetrachloride,[18,19] and catalysts for ammonia synthesis.[20] To avoid interferences by matrix elements and to increase the sensitivity suitable organic complexes of vanadium are often extracted into organic solvents and the organic phase is aspirated directly into the flame (usually nitrous oxide–acetylene). Reagents used include cupferron,[1,6,7,21,22] ammonium pyrrolidine-1-carbodithioate,[23] 8-hydroxyquinoline,[18] 5,7-dichloro-8-hydroxyquinoline,[8] α-benzoinoxime[24] and tetraphenylarsonium chloride,[19] and the solvents include isobutyl methyl ketone,[6,7,21–23,25] butyl acetate,[1,8] isoamyl alcohol,[18] chloroform,[24] benzene[24] and dichloromethane.[19] Also an indirect method has been described, based on the extraction of molybdovanadophosphoric acid into pentanol–ethyl ether mixture (1 : 4), followed by stripping of the molybdate and its determination in a reducing acetylene flame.[26]

Similar remarks apply to the determination of molybdenum in geological and other materials. Thus, atomic-absorption spectrophotometry has been used to determine molyb-

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† Herrn Univ. Prof. Dr. Friedrich Hecht zum 70 Geburtstag hertlichst gewidmet.

denum in uranium and its alloys,[27–31] uranium hexafluoride,[32] fission product and uranium solutions,[33] ferrous alloys,[34,35] iron and steel,[35–39] high-temperature cobalt-base alloys,[40] niobium and tantalum,[41] nickel,[27] metallurgical products,[42] slags,[43] geological samples such as silicates,[44,45] soils,[46] siliceous molybdenum ores,[47] natural waters,[45,48] and brines,[49,50] biological materials,[45,51,52] fertilizers,[53–55] fuels and lubricants,[56,57] and solutions.[58–63] Because interferences due to the presence of large amounts of iron and of other elements can be suppressed by addition of sodium sulphate or other suppressors, most of the methods using atomic-absorption for the determination of larger amounts of molybdenum can be applied directly, *i.e.*, without preliminary separation of the molybdenum from matrix elements. However, in the presence of very small amounts of molybdenum, such as in geological samples or biological material it has been found to be necessary to use extraction to preconcentrate molybdenum before its determination by atomic absorption. Chelates of molybdenum with, for example, 8-hydroxyquinoline,[41,45,48,54] ammonium pyrrolidine-1-carbodithioate,[49,61] ammonium tetramethylenedithiocarbamate,[45] hexahydroazepinium hexahydroazepine-1-carbodithioate[52] and α-benzoinoxime[44] have been extracted into methyl isobutyl ketone,[48,49,54,61] methyl pentyl ketone,[45] butanol,[41] and chloroform[44,52,54] and the extracts directly aspirated into the flame or mineralized.[44] Extraction of molybdenum chloride with pentyl acetate from $>8M$ hydrochloric acid[27] or of molybdenum thiocyanate with isoamyl alcohol[53] have also been used to isolate this element.

The atomic-absorption determination of ppm amounts of vanadium or molybdenum generally requires removal of the matrix elements, either by liquid-liquid extraction (see above) or by ion-exchange. Vanadium can be separated by anion-exchange from hydrochloric acid medium; the vanadium passes through the column. Molybdenum is sorbed quantitatively by that method and can be eluted with a mixed aqueous organic solvent system containing hydrochloric acid.

This paper describes this separation scheme and its application to samples containing from a few ppm to milligram amounts of vanadium and molybdenum.

EXPERIMENTAL

Solutions and reagents

All the reagents were of analytical-reagent grade unless otherwise stated.

Ion-exchanger. Bio-Rad Dowex 1, X8 (100–200 mesh; chloride form). The resin (4 g) was soaked in a few ml of $6M$ hydrochloric acid and the slurry transferred to the ion-exchange column, the same acid being used as a rinse.

Vanadium standard solutions. Vanadyl sulphate pentahydrate (4·967 g) $VOSO_4 . 5H_2O$; dissolved in 5% v/v sulphuric acid and the solution diluted to 1 litre with 5% sulphuric acid; 1 ml of this standard solution contains 1 mg of vanadium. Aliquots are diluted with $6M$ hydrochloric acid to give solutions with vanadium concentrations in the range 1–100 ppm.

Molybdenum standard solutions. Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} . 4H_2O$; 1·8407 g dissolved in $6M$ hydrochloric acid and the solution diluted with $6M$ hydrochloric acid to 1 litre; 1 ml of this standard solution contains 1 mg of molybdenum. Aliquots are diluted with $6M$ hydrochloric acid to give solutions with molybdenum concentrations in the range 1–100 ppm.

Eluent solution. Molybdenum is eluted with a mixture of methanol and $6M$ hydrochloric acid (9 : 1). To avoid the formation of air bubbles in the resin bed, this solution should not be prepared immediately before use but preferably one day in advance.

Aluminum chloride solution. Enough $AlCl_3 . 6H_2O$ is dissolved in $6M$ hydrochloric acid to give a solution containing 4 mg of Al per ml.

Sodium sulphate solution, 10% w/v.

Other reagents. Solid boric acid, methanol. anhydrous sodium carbonate, 1% w/v sodium carbonate solution, $6M$ and concentrated hydrochloric acid, sulphuric acid (1 + 1), concentrated hydrofluoric acid, concentrated nitric acid and concentrated perchloric acid.

Apparatus and operating conditions

A Perkin-Elmer 303 atomic-absorption spectrophotometer (equipped with a Hitachi-Perkin-Elmer Recorder 56 connected to a Perkin-Elmer Recorder read-out accessory) was used with the following instrumental settings.

Vanadium determination

Grating:	ultraviolet
Wavelength:	318·4 nm
Scale expansion:	10 ×
Slit:	4(1 mm, 0·7 nm bandpass)
Source:	vanadium hollow-cathode lamp
Lamp current:	40 mA
Burner:	nitrous oxide-acetylene
Nitrous oxide pressure:	30 psig; 6.0 on flowmeter (arbitrary scale)
Acetylene pressure:	8 psig; 5·5 on flowmeter (arbitrary scale)
Noise suppression:	3

Molybdenum determination

Grating:	ultraviolet
Wavelength:	313·3 nm
Scale expansion:	10 ×
Slit:	4(1 mm, 0·7 nm)
Source:	molybdenum hollow-cathode lamp
Lamp current:	30 mA
Burner:	nitrous oxide-acetylene
Nitrous oxide pressure:	30 psig; 6·0 on flowmeter (arbitrary scale)
Acetylene pressure:	8 psig; 5·5 on flowmeter (arbitrary scale)
Noise suppression:	3

Under these conditions the sensitivity is 1·25 ppm of vanadium for 1% absorption, and 0·5 ppm of molybdenum.

For the spectrophotometric determination of vanadium[64] and molybdenum[65] a Beckman model B spectrophotometer equipped with 1-cm cells was used.

The ion-exchange separations were performed by using columns of the same type and dimensions as described earlier.[66]

Determination of distribution coefficients

The distribution coefficients (K_d-values) and elution characteristics of molybdenum and other adsorbed elements were determined by using the column method.[67,68]

$$K_d = \frac{\bar{V} - V}{m}$$

where $\bar{V}$ = volume of elution peak (ml), V = void volume (0·7 ml when using 1 g of the resin) and m = weight of air-dried resin (g)..

Procedure

Dissolution of sodium diuranate samples. To 1 g of the yellow cake sample add 50 ml of concentrated hydrochloric acid and evaporate the solution to dryness on a steam-bath. Take up the residue in 50 ml of 6*M* hydrochloric acid, filter off the residue of silica and wash it with a few ml of 6*M* hydrochloric acid. If a large amount of silica is present, take up the residue in a 1 : 1 mixture of concentrated hydrofluoric and nitric acid and evaporate the solution to dryness. Dissolve any insoluble fluorides by repeated evaporations on the steam-bath with concentrated hydrochloric acid and an excess of boric acid, evaporate the solution to dryness, take up the residue in 10 ml of 6*M* hydrochloric acid, filter off the boric acid and combine the filtrate with the original filtrate from treatment of the sample with 6*M* hydrochloric acid. Dilute the resulting solution to 100 ml with 6*M* hydrochloric acid and use it for the ion-exchange separation of vanadium and molybdenum (sample solution).

Dissolution of geological samples. (*a*) *Dissolution with acids.* To 1–2 g of the thoroughly homogenized sample in a 250-ml beaker, add 50 ml of concentrated hydrochloric acid and heat the mixture for 2 hr on a steam-bath. Then take the mixture to dryness and, while heating, dissolve the residue in 6*M* hydrochloric acid. Cool to room temperature, filter off the insoluble portion (mainly silica) and wash it with 6*M* hydrochloric acid (filtrate I). Transfer the residue to a plastic beaker and treat it with a 2 : 1 mixture of concentrated hydrofluoric and nitric acid to remove silica. Evaporate this mixture to dryness, and repeat the treatment with hydrofluoric and nitric acid 2 or 3 times if a large amount of residue remains. Then add 6*M* hydrochloric acid and solid boric acid (approximately 2 g) and evaporate the mixture to dryness. This step is repeated twice to completely remove both fluoride and nitrate ions. Take up the residue, with heating, in 6*M* hydrochloric acid, cool to room temperature, filter off the boric acid and wash it with 6*M* hydrochloric acid (filtrate II). Combine filtrates I and II and evaporate them to dryness on a steam-bath. Take up the residue in 6*M* hydrochloric acid (filter off any acid-insoluble portion) and dilute the solution to 100 ml with 6*M* hydrochloric acid. The sample solution thus obtained is used for the ion-exchange separation of vanadium and molybdenum.

(*b*) *Dissolution by alkaline fusion.* Fuse 1 g of the homogenized sample (*e.g.*, uranium-bearing mineral) and 5 g of anhydrous sodium carbonate in a platinum crucible for 30 min and add water to the cold melt. After complete disintegration of the melt (this usually takes 24 hr), filter off the insoluble portion (ferric hydroxide, hydrous oxides of titanium and zirconium, carbonates of the alkaline earth metals *etc*) on a dense filter and discard the residue after washing it with 1% sodium carbonate solution. Acidify the filtrate (containing vanadium and molybdenum) with concentrated hydrochloric acid and precipitate silica in the usual way by evaporating two or three times with concentrated hydrochloric acid. Take up the residue from the last evaporation step in 6*M* hydrochloric acid and after 12 hr filter off the silica and dilute the filtrate to 100 ml with 6*M* hydrochloric acid. From this sample solution vanadium and molybdenum are separated by means of the ion-exchange procedure described below.

Ion-exchange separation

Pass a suitable aliquot of the 6*M* hydrochloric acid sample solution (sorption solution) through the ion-exchange column containing 4 g of the resin (pretreated with 50 ml of 6*M* hydrochloric acid) at a flow-rate which corresponds to the back-pressure of the resin bed. Wash the resin with 80 ml of 6*M* hydrochloric acid and combine this eluate with the effluent obtained from passage of the sorption solution. These combined 6*M* hydrochloric acid effluents contain all the vanadium (vanadium eluate).

After elution of the vanadium, remove the molybdenum quantitatively from the resin by washing it with 600 ml of the eluent solution (molybdenum eluate).

Determination of vanadium

Evaporate an aliquot (if larger amounts of vanadium are expected) or the entire volume (if only a few ppm of vanadium are present) of the vanadium eluate to dryness on a steam-bath. To the residue add 1 ml of the aluminium chloride solution and by means of 6*M* hydrochloric acid transfer the solution to a 10-ml standard flask and dilute it to volume with the same acid. Determine the vanadium content of this solution by atomic-absorption spectrophotometry. For calibration aspirate suitable standard solutions before and after each bath of samples.

In many samples the vanadium was also determined by using a modification of the tungstophosphate photometric procedure which was decribed earlier.[64] Also for the purpose of comparison the vanadium contents of the yellow cake samples have been determined by using a procedure which is based on the titration of vanadium (V) with standardized ferrous ammonium sulphate solution in the presence of barium diphenylaminesulphonate as indicator.[69]

Determination of molybdenum

Depending on the expected molybdenum content, evaporate an aliquot or the entire volume of the molybdenum eluate to dryness on a steam-bath and take up the residue in 10 ml of a 1 : 1 mixture of concentrated nitric and perchloric acid. Heat this solution on the steam-bath to remove nitric acid and then fume off the perchloric acid on a hot-plate or a sand-bath. Take up the residue in 5 ml of sulphuric acid (1 + 1) and heat the solution for 3 hr (or longer) on a steam-bath to completely dissolve the molybdenum. Transfer the solution with water to a 10-ml standard flask containing 1 ml of the sodium sulphate solution. Dilute to volume with water and determine the molybdenum by atomic-absorption spectrophotometry. If iron has not been completely separated by the ion-exchange procedure a white residue of iron sulphate may be present in this solution; it has to be filtered off before the molybdenum determination.

Construct the calibration curve by aspirating suitable molybdenum standard solutions (prepared in exactly the same way as the samples) before and after each batch of samples.

For comparison, many samples were analysed spectrophotometrically by a modification of the thiocyanate method.[65]

RESULTS AND DISCUSSION

By means of anion-exchange in pure aqueous 6*M* hydrochloric acid molybdenum can be separated from vanadium and most of the matrix elements but not from uranium and iron, which show an adsorption behaviour very similar to that of molybdenum, whereas a clean-cut separation from vanadium ($K_d < 1$ in 6*M* hydrochloric acid irrespective of oxidation state) can readily be effected. The distribution coefficients of molybdenum(VI), uranium(VI), and iron(III) in 6*M* hydrochloric acid are 228, 283 and ~10^3 respectively[67,70] so that a separation of these metal ions is impossible at this acidity. The separation is not possible with hydrochloric acid at any concentration nor with systems containing nitric or sulphuric acid. In 0–16*M* nitric acid molybdenum and iron show practically no adsorption on strongly basic anion-exchange resins[67] (uranium has only a small distribution coefficient and hence cannot be separated readily from the molybdenum). Furthermore, the solubility of molybdenum in nitric acid media is very low owing to the formation of sparingly soluble molybdic acids. Molybdenum is more soluble in sulphuric acid but cannot be separated from uranium because both elements are strongly retained by the anion-exchanger from 0·05–1·0*N* sulphuric acid.[67] It is also difficult to elute the molybdenum which is co-adsorbed with the uranium.[71]

The conditions for molybdenum separation are considerably improved if mixed aqueous–organic media are used. Organic solvent systems containing hydrochloric acid are the most suitable because molybdenum is readily soluble in them, and there is less hydrolysis than in the presence of other mineral acids. Most important, however, is the effect on the K_d-values. From Table 1 it is seen that the stepwise replacement of 6*M* hydrochloric acid by methanol causes the distribution coefficient of molybdenum to decrease steadily, its K_d-value reaching a minimum in a 9 : 1 mixture of methanol and 6*M* hydrochloric acid (the eluent solution used in the procedure). In this medium the elution characteristics of molybdenum are optimal (see Table 1) and the K_d-values of iron(III) and uranium(VI), 250 and ~10^3 respectively, are sufficiently high to allow the separation of these two elements from molybdenum. Similar conditions exist if the hydrochloric acid concentration is varied but the methanol content kept constant. Table 2 shows that the 6*M* hydrochloric acid mixture is best, although at lower acidities the K_d-values of molybdenum are even lower. From these mixtures, however, uranium and iron are also much less strongly adsorbed so that these media are less suitable for separations.

Table 1. Elution characteristics of molybdenum (0·5 mg) in hydrochloric acid–methanol solutions (1-g column of Dowex 1, X8)

Composition of mixtures % *v/v*	BTV *ml*	$\bar{V}$ *ml*	K_d	EV *ml*
100% 6*M* HCl- 0% methanol	>100	229	(228·3)	>300
90% 6*M* HCl–10% methanol	95	190	(189.3)	>300
80% 6*M* HCl–20% methanol	90	180	(179·3)	>300
70% 6*M* HCl–30% methanol	85	160	(159·3)	>250
60% 6*M* HCl–40% methanol	60	120	(119·3)	>240
50% 6*M* HCl–50% methanol	45	100	(99·3)	240
40% 6*M* HCl–60% methanol	30	70	(69.3)	205
30% 6*M* HCl–70% methanol	20	55	(54·3)	170
20% 6*M* HCl–80% methanol	15	40	(39·3)	160
10% 6*M* HCl–90% methanol	11	25	(24·3)	90
5% 6*M* HCl–95% methanol	11	26	(25·3)	106

BTV = breakthrough volume; $\bar{V}$ = volume of elution peak; K_d = distribution coefficient = $\bar{V}$ – 0·7; EV = elution volume.

The methanol can be replaced by other aliphatic alcohols, methyl glycol (monomethyl ether of ethylene glycol), acetone or tetrahydrofuran, but a disadvantage of these solvents,

Table 2. Elution characteristics of molybdenum (0·5 mg) in 90% methanol–10% hydrochloric acid mixtures (v/v) (1-g column of Dowex 1, X8)

Composition of mixtures % *v/v*	BTV *ml*	$\bar{V}$ *ml*	K_d	EV *ml*
90% methanol–10% 1*M* HCl	3	10	(9·3)	76
90% methanol–10% 3*M* HCl	6	13	(12·3)	91
90% methanol–10% 6*M* HCl	11	25	(24·3)	90
90% methanol–10% 9*M* HCl	15	40	(39.3)	135
90% methanol–10% 12*M* HCl	19	52	(51·3)	155

Table 3. Results of determinations of vanadium and molybdenum in Mexican yellow cake samples

Sample No.	Vanadium content, %			Molybdenum content, %	
	A	B	C	D	E
1	2·10 2·39	2·25 2·31	2·26 2·15	2·80	2·76
2	2·40 2·68	2·65 2·66	2·67 2·64	1·01	1·01
3	3·05 2·83	2·80 2·83	2·88 2·86	1·35 1·44	1·47
4	2·46	2·22 2·32	2·43 2·32	2·41 2·38	2·35
5	2·64	2·62 2·72	2·64 2·56 2·54	2·74 2·71	2·80
6	2·71	2·72	2·67	1·57	1·56
7	3·05 2·92 2·92 2·93	2·40 2·94	2·92 2·92 2·88 2·85	1·12	1·14
8	2·59	2·42 2·68	2·59 2·56	3·82 3·69	3·69
9	2·38	2·42	2·43	1·42	1·45
10	2·70	2·70	2·67	1·47	1·73

A = Vanadium content determined by atomic-absorption spectrophotometry
B = Vanadium content determined by spectrophotometry
C = Vanadium content determined titrimetrically
D = Molybdenum content determined by atomic-absorption spectrophotometry
E = Molybdenum content determined by spectrophotometry

especially the higher alcohols and methyl glycol, is their high viscosity, which reduces the flow-rate through the column, and hence molybdenum cannot be eluted rapidly.

The separation of molybdenum from iron is not quantitative if an aliquot of the sample solution containing more than about 200 mg of an iron-rich sample is passed through the anion-exchange column (all other conditions being the same). Part of the iron passes into the methanolic molybdenum eluate. This is due to the decrease of the distribution coefficient of iron from about 10^3 in 6*M* hydrochloric acid to 250 in the eluent solution, which means a considerable decrease of the break-through volume of iron, which was found to be 740 ml when the column (4 g) was loaded with 10 mg of iron. Thus, on loading the column with for example 100 mg of iron it is evident that part of the iron is eluted together with the molybdenum (under these conditions the break-through volume is 110 ml). This co-elution of iron is indicated by a yellow colour in the eluate.

Since iron, even in large amounts, does not interfere with the determination of molybdenum by atomic-absorption it is possible to isolate molybdenum from aliquots of sample solutions containing up to 1 g of the original sample provided that this does not contain very large amounts of molybdenum and/or uranium (as for example molybdenite and yellow cake), in which case the capacity of the resin for molybdenum and/or uranium might be exceeded and part of the molybdenum pass into the 6*M* hydrochloric acid effluent. If a large amount of uranium is present in the sorption solution the resin is overloaded with the anionic chloride complex of uranium which replaces molybdenum from the resin. Therefore, the aliquot of the 6*M* hydrochloric acid sample solution from materials rich in molybdenum and/or uranium should not contain larger amounts of these two elements than those which are contained in 10–50 mg of the original sample.

While iron does not disturb the atomic-absorption determination of molybdenum it considerably enhances the vanadium absorbance.[1] A similar behaviour is shown by titanium and aluminum. The enhancement by aluminum is constant for ratios of $Al : V > 25 : 1$ and in the presence of this relative concentration of aluminium, 10000 ppm of iron and 600 ppm of titanium no longer cause enhancement, nor do 400 ppm of zirconium, tin, antimony, or molybdenum or 600 ppm of nickel cause any interference.[1] Although iron, molybdenum, tin and antimony are quantitatively separated from the vanadium by adsorption on the anion-exchanger the addition of excess of aluminum chloride to the final solution used for vanadium determination was found to be necessary because many of the samples analysed contained relatively large amounts of titanium, which passes into the 6*M* hydrochloric acid effluent together with the vanadium. Copper, which is co-eluted with the vanadium, was also found not to interfere with the vanadium determination.

The addition of sodium sulphate to the final solution used for molybdenum determination increases the sensitivity[62] of the method and suppresses the influence of foreign ions, including Fe ($<$5000 ppm), Al, Mn, Ni, Co, Cu, W ($<$500 ppm) and Ti ($<$100 ppm).[37] Furthermore, in the absence of excess of sodium sulphate the calibration curve is not rectilinear even at molybdenum concentrations as low as 1 ppm but it is linear in the presence of alkali metal sulphate.

The suitability of the anion-exchange separation method in combination with the atomic-absorption technique described in this paper for the determination of vanadium and molybdenum was tested by analysing numerous samples with contents ranging from a few ppm to milligram amounts of vanadium and molybdenum. The results of these investigations are shown in Tables 3–10 from which it is seen that in practically all cases very good agreement of results was obtained. For comparison the contents of these two elements were

Table 4. Results of vanadium determinations in uranium-bearing Mexican minerals (with uranium contents ranging from 0·06 to 0·4 %)

Sample No.	Vanadium content, %			
	A	B	C	D
1	0·019	0·018	0·016	0·018
	0·019	0·019		
2	0·032	0·030	0·026	0·038
	0·032	0·030		0·039
3	0·018	0·018	0·016	0·018
	0·019	0·018		0·020
4	0·045	0·045	0·040	0·041
	0·047	0·044		0·045
5	0·072	0·072	0·071	0·067
	0·075	0·070		0·068
6	0·150	0·149	0·148	0·150
	0·154	0·152		0·154
7	0·007	0·0065	0·0055	0·0067
	0·0067	0·007		0·0075
8	0·074	0·074	0·071	0·074
	0·075	0·070		0·075
9	0·148	0·147	0·146	0·144
	0·151	0·141		0·146
10	0·104	0·106	0·101	0·098
	0·105	0·100		0·099

A = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange
B = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange and deduction of vanadium-spike which was added before the dissolution of the sample
C = Vanadium content determined by atomic-absorption spectrophotometry without preliminary separation of vanadium by anion-exchange
D = Vanadium content determined by spectrophotometry after separation of vanadium by anion-exchange.

also determined in a large number of samples by spectrophotometric methods (for vanadium and molybdenum)[64,65] and a titrimetric procedure (for vanadium).[69]

The results for the yellow cake samples (Table 3) generally show very good agreement irrespective of the method used for the final determination.

Some uranium-bearing Mexican minerals were analysed and the results are shown in Tables 4 and 5. The results in column C of Table 4 show that direct analysis of the samples of low vanadium concentrations gave low results. This is due to the effect of the matrix elements on the absorbance of vanadium, which is more pronounced at low than at high concentrations of this element. There is no comparable matrix effect on the molybdenum determination (Table 5). Table 5 also shows that the acid and alkali fusion decomposition procedures work equally well.

Table 5. Results of molybdenum determinations in uranium-bearing Mexican minerals (with uranium contents ranging from 0·06 to 0·4%)

Sample No.	Molybdenum content, %				
	A	B	C	D	E
1	0·023 0·025	0·024	0·024	0·024	0·023 0·025
2	0·0053 0·0054	0·0055 0·0054	0·0053	0·005	0·005 0·006
3	0·0089 0·0087	0·0086 0·0099	0·0087	0·008	0·010 0·012
4	0·329 0·335	0·332 0·335	0·0348	0·310	0·330 0·335
5	0·103 0·114	0·105	0·117	0·108	0·109 0·115
6	0·403 0·409	0·353	0·475	0·390	0·398 0·409
7	0·019 0·021	0·022	0·021	0·020	0·021 0·023
8	0·130 0·133	0·123 0·123	0·141	0·123	0·132 0·135
9	0·125 0·130	0·130	0·133	0·120	0·125 0·128
10	0·819 0·782	0·769	0·813	0·726	0·818 0·825

A = Molybdenum content determined by atomic-absorption spectrophotometry after separation of molybdenum by anion-exchange
B = Molybdenum content determined by atomic-absorption spectrophotometry after separation of molybdenum by anion-exchange and deduction of molybdenum-spike which was added before the dissolution of the sample
C = Molybdenum content determined by atomic-absorption spectrophotometry without preliminary separation of molybdenum by anion-exchange
D = Molybdenum content determined by atomic-absorption spectrophotometry after separation of molybdenum by anion-exchange from samples which were dissolved by alkaline fusion
E = Molybdenum content determined by spectrophotometry after separation of molybdenum by anion-exchange

Table 6. Results of determinations of vanadium and molybdenum in IAEA uranium-standard samples[70]

Sample	Vanadium content, %		Molybdenum content, %	
	A	B	C	D
Soil-2, Shale (Sweden)	0·0130	0·0138 (150)	0·00074	0·00073 (10)
Soil-3, Limestone (Iran)	0·0025	0·0024 (30)	0·00018	0·00015 (2)
S-1, Torbernite (Australia)	0·0089	0·0091 (100)	0·0024	0·0021 (25)
S-2, Torbernite (Spain)	0·0029	0·00285 (30)	0·00125	0·00113 (10)
S-3, Carnotite (U.S.A.)	0·328	0·342 (1500)	0·0011	0·0010 (5)

A = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange
B = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange and deduction of vanadium-spike which was added before the dissolution of the sample (the number in parentheses gives the μg of vanadium which were added as spike)
C = Molybdenum content determined by atomic-absorption spectrophometry after separation of molybdenum by anion-exchange
D = Molybdenum content determined by atomic-absorption spectrophotometry after separation of molybdenum by anion-exchange and deduction of molybdenum-spike which was added before the dissolution of the sample (the number in parentheses gives the μg of molybdenum which were added as spike).

Table 7. Results of determinations of vanadium and molybdenum in Canadian radioactive ore standards[72]

Sample	Vanadium content, %		Molybdenum content, %	
	A	B	A	B
D1	0·0025	0·00233 (30)	0·00044	0·00038 (5)
D2	0·0015	0·00135 (20)	0·00054	0·00048 (10)
BL1	0·0217	0·0205 (200)	0·0035	0·0033 (50)
BL2	0·0840	0·0843 (800)	0·00375	0·0035 (50)
BL3	0·0830	0·0838 (800)	0·0041	0·0038 (50)
BL4	0·0720	0·0688 (800)	0·0037	0·0033 (50)

A = Vanadium or molybdenum content determined by atomic-absorption spectrophotometry after separation of these two elements by anion-exchange

B = Vanadium or molybdenum content determined by atomic-absorption spectrophotometry after separation of these two elements by anion-exchange and deduction of vanadium or molybdenum spikes which were added before the dissolution of the sample (the number in parentheses gives the μg of vanadium or molybdenum which were added as spikes)

Table 8. Results of vanadium determinations in geological samples from the Institute of Geological Sciences, London

Sample material	Vanadium content, *ppm*	
	A	B
Marl Slate; Fishburn, Durham	800	795 (400)
Marl Slate; Claxheugh, Durham	880	894 (1000)
IGS 6 (molybdenite–quartz mixture)	2·0	2·0 (2)
IGS 7 (molybdenite–quartz mixture)	2·0	1·8 (2)
IGS 8 (molybdenite concentrate)	9·8	9·6 (10)

A = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange

B = Vanadium content determined by atomic-absorption spectrophotometry after separation of vanadium by anion-exchange and deduction of vanadium-spike which was added before the dissolution of the sample (the number in parentheses gives the μg of vanadium which were added as spike)

Analyses of other uranium-bearing minerals and radioactive ore standards are shown in Tables 6 and 7, and of geological samples (obtained from the Institute of Geological Sciences, London) in Tables 8 and 9. Agreement with results obtained in other laboratories is good except for molybdenum in sample IGS 8.

The results for the geochemical standards obtained from the Centre de Recherches Pétrographiques et Géochimiques also agree well with those from other laboratories (Table 10).

Because the anion-exchange separation can be performed more or less automatically, numerous samples can be analysed simultaneously, *i.e.*, the procedure is very well suited for the routine determination of vanadium and molybdenum by atomic-absorption spectrophotometry.

Table 9. Results of determination of % molybdenum in geological samples from the Institute of Geological Sciences, London

Sample material	This method	Results obtained in other laboratories[44]
Marl Slate; Fishburn, Durham	0·0090 0·0085	0·0087; atomic-absorption 0·0084; atomic-absorption 0·0092; spectrophotometry 0·0107; X-ray fluorescence 0·0100; emission spectrography
Marl Slate; Claxheugh, Durham	0·0056 0·0054	0·0055; atomic-absorption 0·0050; atomic-absorption 0·0054; spectrophotometry 0·0070; X-ray fluorescence 0·0050; emission spectrography
IGS 6 (molybdenite–quartz mixture)	0·134	0·138*; 0·145† (0·034–0·22)§
IGS 7 (molybdenite–quartz mixture)	1·24	1·24*; 1·21† (0·69–1·44)§
IGS 8 (molybdenite concentrate)	54·2 55·0	57·1*; 56·86† (50·6–58·5)§

* Accepted mean
† Mean % Mo
§ Range of values

Table 10. Results of determinations of vanadium and molybdenum in geochemical standards from the Centre de Recherches Pétrographiques et Géochimiques

Sample	Vanadium content, *ppm*		Molybdenum content, *ppm*	
	A	B	A	B
Granite GA	43	36	0·9	1
Granite GH	5	5	2·9	4
Basalte BR	248	240	2·4	3
Biotite Mica-Fe	134	135	2·1	<1·1; <3; <7; <10; 1·7; 51
Phlogopite Mica-Mg	86	75; 88	0·5	—
Diorite DR-N	225	225	2·3	<7; 3; 5; 6
Serpentine UB-N	68	100	1·1	<3; <3; <7; 6
Bauxite BX-N	365	275; 300 395; 450	7·8	<7; 7; 12
Disthène DT-N		128; 155; 180	1·1	<5; <7; 5
Verre Synthetique VS-N*	1169	902–1857	915	918–1100

A = Vanadium or molybdenum content determined by atomic-absorption spectrophotometry after separation of these two elements by anion-exchange
B = Vanadium or molybdenum content determined in other laboratories[73,74]

* The vanadium and molybdenum contents of this synthetic glass standard are given in ppm V_2O_5 and ppm MoO_3 respectively. Theoretically this sample should contain 1000 ppm of each oxide

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Zusammenfassung—Es wird ein Verfahren zur Bestimmung von Vanadium und Molybdän bis herauf zum Milligramm-Bereich durch Atomabsorptions-Spektrophotometrie in Uranoxidkonzentraten, uranführenden Mineralien und geochemischen Standards beschrieben. Nach dem Aufschluß mit Säuren werden diese beiden Elemente voneinander und von den Hauptbestandteilen durch Anionenaustausch in 6 M Salzsäure an dem stark basischen Anionenaustauschharz Dowex 1, × 8 (Chloridform) getrennt. Vanadium wird nicht adsorbiert und geht in die durchlaufende Lösung, während Molybdän am Harz adsorbiert wird. Zur Elution von Molybdän wird ein Gemisch von Methanol und 6 M Salzsäure (9:1 V/V) verwendet. Nach dem Eindampfen der durchgelaufenen 6 M Salzsäure und des wäßrig-organischen Eluats werden Vanadium und Molybdän durch Atomabsorptions-Spektrophotometrie bestimmt. Das Verfahren wurde getestet, indem zahlreiche Proben mit Gehalten zwischen einigen ppm und Milligramm-Mengen Vanadium und Molybdän analysiert wurden. Zum Vergleich wurde die Konzentration dieser beiden Elemente in einer großen Anzahl von Proben mit spektrophotometrischen und titrimetrischen Verfahren bestimmt. In allen Fällen stimmten die Ergbenisse sehr gut überein.

Résumé—On décrit une méthode pour le dosage du vanadium et du molybdène par spectrophotométrie d'absorption atomique, jusqu'au niveau du milligramme, dans des échantillons de gâteau jaune, de minéraux uranifères et d'étalons géochimiques. Après attaque aux acides, ces deux éléments sont séparés l'un de l'autre et des éléments de la matrice au moyen d'un échange d'anions en acide chlorhydrique 6*M* sur la résine échangeuse d'anions fortement basique Dowex 1-X8 (forme chlorure). Le vanadium n'est pas adsorbé et passe dans l'effluent tandis que le molybdène est adsorbé sur la résine. Pour l'élution du molybdène, on utilise un système solvant mixte aqueuxorganique consistant en méthanol et acide chlorhydrique 6*M* (9:1 v/v). Après évaporation de l'effluent acide chlorhydrique 6*M* et de l'éluat mixte aqueux-organique, le vanadium et le molybdène sont déterminés par spectrophotométrie d'absorption atomique. La méthode a été essayée en analysant de nombreux échantillons avec des teneurs en vanadium et molybdène allant de quelques p.p.m. à des quantités de l'ordre du milligramme. Pour comparaison, les concentrations en ces deux éléments ont été déterminées dans un grand nombre d'échantillons par des techniques spectrophotométriques et titrimétriques. Dans tous les cas on a obtenu un très bon accord des résultats.

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AUTOMATED DETERMINATION OF FLUORIDE ION IN THE PARTS PER MILLIARD RANGE

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Summary—Fluoride, down to 2 ppM, has been determined by automated direct potentiometry using a fluoride ion-selective electrode. The method reduces the dilution and contamination effects of TISAB and takes the electrode response-time into consideration. The relative standard deviation for water samples is 1·5–1·8% and the recovery varies from 96 to 107%.

In some environmental studies the need arose for the determination of fluoride ion in water samples down to the parts per milliard (ppM) level. Of all the ion-selective electrodes developed in recent years, the fluoride electrode has probably been the most outstanding. It exhibits Nernstian response, in media ranging from neutral to moderately acidic, over the fluoride concentration range from 1*M* down to 10^{-5} or $10^{-6}M$.[1,2] The detection limit is *ca.* $10^{-6}M$ in a solution with an ionic strength of 2, but in pure sodium fluoride it may even be $10^{-7}M$.[3,4] Various ions present in solution affect the electrode potential through changes in the fluoride ion activity.[5,6,7] An elegant and rapid method based on a 1:1 dilution of both samples and standards with total ionic strength adjustment buffer (TISAB) seems to have largely solved these difficulties.[8] The later modification of TISAB by replacing citrate with 1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid (DCTA) improved the method significantly.[9] Sixteen or so papers covering water-sample analyis have been published. The Federal Water Pollution Control Administration critically evaluated the methods for the determination of fluoride in water and reported that the fluoride electrode method is significantly more precise and accurate than the other methods and, because of the convenience of electrode operation, is the method of choice.[10]

The practical detection limit achieved with a manual procedure and commercially available TISAB in our laboratories was 100 ppM ($5 \times 10^{-6}M$) of fluoride ion. The need for the determination of fluoride in the ppM range ($10^{-7}M$) led to the development of the method described in this paper.

EXPERIMENTAL

Reagents

All chemicals were of reagent grade. Only fluoride-free chemicals were selected. Demineralized doubly distilled water was used.

The following *total ionic strength adjusting buffers* (TISAB) were prepared (and used).

1. Orion No. 94-09-09 TISAB.
2. Common TISAB. In 500 ml of distilled water were dissolved, with stirring, 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of disodium DCTA. The solution was adjusted to pH 5·5 with 50% sodium hydroxide solution and then diluted to 1000 ml with water.

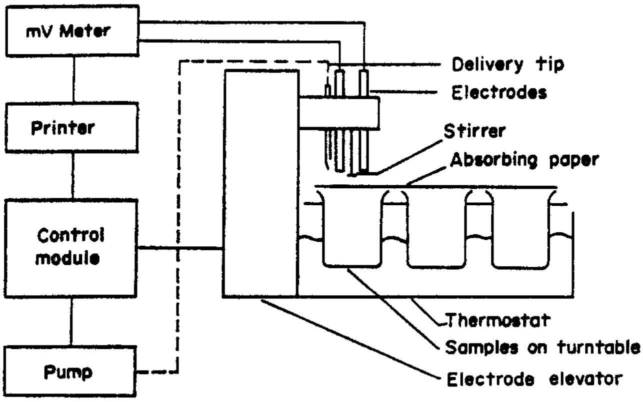

Fig. 1. Block diagram of equipment assembly.

3. Modified TISAB (1). Sodium hydroxide (68 g) and DCTA (4 g) were dissolved in 500 ml of demineralized doubly-distilled water and mixed with 120 g of glacial acetic acid. After adjustment of the pH to 5·5 the solution was diluted to 1000 ml with the demineralized doubly-distilled water.
4. Modified TISAB (2). The concentration of TISAB (1) was increased by a factor of 3. The resulting pH of TISAB (2) is over 6 and must not be adjusted. After mixing of 10 ml of TISAB (2) with 50 ml of sample, the pH reaches the correct value of 5·5.

Apparatus

A combination fluoride-electrode (Orion Model 96-09) was used in this study. All results reported were obtained with a modified version of the automated apparatus for direct potentiometry described in a previous paper.[11] A new apparatus control module was designed, permitting greater flexibility of automatic timing, since it is programmable for almost any desired timing cycle. In addition, the apparatus consists of an Orion 801 digital mV/pH meter, Orion 751 digital printer, Fisher 9-319-50 electrode–elevator–turntable assembly, and a "Desaga" peristaltic pump. The block diagram of the apparatus is shown in Fig. 1. The most prominent advantages of the apparatus are: allowance for the response-time of the electrode, constant temperature-control, absence of cross-contamination and simplicity in operation. It is better suited than the automated potentiometric flow-through system, to the specific requirements of ion-selective electrodes.

Procedure

Standards and samples (50·0 ml), pipetted into 200-ml Berzelius beakers, were placed in the turntable unit of the apparatus. The immersion of the electrode, the addition of TISAB (50 or 10 ml), stirring and print-out of the results (in mV) after the preselected time (10 min), then the rinsing of the electrodes and changing of samples, was provided automatically by the apparatus. A sampling rate of 6 samples/hr was found to be optimal for concentrations lower than $10^{-6}M$. This sampling rate allows 10 min for the stabilization of the electrode potential.

RESULTS AND DISCUSSION

The derivation of the detection limit of the fluoride-ion electrode from the solubility product of the lanthanum fluoride crystal (approximately 10^{-25}) indicates a significantly lower detection limit than the values actually obtained and cited in the literature.

The calibration curve for pure sodium fluoride solution (curve 1 in Fig. 2) shows a Nernstian response from 1000 down to 5 ppM. In contrast, a calibration curve prepared with commercial TISAB (curve 2, Fig. 2) indicates that the detection limit of the fluoride electrode is some hundreds of ppM. This observation indicates that the presence of TISAB significantly influences the detection limit of the fluoride electrode.

According to Ross[13] the presence of a species which forms a very stable complex with one

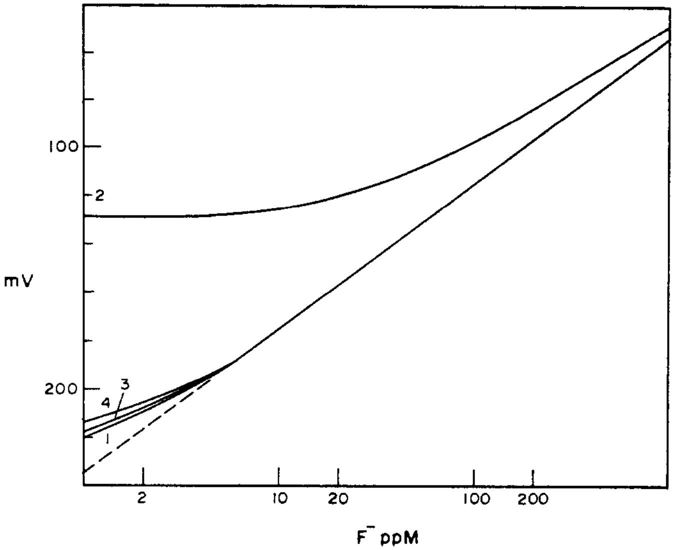

Fig. 2. Calibration curves for F^- in different media *1*—NaF; *2*—NaF in commercial TISAB; *3*—NaF in 0·01*M* DCTA; *4*—NaF in 0·05*M* DCTA.

of the component ions of the membrane, *e.g.*, citrate, EDTA or DCTA, increases the detection limit of the fluoride electrode. To confirm this, a calibration curve for sodium fluoride was prepared for 0·01*M* and 0·05*M* DCTA background. In Fig. 2 (curves 3 and 4) it can be seen that DCTA only mildly affects the detection limit of the electrode, and the calibration curve is nearly identical with the curve obtained for a pure sodium fluoride solution. To illustrate this point further, the commonly used TISAB was prepared from selected, "fluoride-free" chemicals. The calibration curve for sodium fluoride in the background of this TISAB, shown as curve 1 in Fig. 3, indicates that the detection limit decreased to 20 ppM.

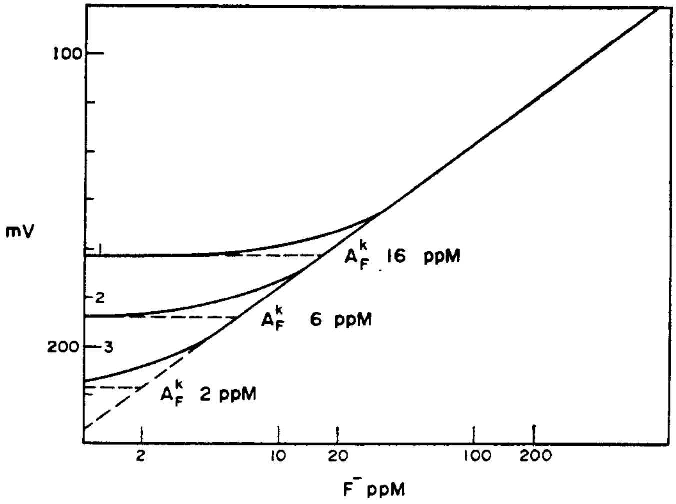

Fig. 3. Calibration curves for F^- in different TISAB solutions. *1*—NaF in "fluoride-free" TISAB;*2*—NaF in modified TISAB(1); *3*—NaF in modified TISAB(2).

It appears that the high detection limit of the method has been caused, to a certain degree, by the contamination of the samples with the fluoride present in the components of common TISAB.[14]

During the search for "fluoride-free" chemicals there were many indications that the main contributors of the fluoride ion were distilled water and sodium chloride. Sodium chloride as well as other chemicals suitable to replace it (potassium chloride or nitrate, sodium nitrate or acetate, *etc.*) showed, in fact, some differences in the fluoride ion contents, but in all cases the level of fluoride ion was not acceptable for the measurements at the ppM level. However, we found that the sodium hydroxide and acetic acid were practically free of fluoride ion.

In order to eliminate the contamination of the sample, the modified TISAB (1) was prepared. To maintain the buffering and ionic-strength adjusting capacity of the TISAB, the concentrations of acetic acid and sodium hydroxide were increased, eliminating the need for addition of sodium chloride. The water used for the preparation was demineralized and doubly distilled. The calibration curve of sodium fluoride in the background of modified TISAB (1) (curve 2, Fig. 3) shows an improvement of the detection limit to 10 ppM of F^- ion.

It can, however, be argued that the 1:1 dilution of the sample with TISAB was a factor influencing the detection limit. Therefore, to minimize this dilution effect, a second, threefold more concentrated modification of TISAB (1) was used. A 1:5 mixing ratio of TISAB (2) with sample was found to be the most convenient, maintaining the total ionic strength of the sample at 1*M*. In this case the calibration curve 3 in Fig. 3 shows the Nernstian response of the electrode down to a concentration of 5 ppM and a practical detection limit of 2 ppM of fluoride ion.

For this reason, the values of $A_F{}^0$ (zero activity of fluoride ion) commonly used in the literature [13] to describe the lower detection limit of the electrode have been replaced in Fig. 3 by values of $A_F{}^k$, where $A_F{}^k$ signifies a point on the potential–activity curve where the activity of the fluoride remains constant under given experimental conditions.

These results lead to the conclusion that the improvement of the detection limit from 200 to 2 ppM has been achieved (*a*) by limitation of the contamination of the samples through the use of the modified fluoride-free TISAB (2), (*b*) by reduction of the dilution of the sample, and (*c*) by standardization of the measurements through automated procedures.

The precision of the determination of fluoride ion was estimated through the measurement of 10 samples each at the following concentrations: 1,2,5,10,20,50,100,500,1000 ppM. The relative standard deviations were calculated and are summarized in Table 1. They are about 2% except for the two lowest concentrations.

Table 1. Precision of the determination of fluoride ion

F^- in the sample, *ppM*	Relative standard deviation, %*	F^- in the sample, *ppM*	Relative standard deviation, %*
1	10·0	50	1·8
2	4·1	100	1·6
5	2·0	500	1·6
10	1·8	1000	1·7
20	1·7		

* Ten determinations at each concentration.

Table 2. Recovery of fluoride ion in synthetic lake water samples

Originally present, *ppM*	Added, *ppM*	Total, *ppM*	Found, *ppM*	Recovery, %
2	5	7	7·5	107
2	20	22	23	105
4	5	9	9	100
4	20	24	25	104
10	5	15	15	100
10	20	30	29	97
21	5	26	25	96
21	20	41	40	98
54	5	59	60	102
54	20	74	75	101

The results of the determination of fluoride ion in water samples are presented in Table 2. Ten samples of synthetic lake water, prepared from chemicals containing traces of fluoride, were analysed for fluoride-ion content *via* the ion-selective electrode as well as by the ASTM D1179-68 SPADNS method. The mean value of six determinations (3 by each method) were considered to give the "originally present" content of fluoride ion in the samples. Known amounts of fluoride, in the concentration range from 1 to 500 ppM were added and the solutions were analysed again. The recovery of fluoride ion was in the range 96–107%.

Ten samples of natural water were analysed in the same manner. The content of possible interfering ions was in the following ranges: 10–200 ppm Ca^{2+}, 2–20 ppm Mg^{2+}, 1–10 ppM Fe^{3+}, and 2–50 ppM Al^{3+}. The recovery of fluoride ion was 92–107% (Table 3).

Table 3. Recovery of fluoride ion in natural water samples

Originally present, *ppM*	Added, *ppM*	Total, *ppM*	Found, *ppM*	Recovery, %
3	10	13	12	92
5	10	15	16	107
7	10	17	18	106
11	10	21	22	105
16	10	26	25	96
22	10	32	31	97
48	10	58	60	103
85	10	95	93	98
94	10	104	100	96
123	10	133	135	102

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DISTINGUISHING POLYFUNCTIONAL FROM MONOFUNCTIONAL ACIDS AND BASES BY ACID–BASE TITRIMETRY, MULTIPARAMETRIC CURVE-FITTING, AND DEVIATION-PATTERN RECOGNITION

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Summary—A new technique for distinguishing diacidic from monoacidic weak bases (or dibasic from monobasic weak acids) is based on fitting the data obtained in a potentiometric acid–base titration to theoretical equations for the titration of a monoacidic base (or monobasic acid). If the substance titrated is not monofunctional the best fit to these equations will involve systematic deviations that, when plotted against the volume of reagent, yield a "deviation pattern" with a shape characteristic of polyfunctional behaviour. Ancillary criteria based on the values of the parameters obtained from the fit are also described. There is a range of uncertainty associated with each of these criteria in which the ratios of successive dissociation constants are so close to the statistical values that it is impossible in the face of the errors of measurement to decide whether the substance is monofunctional or polyfunctional. If the data from one titration prove to lie within that range, the decision may be based on the results of a second titration performed at a different ionic strength. Further fitting to the equations describing more complex behaviour provides a basis for distinguishing non-statistical difunctional substances from trifunctional ones, trifunctional ones from tetrafunctional ones, and so on.

There has been considerable discussion of the problems that arise in attempting to decide whether an unknown acid or base is monofunctional or polyfunctional. Sometimes the decision can be made by inspecting the titration curve obtained in a potentiometric acid–base titration; for example, a dibasic acid with dissociation constants which are not too large, too small, or too nearly equal gives a curve showing two distinct stages of neutralization and having a point of maximum slope very near each of the two equivalence points. As the value of the ratio K_1/K_2 decreases, the two stages of neutralization become harder to discern; the inflection between them deteriorates and may disappear completely; and casual inspection no longer serves to distinguish the curve from the one that would be obtained if the acid were monobasic. There is a value of this ratio (or, more generally, a set of values of the ratios of the successive dissociation constants K_i/K_{i+1} of a polybasic acid) for which the curve is exactly identical with that of a monobasic acid, so that the distinction becomes impossible. Should K_i/K_{i+1} be smaller than these "statistical" values,[1–3] differences from the monobasic-acid curve reappear, and the distinction again becomes theoretically possible.

Limiting the discussion to dibasic acids for convenience and defining a parameter m by the equation

$$m = K_1/K_2 \tag{1}$$

there are thus four possible cases:

1. $m > 10m_{\text{stat}}$, where m_{stat} is the statistical ratio, 4.[1-3]
2. $m_{\text{stat}} < m < 10m_{\text{stat}}$
3. $m = m_{\text{stat}}$
4. $m < m_{\text{stat}}$

In the first case the distinction is easy and requires no discussion; in the third it is impossible and discussion would be fruitless.

To deal with the second and fourth, in which only one point of maximum slope exists or can be discerned on the titration curve, Sturrock[4] proposed a criterion based on the value of the quantity Δ(pH) defined by the equation

$$\Delta(\text{pH}) = \text{pH}_{V/V^*=3/4} - \text{pH}_{V/V^*=1/4} \tag{2}$$

where V is the volume of reagent added and V^* is the volume consumed at the single identifiable end-point. It was originally suggested that Δ(pH) is equal to 0·954 ($=\log_{10} 9$) for a monobasic acid, but exceeds this value for a polybasic one, but further examination by Lomax and Bard,[5] Hamann,[6] and Meites[3] has shown this to be oversimplified: the value of 0·954 is the largest that can be obtained with a monobasic acid. Both fairly strong and fairly weak monobasic acids give values of Δ(pH) that are not only smaller than 0·954 but also dependent on the concentrations of acid and base employed. Moreover, although a dibasic acid for which m/m_{stat} exceeds 1 will give a value of Δ(pH) exceeding that for an appropriately chosen monobasic acid under comparable conditions, one for which m/m_{stat} is smaller than 1 will give a value of Δ(pH) smaller than that for a monobasic acid.

A further difficulty is that unless the full titration curve has been recorded automatically, the two individual pH-values needed for the calculation of Δ(pH) from equation (2) must be obtained by interpolation. Values of Δ(pH) are consequently afflicted by errors that depend on both the precision of the measured pH-values and their spacing along the titration curve. A crude estimate of their magnitude may be made by supposing that measurements are made at intervals of 10% of the equivalent volume of reagent in the titration of a monobasic or "statistical" polybasic acid under such conditions that the theoretical value of Δ(pH) is 0·954. The value of $\text{pH}_{V/V^*=3/4}$ will then have to be obtained by interpolation between the experimental points at $V/V^* = 0{\cdot}7$ and 0·8. If there is no error of measurement the pH-values at these points will differ by 0·234. It is reasonable to suppose that the interpolated pH-value halfway between these points will have a standard error of about one-fifth of this difference, or say ±0·05. As the standard error of $\text{pH}_{V/V^*=1/4}$ will have the same value, that of Δ(pH) may be taken as ±0·07.

The corresponding uncertainty in m may be calculated from an empirical equation relating Δ(pH) to m;[3] for a statistical dibasic acid under conditions such that the theoretical value of Δ(pH) is 0·954, the value of $dm/d\Delta(\text{pH})$ is 0·0558. Since $m_{\text{stat}} = 4$ for a dibasic acid, it may be concluded that a dibasic acid for which m/m_{stat} lies in the range $0{\cdot}7 < m/m_{\text{stat}} < 1{\cdot}3$ cannot reliably be distinguished from a monobasic one by means of the value of Δ(pH). It may further be concluded that this is the minimum width of this range: as the values of K_1 and K_2 increase or decrease, so that the theoretical value of Δ(pH) for the corresponding monobasic acid decreases below 0·954, discrimination between dibasic and monobasic acids becomes more rather than less difficult. For example, the curve obtained in titrating a dibasic acid for which K_1 was 10^4 and K_2 was 10^2 could not be distinguished from that for a monobasic strong acid despite the fact that m/m_{stat} for the dibasic acid would far exceed 1.

Dibasic acids for which both K_1 and K_2 are very large are not common, but those of more moderate strengths for which m/m_{stat} lies between 0·7 and 1·3, at least under some conditions, are far more so. The values of K_1 and K_2 that are relevant are not the thermodynamic constants K_i^0 but the concentration constants defined by equations of the form

$$K_i = \frac{[H^+][H_{2-i}X^{(i-z)-}]}{[H_{3-i}X^{(i-z-1)-}]} = \frac{y_{H_{3-i}X^{(i-z-1)-}}}{y_{H^+}y_{H_{2-i}X^{(i-z)-}}} K_i^0 \tag{3}$$

where the y's denote single-ion molarity activity coefficients and z denotes the charge on the diprotonated species H_2X^{z+}. Consequently the ratio K_1/K_2 is given by

$$\frac{K_1}{K_2} = \frac{y_{i-z-1}^2}{y_{i-z}y_{i-z-2}} \frac{K_1^0}{K_2^0} \tag{4}$$

where the subscripts give the numerical values of the charges on the ions to which the activity coefficients pertain. According to the Debye-Hückel limiting law, the activity-coefficient term in equation (4) decreases as the ionic strength increases, and does so at the same rate if z is either $+2$, $+1$, or 0 but more rapidly if z has any other value. Hence even an acid for which the ratio K_1^0/K_2^0 is well above the statistical value may be impossible to distinguish from a monobasic one by applying the Δ(pH) criterion to data obtained in a titration at a finite ionic strength.

Enough has been said to indicate that this criterion is a very weak reed. This manuscript describes a completely different approach. It is suggested that the data obtained in a titration at constant ionic strength be fitted to the equation that describes the titration curve of a monofunctional compound, employing multiparametric curve-fitting to find the values of the parameters in that equation that yield the best fit. That equation and those parameters may then be combined to obtain a set of calculated values of the pH at each of the experimental points. The deviations of these from the measured values are plotted against either the volume of reagent or the titration parameter f $(= V/V^*)$, which is proportional to the volume of reagent. If the substance titrated is truly monofunctional, the points on this plot will be randomly scattered around the volume or f axis. If it is polyfunctional and if the ratios of the dissociation constants differ from the statistical values, the points will instead be scattered around a curve having a shape characteristic of the functionality. There is still a range over which the pattern that is characteristic of, say, a difunctional compound will be masked by random experimental errors. The range of values of m over which this can happen depends on the precision of measurement of the pH-values but is unlikely to be as wide as the range of uncertainty for the Δ(pH) criterion. Should the data obtained in one titration prove to lie within this range, the fact that the ratio of two successive dissociation constants depends on ionic strength can be turned to advantage by performing a titration at a different ionic strength and subjecting the data obtained from it to a similar analysis.

The calculations, the deviation patterns, and several ancillary criteria made possible by the calculations are described in detail for difunctional substances. Although the prior literature has dealt exclusively with the problem of distinguishing monobasic from polybasic acids, we shall consider that of distinguishing monoacidic from polyacidic bases. This is because of a wish to facilitate comparison of the present work with the results obtained by applying multiparametric curve-fitting to data obtained in acidimetric titrations of very dilute solutions of monoacidic bases,[7] which will be described in a later communication. What is said here about titrations of monoacidic and diacidic bases can of course be applied *mutatis mutandis* to those of monobasic and dibasic acids.

EXPERIMENTAL

Computation

All the numerical computations described here were performed on a PDP8/I minicomputer (Digital Equipment Corporation, Maynard, Mass.). For reasons irrelevant to this work the computer is operated in a multi-user configuration and in a language in which execution of the multiparametric curve-fitting programme previously described[8] is inconveniently slow. It has therefore been supplanted by another programme, based on the method of steepest descent rather than on that of pit-mapping, and very much faster in operation.

Except in a few cases that will be discussed separately, it was assumed that 100 ml ($= V_b^0$) of a 0·1000M ($= C_b^0$) solution of a weak diacidic base X^{2-} was titrated with 1·000M ($= C_a^0$) solution of a strong monobasic acid. The formal dissociation constants K_1 and K_2 of the diprotonated acid H_2X were taken as

$$K_1 = 10^{-4}(m/m_{stat})^{1/2} \tag{5a}$$

and

$$K_2 = 10^{-4}/(m/m_{stat})^{1/2} \tag{5b}$$

so that $(K_1K_2)^{1/2}$ was always 10^{-4}. The titration-curve equation

$$[H^+]^4 + \left(K_1 + \frac{2V_b^0C_b^0 - V_aC_a}{V_b^0 + V_a}\right)[H^+]^3 + \left(K_1K_2 - K_w + K_1\frac{V_b^0C_b^0 - V_aC_a}{V_b^0 + V_a}\right)[H^+]^2 - \left(K_1K_w + K_1K_2\frac{V_aC_a}{V_b^0 + V_a}\right)[H^+] - K_1K_2K_w = 0 \tag{6a}$$

was solved for $[H^+]$ at each of twelve points, where the volume of acid V_a was 1, 3, ..., 21, 23 ml. This number and spacing of points would be relatively easy to obtain in an actual titration. The resulting values of $[H^+]$ were combined with the equation

$$\mathrm{pH} = -\log_{10}[H^+] \tag{6b}$$

to obtain a set of synthetic data representing the titration of X^{2-} in a hypothetical medium in which the activity coefficient of hydrogen ion was known to be 1. Such sets of data were calculated at intervals of a few per cent in m/m_{stat} over the range $0{\cdot}5 < m/m_{stat} < 10$. Near the upper end of this range a poorly marked region of maximum slope could just be discerned in the vicinity of the first (HX^-) equivalence point, but otherwise the second (H_2X) equivalence point was the only one that could be identified. A fairly typical curve is shown by the open circles in Fig. 1, where many additional points are given so as to define its entire course.

The "data" thus obtained were then subjected to multiparametric curve-fitting, using the equations

$$[H^+]^2 + \left(K_a + \frac{V_b^0C_b^0 - V_aC_a}{V_b^0 + V_a}\right)[H^+] - \frac{V_aC_a}{V_b^0 + V_a}K_a = 0 \tag{7a}$$

and

$$\mathrm{pH} = -\log_{10}(y_{H^+}[H^+]) \tag{7b}$$

appropriate to the hypothesis that the base being titrated is monoacidic and sufficiently strong to permit neglecting the concentration of hydroxyl ion at every point, and the best values of the parameters C_b^0, K_a, and y_{H^+} were obtained. With $m/m_{stat} = 1$ the standard deviation from regression was of the order of 10^{-6} pH unit and the results were $C_b^0 = 0{\cdot}199997$, $K_a = 1{\cdot}00008 \times 10^{-4}$, and $y_{H^+} = 1{\cdot}00002$, in agreement with the expected values, 0·2, 1×10^{-4}, and 1.

RESULTS AND DISCUSSION

For any value of m/m_{stat} other than 1, the fit to equations (7a) and (7b) naturally involves larger and systematic errors. The behaviour of these may be deduced by comparing the curve in Fig. 1, which represents the best fit obtainable on the hypothesis of monofunctionality, with the "experimental" points shown by the open circles. As long as m/m_{stat} exceeds 1, the best monofunctional fit lies below the "experimental" curve near the start of the titration, crosses it three times, and finally lies above it after the second equivalence point has been passed. A striking feature of this fit is that the computed value of C_b^0 is

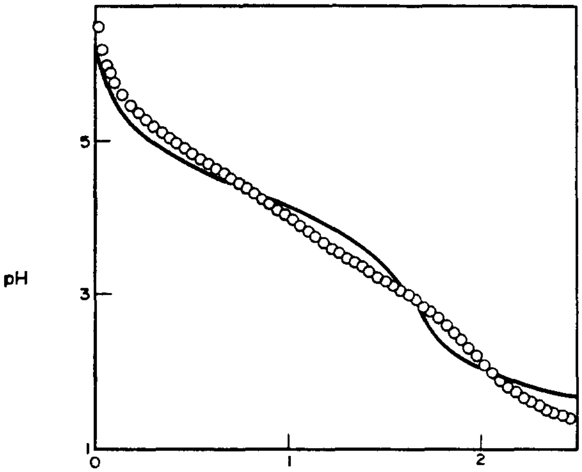

Fig. 1. The open circles represent calculated pH-values during the titration of 100 ml of a 0·1000*M* solution of the diacidic base X^{2-} with a 1·000*M* solution of a strong monobasic acid. The dissociation constants of the acid H_2X were assumed to be $K_1 = 6{\cdot}325 \times 10^{-4}$ and $K_2 = 1{\cdot}581 \times 10^{-5}$, corresponding to $m/m_{stat} = 10$. The solid curve shows the best fit obtainable on the assumption that the base is monoacidic. It corresponds to $C_b{}^0 = 0{\cdot}165$, $K_a = 1{\cdot}63 \times 10^{-4}$ and $y_{H^+} = 0{\cdot}292$ in equations (7a) and (7b).

less than twice the actual one: the equivalence point occurs earlier on the best monofunctional fit than it does on the experimental curve if $m/m_{stat} > 1$. Qualitatively but trivially different phenomena are observed if $m/m_{stat} < 1$ and are described in a later paragraph.

Figure 2 shows the deviation pattern[9] derived from Fig. 1: its ordinate corresponds to the difference between the measured pH and the value calculated from equations (7a) and (7b) with the values of $C_b{}^0$, K_a, and y_{H^+} that yield the best monofunctional fit. Variations of m/m_{stat} affect the amplitude of this pattern, and also, though to a much smaller extent, the widths of the peaks on it, but do not alter its general shape. With any given value of m/m_{stat} the deviations in any limited portion of the curve may be made smaller than those shown in Fig. 2 by taking data more densely in that region than in any other, thereby giving it greater weight in the fit. However, improving the fit in that region merely makes it worse elsewhere: the deviation pattern may be shifted in any direction but its general shape remains unchanged. As would be expected, a deviation pattern of the same shape is also obtained from the titration of a mixture of two monoacidic bases having conjugate acids with different dissociation constants, but in this case it will differ slightly from the one shown in Fig. 2, even if the points are equally spaced along the volume axis and evenly distributed around the first equivalence point, unless the initial concentrations of the two bases are the same.

The shape of the deviation pattern thus obtained is, in short, proof that two (or, as will be shown below, more than two) neutralization steps are involved in the titration. To decide how far m/m_{stat} must differ from 1 to permit recognition of the pattern in the face of the random errors of measurement superimposed on it, it is necessary to compare the height of the pattern with the standard error that may be expected in a single measurement. This error may be estimated with the aid of data obtained in titrations of potassium acetate with hydrochloric acid.[7] The ionic strength was kept large and constant by adding potassium

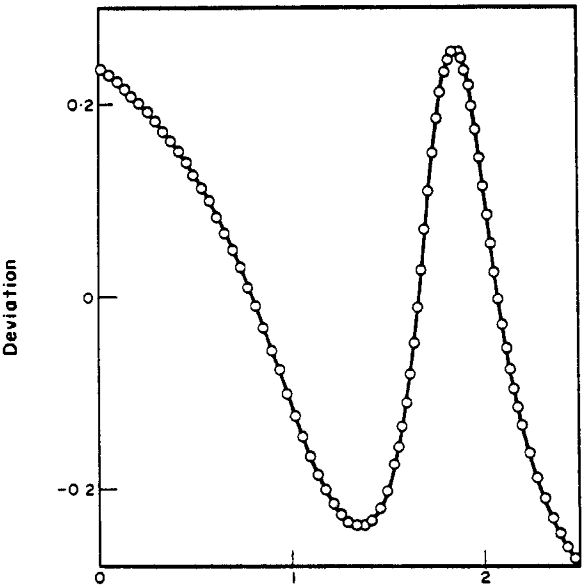

Fig. 2. Deviation pattern obtained from the curves in Fig. 1.

chloride, carbon dioxide was excluded by passing nitrogen through the titration mixture, and the pH-measurements were made with a Corning 012 glass-electrode meter that could be read to 0·001 unit. All reasonable precautions were thus taken to ensure conformity to equations (7a) and (7b), with the result that the standard deviation of a single measured pH-value from the best fit that could be secured to those equations was found to lie between 0·002 and 0·008 pH unit in successive titrations. We consider the average of these values, say 0·005, to be a fair representation of what may be expected.

If the experimental points are reasonably dense it seems probable that the characteristic shape of the deviation pattern can be recognized without difficulty if the vertical distance between the apices of the peaks near $f = 1{\cdot}3$ and $1{\cdot}9$ exceeds four or five times the standard error of a single measurement, or say, 0·025 pH unit. Under the conditions assumed in these computations the overall height, thus defined, of the deviation pattern is found by interpolation to be 0·025 unit when $m/m_{\text{stat}} = 0{\cdot}91$ or $1{\cdot}10$. Under these conditions it should therefore be possible to distinguish any diacidic base from a monoacidic one, on the basis of a single titration, unless the ratio lies in the range $1{\cdot}00 \pm 0{\cdot}10$.

Figure 3, which shows how the parameters of the best monofunctional fit vary with m/m_{stat}, suggests two auxiliary criteria that may be useful in certain circumstances. If the concentration of the base being titrated is evaluated independently from the location of the end-point, it may be compared with the value obtained from the best monofunctional fit. From the end-point it is possible to calculate $C_b{}^0/j$, where j is the unknown functionality of the base. When $m/m_{\text{stat}} = 1$, the value of $C_b{}^0$ obtained from the monofunctional fit is exactly twice that of $C_b{}^0/j$ obtained from the location of the end-point, but the ratio is smaller than 2 if $m/m_{\text{stat}} > 1$ and greater than 2 if $m/m_{\text{stat}} < 1$. A corollary of this criterion is that varying the ionic strength in replicate titrations will not alter the value of $C_b{}^0$ if the base is monoacidic but will do so if it is diacidic (or polyacidic) because this will alter the

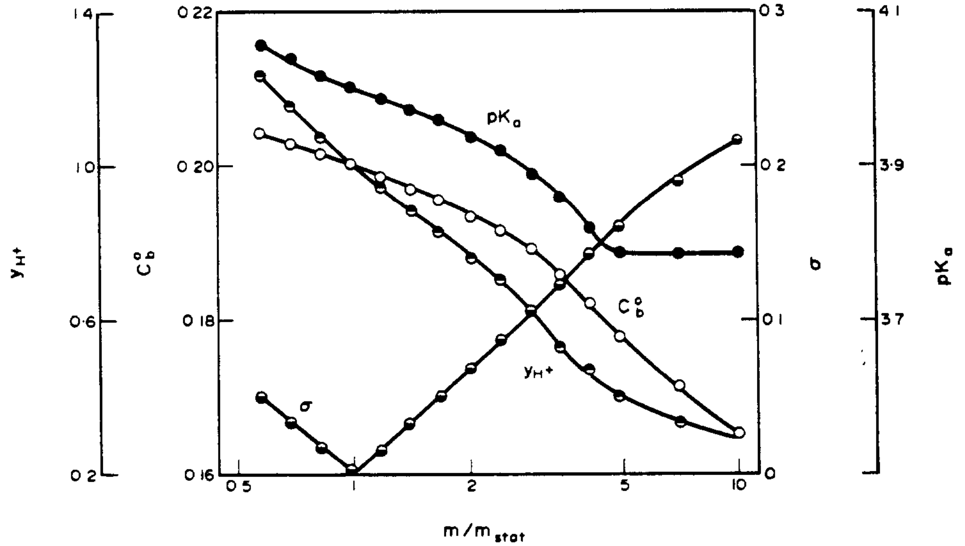

Fig. 3. Effects of the value of m/m_{stat} for a diacidic base on the values of the parameters in the best obtainable fit to equations (7a) and (7b) and on the standard deviation of a single "experimental" value from that best fit, under the conditions of Fig. 1.

ratio m/m_{stat}. A second criterion is that if the apparent activity coefficient of hydrogen ion is known for the titration medium employed [as will be the case if a titration of an authentically monoacidic base is performed in that medium and if y_{H^+} is evaluated by fitting the data to equations (7a) and (7b)] it may be compared with the value of y_{H^+} obtained from the best monofunctional fit. When $m/m_{stat} = 1$ the two are identical, but the best monofunctional fit gives too small a value of y_{H^+} if $m/m_{stat} > 1$ and too large a value if $m/m_{stat} < 1$. In a typical set of titrations of acetate with hydrochloric acid[7] in solutions containing enough potassium chloride to give $\mu = 3{\cdot}0\ M$, the mean value of y_{H^+} was 1·746 and its standard deviation was 0·029, or 1·7 %. It is the relative standard deviation that is appropriate because of the form of equation (7b). If a relative deviation of 7 %, approximately four times the relative standard deviation, is regarded as significant, it should be possible by means of this criterion alone to distinguish any diacidic base from a monoacidic one, on the basis of a single titration, unless m/m_{stat} lies between about 0·83 and 1·2. The prospective user of the second of these criteria should be aware that y_{H^+} varies with temperature, and should have available the values of y_{H^+} in several media of different ionic strengths so that, if one titration fails to reveal that a base is polyfunctional, a second can be performed in another medium to provide a further test.

To escape recognition by these criteria, which even though conservatively formulated are all more sensitive than the one based on Δ(pH), a diacidic base must have a value of m/m_{stat} that is not only very close to 1 but that is also nearly independent of ionic strength over the range examined. Although there are some diacidic bases in which the charged sites are so remote that there is no appreciable overlapping of the ionic atmospheres surrounding them, and for which the variations of m/m_{stat} with ionic strength are smaller than those that the Debye-Hückel equation would predict if it were too rigidly applied, the probability seems to be very small that there can be any diacidic base that the proposed procedure would not prove to be diacidic unless either:

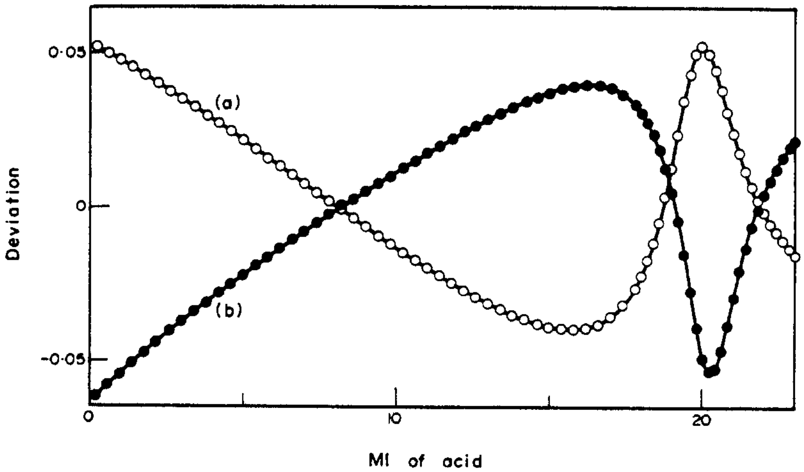

Fig. 4. Deviation patterns for diacidic bases having m/m_{stat} = (*a*) 1·406 and (*b*) 0·689, under the conditions of Fig. 1.

(*a*) pK_1 for the corresponding dibasic acid is extremely small (*i.e.*, so small that the second step of neutralization does not occur to an extent sufficiently large to be detected), *or*

(*b*) both pK_1 and pK_2 are so small that neither step can be detected.

In the first of these cases the proposed criteria would classify the base as monofunctional; in the second they would classify it as zero-functional. Evidently an approach similar to the one described here, but based on titrations with an acid stronger than hydronium ion in a solvent less protophilic than water, would be needed in these cases and would have to be based on considerably different equations.

Allusion was made above to the fact that the shape of the deviation pattern for a diacidic base depends on whether m/m_{stat} is larger or smaller than 1. The nature of this dependence is shown by Fig. 4, on which it seems unnecessary to comment in detail.

A special advantage of the deviation-pattern approach over that based on Δ(pH) is that the former has some ability to discriminate among di-, tri-, and other polyacidic bases whereas the latter has none. To illustrate the proper use of the technique for this purpose we may begin by considering Fig. 5, in which curve *a* shows the deviation pattern obtained in the titration of a triacidic base while curve *b* shows the one obtained in that of a tetra-acidic base. These two patterns, which represent the systematic errors incurred by assuming the bases to be monoacidic, are not exactly identical either with each other or with Fig. 4a for a diacidic base. However, as they do have the same general form, and as minor variations of form will be harder to perceive if the number of points used in constructing the curve is smaller than it is in these figures, the experimenter who obtains a deviation pattern of this general shape is justified in concluding that the base is polyacidic but is unlikely to be able to tell whether it is diacidic or triacidic.

Further interpretation may be made by assuming the base to be diacidic, fitting the data to equations (6a) and (7b), and examining the deviation pattern obtained by plotting the dependence on V_b of the difference between the measured pH and the one calculated from those equations with the aid of the values of the four parameters (C_b^0, K_1, K_2, and y_{H^+})

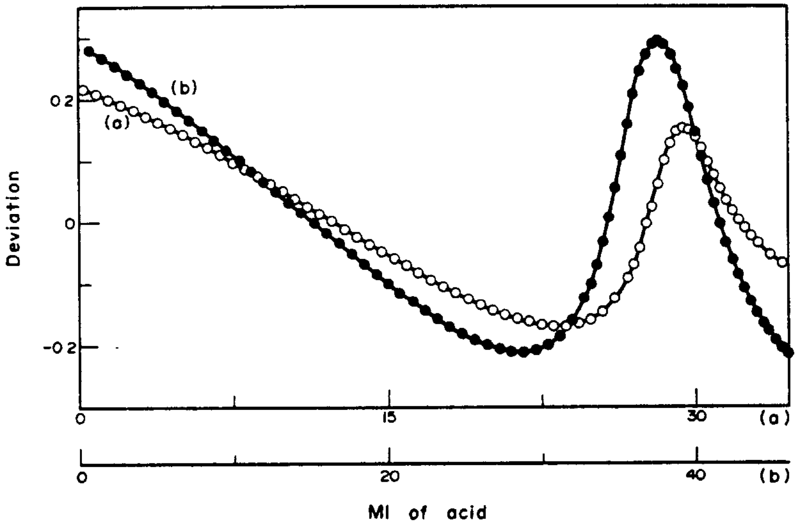

Fig. 5. Deviation patterns for (*a*) a triacidic and (*b*) a tetra-acidic base. As in Fig. 1, it was assumed that 100 ml of a 0·1000*M* solution of the base was titrated with 1·000*M* strong monobasic acid, and that the geometric mean of the dissociation constants of each of the corresponding acids was 10^{-4}. Each ratio of successive dissociation constants was assumed to be twice the corresponding statistical value, so that $K_1 = 6 \times 10^{-4}$, $K_2 = 1 \times 10^{-4}$, and $K_3 = 1.67 \times 10^{-5}$ for the tribasic acid and $K_1 = 1{\cdot}13 \times 10^{-3}$, $K_2 = 2{\cdot}12 \times 10^{-4}$, $K_3 = 4{\cdot}71 \times 10^{-5}$, and $K_4 = 8{\cdot}84 \times 10^{-6}$ for the tetrabasic one. The best fits to equations (7a) and (7b), which were used to construct these plots and which entail the assumption that the base is monoacidic, had the following parameters: (*a*) $C_b{}^0 = 0{\cdot}284$, $K_b = 1{\cdot}24 \times 10^{-4}$, and $y_{H^+} = 0{\cdot}638$; (*b*) $C_b{}^0 = 0{\cdot}355$, $K_b = 1{\cdot}70 \times 10^{-4}$, and $y_{H^+} = 0{\cdot}361$.

obtained.* If the base is truly diacidic, the points will scatter randomly around the volume axis; if it is triacidic the pattern shown in Fig. 6 will result unless its K_i/K_{i+1} ratios have nearly or exactly the statistical ratios ($K_1/K_2 = 3$, $K_2/K_3 = 3$),[3] in which case no systematic deviations will be perceptible and the ratio of the calculated values of K_1 and K_2 will be nearly or exactly equal to 4. This permits non-statistical triacidic bases to be distinguished from non-statistical diacidic ones. However, this deviation pattern for a triacidic base is again generally similar to that for a tetra-acidic base, and so to distinguish between these it is necessary to perform a fit to the equations for the titration of a triacidic base, and so on. An eventual limit to the possibility of distinguishing between a *j*-acidic and a (*j* + 1)-acidic base in this way is set by the fact that the height of the deviation pattern decreases as *j* increases.

In general, one makes the most economical assumption consistent with the prior information—that, for example, the base is monoacidic if nothing is known about it, or that it is diacidic if the deviation pattern based on the first assumption shows that it is not monoacidic. One then performs a fit to the equations that follow from that assumption, employs the values obtained for the parameters in those equations to construct a deviation plot in the manner here outlined, and inspects that plot for a pattern that signifies that the behaviour is more complex than it is assumed to be.

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* If the base is sufficiently weak, the terms in K_w in equation (6a) may be ignored, reducing it to a cubic, as was done in writing equation (7a). Otherwise it may be necessary to insert a value of K_w appropriate to the medium employed for the titration, or to take K_w as a fifth parameter to be evaluated if a prior value is unavailable.

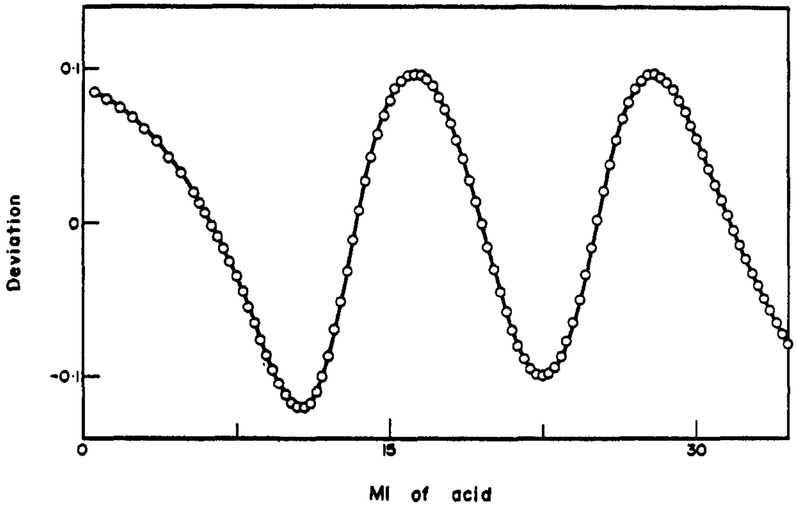

Fig. 6. Deviation patterns showing how the titration curve for a non-statistical triacidic base deviates from the best fit that can be obtained by assuming it to be diacidic. The triacidic base was assumed to have $C_b{}^0 = 0{\cdot}1000M$, $K_1 = 4{\cdot}30 \times 10^{-3}$, $K_2 = 1{\cdot}00 \times 10^{-4}$, and $K_3 = 2{\cdot}32 \times 10^{-6}$ (so that each $m/m_{\text{stat}} = 14{\cdot}35$ as for citrate ion at infinite dilution), and $y_{H^+} = 1$; the parameters in the best fit to equations (6a) and (7b) were $C_b{}^0 = 0{\cdot}1272M$, $K_1 = 9{\cdot}39 \times 10^{-4}$, $K_2 = 7{\cdot}39 \times 10^{-6}$, and $y_{H^+} = 0{\cdot}493$.

One might envision attempting to shorten this procedure by beginning with the assumption that the base is diacidic, expecting to obtain a deviation pattern of one form if it is monoacidic but of another form if it is tri- or polyacidic. This is unwise because the titration curve for any monoacidic base can be fitted by the equations for that of a diacidic one; the fit will yield $K_1/K_2 = 4$. The observation of a characteristic pattern of deviations accordingly has to be replaced by scrutiny of the ratio K_1/K_2, which provides much less information.

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Zusammenfassung—Ein neues Verfahren zur Unterscheidung von zweisäurigen und einsäurigen schwachen Basen (oder von zweibasigen und einbasigen schwachen Säuren) beruht darauf, daß die bei einer potentiometrischen Säure-Basen-Titration erhaltenen Daten an theoretische Gleichungen zur Titration einer einsäurigen Base (oder einbasigen Säure) angepaßt werden. Ist die titrierte Substanz nicht monofunktionell, dann ergibt die beste Anpassung an diese Gleichungen systematische Abweichungen, die, gegen das Volumen an Reagens aufgetragen, ein

"Abweichungsmuster" ergeben, das eine für polyfunktionelles Verhalten charakteristische Formhat. Es werden auch Hilfsmerkmale angegeben, die auf den Werten der aus der Anpassung gewonnenen Parameter beruhen. Mit jedem dieser Kriterien ist ein Unsicherheitsbereich verbunden, in dem das Verhältnis der aufeinanderfolgenden Dissoziationskonstanten so nahe beim statistischen Wert liegt, daß es angesichts der Meßfehler nicht möglich ist, zu entscheiden, ob die Substanz monofunktionell oder polyfunktionell ist. Liegen die Daten einer Titration innerhalb dieses Bereichs, dann kann man die Entscheidung auf Grund einer zweiten Titration bei einer anderen Ionenstärke treffen. Paßt man weiter auch an Gleichungen an, die kompliziertere Verhalten beschreiben, dann kann man nichtstatistische difunktionelle Substanzen von trifunktionellen unterscheiden, trifunktionelle von tetrafunktionellen und so weiter.

Résumé—Une nouvelle technique pour distinguer les bases faibles diacides des monoacides (ou les acides faibles dibasiques des monobasiques) est basée sur l'ajustement des données obtenues dans un titrage potentiométrique acide–base à des équations théoriques pour le titrage d'une base monoacide (ou d'un acide monobasique). Si la substance titrée n'est pas monofonctionnelle, le meilleur ajustement à ces équations aura pour conséquence des écarts systématiques qui, lorsqu'ils sont tracés par rapport au volume de réactif, donnent un "diagramme d'écart" avec une allure caractéristique du comportement polyfonctionnel. On décrit aussi des critères secondaires basés sur les valeurs des paramètres obtenues de l'ajustement. Il y a un domaine d'incertitude associé à chacun de ces critères dans lequel les rapports de constantes de dissociation successives sont si voisins des valeurs statistiques qu'il est impossible en face des erreurs de mesure de décider si la substance est monofonctionnelle ou polyfonctionnelle. S'il s'avère que les données d'un titrage se situent dans ce domaine, la décision peut être basée sur les résultats d'un second titrage réalisé à une force ionique différente. Un nouvel adjustement aux équations décrivant un comportement plus complexe fournit une base pour distinguer des substances bifonctionnelles non-statistiques de substances trifonctionnelles, les trifonctionnelles des tétrafonctionnelles, et ainsi de suite.

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AMPEROMETRICALLY INDICATED "PSEUDOTITRATIONS"—I

COMPLEXOMETRIC DETERMINATION OF CHROMIUM(III)

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Summary—In the pseudotitration no reaction takes place between titrand and titrant in the bulk of the solution. An amperometric indicating system, which generates a small amount of redox catalyst in the vicinity of the electrode, does enable an end-point to be found. Bulk concentrations and diffusion constants are the controlling parameters. This method allows to utilize slow, thermodynamically favourable reactions for titrating purposes. The principle is demonstrated by the direct titration of chromium(III) with EDTA at room temperature.

A necessary condition for the successful application of the substitution reaction

$$\mathrm{MeX} + \mathrm{Y} \rightleftharpoons \mathrm{MeY} + \mathrm{X} \tag{1}$$

for the determination of the metal Me is not only a high value of the equilibrium constant of the reaction, but also a sufficiently high reaction rate. If this latter condition is not fulfilled, a back-titration may be tried, in which the slow reaction is accelerated by an excess of titrant and, if need be, also by boiling the solution.

Such extreme conditions often cause complications in the titration reaction, or they may change the reactivity of other species present, thus increasing the error of the determination. This, together with errors arising from the necessity of using a back-titration, may result in lower accuracy than that of a direct titration.

A direct titration based on a slow reaction (1) may be possible if a catalyst is available, but most effective catalysts are unstable substances which are difficult to prepare and handle under normal titration conditions. Voltamperometric indication (at constant voltage or current) enables one not only to follow the course of the reaction, but also to generate a catalyst electrolytically. The amount of catalyst generated under these conditions is very small but its concentration in the diffusion layer round the electrode is sufficiently high for the reaction (1) to proceed quantitatively in this layer. In the bulk of the solution the reaction may proceed immeasurably slowly since the concentration of the catalyst there is virtually zero. Under these conditions of "pseudotitration", however, the indicating electrode shows the state of the reaction as if completed in the bulk of the solution. The stoichiometric conditions in pseudotitrations are slightly different from those in normal titrations in that the reactants are conveyed to the reaction site by diffusion or controlled convection. The stoichiometry of the reaction is therefore determined not only by the molar ratio, but also by the ratio of the diffusion coefficients of the reacting components.

Much attention has been paid in the literature to the acceleration of slow reactions by means of redox catalysis.[1] The titrand should be one component of a redox couple, the other component of which reacts rapidly with the titrant. Typical examples of redox catalysis are the substitution reactions of chromium(III) complexes catalysed by chromium(II).[1,2] Of these, the substitution by EDTA of other ligands co-ordinated to chromium(III) is important analytically. The redox catalysis of such a reaction for the hexa-aquochromium(III) ion may be simply described by the following equations.

$$\mathrm{Cr(III)} + \mathrm{Y} \rightleftharpoons \mathrm{Cr(III)Y} \tag{2}$$

$$\mathrm{Cr(III)} + e^- \rightleftharpoons \mathrm{Cr(II)} \tag{3}$$

$$\mathrm{Cr(II)} + \mathrm{Y} \rightleftharpoons \mathrm{Cr(II)Y} \tag{4}$$

$$\mathrm{Cr(III)} + \mathrm{Cr(II)Y} \rightleftharpoons \mathrm{Cr(III)Y} + \mathrm{Cr(II)} \tag{5}$$

The electrolytic generation of the catalyst chromium(II) is important because this is not stable in solution, reacting with dissolved oxygen or with water to be re-oxidized to chromium(III). The catalysis is effective because both reactions (4) and (5) are considerably faster than reaction (2).

EXPERIMENTAL

Reagents

Analytical-reagent grade chemicals were used. Stock solutions of chromium(III) were prepared by dissolving potassium chromium alum in 0·05*M* sulphuric acid, to prevent the formation of polynuclear complexes. When it was necessary to work in the absence of additional acid, the solutions were prepared immediately before use. The solutions were analysed for chromium spectrophotometrically[3] after oxidation with peroxide to chromium(VI). The Britton–Robinson and acetate buffers were used. Solutions were de-aerated by bubbling with nitrogen purified by passage through a chromium(II) solution.

Apparatus

Polarographic measurements were made on the recording polarograph OH-102, and potentiometric measurements with the pH-meter OP-205, (Radelkis, Budapest). The drop-time of the DME was 2·8 sec and the flow-rate 2·93 mg/sec in short circuit with the SCE and with 64 cm height of mercury column. A Zeiss Specord UV-VIS spectrophotometer was also used, and all measurements were made at room temperature, about 25°.

RESULTS

The amperometric titration curve

The optimum working potential for the amperometric titration is determined by the polarographic *i–E* curves, The hexa-aquochromium(III) ion is reduced at half-wave potential about −0·9 V *vs.* the SCE, at pH 4–5, giving an irreversible one-electron wave. The redox system Cr(III)EDTA–Cr(II)EDTA has a reversible half-wave potential at about −1.2 V. With addition of EDTA during the titration, the hexa-aquochromium(III) reduction wave decreases and the more negative one of chromium(III)EDTA increases. The most suitable potential was −1·075 V, approximately in the middle of the current plateau between the waves, where the shape of the titration curve and hence the accuracy of the titration were least affected by changes in potential or pH.

The titration curve is L-shaped, with the equivalence point lying at the intersection of the two branches. Since no reaction actually occurs in the bulk of the solution, one cannot really speak of a true equivalence point. From the Ilkovič equation one can conclude that

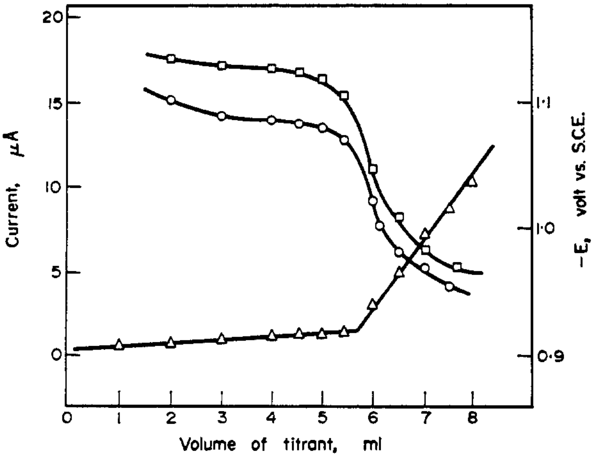

Fig. 1. Comparison of amperometric and potentiometric indication with constant current in the pseudotitration of chromium(III) with EDTA; pH 4·1; 0·25*M* Na_2SO_4;
△ dependence of the current at potential −1·05 V *vs.* SCE on the volume of titrant
⊙ dependence of potential of DME *vs.* SCE on the volume of titrant, polarizing current 1·45 μA
☐ dependence of potential of DME *vs.* SCE on the volume of titrant, polarizing current 2·90 μA.

the equivalence-point for this pseudotitration is given by the stoichiometric ratio, in this case 1:1, multiplied by the factor $\sqrt{D_{EDTA}/D_{Cr(III)}}$, these being the diffusion coefficients for EDTA and the Cr(III) aquo-ion respectively. In this case, this ratio is approximately equal to unity.

Potentiometric titration with constant current

The advantages of the electrolytic generation of a redox catalyst can also be made use of when the indicating electrode is polarized by a small constant current and its potential is measured during the titration. Figure 1 shows examples of such curves for two different polarizing currents. For comparison purposes the amperometric titration curve is also shown. Figure 1 also shows that it should be possible to titrate EDTA with Cr(III).

In practice the amperometric titration is to be preferred to the potentiometric one at constant current, which gives rise to a systematic error since the polarization current cannot be held at a small enough value. In addition, the potential break is rather small, and with the DME the potential varies with the size of the drop and must be measured just before the drop falls off, or an overdamped measuring system must be used.

Accuracy of the pseudotitration

The titrations should be performed at pH 3·2–4·6. The lower limit is determined by the stability of the Cr(III)EDTA complex,[4] and the upper by the fact that the hexa-aquochromium(III) ion polymerizes at higher pH values and may even be partially precipitated. The shape of the titration curve remains unchanged in supporting electrolytes of perchlorate, chloride or sulphate, as long as the concentration is high enough to eliminate the migration current, and the buffer capacity is also not critical. It is important, however, particularly for small amounts of chromium, to remove dissolved oxygen completely from the solution.

Table 1. Statistical evaluation of the pseudotitration of chromium(III)

Chromium(III)		Relative error, %	No. of determinations	Limits of confidence for 95% probability	
taken, µg	found (mean), µg			µg	%
7800	7790	0·13	8	±80	99.9± 1·0
781	776	0·64	8	±11	99·4± 1·4
78	77	1·3	8	±1.4	98·7± 1·8

The titration results have been evaluated statistically by the method of Dean and Dixon[5] for solutions of chromium(III) in 0·25*M* sodium sulphate with an acetate buffer at pH 4·4 and are given in Table 1.

DISCUSSION

Complexometric determinations of chromium have hitherto been performed as back-titrations. For visual back-titrations with metallochromic indicators, salts of Zn^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Th^{4+} have been used.[6] In the back-titration with Pb^{2+} the end-point has beeen indicated by the precipitation of lead chromate.[7] The intense colour of the chromium(III)EDTA complex is a serious drawback of the visual titration. A potentiometric back-titration with Zn^{2+} eliminates this problem,[8] but some difficulties still remain in connection with heating the solution and carrying out the back-titration. These difficulties were not solved by an amperometrically indicated back-titration either.[9] Chiacchierini[10] described a direct amperometric titration of chromium(III) with various chelating agents. The shapes of the titration curves led him to the erroneous conclusion that the complexometric titration reactions were in fact fast in the bulk of the solution even at room temperature (25°). As may be seen from Fig. 2, however, the spectrum remains practically unchanged during the time required for a titration, from which we may conclude that the reaction in the bulk of the solution may be neglected. Moreover, in the paper quoted,[10] chromium(III) was introduced as the nitrate. This causes considerable complications in the titration curve, since chromium(II)EDTA reacts with nitrate,[11,12] causing an increase in the indicating current. This increase depends not only on the nitrate concentration but also on the chromium(II) concentration and on the pH of the solution,[13] so that in the unbuffered media used [10] various factors contributed to the changes in the shape of the titration curve.

The changes in the chromium(III) polargraphic curve on addition of EDTA and in the shape of the amperometric titration curve have here been explained by redox catalysis of the substitution reaction between hexa-aquochromium(III) and EDTA. Another explanation of these changes has been put forward by Tanaka and Ebata.[14]

$$\mathrm{Cr(III)} + e^- \overset{E_1}{\rightleftharpoons} \mathrm{Cr(II)} \tag{6}$$

$$\mathrm{Cr(II)} + \mathrm{EDTA} \rightleftharpoons \mathrm{Cr(II)EDTA} \tag{7}$$

$$\mathrm{Cr(II)EDTA} \overset{E_2}{\rightleftharpoons} \mathrm{Cr(III)EDTA} + e^- \tag{8}$$

Chromium(II) formed by the electrolytic reduction of chromium(III) as in reaction (6) is in rapid equilibrium with its EDTA complex.[6] Since the reversible half-wave potential E_2 is

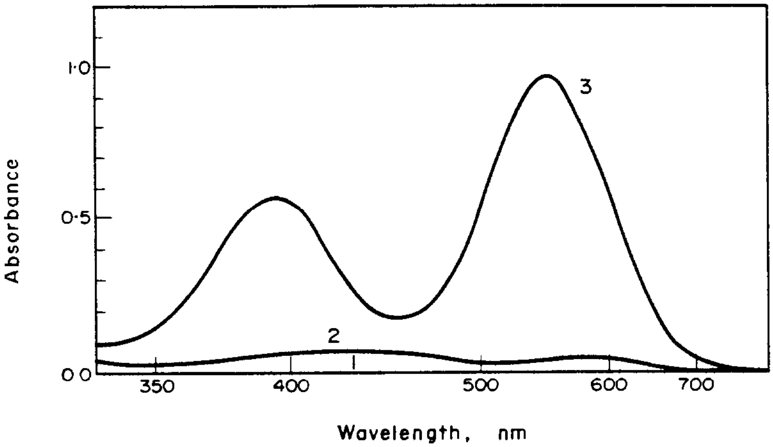

Fig. 2. Comparison of absorption spectrum of Cr(III) before and after the pseudotitration; Britton-Robinson buffer pH 4·40, temperature 20°C, light-path 5 cm.

1. Spectrum of 1mM $KCr(SO_4)_2$.
2. Spectrum of 1mM $KCr(SO_4)_2$ and 1·2 mM EDTA, 20 min after mixing.
3. Spectrum of solution 2 after 15 min boiling.

more negative than the potential E_1 for the irreversible reduction of the hexa-aquochromium(III) complex, the chromium(II)EDTA complex is oxidized at potentials between E_1 and E_2, and the corresponding oxidation current is subtracted from the reduction current of chromium(III). At potentials above E_2 the reduction wave of chromium(III)EDTA may be observed.

It is difficult to determine which of the mechanisms is responsible for the changes in the polarographic wave used for the pseudotitration. Most likely both mechanisms—the catalytic one and that just discussed—are competitive and parallel.

It has been observed that the pseudotitration of chromium(III) may also be performed with other chelating agents as well as metal chelates as titrants. Our studies have also shown that the pseudotitration may be carried out in the presence of other ions which react with these reagents.[15]

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Zusammenfassung—Bie der Pseudotitration findet in der Hauptmenge der Lösung Keine Reaktion zwischen Titrand und Titrant statt; ein amperometrisches Anzeigesystem, das eine kleine Menge Redoxkatalysator in der Nachbarschaft der Elektrode erzuegt, erlaubt jedoch, einen Endpunkt zu finden. Die verschiedenen Ionen in der Lösung diffundieren zur Elektrode, wo eine Reaktion mit sehr geringem Umsatz katalysiert wird. Die dafür wesentlichen Parameter sind die Konzentrationen in der Hauptmenge der Lösung und die Diffusionskonstanten. Das Prinzip wird demonstriert an der direkten Titration von Chrom(III) mit EDTA bei Raumtemperatur.

Résumé—Dans le pseudotitrage, il n'y a pas de réaction entre le produit à titrer et l'agent de titrage au sein de la solution, mais un système indicateur ampérométrique, qui engendre une petite quantité de catalyseur redox au voisinage de l'électrode, permet de trouver un point de fin de dosage. Les divers ions de la solution diffusent vers l'électrode où la réaction est catalysée sur une très petite échelle. Les concentrations globales et les constantes de diffusion sont les paramètres régulateurs. On démontre le principe par le titrage direct du chrome (III) à l'EDTA à température ambiante.

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AMPEROMETRICALLY INDICATED "PSEUDOTITRATIONS"—II*

DETERMINATION OF CHROMIUM(III) IN THE PRESENCE OF OTHER REACTING METAL IONS

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Summary—Chromium(III) may be determined complexometrically in a pseudotitration in which no reaction takes place in the bulk of the solution. Redox catalyzed titration reaction proceeds only in the vicinity of the indicating electrode. The titration curves for solutions containing additional metal ions which react with EDTA are discussed and classified according to their reduction potentials, equilibrium, constants and reaction rates. In certain combinations two or more metals may be determined simultaneously from one titration curve. Examples given are Cr/Hg, Cr/Cd, and Cr/Zn.

In the first paper[1] the principle of amperometrically indicated pseudotitration was explained for the case of the complexometric determination of chromium(III). This paper deals with its application in the presence of other electroactive cations which react with EDTA. In such cases it is often possible to determine the amounts of two or more components in a single titration. In the presence of another electroactive ion the shape of the titration curve changes, depending on the polarographic half-wave potential for the reduction of the additional ion and its EDTA complex, as well as on the stability of this complex compared with that of the chromium(III)EDTA complex. The influence of the additional components on the shape of the titration curve may be classified under one of the four following headings.

1. *The additional ion and its EDTA complex are both reduced at potentials more positive than is chromium(III).*

Figure 1 shows schematically the polarographic curves at different stages of the titration, and also the titration curve for the case where the additional ion Me(I) and its complex Me(I)EDTA undergo a one-electron reduction to the metal. The additional ion is titrated in the bulk of the solution and the course of the titration may be followed from the changes in the current when the potential of the indicating electrode lies in the region E_2 (Fig. 1). Independently of this titration the pseudotitration of chromium(III) takes place and can be followed by measuring in the potential region E_1. The shape of the titration curve does not depend on the value of the stability constant of Me(I)EDTA, because at the potential for reduction of chromium(III) the EDTA is liberated by reduction of Me(I)EDTA to the metal at the indicator electrode, and the pseudotitration of chromium(III) may be carried out without any interference.

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* Part I: *Talanta*, 1973, **20**, 1185.

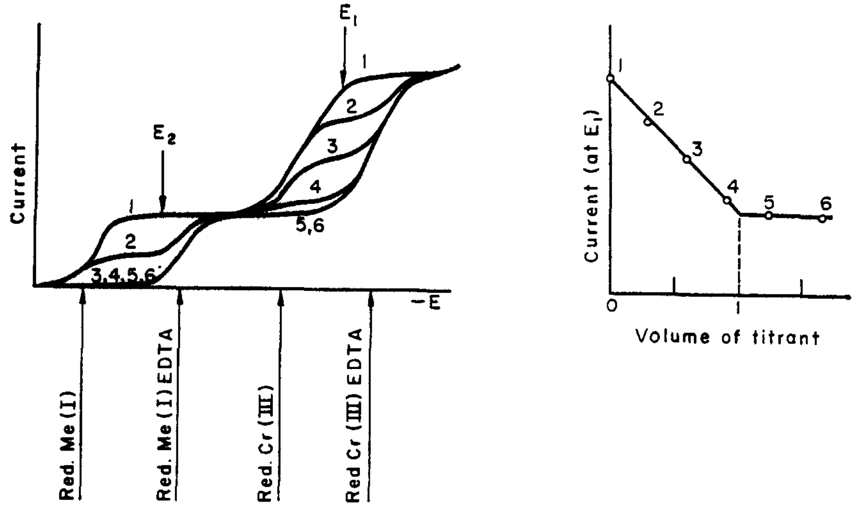

Fig. 1. Schematic representation of the titration of Me(I) and Cr(III) with EDTA: case 1.

If the additional ion is reduced to the metal with the gain of more than one electron (an n-electron transfer) and if the ion reacts with EDTA in a 1:1 molar ratio (which is usually the case) the current decrease in the region E_2 will be n times the decrease in the region E_1 (Fig. 1).

2. *The additional ion is reduced at potentials more positive than chromium(III) while its EDTA complex is reduced at potentials more negative than is chromium(III)EDTA.*

This situation is represented in Fig. 2. For reasons of simplicity it is considered that the EDTA complex of the additional ion is not reduced in the polarographically accessible potential region. Unlike the first case, free EDTA is not available for the pseudotitration of

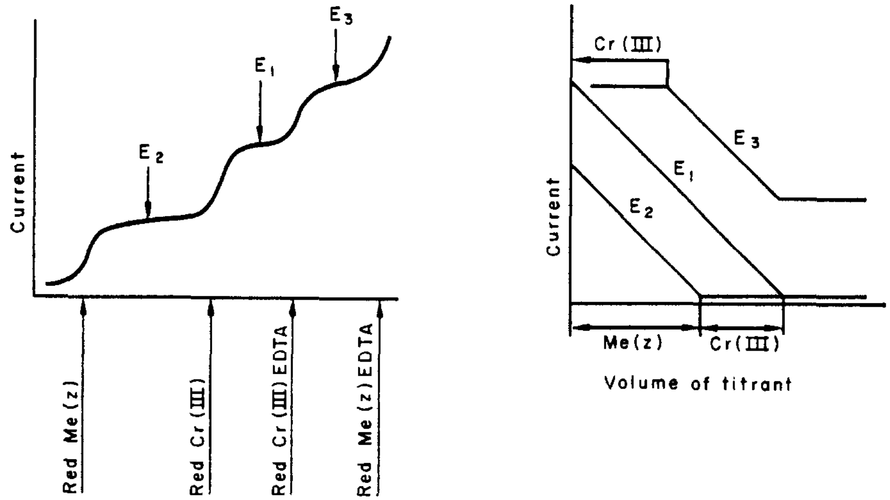

Fig. 2a. Schematic representation of the titration of Me(Z) and Cr(III) with EDTA; case 2a.

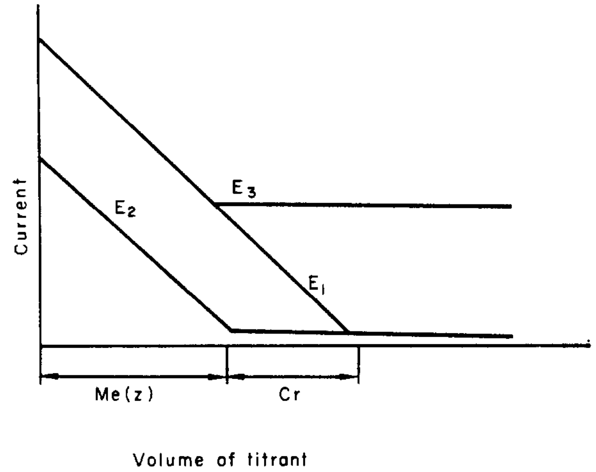

Fig. 2b. Schematic representation of the titration of Me(Z) and Cr(III) with EDTA; case *2b*. The current–potential curve is identical with that for case *2a*.

chromium(III), even at the indicating electrode. This is in fact a replacement pseudotitration:

$$\text{Me(Z)EDTA} + \text{Cr(III)} \rightleftharpoons \text{Cr(III)EDTA} + \text{Me(Z)} \tag{1}$$

where Z denotes the oxidation state of the additional metal ion. The reaction is catalysed by the chromium(II) generated at the indicating electrode:

$$\text{Me(Z)EDTA} + \text{Cr(II)} \xrightarrow{k_1} \text{Cr(II)EDTA} + \text{Me(Z)} \tag{2}$$

$$\text{Cr(III)} + \text{Cr(II)EDTA} \xrightarrow{k_2} \text{Cr(III)EDTA} + \text{Cr(II)} \tag{3}$$

We may now consider three variants of this case, depending on the rate of reaction (1):

2a. Reaction (1), catalysed by chromium(II), proceeds quantitatively. The wave due to Me(Z) decreases as it is titrated with EDTA forming Me(Z)EDTA. According to reaction (1), the chromium(III) wave should also decrease, but the same reaction liberates an equivalent amount of Me(Z), electrode reduction of which makes up the wave-height to the initial value of the chromium(III) wave [for the case of a one-electron reduction of Me(Z)]. The reduction wave for chromium(III)EDTA increases in the course of the titration approximately to the initial value for chromium(III). The shape of the titration curve (Fig. *2a*) follows from this balance. The amount of chromium(III) may be determined from the difference in the volumes corresponding to the intersection points of the linear branches of the titration curves at the potentials E_1 and E_2, or from the volume corresponding to the intersection point at potential E_3.

2b. Reaction (1) does not proceed from left to right. Me(Z) is titrated with EDTA and its wave-height decreases. The chromium(III) wave height is constant at first, and then decreases after Me(Z) has been titrated. The current balance for this variant at different potentials can be seen in Fig. 2b. The fact that reaction (1) does not proceed may be attributable to a small equilibrium constant, or to kinetic causes. The indicating system can record reaction (1) as finished only if it is completed during the drop-time of the DME, so it must be effectively catalysed according to reactions (2) and (3). Consequently, the extent of applicability

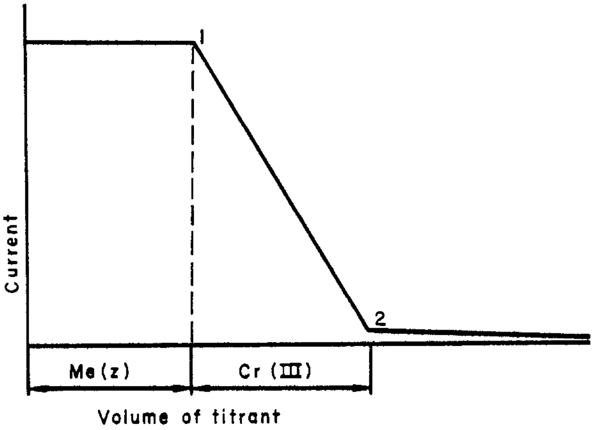

Fig. 3. Schematic representation of the titration of Me(Z) and Cr(III) with EDTA; case 3*b*.

of reaction (1) depends, for the given rate constant[2] for reaction (3), $k_2 = 2 \times 10^4$ l. mole^{-1}. sec^{-1} at 25°, $\mu = 1$, on the equilibrium and rate constant of reaction (2).

2*c*. *Reaction* (*1*) *proceeds, but slowly or incompletely.* It is possible to use the results of amperometric experiments for the determination of equilibrium or rate constants for the reactions involved, depending on whether reaction (1) is thermodynamically or kinetically controlled. This case is, of course, analytically less important.

It should be mentioned that in case 2 it makes little difference whether the species Me(Z) is reduced to the metal or to an ion in a lower oxidation state. Current balance is partly changed in the case of multi-electron reduction of the additional ion, but the determination may still be carried out. In addition, it is possible to determine both components simultaneously from the titration curve for potential E_1.

3. *The additional ion and its EDTA complex are reduced at potentials more negative than its chromium(III)EDTA*

For this case there are also three possible variants:

3*a*. *Reaction* (*1*) *proceeds quatitatively.* The titration curve will be L-shaped as if no additional ion were present in the solution.

3*b*. *Reaction* (*1*) *does not proceed from left to right.* The titration curve will have the shape shown in Fig. 3. Consumption of titrant for the pseudotitration of chromium(III) is measured starting at point *1*, where the titration of the more negatively reduced ion is finished. Variant 3*b* may also arise for kinetic reasons, as in case 2*b*.

3*c*. *Reaction* (*1*) *is slow or incomplete.* This case has similar implications to case 2*c* already discussed.

For additional ions in case 3 the shape of the titration curve depends neither on the type of the reduction nor on the number of electrons transfered.

4. *The additional ion and/or its EDTA complex can be reduced at a potential in the same region as chromium(III) and its EDTA complex.*

In such cases the shape of the titration curve is rather complicated, and the conditions for following the pseudotitration have to be chosen according to the current balance for each individual set of circumstances.

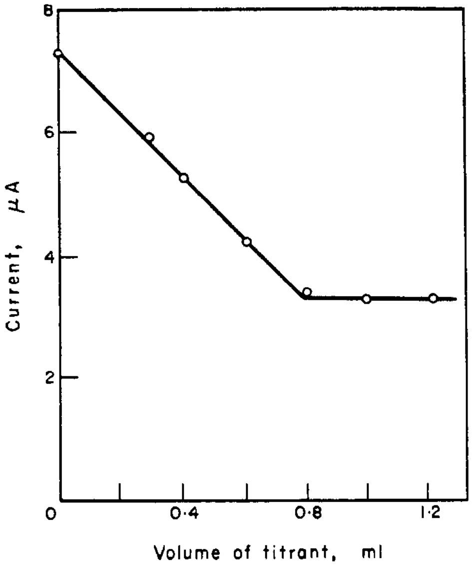

Fig. 4. The titration curve for the complexometric determination of 20 ml of 0·95m*M* Hg(II) and 1·95m*M* Cr(III) with 0·05*M* EDTA in acetate buffer, pH 4·0 potential −1·08 V *vs*. SCE.

EXPERIMENTAL

Chemicals, procedures and apparatus have been described in the preceding paper.[1]

RESULTS AND DISCUSSION

Determination of chromium(III) in the presence of mercury(II)—case 1

Figure 4 shows the shape of the titration curve. The end-point is obvious and the results show excellent agreement with the actual concentrations.

Determination of chromium(III) in the presence of cadmium(II)—case 2

This classification is only approximate, since the cadmium(II)EDTA complex is reduced at about the same potential as the chromium(III)EDTA complex. Consequently at this potential a small cathodic current flows through the system corresponding to the reduction of cadmium(II)EDTA even after the titration of both components is finished (Fig. 5. curve *2*). Cadmium(II) is reduced in a two-electron step while chromium(III) gains only one electron, so the curve shows two breaks, the first indicating the end-point of the cadmium titration, and the second that of the chromium pseudotitration.

The accuracy of determination of both equivalence points from a single curve (curve *2* in Fig. 5) is increased substantially upon addition of nitrate to the solution. As can be seen in Fig. 6, the middle part of the titration curve becomes convex, thus decreasing the angles of the two breaks. The change in shape is caused by the reaction of chromium(II)EDTA with nitrate near the indicating electrode, leading to an increase in the electrolytic current.[3,4] The optimum nitrate concentration for such a modification of the titration curve lies slightly above that of the chromium(III) present.

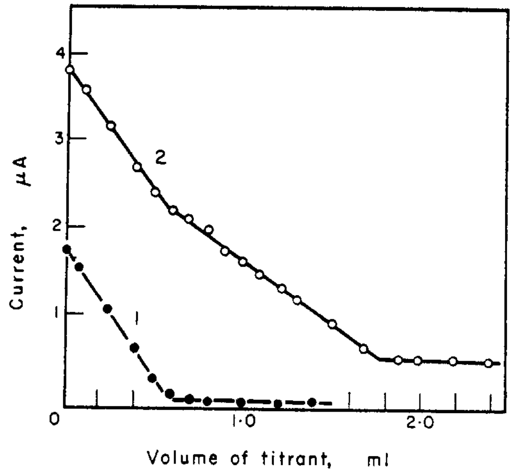

Fig. 5. The titration curves for the complexometric determination of 12 ml of 0·50mM Cd(II) and 0·975mM Cr(III) with 0·01M EDTA in Britton-Robinson buffer, pH 4·2 and ionic strength 0·2M. Titration curve *1* was obtained at the potential −0·7 V *vs.* SCE, curve *2* at −1·075 V.

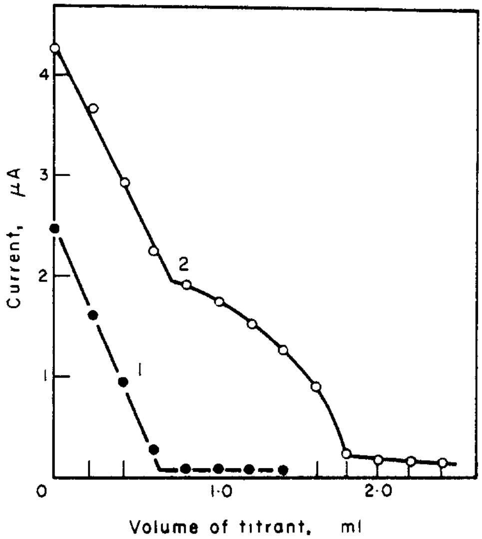

Fig. 6. Titration curves for complexometric determination of 12 ml of 0·58mM Cd(II) and 0·92mM Cr(III) with 0·01M EDTA in the presence of nitrate (1·16)mM) in Britton-Robinson buffer, pH 4·6 and ionic strength 0·2M. Titration curve *1* was obtained at the potential −0·725 V *vs.* SCE, curve *2* at −1·025 V.

Determination of chromium(III) in the presence of zinc(II)—case 2b

The half-wave potential for the reduction of zinc almost coincides with that of chromium(III), so that a titration curve may be obtained by measuring in the region of potential E_2 (Fig. 2*b*). Owing to the different number of electrons involved, the titration curve at the potential E_1 (Fig. 2*b*) exhibits two breaks for the two components being titrated (curve *1* in

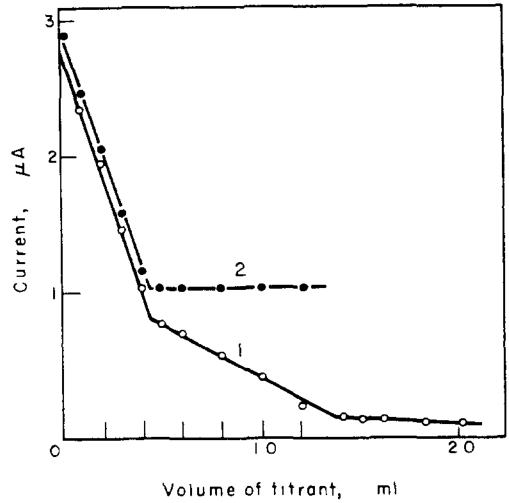

Fig. 7. Titration curves for the complexometric determination of 12 ml of 0·37m*M* Zn(II) and 0·72m*M* Cr(III) with 0·01*M* EDTA in Britton–Robinson buffer, pH 4·5 and ionic strength 0·2*M*. Titration curve *1* was obtained at the potential −1·1 V *vs*. SCE, curve *2* at −1·325 V.

Fig. 7). The first break indicates the end-point for the zinc titration, which can also be obtained from curve *2* obtained by measuring at potential E_3 (Fig. 2*b*). The similarity between curves *1* and *2* (Fig. 7) before the first equivalence point (except for a small discrepancy due to the difference in the charging currents at the two potentials) allows one to classify the determination as type 2*b*.

A comparison of the stability constants of the chromium(III)EDTA and Zn(II)EDTA complexes shows that the assignment to variant 2*b* must be based on kinetic reasons.

During a typical titration experiment the spectrum of the solution containing chromium (III) remained unchanged, indicating that the amperometrically indicated complexometric titration does not take place in the bulk of the solution and consequently that it is indeed a pseudotitration. The determination of chromium(III) by titration in the presence of other combinations of ions is at present the subject of further study in our laboratories.

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Zusammenfassung—Chrom(III) kann komplexometrisch in einer Pseudotitration bestimmt werden; bei findet in der Hauptmenge der Lösung keine, an der Oberfläche der Anzeigeelektrode jedoch in sehr geringem Ausmaß eine katalysierte Reaktion statt. Die Tirtationskurven von Lösungen, die zusätzliche mit EDTA reagierende Metallionin enthalten, werden diskutiert und entsprecheed den verschiedenen Reduktionspotentialent Gleichgewichtskonstanten und Reaktionsgeschwindigkeiten eingeordnet. In bestimmten Kombinationen können zwei oder meherre Metalle nevenineander aus einer Titrationskurve bestimmt werden. Es werden die Beispiele Cr/Hg, Cr/Cd und Cr/Zn angegeben.

Résumé—On peut doser le chrome (III) complexométriquement dans un pseudotitrage, où il ne se produit pas de réaction au sein de la solution, mais où il s'en produit une à un très petit degré quand elle est catalysée à la surface de l'électrode indicatrice. On discute des courbes de titrage pour des solutions contenant des ions métalliques supplémentaires qui réagissent avec l'EDTA et les classe selon les divers potentiels de réduction, constantes d'équilibre et vitesses de réaction. Dans certaines combinaisons on peut déterminer simultanément deux ou davantage de métaux à partir d'une courbe de titrage. Les exemples donnés sont Cr/Hg, Cr/Cd et Cr/Zn.

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ANION-EXCHANGE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN GEOLOGICAL SAMPLES

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Summary—To determine thorium in geological samples it is first separated from all matrix elements by means of anion-exchange. After elution thorium is determined spectrophotometrically by using thoronol or arsenazo III. The suitability of the method for the determination of both trace and larger amounts of thorium was tested by analysing numerous geochemical standard samples with thorium contents in the range of 1–1000 ppm. In all cases very good agreement was obtained.

Spectrophotometric methods are employed extensively for the determination of amounts of thorium in the ppm range in geological materials.[1,2,3]. Thorium reacts with many organic reagents to form intensely coloured complexes, of which those with thoronol and arsenazo III (because of the high sensitivity of these reagents for thorium) have gained widespread analytical application.[1,2]

Both reagents can be applied to the determination of thorium provided that interfering elements such as zirconium, titanium, uranium and the rare-earth metals are virtually absent. When the thoronol method is used additional interferences are observed in the presence of phosphate, fluoride and sulphate. It is necessary if the sample material contains only a few ppm of thorium, to separate it before determination, removing both interfering ions and matrix elements. For this purpose, liquid-liquid extraction from nitrate solution is employed, using solvents such as mesityl oxide or tributyl phosphate.[3] These procedures have the disadvantage that the interfering elements (especially titanium and the rare earth metals) are not completely separated from thorium so that a limit is set for the determination of very low thorium concentrations. Similar difficulties are encountered if the thorium is separated from hydrochloric acid solutions either by extraction with long-chain aliphatic amines (e.g., Alamine 336[1]) or by anion-exchange on a strongly basic anion-exchanger (*e.g.*, Dowex 1[3]).

Much more favourable conditions for the separation of thorium exist, however, if thorium is adsorbed on Dowex 1 from 8*M* nitric acid. This adsorption as the anionic nitrate complex allows thorium to be separated quantitatively from most elements.[2–4] After elution with 6*M* hydrochloric acid thorium can be determined spectrophotometrically by means of the thoronol or arsenazo III method. Before the determination of thorium it is necessary to destroy organic matter in the eluate by oxidative wet-ashing. Otherwise, thorium is partly or completely complexed so that the spectrophotometric determination gives inaccurate and non-reproducible results (especially if only a few micrograms of thorium are present).

EXPERIMENTAL

Solutions and Reagents

Ion-exchanger. The strongly basic anion-exchanger Dowex 1, X8 (100–200 mesh; chloride form) was used. To obtain the nitrate form of the resin, approximately 5 g of the exchanger were transferred to a column and washed with 8*M* nitric acid until no more chloride is detectable in the effluent.

Standard thorium solution. Thorium nitrate hexahydrate (12·67 g) was dissolved in 8*M* nitric acid and the solution diluted with the same acid to give a thorium concentration of 5·0 mg/ml, and checked by titration with EDTA. A standard solution which contained 50 μg/ml of thorium was prepared by dilution with 8*M* nitric acid . The standard solution for construction of the thoronol calibration curve contained 10 μg thorium per ml of 0.1*M* hydrochloric acid. It was prepared by evaporation of 2 ml of the concentrated standard solution (5.0 mg/ml) on a steam bath and dissolution of the residue in 1 litre of 0.1*M* hydrochloric acid. For construction of the arsenazo III calibration curve, it is necessary to dilute this solution further and to remove the nitrate ion by evaporation in the presence of formic acid and hydrochloric acid (see *Procedure—arsenazo III method*).

Thoronol reagent 0.1% *aqueous solution.* Thoronol is [1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulphonic acid.

Arsenazo III reagent 0.2% *aqueous solution.* It is preferable to use a solution of this azo-dye which is not more than two weeks old.

Potassium permanganate 2% *aqueous solution.*

Nitric acid 8*M*. Prepared by mixing concentrated nitric acid (about 16*M*) with distilled water in 1:1 ratio. To prevent the formation of gas bubbles in the ion-exchange columns this acid should not be used immediately following its preparation but after it has been allowed to cool.

Other reagents. Solid crystalline boric acid, ascorbic acid, concentrated formic acid, 0.1, 1.0, 6*M* and concentrated hydrochloric acid (37%), concentrated hydrofluoric acid (40%), and 1*M* and concentrated nitric acid (65%).

Apparatus

The ion-exchange separations of thorium were performed on columns of the type and dimensions described earlier.[5]

Procedures

Dissolution of samples. A 0·5–2·0 g sample, in a plastic beaker, is moistened with a few ml of water and 30 ml each of concentrated nitric acid and concentrated hydrofluoric acid are added. The mixture is evaporated to dryness on a steam-bath (stirring intermittently with a plastic rod speeds up dissolution) and the residue is treated once more with 60 ml of the 1:1 mixture of nitric and hydrofluoric acid (if silica is not completely removed after the evaporation of this mixture, this dissolution step has to be repeated a third time). To the final evaporation residue (free from silica) 50 ml of concentrated nitric acid are added and fluoride is removed by evaporation of the solution in the presence of 5 g of boric acid. If this residue does not contain an excess of boric acid it is necessary to repeat the evaporation with concentrated nitric acid using another 5 g of boric acid) is taken up in 1*M* nitric acid, excess of boric acid is filtered off and washed with 1*M* nitric acid, and the filtrate is diluted with an equal volume of concentrated nitric acid. The resulting sorption solution should be clear and free from hydrous oxides of titanium and zirconium *etc*. Turbid solutions should be filtered, preferably several hours after their preparation, before being passed through the ion-exchange columns.

Ion-exchange separation. The sorption solution is passed at room temperature through the ion-exchange column containing about 5 g of the resin in the nitrate form (pretreated with 8*M* nitric acid), at a flow-rate which corresponds to the back-pressure of the resin bed (approximately 2–3 ml/min). The resin is washed in portions with a total of 200 ml of 8*M* nitric acid in order to remove all elements accompanying the thorium, including those which are weakly retained by the resin, *e.g.*, uranium. The adsorbed thorium is then eluted with 200 ml of 6*M* hydrochloric acid and the eluate is evaporated to dryness on a steam-bath. To the residue 5 ml each of 1*M* hydrochloric acid and 2% potassium permanganate solution are added and the solution is evaporated on the steam-bath to destroy organic matter. The residue (which may contain manganese dioxide) is taken up in 10 ml of concentrated hydrochloric acid and the solution is evaporated to dryness on the steam-bath.

To regenerate the resin (reconversion into the nitrate form) after the elution of thorium, the column is washed with 8*M* nitric acid until no more chloride can be detected in the effluent. Following this regeneration the column can be used for another separation of thorium.

Thoronol method. The residue containing manganese(II) chloride and the thorium is dissolved in 5 ml of 0.1*M* hydrochloric acid and after the addition of 1 ml of 0.1% thoronol reagent the solution is diluted with 0·1*M* hydrochloric acid to 10 ml in a standard flask. To eliminate possible interference due to traces of iron(III) contained in the reagents which are used to destroy organic matter, and to dissolve manganese dioxide, a few crystals of ascorbic acid are added to this final solution and then its extinction is measured at 545 nm, with a reagent blank solution as reference. The thorium content is obtained by comparison with a calibration curve covering the concentration range 0–10 μg/ml. An absorbance of 0.042–0.045 is given by 1 μg/ml.

Arsenazo III method. To the residue containing manganese(II) chloride and the thorium a few drops of concentrated formic acid and 10 ml of concentrated hydrochloric acid are added and the solution is evaporated to dryness on the steam-bath (removal of nitrate). The residue is taken up in 5 ml of concentrated hydrochloric acid and transferred to a 10-ml standard flask and after the addition of 1 ml of 0.2% arsenazo III reagent the solution is diluted to 10 ml with water. The absorbance of this solution is measured at 660 nm, with a reagent blank solution as reference. The thorium content is obtained by comparison with a calibration curve for the concentration range 0 — 1.15 μg/ml. An absorbance of 0.210 is given by 1 μg/ml.

RESULTS AND DISCUSSION

In pure aqueous nitric acid systems at high acidities thorium forms a stable anionic nitrate complex[3] of the formula $[Th(NO_3)_6]^{2-}$ which can be adsorbed on strongly basic anion-exchange resins. Thus, thorium can be separated from other metal ions which do not form stable anionic nitrate complexes. This separation is best performed in 5–10*M* nitric acid solutions because the distribution coefficients of thorium, *e.g.*, on Dowex 1, are highest at these acid concentrations. In the sorption solution (about 8*M* in nitric acid), for example, the distribution coefficient of thorium has a value of about 300 while under the same conditions uranium is only slightly adsorbed (distribution coefficient = 10–18).[3] Consequently this medium is suitable for the separation of ppm-levels of thorium from large amounts of uranium. At a nitric acid concentration of 8*M* it is also possible to separate thorium from practically all elements occurring in mineral matrices, except gold, which is co-adsorbed with the thorium but is not removed from the resin during elution of the thorium with 6*M* hydrochloric acid. After its elution from the anion-exchange resin it is possible to determine thorium by using the thoronol or arsenazo III methods because the most serious interferences, *i.e.*, titanium, zirconium, uranium, rare-earth metals, phosphate, fluoride and sulphate are separated quantitatively from the thorium.

It must be stressed that if a turbid sorption solution is passed through the ion-exchange column the turbidity is retained at the top of the resin bed (or on the pad of glass-wool which is used to keep the bed in position) and is not removed quantitatively by subsequent washing with 8*M* nitric acid. Such turbidities or precipitates are usually caused by hydrous oxides of titanium and zirconium or by molybdic acid, which are formed from the fluorides in treatment of the dissolved samples with the mixture consisting of nitric acid and boric acid (the residues from the dissolved samples have to be treated with excess of boric acid and concentrated nitric acid in order to dissolve the insoluble fluorides of the alkaline earths and rare-earth metals, otherwise thorium is lost by co-precipitation with these fluorides). The presence of hydrous oxides in the ion-exchange column is highly undesirable because they are readily soluble in the 6*M* hydrochloric acid which is used for the elution of thorium and hence titanium and zirconium pass into the elutate together with thorium and interfere seriously with the spectrophotometric determination of thorium. Thus, negative errors are usually obtained because of the presence of relatively large amounts of titanium in most minerals. Furthermore, titanium readily forms hydrous oxides which are sparingly soluble in 8*M* nitric acid, so that turbidity or precipitation occurs frequently in sorption solutions which have not been filtered properly. In contrast to titanium and zirconium which are not adsorbed on the anion-exchanger from 6*M* hydrochloric acid the molybdenum chloride which is formed on dissolution of a precipitate of molybdic acid is strongly retained by the exchanger[5] and hence is not eluted together with the thorium.

In order to avoid the interferences mentioned above, it is necessary to carry out very carefully the filtration of the $1M$ nitric acid containing the evaporation residue and boric acid. If a turbid filtrate is obtained, it is allowed to stand overnight and filtered. To this filtrate an equal volume of concentrated nitric acid is added and the solution is allowed to stand for several hours before it is passed through the ion-exchange column. If the solution should become turbid during this time or if a precipitate is formed the sorption solution is filtered and then passed through the column. A very slight turbidity of the sorption solution can be eliminated sometimes by dilution of the solution with $8M$ nitric acid but care has to be taken that the volume of this diluted solution does not exceed 300–400 ml so that during the subsequent washing of the resin with $8M$ nitric acid which follows the sorption of thorium the breakthrough capacity of the resin for thorium is not exceeded.

For the elution of thorium adsorbed on strongly basic anion-exchange resins dilute mineral acids and water have been recommended[3] but these eluents are much less effective than $6M$ hydrochloric acid. Thus, when $6M$ hydrochloric acid is used as the eluting agent for thorium, an eluate is obtained which contains only thorium, provided that this was adsorbed on the resin from a completely clear sorption solution.

Although not contaminated with other metal ions the thorium eluate always contains varying quantities of chelating organic substances originating from the resin, which have to be destroyed before thorium is determined spectrophotometrically. Otherwise, these organic substances are able to mask a portion or the entire amount of the thorium present; this situation is not changed after repeated evaporations with *aqua regia*. The quantitative destruction of the organic substances is achieved with potassium permanganate and hydrochloric acid, and thorium can then be determined free from interferences. The organic matter can also be completely destroyed by fuming with excess of perchloric acid.[2]

Because nitrate may still be present in the evaporation residue after the destruction of the organic substances and subsequent evaporation with concentrated hydrochloric acid, it is destroyed by treatment of the residue with concentrated formic acid in the presence of concentrated hydrochloric acid before thorium is determined by use of the arsenazo III method. If this method is employed in the presence of nitrate (even if present in traces only) part of the arsenazo III is destroyed oxidatively so that the amount of dye remaining is not sufficient to react quantitatively with the thorium (even if not more than 5 μg of thorium are present in 10 ml of solution). Another method of avoiding the effect of nitrate is to carry out the measurement of thorium in the presence of ascorbic acid.[1]

When using the arsenazo III method it has also to be taken into consideration that old solutions of the dye (older than about 2 weeks) give lower absorbances for thorium and furthermore turbid measuring solutions are obtained because a precipitate may form in the dye solution. It is necessary to use a recently prepared dye solution and to construct the calibration curve at the same time. Since the results obtained by use of the arsenazo III method are dependent on the acid concentration in the test solution (increase in absorbance with increasing concentration of hydrochloric acid or chloride salts) care has to be taken in preparation of the calibration curve that the standards contain the same amounts of manganese chloride as the test solutions. If this is not done, a positive error of about 15% may be obtained. The standards are prepared by evaporation of aliquots of the dilute thorium standard solutions and then the residues are treated in exactly the same way as those obtained after evaporation of thorium eluates.

The results of thorium determinations in uranium-bearing minerals, standard samples and geochemical standards are shown in Tables 1, 2 and 3.

Table 1. Results of thorium determination in IAEA standard uranium samples and geological standards

Sample	Thoronol method Thorium content *ppm*		Arsenazo III method Thorium content (*ppm*)		Results of other authors, *ppm*
Soil-1, Shale	7.75	8.00*	8.08	8.50*	—
(Germany)[5] (IAEA)	7.60				
Soil-2, Shale	5.00	5.08*	5.52	5.95*	—
(Sweden)[5] (IAEA)	5.10				
Soil-3, Limestone	0.75	0.80*	0.98	1.13*	—
(Iran)[5] (IAEA)	0.75				
S-1, Torbernite (Australia)[5] (IAEA)	3.50	3.60*	3.61	3.40*	—
S-2, Torbernite	3.25	3.10*	3.40	3.82*	10.0†
(Spain)[5] (IAEA)	3.85				
S-3, Carnotite (U.S.A.)[5] (IAEA)	2.70	2.60*	2.76	2.97*	4.0†
U.S. Geological Survey Standrad G-1	—	—	35.0	—	21-80[6]
U.S. Geological Survey Standard W-1	—	—	5.0	—	1.8-5[6]
New Brunswick Laboratory, USAEC Analysed Sample No. 83	117	115§	92.0	112‡	100

* After deduction of 2.0 μg of Th which was added as a spike.

† Thorium content (ppm ThO_2) found by semi-quantitative spectrographic analysis.

‡ After deduction of 5.0 μg of Th which was added as a spike.

§ After deduction of 20.0 μg of Th which was added as a spike.

Table 2. Results of thorium determinations in geochemical standards from the Centre de Recherches Pétrographiques et Géochimiques

Sample	Thorium content, *ppm*		Results obtained in other laboratories,[7] *ppm*
Granite GA	17	18.5*	15§
Granite GH	56	59.0*	9.5; 54.1; 72; 110; 155
Basalte BR	15	15.6*	12.6; 21; 57
Biotite Mica-Fe	60.5	60.0*	55; 60; 170
Phlogopite Mica-Mg	1.8‡	2.1†‡	1
Diorite DR-N	11	12.5*	22
Serpentine UB-N	2.0‡	3.0†‡	—
Bauxite BX-N	45.5	43.0*	65
Disthène DT-N	11.6	13.0*	—

* After deduction of 10 μg of Th/g added as a spike before dissolution of the sample.

† After deduction of 2.5 μg of Th/g added as a spike before dissolution of the sample.

‡ Thorium determined in these samples by means of the arsenazo III method while in all others the thoronol procedure was used.

§ Established with 5 results.

Table 3. Results of thorium determinations in Canadian radioactive-ore standards

No. of determination	Thorium content, *ppm*					
	D1	D2	BL1	BL2	BL3	BL4
1	78.7	1250	24.0	23.0	30.0	20.0
2	81.2	1200	27.0	18.0	28.5	21.5
3	80.0	1150	22.0	20.5	30.5	18.0
4	80.0	1180	23.0	19.0	26.0	20.0
5	92.0	1390	18.0	21.5	30.0	22.5
6	76.0	1300	31.0	20.0	34.0	18.5
7	73.0	1340	22.0	18.0	30.0	20.0
8	85.0	1180	34.0	18.5	26.0	21.5
9	87.0	1140	27.0	21.5	30.5	20.5
10	100.0	1190	22.0	17.0	30.0	20.0
11*	80.0	1140	26.0	18.0	29.0	22.0
Arithmetic means† A	82.3	1234	22.8	20.4	29.0	20.4
Arithmetic means† B	84.2	1230	27.2	19.0	30.1	20.1
CDEMR‡	80.0	1100	15.0	13.0	14.0	12.0
AAEC§	62.0	1043	16.0	18.0	18.0	14.0

* The results of these thorium determinations were obtained by analyzing batches of the same samples which were made available by the Australian Atomic Energy Commission.

†Arithmetic mean A was obtained from the results of thorium determinations 1–5 while mean B was calculated from determinations 6–10.

‡Approximate thorium contents (in ppm) as given by the Canada Department of Energy, Mines and Resources, Mines Branch, Ottawa, Ontario, Canada.

§ Thorium contents (in ppm) as determined in the Inorganic Chemistry Section of the Australian Atomic Energy Commission, Research Establishment, Lucas Heights, N.S.W., Australia.

These results show that good agreement between the thorium values irrespective of the spectrophotometric method used. From Tables 1 and 2 it is seen that larger deviations in the results are observed when the thorium contents are in the range of 1 ppm or lower than at higher thorium concentrations as would be expected.

The Canadian radioactive-ore standards in which thorium contents of the magnitude shown in Table 3 were found have the following approximate mineralogical compositions. D1 is a quartz pebble conglomerate with a pebble-to-matrix ratio of about 2:1. The pebbles are mainly quartz, while the matrix consists of quartz, sericite, feldspar, chlorite, pyrite, and the uranium-containing minerals brannerite, uraninite and monazite, along with minor amounts of thucholite, uranothorite and coffinite. The ore also contains rare earths, the yttrium and heavy rare earths being associated with the uraninite and brannerite, while the light rare earths are found in the monazite. D2 is an arkose sandstone believed to have essentially the same radioactive minerals as D1. BL1, 2, 3 and 4 were selected from ores which consist of reddish-brown mylonitized oligoclase, saturated with dusty haematite. Gangue minerals include calcite, chlorite, quartz, and some pyrite and other sulphides. The major uranium mineral is pitchblende. Vanadium is also present, as the iron vanadate, nolanite.

The samples were made available in two different containers for each sample. Each pair of samples was analysed in quintuplicate, one of each, each day, using 5 weighed portions of the sample. All the results (determinations 1–11) listed in Table 3 were obtained by employing the anion-exchange procedure followed by spectrophotometric measurement of the thorium by the thoronol method.

Because of the fact that the method described in this paper is based on the enrichment and isolation of thorium on anion-exchange columns, which can be performed more or less automatically, it is possible to analyse numerous samples simultaneously, *i.e.*, the procedure is very well suited for the routine determination of thorium.

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Zusammenfassung—Um Thorium in geologischen Proben zu bestimmen, wird es zuerst von allen Hauptbestandteilen durch Anionenaustausch abgetrennt. Nach der Elution wird das Thorium spektrophotometrisch mit Thoronol oder Arseazo III bestimmt. Die Eignung der Methode zur Bestimmung von Spuren und größeren Mengen Thorium wurde geprüft, indem zahlreiche geologische Standardproben mit Throiumgehalten von 1–1000 ppm analysiert wurden. Es wurde in allen Fällen sehr gute Übereinstimmung erzielt.

Résumé—Pour déterminer le thorium dans des échantillons géologiques, on le sépare d'abord de tous les éléments de la matrice au moyen d'échange d'anions. Après élution, on dose le thorium spectrophotométriquement en utilisant le thoronol ou l'arsenazo III. On a essayé la valeur de la méthode pour le dosage tant de traces que de quantités plus importantes de thorium en analysant de nombreux échantillons standard géochimiques avec des teneurs en thorium de 1 à 1000 ppm. Dans tous les cas, on a obtenu un très bon accord.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM BY EXTRACTION OF A GREEN MOLYBDENUM(V) SPECIES

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Methods for the determination of milligram amounts of molybdenum in natural and industrial samples by gravimetry or titrimetry require its prior separation from several elements.[1] The gravimetric methods areo ften tedious. The colorimetric methods are generally suitable for microgram amounts of molybdenum.[1] The colorimetric thiocyanate method is used for the rapid determination of 1–6% of molybdenum but there are difficulties and inaccuracies[2] and separation from several interfering elements is necessary.[3]

Molybdenum forms a brown Mo(V) species in sulphuric acid and also a green one at higher concentrations of hydrochloric acid.[4] The former species has been used for the determination of milligram amounts of molybdenum.[4–7] The method presented below makes use of the green species, which is extractable by organic solvents.

EXPERIMENTAL

Reagents and test solutions

Solutions of the elements. Molybdenum solution was prepared by dissolving sodium molybdate dihydrate in water to give 10 mg of Mo per ml, and standardized by the oxinate method.[1] Solutions of other ions were prepared by dissolving their easily available salts to give 10 or 20 mg of ion per ml, and standardized by conventional methods.[8]

Isoamyl acetate. The fraction distilling at up to 130° was used.

Hydrazine sulphate.

Samples. Synthetic samples were prepared by mixing hydrochloric or sulphuric acid solutions of the ions to give the required composition (Table 3).

Ferromolybdenum. Finely powdered sample (0·1 g) was dissolved in 3 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric acid by gentle warming. Nitrate was destroyed by careful addition of solid hydrazine sulphate. The solution was then subjected to the procedure.

Procedure

To a hot 10-ml aliquot of sample solution containing not more than 135 mg of molybdenum and other ions (in $5{\cdot}5M$ hydrochloric acid) add solid hydrazine sulphate (1 mg for mg of each reducible ion) and boil the solution for 2 min in a 50-ml covered beaker, with occasional stirring. Cool the solution under tap water, transfer it to a 100-ml separatory funnel, adjust it to be $7M$ in hydrochloric acid in a final 20-ml volume (adding the acid last) and mix well. Then extract with one 10-ml and three 5-ml portions of isoamyl acetate, shaking each time for 1 min. Two extractions, each with 10 ml of solvent, are sufficient for up to 10 mg of molybdenum. Combine the extracts and dilute to 25 ml in a volumetric flask. Pass the solution through a Whatman No. 41 filter paper, rejecting the first few drops, and measure the absorbance at 720 nm against a similarly treated reagent blank, within 45 min.

Samples containing iron. To the hot solution, after reduction of molybdenum by hydrazine sulphate, add concentrated stannous chloride solution dropwise in calculated slight excess to reduce all the iron(III) (approximately known). Before repeating the extraction with the solvent, add a drop or two of the stannous chloride solution to reduce any iron oxidized during the previous equilibration.

Samples containing tungsten. Add enough tartaric acid to the neutral or just alkaline sample solution to mask all the tungsten and then apply the procedure.

Samples containing copper. After reduction of molybdenum, add enough thiourea to mask the copper.

RESULTS AND DISCUSSION

Effect of varying experimental conditions

Reductants other than hydrazine are not suitable—metallic mercury forms insoluble mercurous chloride, making phase separation difficult, stannous chloride does not produce a single oxidation state,[9] and ascorbic acid in excess suppresses the extraction. The effect of conditions of reduction and extraction on the green Mo(V) absorbance is shown in Table 1. Solvent extraction of molybdenum solutions obtained by reduction in <5*M* hydrochloric acid and below the boiling point, gives a slightly different green colour in the solvent phase; a back-wash from the solvent shows a blue colour indicating that some "molybdenum blue" is still present after reduction under these conditions. If the reduction is carried out in >5*M* hydrochloric acid and at boiling point, a back-extraction from the green solvent phase gives a brown to orange colour. Molybdenum blue, once formed, is sufficiently stable even in 7*M* hydrochloric acid, hence its formation should be prevented by carrying out the reduction in >5*M* hydrochloric acid. The presence of even small amounts of molybdenum blue enhances the absorbance at 720 nm as it has very much higher molar absorptivity than the green Mo(V). This can be seen from Table 1. Reduction with hydrazine is complete in 2 min and gives a single oxidation state, Mo(V).[10] At hydrochloric acid concentrations >5*M*, the brown species decreases and the green species increases abruptly.[4] When the aqueous phase is made 7*M* in hydrochloric acid, the acid should be added last, otherwise the absorbance is slightly lowered. Extraction from 7*M* hydrochloric acid gives maximum absorbance. These conditions are incorporated in the procedure and give satisfactory results reproducible to ±0·2 mg.

Table 1. Dependence of the absorbance of green Mo(V) on acidity of the aqueous phase (Mo = 1·976 mg/ml of solvent phase)

[HCl] for reduction, *M*	0·5	1·0	1·5	2·0	3·5	4·5	5·5
Absorbance[*]	0·860	0·430	0·416	0·409	0·390	0·381	0·374
[HCl] for extraction[†], *M*	5·5	6·0	6·5	7·0	7·5	8·0	
Absorbance	0·348	0·360	0·367	0·374	0·370	0·359	

[*] After extraction from 7*M* HCl.

[†] After reduction in 5·5*M* HCl.

The oxygenated solvents, isoamyl acetate , isoamyl alcohol, methyl isobutyl ketone, n-butyl acetate and tri-n-butyl phosphate, extract the green Mo(V) but the absorbance is the highest in isoamyl acetate at 720 nm. Isoamyl acetate also extracts less of the other elements. The absorption maxima at 305 nm and 440 nm are not so useful. Extraction of Mo(V) is complete after the four separate equilibrations. Beer's law is obeyed at 720 nm from 0·08 to 5·4 mg of molybdenum per ml. The absorbance is constant for 45 min. The spectrum matches that known to correspond to H_2MoOCl_5.

Table 2. Extraction of other elements

Element[*]	Colour of extract	Absorbance
Co	Blue	0·298
Cu	Greenish yellow	0·047
Fe	Yellow	0·018
Os[#]	Faintly coloured	0·002
Pd[†]	Orange yellow	0·002
U	Faintly yellow	0·000
Ni, Ru, Pt, Cr, V, Mn, Se, Te, Cu,[§] Fe,[¶] Ce	Colourless	0·000
Nb, Ti, Zr, Re,[‡] Th, Be, Mg, Ca, Ba, Sr, Zn, Al, Pb, Cd, Bi, La, W, Sb, Sn, As	Colourless	0·000

[*] 5 mg/ml, in its normal oxidation state, unless otherwise stated.

[#] 3·75 mg/ml; [†] 1·5 mg/ml; [‡] 0·005 mg/ml.

[§] On adding 2 g of thiourea.

[¶] On adding stannous chloride.

Effect of diverse ions

Sulphate has no effect, and acetate, oxalate, tartrate, citrate, phosphate and EDTA even in saturation amounts, decrease the extraction only slightly. Excess of ascorbic acid gives a dark brown aqueous solution and lowers the extraction of the green species. Fluoride (>25 mg/ml) decreases the extraction considerably.

Except for cobalt and very large amounts of palladium and osmium, other elements do not interfere (Table 2) in the method. Particularly remarkable is the absence of interference from Ti, V, Nb, Cr, W, Fe, Ni, Cu, U and Sb, which have to be separated for most methods of moybdenum determination.

Applications

The wide applicability of the method is shown by the satisfactory analysis of different synthetic samples and of ferromolybdenum (Table 3). Samples weighing 0·2–5 g (not containing cobalt and large amounts of platinum metals) can be directly analysed for 1–60% of molybdenum in 15 min or less with sufficient accuracy for all routine purposes. The method requires only simple reagents and is also useful for rapid series analyses.

Table 3. Analysis of samples by the proposed method

Sample composition*	Mo added, *mg*	Mo found, *mg*	Sample composition*	Mo added, *mg*	Mo found, *mg*
V(100) Ti(40) Mn(30)	19·3	19·1, 19·2	W(50)	9·6	9·7
V(20) Ni(40)	57·9	57·9, 58·0	Ti(100)	20·0	20·0
V(10) Ni(20) Cr(50)	28·9	29·1	Fe(40)	48·3	48·4
Ru(9) Pt(10) Nb(15)	67·6	67·7	Fe(20) Ni(60)†	19·3	19·3
U(100)	25·0	25·0	Fe(1000)	45·6	45·7
W(20)	38·6	38·7	Ferromolybdenum‡	—	58·6%

* Amounts (mg) are given in brackets.
† Analogous to Hastelloy A.
‡ 58·8% by oxinate method.[1]

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Summary—A simple method is described for the rapid spectrophotometric determination of molybdenum in samples containing 1–60% Mo, with satisfactory accuracy. Molybdenum is reduced with excess of hydrazine sulphate in boiling 5·5*M* hydrochloric acid and extracted with isoamyl acetate from 7*M* hydrochloric acid. The green colour is measured at 720 nm against a reagent blank. Beer's law is obeyed over the range 0·08–5·4 mg of molybdenum per ml. Interference from iron and copper is removed by adding stannous chloride and thiourea respectively in slight excess. Titanium, vanadium, niobium, chromium, tungsten, nickel, uranium, and antimony do not interfere even in large amounts. Only cobalt interferes seriously.

Zusammenfassung—Eine einfache Methode wird beschrieben, um Molybdän in Proben, die 1–60% Mo enthalten, rasch und hinreichend genau spektrophotometrisch zu bestimmen. Molybdän wird mit einem Überschuß von Hydrazinsulfat in siedender 5,5M Salzsäure und mit Isoamylacetat aus 7M Salzsäure extrahiert. Die grüne Farbe wird bei 720 nm gegen eine Reagentien-Blindprobe gemessen. Das Beersche Gesetz wird im Bereich 0,08–5,4 mg Molybdän pro ml befolgt. Die Störung durch Eisen bzw. Kupfer wird beseitigt, indem man Zinn(II)-chlorid bzw. Thioharnstoff in schwachem Überschuß zugibt. Titan, Vanadium, Niob, Chrom, Wolfram, Nickel, Uran und Antimon stören auch in großen Mengen nicht. Nur Kobalt stört in erheblichem Ausmaß.

Résumé—On décrit une méthode simple pour le dosage spectrophotométrique rapide du molybdène dans des échantillons contenant 1–6p% de Mo, avec une précision satisfaisante. Le molybdène est réduit par un excès de sulfate d'hydrazine en acide chlorhydrique 5, 5 *M* bouillant et extrait par l'acétate d'isoamyle à partir d'acide chlorhydrique 7*M*. On mesure la coloration verte à 720 nm par rapport à un témoin des réactifs. La loi de Beer est suivie dans le domaine 0,08–5,4 mg de molybdène par ml. On élimine l'interférence du fer et du cuivre par addition en léger excès de chlorure stanneux et de thiourée respectivement. Les titane, vanadium, niobium, chrome, tungstène, nickel, uranium et antimoine n'interfèrent pas, même en fortes quantités. Seul le cobalt interfère sérieusement.

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THIOTROPOLONE AS A CHROMOGENIC REAGENT FOR THE SIMULTANEOUS DETERMINATION OF COBALT(II) AND NICKEL(II)

(*Received* 20 *March* 1973. *Accepted* 12 *May* 1973)

Thiotropolone (TT) is a chelating agent, the complexes of which with certain metal ions have been isolated.[1] However, no solution studies have been reported. The present paper deals with investigation of the use of thiotropolone as a chromogenic reagent for the simultaneous determination of cobalt and nickel, in metals and alloys. Cobalt and nickel form reddish-brown and violet insoluble complexes respectively, extractable into chloroform and other non-polar solvents.

EXPERIMENTAL

Reagents

Thiotropolone was synthesized by the method of Nozoe *et al.*[2,3] and a stock solution (0.01*M*) in chloroform prepared. Cobalt(II) and nickel(II) solutions were prepared by dissolving the corresponding sulphates in doubly distilled water and standardized gravimetrically.

Acetate buffers, hydrochloric acid and sodium hydroxide were used for pH adjustments. All other chemicals used were of reagent grade.

Procedure

To a suitable aliquot containing 6·0–25·0 μg of cobalt or 7·5–45·7 μg of nickel, add an excess of chloroform solution of thiotropolone, keeping the pH at 7·0. Make the volumes of both phases 10 ml and shake the mixture for 5 min. Separate the organic layer and measure its absorbance (at 500 nm for cobalt and 580 nm for nickel) against the corresponding reagent blank. Read the cobalt or nickel concentration from a previously prepared calibration curve.

RESULTS AND DISCUSSIONS

Absorption spectra, and effect of pH and reagent concentration

The cobalt and nickel complexes exhibit maximum absorbance at 500 and 580 nm rsepectively (Fig. 1). Absorbance due to the reagent is negligible at 580 nm. Therefore subsequent studies on the nickel complex were done with a chloroform blank, but reagent blanks were used for cobalt.

Zusammenfassung—Eine einfache Methode wird beschrieben, um Molybdän in Proben, die 1–60% Mo enthalten, rasch und hinreichend genau spektrophotometrisch zu bestimmen. Molybdän wird mit einem Überschuß von Hydrazinsulfat in siedender 5,5M Salzsäure und mit Isoamylacetat aus 7M Salzsäure extrahiert. Die grüne Farbe wird bei 720 nm gegen eine Reagentien-Blindprobe gemessen. Das Beersche Gesetz wird im Bereich 0,08–5,4 mg Molybdän pro ml befolgt. Die Störung durch Eisen bzw. Kupfer wird beseitigt, indem man Zinn(II)-chlorid bzw. Thioharnstoff in schwachem Überschuß zugibt. Titan, Vanadium, Niob, Chrom, Wolfram, Nickel, Uran und Antimon stören auch in großen Mengen nicht. Nur Kobalt stört in erheblichem Ausmaß.

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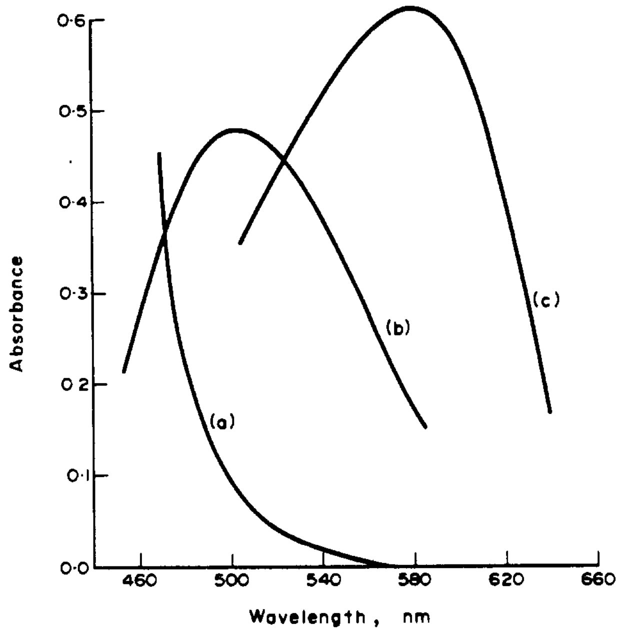

Fig. 1. Absorption spectra
Curve (A) ligand blank *vs.* chloroform [$TT = 2·5 \times 10^{-4}M$]
Curve (B) cobalt complex *vs.* ligand blank [$Co(II) = 2·5 \times 10^{-5}M$, $TT = 2·5 \times 10^{-4}M$]
Curve (C) nickel complex *vs.* ligand blank [$Ni(II) = 5·0 \times 10^{-5}$, $TT = 5·0 \times 10^{-4}M$].

The nickel complex was found to exhibit maximum absorbance over the pH range 6·0–9·0 and the cobalt complex over the pH range 7·0–8·5.

A mole-ratio study revealed that for full colour development, a fivefold molar excess of the reagent is required for cobalt and fourfold for nickel. However, a minimum of a tenfold excess was used in subsequent studies.

Calibration curve, sensitivity and range for accurate determination

Linearity between absorbance and metal ion concentration was observed up to 2·6 ppm of cobalt and 4·7 ppm of nickel. The optimum ranges for accurate determination, as deduced from Ringbom plots, are 0·6–2·5 ppm and 0·75–4·57 ppm for cobalt and nickel respectively.

The sensitivities of the colour reactions (in terms of Sandell's definition) are 0·0031 $\mu g/cm^2$ (at 500 nm) for cobalt and 0·0048 $\mu g/cm^2$ (at 580 nm) for nickel, with molar absorptivities $1·91 \times 10^4$ and $1·21 \times 10^4$ $l \cdot mole^{-1} \cdot cm^{-1}$ respectively.

The precision of the procedures was checked by measuring the absorbance of 8 samples, each containing a final concentration of 1·47 ppm of cobalt or 2.93 ppm of nickel, values approximately in the middle of the optimum ranges. The mean absorbances of the cobalt and nickel complexes were found to be 0·475 and 0·605, with standard deviations of 0·002 and 0·003 respectively.

Composition and apparent instability constants

Job's method of continuous variations and the mole-ratio method indicate the formation of 1:3 (cobalt : TT) and 1:2 (nickel:TT) complexes. The 1 : 3 complex seems to contain tervalent cobalt as do the cobalt chelates with nitrosonaphthols,[4] violuric[5] and thiovioluric acids.[6] That cobalt exists in the tervalent state in the complex is supported by its stability in strongly acidic solutions, a characteristic of a spin-paired d^6 cobalt complexes.[7] The apparent instability constants for cobalt and nickel complexes have been calculated from mole-ratio plots.[8] The values are $1·91 \times 10^{-15}$ and $5·58 \times 10^{-11}$ for cobalt and nickel respectively.

Effect of diverse ions

The general procedure was followed, except that the solutions of foreign ions were added before the reagent solution.

Common anions such as acetate, nitrate, nitrite, chloride, bromide, iodide, sulphate, sulphite, iodate, citrate, tartrate, phosphate, fluoride, thiocyanate and thiourea are tolerated up to 1000–5000-fold molar ratio relative to cobalt or nickel.

Tolerance limits (in ppm) for various cations, in the determination of cobalt, are as follows: Mo(VI), Mn(II), Sb(III), Th(IV), U(VI), each 50; Ca(II), Sr(II), Ba(II), Mg(II) each 500; Sc(III), As(III), V(V), Zr(IV), In(III), Al(III), Ga(III) and Bi(III) each 20.

For nickel, the tolerance limits are Mo(VI), Mn(II) each 100; Sb(III), Th(IV), U(VI) each 50; Ga(III), Bi(III) each 20; Al(III), In(III), As(III), V(V) each 30: Sc(III), Zr(IV) each 40; Ca(II), Sr(II), Ba(II) and Mg(II) each 500.

However, zinc, cadmium, mercury, tin, copper, EDTA, lead, palladium and iron interfere seriously in the determination of either of the metals.

Fe(III) (10 ppm) and Sn (IV)(50 ppm) can be masked with fluoride (1000 ppm); Hg(10 ppm) and Cd(10 ppm) with iodide (500 ppm); Zn(II)(10 ppm) with tartrate (500 ppm); Cu(II) (10 ppm) with thiourea (500 ppm). Pb(II) (50 ppm) can be precipitated with sulphate (500 ppm) and filtered off.

Simultaneous determination of cobalt and nickel

There is a difference of 80 nm in the wavelengths of absorption maximum of the cobalt and nickel complexes. In view of this, the following equations derived by Sandell[9] for simultaneous determination of the two components were employed for the determination of cobalt (A) and nickel (B)

$$K_1^A C_A + K_1^B = A_1 \text{ (total absorbance at 500 nm)}$$

$$K_2^A C_A + K_2^B C_B = A_2 \text{ (total absorbance at 580 nm)}$$

where K_1^A, K_2^A and K_1^B and K_2^B the molar extinction coefficients for cobalt and nickel complexes at 500 and 580 nm respectively are $1{\cdot}91 \times 10^4 (K_1^A)$, $5{\cdot}20 \times 10^3 (K_2^A)$, $4{\cdot}80 \times 10^3 (K_1^B)$ and $1{\cdot}21 \times 10^4\ \text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1} (K_2^B)$. The results for the determination of cobalt and nickel in synthetic mixtures of the two are tabulated below.

Table 1. Simultaneous determination of cobalt and nickel in synthetic mixtures

Cobalt taken, *ppm*	Nickel taken, *ppm*	Cobalt found, *ppm*	Nickel found, *ppm*
2.00	2·50	2·00	2·52
1·50	1·00	1·50	1·01
1·20	1·50	1·20	1·51
1·00	2·00	1·01	2·00
0·60	2·93	0·58	2·94

Determination of cobalt and nickel in alloys

Solutions of a few alloys containing cobalt, nickel, iron and copper were prepared and suitable aliquots of the solutions were taken. Large excesses of thiourea and ammonium fluoride were added in order to mask copper and iron. Determinations were then done as described above, by measuring the absorbances of the solutions at 500 and 580 nm against the corresponding reagent blanks.

The results for a few such determinations are recorded in Table 2.

Table 2. *Determination of cobalt and nickel in alloys*

Alloy	Cobalt reported, %	Nickel reported, %	Cobalt found, %	Nickel found, %
'K' Monel wire	0·51	65·6	0·50	65·0
Nilo-K wire	17·4	29·0	18·2	30·1
Brightray 'B' wire	nil	60·0	nil	60·8

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Summary—Thiotropolone forms chloroform-soluble reddish-brown and violet complexes with cobalt(II) and nickel(II), in the pH range 7·0–8·5 and 6·0–9·0 respectively. Based on this, a sensitive and rapid method for the spectrophotometric determination of traces of cobalt and nickel in metals and alloys has been developed. The two metals can be determined accurately in the range 0·6–2·6 ppm of cobalt and 0·75–4·57 ppm of nickel, simultaneously.

Zusammenfassung—Thiotropolon bildet mit Kobalt(II) und Nickel(II) bei pH 7,0–8,5 bzw. 6,0–9,0 chloroformlösliche rötlichbraune und violette Komplexe. Auf dieser Grundlage wurde ein empfindliches und schnelles Verfahren zur spektrophotometrischen Bestimmung von Kobalt- und Nickelspuren in Metallen und Legierungen entwickelt. Die beiden Metalle können gleichzeitig und genau im Bereich 0,6–2,6 ppm Kobalt und 0,75–4,57 ppm Nickel bestimmt werden.

Résumé—La thiotropolone forme des complexes brun-rougeâtre et violet solubles en chloroforme avec le cobalt(II) et le nickel(II), dans les domaines de pH 7,0–8,5 et 6,0–9,0 respectivement. En se basant sur ceci, on a élaboré une méthode sensible et rapide pour le dosage spectrophotométrique de traces de cobalt et de nickel dans les métaux et alliages. Les deux métaux peuvent être dosés avec précision dans le domaine 0,6–2,6 p.p.m. de cobalt et 0,75–4,57 p.p.m. de nickel, simultanément.

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GRAVIMETRIC DETERMINATION OF CADMIUM WITH *N*-PHENYLBENZOHYDROXAMIC ACID*

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Hydroxamic acids are characterized by remarkable versatility as reagents in organic and inorganic analysis.[1–5] No systematic investigation seems to have been made hitherto of their use for gravimetric determination of cadmium. *N*-Phenylbenzohydroxamic acid has now been found to be satisfactory for this purpose.

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Summary—Thiotropolone forms chloroform-soluble reddish-brown and violet complexes with cobalt(II) and nickel(II), in the pH range 7·0–8·5 and 6·0–9·0 respectively. Based on this, a sensitive and rapid method for the spectrophotometric determination of traces of cobalt and nickel in metals and alloys has been developed. The two metals can be determined accurately in the range 0·6–2·6 ppm of cobalt and 0·75–4·57 ppm of nickel, simultaneously.

Zusammenfassung—Thiotropolon bildet mit Kobalt(II) und Nickel(II) bei pH 7,0–8,5 bzw. 6,0–9,0 chloroformlösliche rötlichbraune und violette Komplexe. Auf dieser Grundlage wurde ein empfindliches und schnelles Verfahren zur spektrophotometrischen Bestimmung von Kobalt- und Nickelspuren in Metallen und Legierungen entwickelt. Die beiden Metalle können gleichzeitig und genau im Bereich 0,6–2,6 ppm Kobalt und 0,75–4,57 ppm Nickel bestimmt werden.

Résumé—La thiotropolone forme des complexes brun-rougeâtre et violet solubles en chloroforme avec le cobalt(II) et le nickel(II), dans les domaines de pH 7,0–8,5 et 6,0–9,0 respectivement. En se basant sur ceci, on a élaboré une méthode sensible et rapide pour le dosage spectrophotométrique de traces de cobalt et de nickel dans les métaux et alliages. Les deux métaux peuvent être dosés avec précision dans le domaine 0,6–2,6 p.p.m. de cobalt et 0,75–4,57 p.p.m. de nickel, simultanément.

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GRAVIMETRIC DETERMINATION OF CADMIUM WITH *N*-PHENYLBENZOHYDROXAMIC ACID*

(*Received* 11 *April* 1973. *Accepted* 19 *May* 1973)

Hydroxamic acids are characterized by remarkable versatility as reagents in organic and inorganic analysis.[1–5] No systematic investigation seems to have been made hitherto of their use for gravimetric determination of cadmium. *N*-Phenylbenzohydroxamic acid has now been found to be satisfactory for this purpose.

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* Presented at the Convention of Chemistry, Allahabad, 1972, India.

EXPERIMENTAL

Reagents

Cadmium solution. Prepared by dissolving cadmium acetate, and standardized volumetrically.[6]

N-*Phenylbenzohydroxamic acid.* Prepared by the method of Priyadarshini and Tandon;[7] m.p. 121° (literature value 121°).

Table 1. Gravimetric determination of Cd with PBHA

Cd taken, *mg*	Cd found, *mg*
6·00	6·05
6·00	5·98
9·00	9·00
15·00	15·03
15·00	14·98

Procedure

In a 1-litre beaker, 6–15 mg of cadmium acetate and 500 ml of water were heated to 60° on a water-bath. Then 20 ml of $\sim 0{\cdot}1M$ PBHA in ethanol were added dropwise (mole ratio Cd : PBHA = 1 : 2) with constant stirring. The pH was adjusted to 5·8–6·5 with ammonium acetate and ammonia. The granular precipitate thus formed was digested for 2–3 hr over a steam-bath, filtered off on a sintered-glass crucible of porosity G4 and washed thoroughly with hot water and finally with 50% aqueous ethanol (10 × 10 ml). The cadmium complex thus obtained was dried at 110° and weighed as $(C_{13}H_{10}NO_2)Cd$.

Separation of cadmium from foreign ions

A mixture containing cadmium(II) (9·0 or 12 mg), and silver(I) (60 mg), lead(II), (80 mg), manganese(II) (80 mg), mercury(II) (60 mg), palladium(II) (100 mg), gallium(III), (100 mg), bismuth(III) (80 mg), lanthanum(III), (80 mg), titanium(IV) (100 mg), zirconium(IV) (100 mg), vanadium(V) (80 mg), or molybdenum(VI) (100 mg) was taken and the foreign metal ion was precipitated in presence of acetate ions at pH below 5·0 by PBHA. The precipitate was filtered off and washed with an acetate solution at pH 5·0. The filtrate and washings were combined and concentrated to about 150 ml, and cadmium was precipitated with PBHA from the solution, collected, washed with 50% aqueous ethanol mixture (15 × 20 ml) and dried at 110°.

Cadmium was also precipitated with PBHA from 150 ml of solution containing beryllium(II) (80 mg), nickel(II) (80 mg), copper(II) (80 mg), zinc(II) (80 mg), aluminium(III) (100 mg), antimony(III) (100 mg) or uranium(VI) (60 mg) in presence of acetate and citrate ions and the complex was washed, dried and weighed as before. The weights quoted in brackets are the maximum amounts of these ions that can be tolerated.

The experimental results are given in Table 1 and 2. The Cd–PBHA complex is fairly soluble in ethanol and chloroform but only sparingly soluble in ether, benzene, carbon tetrachloride, acetone and glacial

Table 2. Separation of Cd from other metals.

Cd taken, *mg*	Foreign ion, *mg*	Masking agent	Cd found, *mg*	Cd taken, *mg*	Foreign ion, *mg*	Masking agent	Cd found, *mg*
9·00	Ag^{+} 60	Acetate	8·98	9·00	Al^{3+} 100	Acetate + citrate	9·01
9·00	Be^{2+} 80	Acetate + citrate	8·99	9·00	Bi^{3+} 80	Acetate	8·98
9·00	Pb^{2+} 80	Acetate	9·01	9·00	Sb^{3+} 100	Acetate + citrate	8·96
9·00	Mn^{2+} 80	Acetate	8·99	9·00	La^{3+} 80	Acetate	9·02
12·00	Ni^{2+} 80	Acetate + citrate	11·96	9·00	Ti^{4+} 100	Acetate	9·00
12·00	Cu^{2+} 80	Acetate + citrate	11·96	9·00	Zr^{4+} 100	Acetate	8·98
12·00	Zn^{2+} 80	Acetate + citrate	12·01	9·00	V^{5+} 80	Acetate	8·97
9·00	Hg^{2+} 60	Acetate	9·00	9·00	Mo^{6+} 100	Acetate	9·00
9·00	Pd^{2+} 100	Acetate	9·03	9·00	U^{6+} 60	Acetate + citrate	9·01
9·00	Ga^{3+} 100	Acetate	9·01				

acetic acid. It is decomposed when treated with conc. sulphuric, perchloric, nitric or hydrochloric acid and melts at 225°. The analytical results indicate the complex to be $(C_{13}H_{10}NO_2)_2Cd$.

Acknowledgement—The author is indebted to Professor A. B. Biswas, Senior Professor of Chemistry, I.I.T. Bombay for his valuable suggestions and for providing facilities.

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Summary—A quantitative gravimetric determination of cadmium in presence of Ag^+, Be^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Mo^{6+} and U^{6+} was made by selective precipitation with *N*-phenylbenzohydroxamic acid from a solution containing 6–15 mg of cadmium acetate at pH 5·8–6·5. The precipitate was weighed directly after drying at 110–120°. The cadmium complex is curdy white, granular and melts at 225°. The analytical results indicate the complex to be $(C_{13}H_{10}NO_2)_2Cd$.

Zusammenfassung—Cadmium wurde in Gegenwart von Ag^+, Be^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Mo^{6+}, und U^{6+} quantitativ gravimetrisch bestimmt. Es wrude selektiv mit N–Phenylbenzhydroxamsäure aus einer Losung gefällt, die 6–15 mg Cadmiumacetat bei pH 5.8—6.5 enthielt. Der Niederschlag wurde nach Trocknen bei 110—120° direkt gewogen. Der Cadmiumkomplex ist käsig weiß und körnig und schmilzt bei 225°. Die analytischen Ergebnisse zeigen, daß der Komplex die Formel $(C_{13}H_{10}NO_2)_2Cd$ hat.

Résumé—On a effectué un dosage gravimétrique quantitatif du cadmium en présence de Ag^+, Be^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Mo^{6+} et U^{6+} par précipitation sélective avec l'acide N-phénylbenzohydroxamique à partir d'une solution contenant 6–15 mg d'acétate de cadmium à pH 5,8–6,5. Le précipité a été pesé directement après séchage à 110–120°. Le complexe de cadmium est blanc caillebоté, granulaire, et fond à 225°. Les résultats analytiques indiquent que le complexe est $(C_{13}H_{10}NO_2)_2Cd$.

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SPECTROSCOPIC DETERMINATION OF SULPHATE IN THE PRESENCE OF EXCESS OF NITRATE AND NITRITE

(*Received* 26 *April* 1973. *Accepted* 15 *May* 1973)

The determination of sulphate in alkali metal sulphates, or of sulphuric acid in the presence of other anions, is important analytically. A survey of the chemical literature indicates that a vast number of methods has been proposed for the determination of sulphate, ranging from classical procedures to modern techniques acetic acid. It is decomposed when treated with conc. sulphuric, perchloric, nitric or hydrochloric acid and melts at 225°. The analytical results indicate the complex to be $(C_{13}H_{10}NO_2)_2Cd$.

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The determination of sulphate in alkali metal sulphates, or of sulphuric acid in the presence of other anions, is important analytically. A survey of the chemical literature indicates that a vast number of methods has been proposed for the determination of sulphate, ranging from classical procedures to modern techniques such as ion-selective electrodes[1] and spectroscopy.[2] Recently, an infrared method using the KBr pellet technique has been successfully applied for the determination of some alkali metal nitrates,[3] carbonates,[4] and sulphates.[5] We have applied the method to the determination of sulphate in the presence of large excesses of nitrate or nitrite.

EXPERIMENTAL

Merck analytical-reagent grade potassium sulphate, potassium nitrate and sodium nitrite were recrystallized from distilled water. These chemicals and Merck spectroscopic grade potassium bromide were dried under vacuum.

Discs were prepared covering the range 0·1–1·0 mg of sulphate and containing 20 mg of potassium nitrate or 5 mg of sodium nitrite and enough potassium bromide to yield a total mass of 200 mg. Each sample was weighed to ±0·01 mg, finely ground in an agate mortar and transferred to a die which was subsequently evacuated and the disc pressed under 15 tons pressure for 5 min. The spectra were then scanned from 1000 to 400 cm^{-1} on a Perkin–Elmer Model 457 infrared spectrophotometer. The absorbances of the band at 619 cm^{-1} were measured.

RESULTS AND DISCUSSION

Nitrite and nitrate do not absorb significantly between 800 and 600 cm^{-1} and therefore sulphate was determined by measuring the absorption of radiation at 619 cm^{-1} by the ν_4 vibration of the sulphate ion. The information for the construction of calibration curves is shown in Table 1. The calibration curves differ considerably in slope, so presumably the intensity of the ν_4 vibration of the sulphate ion is sensitive to chemical environment. Consequently, if both nitrate and nitrite are present the ratio of the two would have to be known and an appropriate calibration curve constructed, or the standard addition technique used.

Table 1. Calibration curves for sulphate in (*a*) presence of 20 mg of KNO_3 and (*b*) 5 mg of $NaNO_2$

Weight of sulphate added, *mg*	0·13	0·25	0·35	0·40	0·52	0·53	0·62	0·95
Absorbance (*a*)	0·100	0·185	0·270	0·306	0·400	—	0·460	—
Absorbance (*b*)	0·075	—	0·205	—	—	0·285	0·355	0·535

Results obtained for synthetic mixtures of sulphate with nitrate or nitrite are shown in Table 2.

Table 2. Determination of sulphate in presence of (*a*) 20 mg of KNO_3 and (*b*) 5 mg of $NaNO_2$.

(*a*) Sulphate taken, *mg*	0·05	0.16	0·17	0·28	0·30	0·38	0·41	0·46	0·48	0·57	0·63	0·68
found, *mg*	0·04	0·15	0·16	0·26	0·30	0·35	0·38	0·44	0·45	0·53	0·60	0·71
(*b*) Sulphate taken, *mg*	0·04	0·06	0·17	0·21	0·33	0·42	0·44	0·50	0·52	0·73		
found, *mg*	0·04	0·07	0·16	0·19	0·35	0·44	0·45	0·46	0·55	0·71		

Sulphate could be determined in the presence of up to a 400-fold molar excess of nitrate and a 60-fold molar excess of nitrite. The maximal amount of nitrate tolerable was a function of the maximal baseline adjustment available and whilst greater than 60-fold molar excess of nitrite did not interfere in the 600–800 cm^{-1} region, a practical difficulty was encountered in mixing the sample, so there was poor dispersion of the sulphate through the sample.

The results indicate that this method for sulphate determination in the presence of nitrate and nitrite compares reasonably with other techniques,[6] the relative standard deviation being about 5%.

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Summary—The KBr pellet technique has been used for the determination of alkali metal sulphate in the presence of large excesses of nitrate and nitrite by measuring the absorption of the sulphate at 619 cm^{-1}. The sulphate can be determined in a 400-fold molar excess of nitrate and a 60-fold molar excess of nitrite with a relative standard deviation of about 5%.

Zusammenfassung—Die KBr-Tablettentechnik wurde zur Bestimmung von Alkalimetallsulfat in Gegenwart großer Überschüsse von Nitrat und Nitrit durch Messung der Absorption von Sulfat bei 619 cm^{-1} verwendet. Das Sulfat kann neben einem 400-fachen molaren Überschuß von Nitrat und einem 60-fachen molaren Überschuß von Nitrit mit einer relativen Standardabweichung von etwa 5% bestimmt werden.

Résumé—La méthode à la pastille de KBr a été utilisée pour le dosage de sulfate de métal alcalin en la présence de grands excès de nitrate et nitrite en mesurant l'absorption du sulfate à 619 cm^{-1}. Le sulfate peut être dosé dans un excès 400 fois molaire de nitrate et un excès 60 fois molaire de nitrite avec un écart type relatif d'environ 5%.

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GRAVIMETRIC DETERMINATION OF URANIUM(VI) WITH PYRIDINE-2,6-DICARBOXYLIC ACID

(*Received* 27 *September* 1972. *Accepted* 12 *May* 1973)

During research on the chemistry of uranyl co-ordination compounds, we found a need for a rapid, simple and precise method for the determination of relatively small amounts of uranium in solution. Many methods have been reported,[1–5] but the gravimetric techniques usually require either ignition of a precipitate to U_3O_8 or else the formation of a stoichiometric complex which can be separated and weighed. The ignition method is of limited precision when small quantities of uranium are involved and most of the complexes present problems in filtration, which makes the process time-consuming.

When studying the formation of complexes of uranyl ion with pyridine-2,6-dicarboxylic acid (H_2L) in aqueous solution,[6] we found that the anionic complex $[UO_2L_2]^{2-}$ can be rapidly precipitated by addition of tetraphenylarsonium chloride (Ph_4AsCl). The precipitate is a crystalline solid, which can be rapidly filtered off and washed. We have devised a method for the gravimetric determination of uranium based on this reaction.

EXPERIMENTAL

Reagents

Uranyl nitrate solution. Approximately 2 g of reagent-grade uranyl nitrate hexahydrate was dissolved in 1 l. of distilled water, and the solution standardized by evaporation of an aliquot in a porcelain crucible under an infrared lamp, ignition at 800° for 5 hr, and weighing of the product as U_3O_8. Analysis of six 25-ml aliquots gave an average value of 23·80 mg of uranium with a standard deviation of 0·11 mg (Table 1).

Tetraphenylarsonium chloride solution. A 1% solution in water was treated with active charcoal to remove the cloudiness due to impurities.

Pyridine-2,6-dicarboxylic acid. The reagent grade chemical was used without further purification.

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Tetraphenylarsonium chloride solution. A 1% solution in water was treated with active charcoal to remove the cloudiness due to impurities.

Pyridine-2,6-dicarboxylic acid. The reagent grade chemical was used without further purification.

Table 1. Determination of uranium as the oxide and as the complex from 25-ml aliquots of uranyl nitrate solution

Weight of U_3O_8, *mg*	U found,* *mg*	Weight of complex,† *mg*	U found,‡ *mg*
28·10	23·83	140·82	23·88
27·98	23·73	140·22	23·78
27·91	23·67	140·62	23·84
28·07	23·80	140·52	23·83
28·12	23·84	140·30	23·79
28·23	23·94	140·20	23·77

* Average value 23·80 mg; s.d. 0·11 mg (calculated from the range[7]).

† In each determination the molar ratio of reagents is: uranyl nitrate:pyridine-2,6-dicarboxylic acid:tetraphenylarsonium chloride = 1:6:6.

‡ Average value 23·81 mg; s.d. 0·04 mg.

Procedure

The required amount of pyridine-2,6-dicarboxylic acid was added to 25 ml of 1% tetraphenylarsonium chloride solution and the mixture heated at 80° and stirred until dissolution was complete. Then 25 ml of the stock uranyl nitrate solution, previously heated to the same temperature, were added rapidly and the resulting solution was left to reach room temperature, during which time (~ 30 min) precipitation took place. The precipitate was filtered off on a medium-porosity sintered-glass crucible, washed with several small portions of cold distilled water and dried to constant weight *in vacuo* (0·1 Torr) for 2 hr. When the precipitation is carried out at room temperature the product is microcrystalline, although still easily collected on a filter.

RESULTS AND DISCUSSION

The pale greenish-yellow crystalline complex obtained as described above displays no tendency to creep. It is soluble in water at above 60° and in methanol but is practically insoluble in chloroform, acetone, ether, carbon tetrachloride and in water at room temperature. The analytical data accord with the formula $(Ph_4As)_2[UO_2L_2].2H_2O$ (calculated: C, 53·03%; N, 1·99%; H, 3·56%; U, 16·96%; found: C, 52·8%; N, 2·0%; H, 3·5%; U, 16·9%).

The presence of two molecules of water was independently confirmed by infrared and thermogravimetric analysis. The infrared spectrum has a broad band in the 3300–3600 cm^{-1} region and the thermogravimetric curve shows clearly the loss of two molecules of water in the range 70–126°.

The results listed in Table 1 indicate that uranium(VI) is quantitatively precipitated.

Effect of reagent concentration

The precipitation was carried out with various amounts of the reagents, the other conditions remaining the same (Table 2). For rapid and complete precipitation of the metal the optimum ratio of reagents required was: uranyl nitrate : pyridine-2,6-dicarboxylic acid : tetraphenylarsonium chloride = 1 : 6 : 6.

Table 2. Effect of reagent concentration*

Molar ratio of reagents			Weight of complex,† *mg*	Precipitation time, *min*
$UO_2(NO_3)_2$	H_2L	Ph_4AsCl		
1	3	3	Incomplete precipitation	Long time
1	3	6	140·20	120
1	6	3	140·50	120
1	6	6	140·27	30
1	15	15	140·41	20

* Each determination was performed on a 25-ml aliquot of standard uranyl nitrate solution.

† Calculated for complete precipitation: 140·29 mg.

Effect of pH

Solutions containing uranium(VI), H_2L and Ph_4AsCl in the ratio 1 : 6 : 6 were adjusted to different pH values with nitric acid (2*M*) or with potassium hydroxide (2*M*), digested as usual and filtered and the pH of the filtrate was measured. The precipitates were washed, dried and weighed in the usual way. The precipitation is complete between pH 2·1 and 6·9. Below pH 2·1 precipitation is incomplete and above pH 6·9 the precipitate is impure, probably because of the presence of uranate.

Precipitation of uranium in the presence of foreign ions

When separation from Na^+, Al^{3+}, Ni^{2+}, Cu^{2+}, Fe^{3+} or Th^{4+} was studied, an equimolar amount of one of these ions with respect to uranyl ion was added as acetate, sulphate, nitrate or chloride to a solution of the reagent, the molar ratios of metal ion : pyridine-2,6-dicarboxylic acid : tetraphenylarsonium chloride being 1 : 6 : 6, in the pH range 2–3. An aliquot of uranyl nitrate solution was added and the uranium determined by the method above.

The results of the analysis of four 25-ml aliquots resulted in an average value of 24·62 mg of uranium with a standard deviation of 0·04 mg. Na^+, Al^{3+}, Cu^{2+}, Ni^{2+}, Cl^-, NO_3^-, SO_4^{2-} and acetate ions do not interfere under these conditions (Table 3), but Fe^{3+} and Th^{4+} do precipitate. The addition of a large excess of EDTA prevents the co-precipitation of thorium and iron to some extent, but the separation is not complete.

Table 3. Determination of 24·62 mg of uranium in the presence of foreign ions

Foreign ion present*	U found,† *mg*	Error, *mg*
CH_3COONa	24·59 ± 0·02	−0·03
Na_2SO_4	24·67 ± 0·04	+0·05
$Cu(NO_3)_2$	24·68 ± 0·06	+0·06
$NiCl_2$	24·54 ± 0·06	−0·08
$AlCl_3$	24·59 ± 0·03	−0·03

* In every experiment an equimolar amount of foreign ion with respect to uranyl ion was added.

† Average values of four determinations.

CONCLUSION

The use of pyridine-2,6-dicarboxylic acid in the presence of tetraphenylarsonium chloride for precipitation of uranium offers the advantage of forming rapidly a highly insoluble crystalline material with a very favourable gravimetric factor. There is a twofold improvement in the precision of the determination compared to the method based on ignition to U_3O_8.

Acknowledgement—We thank Mrs. A. Coin and Mr. A. Berton for technical assistance.

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Summary—Uranium(VI) can be quantitatively precipitated from aqueous solution in the pH range 2·1–6·9 with pyridine-2,6-dicarboxylic acid in the presence of tetraphenylarsonium chloride. This provides a new rapid gravimetric method for uranyl ion as an organic chelate complex of high molecular weight. Sodium, aluminium, copper and nickel as well as nitrate, chloride, sulphate and acetate ions, do not interfere, but iron(III) and thorium(IV) do.

Zusammenfassung—Uran(VI) kann aus wäßriger Lösung bei pH 2,1–6,9 quantitativ mit Pyridin-2,6-dicarbonsäure in Gegenwart von Tetraphenylarsoniumchlorid quantitativ gefällt werden. Dies liefert eine neue rasche Methode zur gravimetrischen Analyse von Uranylionen als organischer Chelatkomplex von hohem Molekulargewicht. Natrium, Aluminium, Kupfer und Nickel sowie Nitrat, Chlorid, Sulfat und Acetat stören nicht, dagegen Eisen(III) und Thorium-(IV).

Résumé—On peut précipiter quantitativement l'uranium (VI) d'une solution aqueuse dans le domaine de pH 2,1–6,9 avec l'acide pyridine 2,6-dicarboxylique en la présence de chlorure de tétraphénylarsonium. Ceci fournit une nouvelle méthode rapide pour l'analyse gravimétrique de l'ion uranyle sous forme d'un complexe chélaté organique de haut poids moléculaire. Les sodium, aluminium, cuivre et nickel, ainsi que les ions nitrate, chlorure, sulfate et acétate n'interfèrent pas, mais le fer (III) et le thorium (IV) gênent.

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QUANTITATIVE MEASUREMENT OF MIXTURES OF HALLUCINOGENS BY FLUOROMETRY AND PHOSPHORIMETRY*

(*Received* 8 *May* 1973. *Accepted* 14 *June* 1973)

Currently, in forensic chemistry, most quantitative drug analyses are performed on as pure a sample as possible. This usually entails at least one chemical separation because most "street" drugs are mixtures. They usually contain one or two drugs and an inert matrix in the form of a tablet. There are many procedures to separate a drug from its matrix,[1] but fewer to separate a mixture of drugs from each other without significant losses. Therefore, it is of interest to look into methods of quantitative analysis not requiring separation of mixtures.

Lysergic acid diethylamide (LSD) has become one of the most widely used illicit drugs. It has also been mixed with many other drugs, either to enhance the physiological effect of the LSD or in order to be sold as some other drug. Many samples of "street" drugs which are examined contain mixtures of LSD and some other hallucinogen.

Fluorometry and phosphorimetry[2,3] offer the advantages of sensitivity, simplicity, accuracy, and relatively inexpensive equipment for the analysis of binary mixtures of LSD and some other hallucinogen. Recent improvements in phosphorimetry[4,5] allow its application to the measurements of analytes in aqueous, snowed matrices, *e.g.*, a predominately aqueous solvent (methanol/water 10/90 v/v). This has enabled workers to use the same solvent for both fluorometric and phosphorimetric measurements.

The present study was carried out to develop methods for the analysis of mixtures containing LSD and other hallucinogens, which are rapid, sensitive, and do not require physical separation (chromatographic) of components.

EXPERIMENTAL

Apparatus

All fluorescence and phosphorescence signals were measured with an Aminco-Bowman spectrophotofluorometer (American Instrument Company, Silver Spring, Maryland) with both fluorescence and phosphorescence cell assemblies and with an RCA 1P21 multiplier phototube powered by a model 244 high-voltage supply (Keithley Instruments Inc., Cleveland, Ohio). A 150-W Hanovia xenon arc lamp was powered by a Harrison model 6268A DC power supply (Hewlett-Packard, Palo Alto, California). The lamp was started by a circuit described by Zweidinger.[6] Signals were measured with a low-noise nanoammeter described previously.[7]

Summary—Uranium(VI) can be quantitatively precipitated from aqueous solution in the pH range 2·1–6·9 with pyridine-2,6-dicarboxylic acid in the presence of tetraphenylarsonium chloride. This provides a new rapid gravimetric method for uranyl ion as an organic chelate complex of high molecular weight. Sodium, aluminium, copper and nickel as well as nitrate, chloride, sulphate and acetate ions, do not interfere, but iron(III) and thorium(IV) do.

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For fluorescence measurements at room temperature, a 1 × 1 cm quartz sample cell was used. Phosphorescence measurements were made at 77° K, using a rotating capillary tube (approximately 4·5 mm diameter and 1·0 mm bore) made from T21 Suprasil quartz capillary tubing (Amersil Inc., Hillside, New Jersey); this cell contained approximately 20 μl and was used under the conditions described in the work by Lukasiewicz, Rozynes, Sanders and Winefordner.[4]

Spectra were checked against available literature data.[8,9] An X–Y recorder (No. 1620–827, American Instruments Company, Silver Spring, Maryland) was used to record all spectra.

Reagents

The following hallucinogens were studied: lysergic acid diethylamide (LSD), 2-5-dimethoxy-4-methylamphetamine (STP or DOM), psilocybin (from NIMH, Center for Studies of Narcotics and Drug Abuse, Rockville, Maryland), mescaline hydrochloride (from Sigma Chemical Company, St. Louis, Missouri), and phencyclidine hydrochloride (from Philips Roxane, Inc., St. Joseph, Missouri). All drugs were used as received, *i.e.*, without purification.

Methanol (Matheson, Coleman and Bell, Manufacturing Chemists, Norwood, Ohio, "Spectroquality" grade) and demineralized water were used as solvents.

Sodium iodide (Fisher Scientific Company, Fair Lawn, New Jersey, "Certified reagent" grade) was used for the heavy-ion effect in phosphorimetry.

Procedures

Stock solutions of the hallucinogenic drugs were prepared in a darkened room at concentrations of 10^{-2}–$10^{-3}M$ in methanol/water (10/90 v/v). For phosphorescence, drug mixtures containing LSD were also prepared in 0·75M sodium iodide. The stock solutions were prepared just before use because LSD was observed to decompose rapidly even when stored in darkness and at 5°. Because heavy-ion effect studies on mescaline hydrochloride and phencyclidine hydrochloride had not previously been performed, two stock solutions of each were prepared, one in methanol/water (10/90 v/v) and 0·75M in sodium iodide, the other in methanol/water (10/90) v/v.

The stock solutions were mixed and successively diluted to $10^{-9}M$ for preparation of the analytical curves. Each mixture was run at three different concentration ratios of LSD to the other hallucinogens: (*a*) 100:1; (*b*)1:1; (*c*) 1:100. The only exceptions were mixtures containing mescaline and phencyclidine, which were run at only two different concentrations because these species are only weakly fluorescent and phosphorescent.

The slit arrangement for fluorescence measurements was 3,2,2,3 (17 and 11 nm spectral half-band passes). A slit arrangement of 3,3,3,3 (17 and 17 nm spectral half-band passes) was used for phosphorescence measurements. In Table 1, the excitation and emission wavelengths at which measurements were made are given.

RESULTS AND DISCUSSION

Fluorometric and phosphorimetric analytical curves (luminescence signal *vs.* analyte concentration) for mixtures containing LSD and other hallucinogens at different concentrations were measured; the results are given in Table 2. All the hallucinogens except mescaline and phencyclidine (PCP) have fluorescence signals (and signal-to-noise ratios) high enough to be analytically useful. The phosphorescence signal of PCP is high enough to be analytically useful although the phosphorescence signal level of mescaline is too low.

Table 1. Excitation and emission wavelengths* (nm) used

Compound	Fluorescence†		Phosphorescence§	
	Excitation	Emission	Excitation	Emission
LSD	330	430	320	515
STP (DOM)	295	340	295	408
Psilocybin	283	352	—‡	—‡
Mescaline	—¶	—¶	281	418
Phencyclidine	—¶	—¶	265	385

* Peak wavelength error ±3 nm.
† In methanol/water (10/90 v/v).
§ In 0·75M NaI, methanol/water (10/90 v/v).
‡ Psilocybin was not measured by phosphorimetry.
¶ Mesacline and phencyclidine were not measured by fluorometry.

Table 2. Fluorometric analytical chacteristics of mixtures of hallucinogens

Hallucinogen		Fluorescence*			
	Slope of anal. curve§	Factor for concentration range of near linearity†		Limit of detection, *ng/ml*‡	
		Literature¶	This work	Literature¶	This work
LSD	0.96,0.94,1.09,1.28	10^3	10^4	6·5	3.6
STP	0·90	10^3	10^4	10	5
Psilocybin	0·89	10^3	10^3	23	23
Phencyclidine (PCP)	—	—	—	2·5 × 10^4¶	—
		Phosphorescence≠			
LSD	0·67,0·80,0·76,0·73	10^4	10^3	8	530
STP	0·99	10^3	10^4	10	33
Psilocybin	—	10^3	—	14	—
Phencyclidine (PCP)	0·98	—	10^2	—	320

* In neutral methanol/water (10/90 v/v) at 298° K.

§ The slopes of the analytical curves for LSD are for mixtures of LSD with STP, psilocybin, PCP, and mescaline, respectively.

† "Near linearity" means region over which analytical curve (log–log plot) deviates less than 1% from linearity. The absolute concentration range extends from the limit of detection to an upper concentration determined by the range factor times the limit of detection.

‡ Limit of detection is defined as the concentration giving a fluorescence of phosphorescence signal (located on the linear part of the analytical curve) that is twice the background noise.

¶ Reference 8.

≠ In 0·75*M* NaI solution in methanol/water (10/90 v/v) at 77° K.

Results for mescaline are therefore not reported. It was not possible to determine LSD and psilocybin by phosphorimetry. The excitation and emission peaks of the two were so close to each other that there would be severe spectral interference.

Limits of detection (defined as the concentration giving a fluorescence or phosphorescence signal twice the background noise) were approximately the same as reported by Aaron, Sanders and Winefordner[9] except for LSD by phosphorimetry (see Table 2). The limit of detection of LSD in this work was approximately 66 times that obtained by Aaron, Sanders and Winefordner.[9] This was a result of a much higher background, which for low concentrations of LSD effectively hid the phosphorescence signal in the noise. However, the high limit of detection for LSD does not present a problem because the normal dose in "street" tablets of LSD is 2–400 μg.[1] The phosphorimetric limit of detection for PCP was found to be about 250 ng/ml. Sodium iodide, which was added to enhance the signal intensity of LSD by the heavy-ion effect, was also found to enhance the phosphorescence signals of PCP and mescaline. The phosphorescence signal level for PCP was increased by a factor of four and for mescaline by a factor of ten. The presence of LSD in a mixture also containing mescaline of PCP prevented reliable measurement of fluorometric signals from either mescaline or PCP, owing to the high background noise level. However, in phosphorimetry, if sodium iodide is present, it would be possible to determine low concentrations of phencyclidine (but not mescaline).

There were no severe fluorescence interferences between the two compounds in the mixtures (see Table 2) *i.e.*, neither component affected the analytical curve for the other. However, in phosphorimetry, there were several cases of rather severe interference and analytical curve slopes appreciably below unity were obtained. It should be stressed, however, that in these cases the slopes were the same whether the ratio of LSD concentration to the other hallucinogen concentration was 100, 1, or 0·01, The reason for the departure from linearity is not known to the authors. However, by proper calibration procedures, such non-linear curves could be used for analytical purposes. The linear dynamic ranges of the analytical curves (see Table 2) compare well with those reported by Aaron, Sanders and Winefordner.[9] The standard deviation of the slopes for all analytical curves was 5%.

Because of the low limits of detection, lack of severe spectral interference, simplicity of procedure, and versatility of application, a combined fluorometric and phosphorimetric method seems appropriate for the quantitative analysis of hallucinogenic drugs in mixtures. It is sensitive, rapid, and does not require separation of the mixture. An examination of the spectra of the mixture can also give information on the identity of the hallucinogens.

The use of fluorometric and phosphorimetric methods foı the analysis of hallucinogenic mixtures should be extended to other drug mixtures. A possible example would be quantitative analysis of a morphine–strychnine mixture by phosphorimetry.[10]

This study was done under ideal conditions in which the drugs were pure and did not have to be extracted from a real sample. A study should be performed on regular "street" drugs to determine if the extraction of the hallucinogens will be satisfactory and which solvents are compatible with the background requirements of fluorescence and phosphorescence. A useful further extension of this work would be the analysis of hallucinogenic mixtures by time-resolved phosphorimetry.[11,12] Such studies are currently in progress.

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Summary—Room temperature fluorometric and low-temperature phosphorimetric analytical curves of hallucinogens in methanol/water solution have been prepared to demonstrate the absence of interference in common binary mixtures of hallucinogenic drugs. Limits of detection and linear dynamic ranges have been determined for drugs in mixtures. Mixtures containing LSD and another hallucinogen such as STP (DOM), psilocybin, mescaline, and phencyclidine have been studied. Detection limits are low, and analytical curves are linear over wide concentration ranges.

Zusammenfassung—Es wurden bei Zimmertemperatur fluorimetrische und bei tiefer Temperatur phosphorimetrische analytische Kurven von Halluzinogenen in Methanol-Wasser-Lösung aufgenommen, um die Abwesenheit von Störungen in gängigen binären Gemischen halluzinogener Drogen zu zeigen. Für Drogen in Gemischen wurden Nachweisgrenzen und lineare dynamische Bereiche ermittelt. Gemische, die LSD und ein anderes Halluzinogen wie STP (DOM), Psilocybin, Mescalin und Phencyclidin (1-(1-Phenylcyclohexyl)-piperidin) enthielten, wurden untersucht. Die Nachweisgrenzen sind niedrig und die analytischen Kurven sind in weiten Konzentrationsbereichen linear.

Résumé—On a préparé des courbes analytiques fluorimétriques à température ambiante et phosphorimétriques à basse température d'hallucinogènes en solution méthanol/eau pour démontrer l'absence d'interférence dans des mélanges binaires communs de drogues hallucinogènes. On a déterminé les limites de détection et les domaines dynamiques linéaires pour des drogues en mélange. On a étudié des mélanges contenant du LSD et un autre hallucinogène tel que STP (DOM), psilocybine, mescaline et phencyclidine. Les limites de détection sont basses, et les courbes analytiques sont linéaires dans de larges domaines de concentrations.

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ANALYTICAL DATA

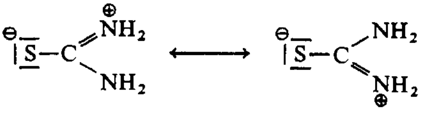
FORMATION AND THERMODYNAMIC PROPERTIES OF COMPLEXES OF Ag(I) WITH THIOUREA AS LIGAND*

(*Received* 30 *December* 1971. *Revised* 14 *May* 1973. *Accepted* 31 *May* 1973)

Thiourea (Tu) has a marked tendency to give co-ordinate bonds with many univalent[1–6] and multivalent[7–9] ions and is therefore considered one of the most important masking agents having sulphur as donor atom. Tu has three potential co-ordination centres, *i.e.*, the two nitrogen atoms and the sulphur atom. Tu almost always co-ordinates through the sulphur atom, although some authors do not exclude co-ordination through the nitrogen atoms for some metal ions such as Cu(I), Pt(II) and Pd(II).[7–8]

Preferential bonding through the sulphur atom is in agreement with some structural characteristics. Sulphur can form both σ and π bonds; moreover, the presence of empty anti-bonding π^* orbitals in Tu leads to a further stabilization of the M–S bond through back-donation from the metal to the ligand.

Finally, factors such as the complete planarity of Tu, including the hydrogen atoms,[5] the C–S and C–N bond lengths, and restricted rotation round the C–N bonds,[10] show a significant contribution of the polar structure to the ground state of Tu.



(1)

The charge separation in this structure decreases the donor capacity of the nitrogen atoms and increases that of the sulphur atom. Some authors have studied the Ag(I)–Tu system and found two- and three-co-ordinate complexes[1–4] for which only the stability constant of $AgTu_3^+$ is known.

Diffractometric studies[5] on a *bis*-Tu(AgCl) crystal showed it to have a very distorted tetrahedral structure with sulphur atoms contiguous to silver ions, at long and short distances alternately; in contrast the Ag–Cl distance was large and the chloride probably bonded ionically.

Here we report the values of the formation constants, obtained in a potentiometric study on the Ag(I)–Tu–H_2O system. The results give definitive information about the chemical species present and their stability in dependence on ionic strength and temperature.

EXPERIMENTAL

The method used by several authors[11–13] is based on mathematical analysis of equation (2), valid in this form only for a mononuclear system.

$$1/\alpha_0 = [\mathrm{Ag}]_{\mathrm{tot}}/[\mathrm{Ag}]_{\mathrm{free}} = \sum_{n=0}^{n=N} \beta_n [\mathrm{Tu}]^n \qquad (2)$$

The $1/\alpha_0$ values were obtained by potentiometric measurements made by using a silver wire electrolytically coated with silver iodide as a measuring electrode, and a cell of the type:

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{Ag}^+\\ \mathrm{Tu}\\ \mathrm{KNO_3}\end{array}\right\|\ \mathrm{KNO_3}\ \mathrm{sat.}\ \big\|\ \mathrm{S.C.E.}$$

---

* Part of this paper was presented at the 2nd Conference on Applied Physical Chemistry, Veszprém, Hungary, August 1971. Research supported by the Consiglio Nazionale delle Richerche.

for which the following relationship is valid:

$$E = E^0 + E_j + k \log [\mathrm{Ag}^+]_{free} \tag{4}$$

The potential difference measurements free for solutions at constant ionic strength ($KNO_3 = 0.25$, 0.5 and 0·75*M*) and containing different amounts of silver nitrate, show a constant value of E_j. The *k* values used in equation (4) to determine $-\log \alpha_0$ are those experimentally found for the specific ionic strengths used, and are in agreement with theoretical values in the Nernst equation. The reproductibility of *E* was ± 2–3 mV.

The $-\log \alpha_0$ values were extrapolated to $[\mathrm{Ag}^+]_{tot} = 0$ at constant Tu concentration and variable $[\mathrm{Ag}^+]_{tot}$ concentration ranging from 5×10^{-3} to $6.25 \times 10^{-5}M$. The expression (2) is then valid and $[\mathrm{Tu}]_{free} = [\mathrm{Tu}]_{tot}$. The pH of the solutions, measured by glass–calomel electrode at 25°, was 6.8. At this value the reaction $\mathrm{Tu} + \mathrm{H}^+ = \mathrm{TuH}^+$ and the hydrolysis of silver ion are negligible.[14]

Reagents

Tu solutions were prepared just before use from Tu that had been recrystallized from ethanol and dried at 85°(m.p. 181–183°). Silver nitrate solutions were kept in dark flasks and standardized periodically by dielectrometric titration with potassium chloride.

Measurements were made at 25, 35 and 45° with 100-ml samples with ionic strength kept constant by means of 0.25, 0.50 and 0.75*M* potassium nitrate.

When stoichiometric amounts of the two reagents were mixed, a white precipitate appeared which blackened immediately. This was accompanied by a smell of hydrogen sulphide and appearance of a metallic film on the surface of the solution. Later it was found that these phenomena arise when the potential of the silver electrode becomes 60–70 mV *vs.* S.C.E.

On the other hand when the silver nitrate solution was added to an excess of Tu, a clear colourless and stable solution was obtained. Before measurement the solutions were equilibrated for 5–6 hr in a thermostat.

RESULTS

Because of the large number of experimental data and calculations, only the final results are given here. Figure 1 shows the dependence of $-\log \alpha_0$ on pTu at 25° and $[KNO_3] = 0.25M$. The value of $\tan \theta =$ $\partial(-\log \alpha_0)/\partial(\mathrm{pTu}) = 3.4$ indicates the formation of AgTu_4^+. The values of α_0 are not quoted here, but mathematical analysis of $1/\alpha_0$ *vs.* $[\mathrm{Tu}]_{free}$ gives the values of the overall formation constants (β_n) of four mononuclear complexes AgTu_n^+. Table 1 gives the values of $\log \beta_n$ at different ionic strength and temperature together with thermodynamic values of $\log \beta_n$ extrapolated to $KNO_3 = 0$, and thermodynamic formation parameters.

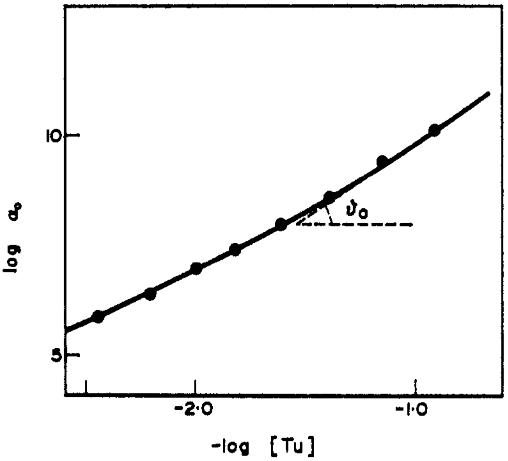


Fig. 1. Relation between $-\log \alpha_0$ and $-\log[\mathrm{Tu}]$ at 25°, $[KNO_3] = 0{\cdot}25M$ and $[\mathrm{Ag}^+] = 0$ ($\tan \theta_0 = 3{\cdot}4$).

Table 1. Over-all stability constants and thermodynamic data.

	T, °C	$KNO_3 = 0·75M$	$KNO_3 = 0·5M$	$KNO_3 = 0·25M$	$KNO_3 = 0$	$\Delta G°$ *kcal/mole*	$\Delta H°$ *kcal/mole*	$\Delta S°$ *cal/mole.deg.*
log β_1	25	7·30	7·18	7·30	7·30	—9·9	—36·9	—90
	35	6·40	6·69	6·48	6·52	—9·1		
	45	5·60	5·60	5·60	5·60	—8·1		
log β_2	25	10·60	10·60	10·36	10·60	—14·4	—25·3	—36
	35	9·92	10·02	9·92	9·92	—14·0		
	45	9·34	9·40	9·34	9·34	—13·7		
log β_3	25	12·68	13·0	12·74	12·80	—17·4	—26·1	—29
	35	11·98	11·90	12·22	12·03	—16·9		
	45	11·53	11·67	11·56	11·59	—16·9		
log β_4	25	13·78	13·75	13·64	13·72	—18·7	—34·1	—51
	35	12·95	13·04	12·92	12·97	—18·3		
	45	12·16	12·24	12·04	12·15	—17·7		

CONCLUSIONS

Four mononuclear complexes of rather high stability have been found in the Ag(I)–Tu–H_2O system. The overall formation constants were 7–10 orders of magnitude greater than those for complexes of silver with organic sulphides as ligand[15] and were similar to those for phosphine ligands.[16] The order $K_1 > K_2 < K_3 > K_4$ indicates a probable change in co-ordination on entrance of the third ligand, confirmed by the sequence of partial heats of formation ($\Delta H_1 < \Delta H_2 > \Delta H_3$); the first two groups are probably co-ordinated linearly to the silver.

The thermodynamic data for the reaction

$$Ag(H_2O)_x^+ + n\,Tu = AgTu_n(H_2O)_y^+ + (x-y)H_2O$$

indicate a markedly higher stability of the Ag–S bond in $AgTu_n^+$ than of the Ag–O bond in the aquo–ion. The large negative entropy term can be explained by a partial release of water molecules in the complexation process.

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Summary—A potentiometric study has been made of the $Ag(I)–CSN_2H_4–H_2O$ system. Mathematical analysis of the formation functions reveals the existence of the complexes $AgCSN_2H_4^+$, $Ag(CSN_2H_4)_2^+$, $Ag(CSN_2H_4)_3^+$ and $Ag(CSN_2H_4)_4^+$ for which the stability constants have been calculated at different ionic strengths and temperatures. No evidence was found for the formation of polynuclear complexes.

Zusammenfassung—Das System $Ag(I)–CSN_2H_4–H_2O$ wurde potentiometrisch untersucht. Die mathematische Analyse der Bildungsfunktionen zeigt die Existenz der Komplexe $AgCSN_2H_4{}^+$, $Ag(CSN_2H_4)_2{}^+$, $Ag(CSN_2H_4)_3{}^+$ und $Ag(CSN_2H_4)_4{}^+$ an. Deren Stabilitätskonstanten wurden bei verschiedenen Ionenstärken und Temperaturen berechnet. Es fand sich kein Hinweis auf die Bildung mehrkerniger Komplexe.

Résumé—On a effectué une étude potentiométrique du système $Ag(I)–CSN_2H_4–H_2O$. L'analyse mathématique des fonctions de formation révèle l'existence des complexes $AgCSN_2H_4{}^+$, $Ag(CSN_2H_4)_2{}^+$, $Ag(CSN_2H_4)_3{}^+$ et $Ag(CSN_2H_4)_4{}^+$ pour lesquels on a calculé les constantes de stabilité à differérentes forces ioniques et températures. On n'a pas trouvé de preuve de la formation de complexes polynucléaires.

Talanta, Vol. 20, p. 1229. Pergamon Press, 1973. Printed in Great Britain

ERRATUM

On page 645 in the July 1973 issue, lines 15 and 16 should be replaced by the following.

und FAT II als flüssige Membranelektroden von Interesse.
Für die schnelle Flüssigkeitschromatographie brauchbare Produkte erhält man durch

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NOTICE

21st CANADIAN SPECTROSCOPY SYMPOSIUM

This symposium will be held in Ottawa, 7–9 October 1974. For further information contact Mr. J. L. Dalton, Secretary, 21st Canadian Spectroscopy Symposium, Department of Energy, Mines and Resources, Mines Branch, 555 Booth Street, Ottawa, Ontario, Canada.

Talanta, Vol. 20, pp. 1231–1260. Pergamon Press ,1973. Printed in Great Britain

TALANTA REVIEW*

THIN-LAYER CHROMATOGRAPHY IN THE HEAVY ORGANIC INDUSTRIES

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(*Received* 7 *February* 1973. *Accepted* 11 *April* 1973)

Summary—The technique of thin-layer chromatography, as practised in the organic industrial laboratory, is described and its applications to the analysis of petroleum hydrocarbons, fuels, lubricants, polymers, plastics and their additives, non-ionic surfactants and explosives are reviewed. The role of thin-layer chromatography in the conservation of the environment is also considered.

Thin-layer chromatography (TLC) is a quick and simple semi-quantitative analytical technique requiring only inexpensive apparatus for many routine applications. Taken in conjunction with other sophisticated analytical techniques, however, it becomes a powerful tool and often plays a vital role in the separation of complex organic mixtures.

Over the last decade, the technique has been widely applied in the following areas

Lipids
Terpenoids and essential oils
Vitamins
Steroids
Alkaloids
Pharmaceuticals
Drugs, antibiotics
Clinical medicine
Plant extracts
Food additives
Insecticides
Proteins, amino acids
Nucleotides, nucleic acids
Sugars
Inorganic ions

These applications have been adequately chronicled in the several textbooks on TLC, such as those edited by Stahl[1] and Kirchner.[2] Applications in industrial organic analysis have been much less adequately treated, however, and, if mentioned, are usually tucked away under such headings as " Miscellaneous ". The object of this review is to help to redress this imbalance. The range of industrial applications it is intended to cover mainly derives from the petroleum and coal industries and includes fuels, lubricants, polymers, plastics, additives and other manufactured chemicals. Not only does TLC play a part in the research, development and process and quality control of these materials, it also fulfils vital roles in analytical schemes devised to unravel the composition of unknown mixtures. TLC is also useful in problems concerned with conservation of the environment.

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* For reprints of this Review see Publishers announcement near the end of this issue.

HISTORICAL

Although Izmailov and Shraiber[3] first used TLC in 1938 to separate plant extracts, for the next twenty years bed-layer chromatography was dominated by paper chromatography, introduced in 1944 by Consden, Gordon and Martin.[4] This technique was much used in, for example, the biochemical field, where it was ideal for the separation, by partition chromatography, of hydrophilic solutes between an aqueous mobile phase and the water held by the cellulose support, *i.e.*, the paper. Paper chromatography did not enjoy wide spread popularity in the organic industrial laboratory—the procedure was too slow for most applications and the mainly hydrophobic samples were not amenable to the hydrophilic systems which had been evolved.

In contrast, the industrial organic analyst during the 1950's was deeply involved in applying the rapidly developing and enormously successful technique of gas chromatography, but by the early 1960's the limitations of this technique for the analysis of increasingly involatile materials became apparent. At about the same time the emergence of TLC as a successful technique for the separation of lipophilic mixtures was noted. The last ten years have seen the establishment of TLC as the second most widely-used separation technique in many analytical organic chemistry laboratories.

GENERAL TECHNIQUE

A recent account of the practice of TLC in the industrial organic laboratory, based on experience at the Esso Research Centre, Abingdon, has been given by Perry, Amos and Brewer[5] to which the reader is referred for fuller details. The technique, in outline, involves the application of microgram quantities of sample components in the form of dilute, typically 1–5%, solutions to a thin layer of stationary phase bound to a supporting plate, usually glass. The most common stationary phase is silica gel; alumina is also often used, both acting as adsorbents. However, many examples have been reported (see "Applications") involving separations by normal partition chromatography (*e.g.*, on cellulose as the stationary phase), reversed-phase partition chromatography (*e.g.*, by using a non-adsorbent support such as kieselguhr, impregnated with high-boiling non-polar organic liquids such as squalane), ion-exchange chromatography and gel exclusion chromatography (using swollen organic gels of known pore size as the stationary phase). In the early days, TLC plates were prepared in the laboratory, but nowadays many brands of precoated plates are commercially available.[5,6]

After sample application, the plate is placed in a developing tank containing a few mm depth of the appropriate mobile phase which then travels through the layer by capillary action. In doing so, it carries with it the sample components, which travel at different rates depending on their distribution coefficients between the stationary and mobile phases. Various methods of development have been described[1,2,5] and several types of development tank are commercially available.[1]

Development is most conveniently carried out by ascending chromatography with the plate standing vertically in either a sandwich-type chamber or in a glass tank. The choice of mobile phase depends first upon the chromatographic mechanism to be exploited and secondly on the chemical nature of the sample. Other factors which must be considered in choosing a mobile phase include volatility, viscosity, solubility of the solute and possible mobile–stationary phase interaction. All these factors have been discussed recently.[5] For example, to carry out a separation by adsorption chromatography with a silica stationary phase one would try out a series of volatile solvents of gradually increasing eluent strength, using mixtures if necessary, until an optimum separation is achieved and the components of interest lie between one-fifth and four-fifths of the length of the developed chromatogram. A typical series of solvents in order of increasing polarity in adsorption chromatography would be n-pentane, carbon tetrachloride, toluene, diethyl ether, chloroform, ethyl acetate, nitromethane, pyridine, methanol and acetic acid.

Development is stopped by removing the plate from the chamber when the mobile phase has reached a predetermined position, and the plate is then allowed to dry. The separated solutes are located, if not already visible, by viewing under ultraviolet light or by spraying with a chemical solution that will react with the solute to give a characteristic colour when viewed in normal or ultraviolet light.

Gradient techniques may also be used, the gradient being applied by varying the activity of the stationary phase, the eluent strength of the mobile phase, or the temperature.

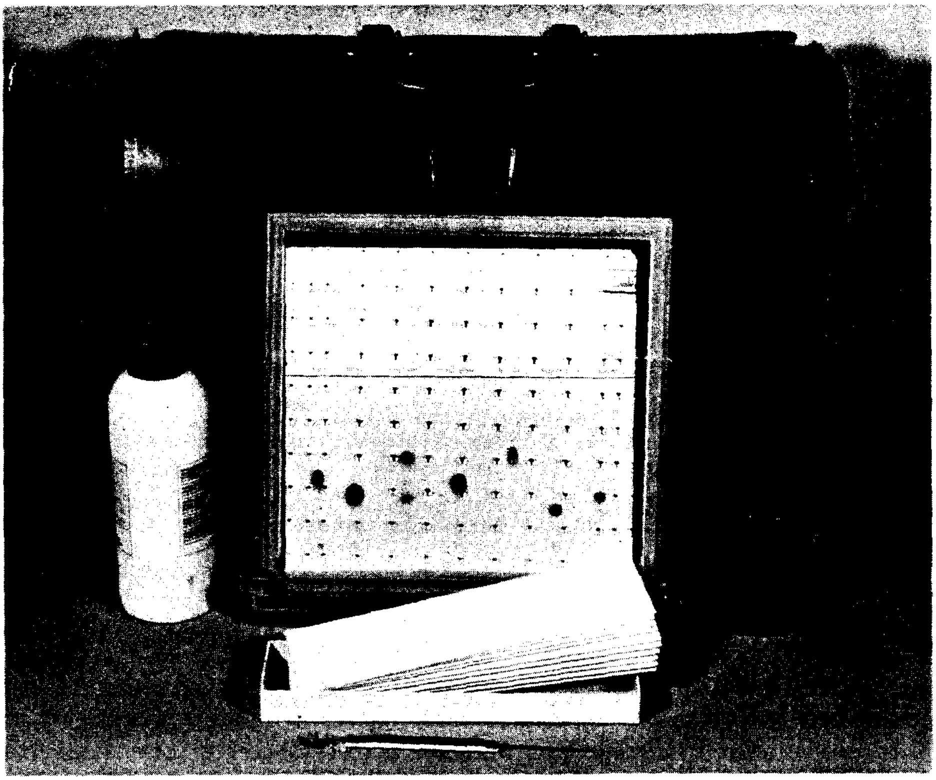

Fig. 1. Equipment suitable for field use

GENERAL APPLICATIONS

The use of TLC in industrial organic analysis falls into three main categories, for monitoring a chemical process, for identification of unknown components or in quantitative analysis. The general principles of these three different types of application will now be considered in turn.

For process monitoring

In this application, full advantage is taken of the speed and simplicity of the technique. All that may be required is a packet of precoated plates, a microsyringe, a simple sandwich-type development chamber, a bottle of solvent and a pressurized can of revealing reagent. As can be seen from Fig. 1 this can be easily packed away in a briefcase, demonstrating that this technique can be readily adapted to field use. Examples of this type of application include the following.

Chemical synthesis. Here, conditions are first established for obtaining a thin-layer chromatogram of the reactants. As the reaction proceeds, samples are taken at regular intervals and chromatographed. The disappearance of spots due to the reactants and the appearance of fresh spots due to the products are noted. If the position of the reaction product, or more usually its behaviour with a chromogenic reagent, can be predicted, its appearance can be observed. Furthermore, spots due to undesirable by-products may be detected at an early

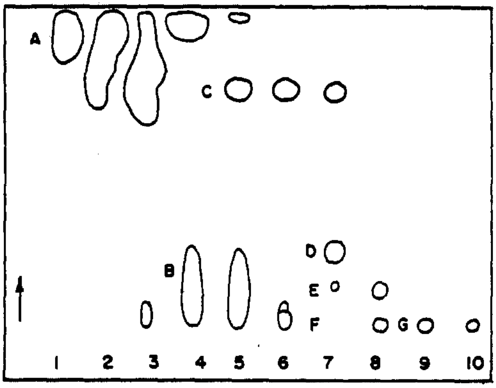

Fig. 2. TLC chromatogram of lubricating oil fractions 1–10. Adsorbent, Merck silica gel G; mobile phase, benzene; revealed by phosphomolybdic acid reagent. A = base oil; B = zinc dialkyldithiophosphate; C = isopropyl oleate; D. E, F = alkyl phenols; G = amine.

stage and appropriate corrective action taken. Some typical examples are discussed in the section on explosives.

Purification. Arising from the use of TLC in chemical synthesis, the technique can be used to monitor progress during the various work-up procedures required for the purification of the final product and can even be used to establish a specification limit. This is especially valuable in cases where an undesirable impurity has an R_F value fairly close to that of the required product. By comparing solutions of known increasing dilutions it can be established at which concentration the impurity in question can no longer be seen under standard chromatographic conditions.

The use of TLC as a monitor for the fractionation of a complex sample on a large scale liquid chromatographic column is illustrated by the work of Killer and Amos.[8] A lubricating oil was chromatographed into 10 fractions on an activated silica column, a tiny portion of each fraction being spotted on to a silica gel TLC plate. The chromatogram (Fig. 2) gives an insight into the relative concentrations of the different components in the mixture.

Additive depletion studies. Manufactured chemicals are added to many industrial products to improve their properties. Such products may be used in a hostile environment and their deterioration can conveniently be monitored by TLC, enabling onset of failure to be predicted and avoided. As an example, Killer and Amos[9] studied the thermal decomposition of zinc di-isopropyl dithiophosphate, a compound of the type commonly used as antioxidant antiwear additives in lubricating oils. This was followed up by studying the behaviour of a similar additive in service by taking oil samples from an engine after each successive 1000 miles. The observed degradation of the additive and the appearance of fresh spots could be correlated with oil quality and the condition of the engine.

Qualitative analysis

The identification of unknown compounds by TLC is based on R_F values and specific colour reactions; confirmation is obtained by isolation of the separated components from the stationary phase and positive identification by an ancillary technique such as infrared spectroscopy or mass spectrometry.

Identification by R_F *values.* The position of a solute spot on a developed TLC plate is described by measuring its R_F value, defined as

$$R_F = \frac{\text{Distance moved by solute from point of application}}{\text{Distance moved by mobile phase from point of application}}$$

R_F values therefore vary from 0·00 (no movement) to 1·00 (movement with solvent front). The precision with which this measurement can be made (*i.e.*, reproducibility from laboratory to laboratory) is rather poor. This is because of the many factors which can affect the R_F value.[5] In adsorption chromatography, for example, such factors as the quality of the adsorbent (surface properties, surface area and particle size), activity of adsorbent, layer thickness, purity of the mobile phase, exposure of the adsorbent to solvent vapour in the developing tank, effect of temperature, position of starting point in relation to depth of mobile phase in the developing tank, development time, mobile phase velocity, sample size and complexity of the sample, all influence the measured R_F value. To make matters worse, difficulties may be encountered in determining the position of the true mass centre of the spots, particularly when they are not symmetrical. As a result, the TLC procedure must be carefully standardized if R_F values are to be measured, and several such procedures have been described.[5,9,10].

Tables of R_F values are regularly published[11] which, taken in conjunction with behaviour with specific revealing reagents, are used to make a tentative identification of a separated solute. In spite of the poor reproducibility of R_F values, the published tables are useful because they indicate whether it is possible to separate a particular group of compounds and they also serve as a guide as to the conditions to be chosen when attempting to carry out a similar separation for the first time.

Identification by chromogenic reagents. Colourless solutes on a developed chromatogram are revealed by spraying the plate with a solution of a reagent that will form a coloured derivative with the solute. Whilst some reagents, *e.g.*, phosphomolybdic or sulphuric acid, form coloured derivatives with most organic compounds (these two give rise to blue and charred spots respectively), many reagents can be chosen that will react with one or more specific functional groups to give a characteristically coloured derivative. For example, 2,6-dichloroquinone-4-chloroimine has been extensively studied[12] and produces a variety of intense colours with primary, secondary and tertiary aromatic amines, carbazoles, primary and secondary aliphatic amines, aromatic hydrocarbons and phenols. Amines, amine oxides and other oxidized nitrogen compounds give weak or negative reactions, as do aromatic compounds with electron-attracting groups. This reagent is widely used for the detection of antioxidants. Further colour changes may occur on spraying with borax solution. Table 1 gives a selection of chromogenic spray reagents which may be used for the identification of specific functional groups. Other examples and further details on their preparation will be found elsewhere.[5]

Identification after removal from the stationary phase. The combination of TLC with other sensitive instrumental methods, particularly infrared spectroscopy, mass spectrometry and gas chromatography, provides a powerful identification tool for identifying complex organic mixtures. The sample sizes required by these techniques are compatible with the microgram amounts of material readily separable by TLC. When using these high-sensitivity identification techniques special care must be taken to avoid solute contamination.[13] Adsorbents and solvents must be especially pure, atmospheric pollution and contamination by plasticizers must be avoided, and sample handling must be reduced to a minimum.

An effective way of carrying out this task[13,14] is to chromatograph on a specially purified adsorbent, using redistilled solvent. The area of stationary phase bearing the separated com-

Table 1

Functional group	Reagents and reactions
Acids and bases	indicators, *e.g.*, Bromocresol Green, Methyl Orange
Alcohols	ceric ammonium nitrate, vanadium oxinate
Aldehydes and ketones	hydrazone formation with 2,4-dinitrophenylhydrazine
Amides, anhydrides, esters	hydroxamic acid/ferric ion reaction
Aliphatic amines	cobalt thiocyanate, ninhydrin
Aromatic amines and phenols Antioxidants	azo-dye formation with diazonium salts; coupling reactions with 2,6-dichloroquinone-4-chloroimine.
Peroxides	*N*,*N*-dimethyl-*p*-phenylene diammonium dichloride
Phosphorus compounds	molybdenum blue formation with ammonium molybdate
Polynuclear aromatics	fluorescence under long-wave ultraviolet light
Sulphate and sulphonate esters	Pinacryptol Yellow
Sulphur-containing compounds	palladium chloride

ponent is transferred, by microspatula, to a capillary tube. The solute is eluted, by percolating, drop by drop, a polar solvent such as acetone through the tube into the sampling accessory of the appropriate identification instrument. This could be, for example, the direct insertion probe of a mass spectrometer, or a small pile of potassium bromide powder which is then used to prepare a microdisc suitable for infrared spectroscopy.

Quantitative analysis

Quantitative analysis[5,15] in TLC can be carried out either directly on the plate or after elution of the separated solutes from the stationary phase. To obtain an error of less than 10% requires a considerable amount of skill and patience on the part of the experimenter and also requires the use of ancillary equipment. In addition, the component to be measured needs to be well separated from other components and must either possess a chromophoric group or react quantitatively with a chromogenic reagent.

All this detracts from the basic simplicity of the technique and it seems likely that routine quantitative TLC will soon be superseded by the rapidly emerging technique of high-performance column chromatography.[5] Nevertheless, many highly successful quantitative TLC applications have been reported, with precisions of 5% or better.

The simplest, and often adequate though the least precise, technique of quantitative analysis is by visually comparing the size and intensity of the sample spots with those from a series of standard solutions of similar composition. An improvement in precision is achieved by measuring the areas of the spots, *e.g.*, by planimetry, photographing or copying onto tracing paper, cutting out and weighing, or by copying onto millimetre-squared paper and counting the number of squares. The amount of material in the sample spot is found by interpolation, after plotting an appropriate function such as the logarithm of the weight of material in the standard spots *vs.* square root of the spot areas, to obtain a straight line or (more usually) a smooth calibration curve.

Such methods of measuring spot areas are tedious and time-consuming and better results are obtained more quickly by densitometry. In this technique, an integrated function of spot area and intensity is measured by scanning the TLC spot with a beam of light. The reflected or (more usually) the transmitted light is directed to a photomultiplier and the difference in intensity between this and the incident light is measured electrically and indicated on a strip-chart recorder. A symmetrical spot would give rise to a Gaussian peak, the height of which would be proportional to the intensity of the spot, and the peak-width proportional to the spot diameter. As before, some function of the peak areas of a series of reference solutions is plotted against the weight of solute per spot to obtain the calibration curve.

The quantitative methods described so far suffer from several sources of error inherent in the TLC procedure itself. Major sources of error arise from the difficulty in applying a reproducible amount of sample to the layer, variations in layer thickness, and, which is probably the most important source of error, the difficulty of spraying a plate uniformly and ensuring that a reproducible, quantitative reaction between solute and chromogenic reagent occurs to produce a spot with a colour that is stable long enough for evaluation.

The highest accuracies in quantitative TLC have been reported for use of fluorimetry in which a fluorescent spot on a dark background is scanned under ultraviolet light. The preparation of the chromatogram, the mechanics of scanning and interpretation of the results are the same as in densitometry. Highest accuracies are achieved with naturally fluorescing compounds such as the polynuclear aromatics that do not require treatment with a chromogenic reagent, thus eliminating the major source of error. The application of *in situ* fluorimetry to the determination of atmospheric pollutants has been described by Sawicki[16] in a previous review article.

A number of densitometers and fluorimeters are commercially available. The modes of action of some of them have been compared in a recent review article by Lefar and Lewis.[17] In general, it can be said that the errors involved in producing reproducible chromatographic spots far outweigh the instrumental errors.

The most widely reported method of quantitative TLC involves spectrophotometric determination of the solute after it has been eluted from the stationary phase. Although more time-consuming than densitometry, and subject to many errors, it presumably owes its popularity to the fact that a spectrophotometer is a standard piece of equipment in most laboratories. Errors arise mainly from incomplete recovery from the stationary phase, and interference from impurities in the stationary phase. These are much more more serious in ultraviolet than in visible-region spectrophotometry. A number of workers[18,19] have compared spectrophotometry with densitometry and conclude that the precision of the two methods is similar, with relative standard deviations in the 3–5% region. Some examples are described in the section on plastics and polymers.

APPLICATIONS IN PETROLEUM ANALYSIS

The use of TLC in the analysis of petroleum and its products has been described in some detail by Killer and Amos[8] and by Coates.[7] Applications can be divided into two main parts, those concerned with the composition of the hydrocarbon oil itself and, more importantly, qualitative or semi-quantitative determination of the various chemicals that are added to petroleum products to enhance their useful properties.

Hydrocarbon types

Non-volatile oils can be separated, to some extent, according to class of compound, on layers of silica or alumina, with C_5–C_7 paraffins or cycloparaffins as mobile phase. Saturated compounds, being unadsorbed, travel with the solvent front, closely followed, in order, by mono-, di-, and tricyclic aromatics. Naturally-occurring sulphur compounds (sulphides, thiophenes) travel with the aromatics.

Difficulties are encountered[8] in obtaining regularly shaped spots, particularly of the saturated hydrocarbons, for samples of high viscosity in the range from gas–oil to lubricating oil. This is because the solvent front passes so quickly over the substance on the starting line that the separated zones have no time to distribute themselves evenly over the adsorbent surface. This problem may be overcome by applying the sample solution to an adsorbent surface pre-wetted by a relatively high-viscosity mobile phase such as cyclohexane. This process is best achieved by using the horizontal "BN chamber" for development of the chromatogram. Aromatics are detected either by their fluorescence or fluorescence-quenching characteristics when viewed under ultraviolet light (long-wave and short-wave respectively), whilst saturated compounds are revealed by spraying the plate with 5% potassium dichromate in 40% sulphuric acid.

Olefins are only separable from saturated compounds on silica gel plates impregnated with silver nitrate. A more impressive separation is obtained after prior conversion of the olefins into their mercuric acetate derivatives by the procedures of Braun[20] and Prey *et al*,[21] After the sample containing olefin has been allowed to stand with an alcoholic solution of mercuric acetate for 30 min, the reaction mixture is chromatographed on a silica gel plate with a mobile phase of n-propanol–triethylamine–water (50:25:25 v/v). The adducts are revealed as violet spots on a pink background after spraying with a 2% alcoholic solution of diphenylcarbazone. Less than 0·1 μg of mercuric adduct can be detected, which means that less than 0·1% of olefin in a petroleum product can be detected.

The usefulness of TLC is generally restricted to identification of different product types, *e.g.*, in tracing possible sources of pollution. Crump[22] was able to classify oils into four groups—mineral oils, synthetic esters, naturally-occurring glycerides (*e.g.*, olive, mustard, and sulphurized sperm oils) and others and thus was able to recommend procedures for detecting contamination of edible oils by lubricants.[23] The samples were chromatographed on layers of silica gel and developed with chloroform–benzene (70:30 v/v). After development, the plates were examined under ultraviolet light, mineral oils being revealed as blue fluorescent zones of high R_F value. The plates were then sprayed with concentrated sulphuric acid, heated at 120° for 15 min and then re-examined under ultraviolet light; esters and glycerides appeared as grey spots of lower R_F value. Silicone oils were not revealed by these procedures but could be detected by respraying the plate with chromic acid followed by a further heating treatment. Similarly, petroleum oil diluents in coal-tar creosote were measured[24] down to the 0·25% level, by chromatography on Merck silica gel H with hexane as mobile phase. The mineral oils were revealed as brown spots by spraying with an α-cyclodextrin solution followed by exposure to iodine vapour. A similar application is the estimation of mineral oil contamination in synthetic hydraulic fluids.[7] This is of vital importance in the aircraft industry.

Heavy oils, particularly petroleum resins, can be characterized by use of a 3-stage discontinuous layer-gradient plate.[25] The plates consist of three parallel sections coated, in order, with Florisil, alumina and silica gel and developed in the direction from the Florisil towards the silica. Various solvent combinations are utilized according to the type of separation required. For example, with cyclohexane–benzene–ethyl acetate (105:1:1 v/v) a chromatogram containing one of the separated cuts in each stage is obtained whilst petroleum ether–ethyl acetate–acetone (380:1:1 v/v) produces a separation between saturated compounds and monocyclic aromatics within the silica-coated portion. Semi-quantitative information is obtained from the completed chromatogram by measuring the size of the bands with a ruler or photoelectric scanner.

The most extensively used application of TLC in hydrocarbon analysis lies in the detection and determination of polynuclear aromatic hydrocarbons, particularly the carcinogenic benz[*a*]pyrene.

Lubricating oil additives

The most successful application of TLC in the petroleum industry has been in lubricating oil additive analysis.[7,8,26] These applications can be classified as follows.

(*i*) Detection and determination of additives in unknown products.
(*ii*) Monitoring the preparation of additives.
(*iii*) Blending control.
(*iv*) Following additive depletion in used oils.

TLC can provide information on the additives in a drop of oil, which may be either impossible or time-consuming to get in any other way. For example, whilst the infrared spectrum of an oil containing an overbased detergent-additive may be completely dominated by carbonate absorption bands, a rapid TLC test will establish whether the additive is of a sulphonate or phenate type. Similarly, the infrared spectrum of a oil containing several additives may be too complex to interpret, whereas TLC of the same oil rapidly separates the additive components and, with the help of specific spray reagents, provides valuable information on the type and quantity of specific additives present.

Table 2. Lubricant additive types

Function	Compound type
Antioxidants	hindered phenols, bis phenols and amines, phenothiazine derivatives.
Detergents, dispersants	calcium or barium sulphonates, phenates, bis phenates, sulphurized phenates, phosphosulphurized phenates, salicylates, carboxylates, polyisobutenyl polyamides.
Antiwear, load bearing	zinc dialkyldithiophosphates, dithiocarbamates, phosphate and carboxylate esters, amine salts, sulphurized unsaturated esters and terpenes.
Corrosion inhibitors	colloidal carbonates (incorporated in detergent inhibitors), alkanolamines, *N*-substituted benzotriazole and mercaptobenzthiazole derivatives, carboxylic acids.
Viscosity index improvers; pour point depressants	high molecular-weight polymers not separable by TLC.

Some common additive types found in lubricating oils are given in Table 2. In many instances, the additives are not discrete chemical compounds but complex reaction mixtures of natural products (*e.g.*, sulphurized sperm oil), but because adsorption chromatography separates by compound type, and not by molecular weight, relatively simple and identifiable chromatograms are usually obtained. The total additive content of modern lubricants may range from about 0·1% of a simple antioxidant to more than 10% of a complex mixture, depending upon the environment in which the lubricant is to be used.

Additives in unknown products. An analysis scheme, based on TLC, of a complex lubricant, is illustrated in Fig. 3.

A useful first step is an elemental analysis on the original sample for metals, phosphorus, chlorine and boron. X-ray fluorescence, ultraviolet emission and atomic-absorption spectroscopy are the techniques most commonly used. Since hydrocarbon oil contains naturally-

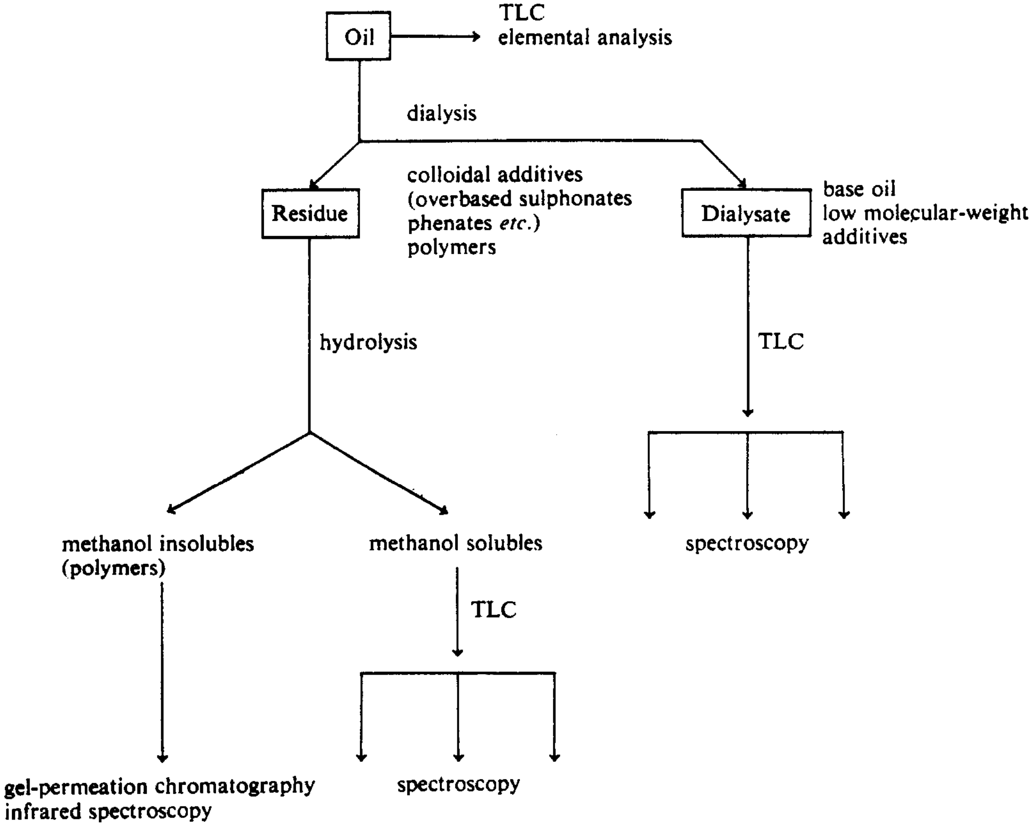

Fig. 3

occurring sulphur and nitrogen compounds, the determination of these elements is delayed until the dialysis residue has been obtained. If the oil is low in carbonate and polymer content, TLC can be applied directly to the sample. However, high carbonate and polymer concentrations produce smears on the plate which interfere with effective chromatographic separation. They can be removed from the sample by dialysis[27] followed by hydrolysis of the dialysis residue. Polymers are removed by precipitation with methanol and characterized by gel-permeation chromatography and infrared spectroscopy. The methanol-soluble fraction, containing phenols, sulphonic and carboxylic acids can then be examined by TLC. The dialysate, containing the hydrocarbon base oil and low molecular-weight ($<$ 1000) additives are also examined by TLC and the separated spots are scraped off, eluted with acetone and identified by infrared and mass spectrometry.

Table 3 summarizes the sequence of experiments carried out to locate the additive types present in an unknown sample. The use of specific spray reagents provides valuable information on the likely additive types present, and where the presence of a well-known additive is suspected, the simultaneous chromatography of a reference additive often renders the spectroscopic identification of the eluted spot a formality which can be dispensed with.

Lynes[28] found TLC to be a rapid method for the identification of alkanolamines used as corrosion inhibitors in hydraulic brake fluids and cutting oils, and their salts (*e.g.*, oleate, stearate, naphthenate) which are used as emulsifiers and detergents. The best chromatographic system was found to be dichloromethane–ethanol–ammonia (43:43:15 v/v) on

Table 3. Guidelines for choice of mobile phase and revealing reagents for location of lubricant additives, using silica gel as stationary phase

Mobile phase	Revealing reagent	Spot colour	Conclusions
		(R_F 0·3–0·8)	
low boiling alkanes	phosphomolybdic acid	blue–black	hydrocarbon base oil
(+3–5% ether or ethyl acetate);	+heat;		
carbon tetrachloride	2,6-dichloroquinone-4-chloroimine	yellow–red–mauve–blue	phenolic antioxidants
	diazotized *p*-nitroaniline	yellow–brown	
toluene	ninhydrin + heat	pink–mauve	amines
	cobalt thiocyanate	blue	
	diazotized *p*-nitroaniline	yellow–red–brown	phenols, aromatic amines
	palladium chloride	dark blue	phenothiazines
heptane–ethyl acetate (50:50 v/v)	2,6,-dichloroquinone-4-chloroimine	grey–brown	benzotriazoles
		orange	mercaptobenzthiazoles
	iodine	brown	esters
dichloromethane			
hexane–ether–methanol (70:30:5 v/v)	sodium molybdate	blue	phosphate esters
heptane–ethyl acetate–acetic acid (60:25:15 v/v)	dithizone	pink	zinc dialkyldithiophosphates
toluene–methyl ethyl ketone–acetic acid–pyridine (60:20:10:10 v/v)	palladium chloride	brown	sulphurized additives
methyl acetate–ethanol–ammonia (70:20:10 v/v)	Pinacryptol Yellow (view at λ = 360 nm)	dull orange fluorescence	natural sulphonates
chloroform–ammonia–isopropyl alcohol (25:25:50 v/v)		bright yellow–orange fluorescence	synthetic sulphonates
isopropyl alcohol–ammonia (80:20 v/v)		black absorbing spots	phenates, salicylates, zinc dialkyldithiocarbonates
		green fluorescence	carboxylates
	diazotized *p*-nitroaniline	brown	phenates, salicylates
	palladium chloride	brown	sulphurized phenates
	ninhydrin + heat	pink	amine salts

silica gel. Solutions of 0·2% ninhydrin and alizarin in acetone were used to reveal the separated alkanolamines. By means of the characteristic colours produced, and differences in R_F values, it was possible to distinguish between the primary, secondary and tertiary amines. Extra spots were obtained when the acid salts were chromatographed.

The alkyl groups of zinc dialkyl dithiophosphates can be tentatively identified by their R_F values. To maximize differentiation of R_F values, a hydrocarbon solution of the additive is first shaken with diethylamine and the resulting alkylammonium salts are chromatographed on an activated alumina G plate with n-hexane–acetone–ethanol–triethylamine (20:30:1:1 v/v) as mobile phase.[29] The spots are revealed by spraying first with an iodine–azide solution, followed by a starch solution. R_F values increase with increasing size of the alkyl groups. A more informative and sophisticated method is to chromatograph the additives directly on layers of silica gel[8,30] using heptane–acetic acid (95:5 v/v) as mobile phase. After development, the spots are eluted with acetone directly into a pyrolysis unit coupled to a gas chromatograph. The separated sample is pyrolysed and the products swept into the column. The olefins so formed are separated and identified by retention values, from which the structure of the original dialkyldithiophosphate can be deduced.

Diamond[31] distinguished the various n-(C_1–C_{12}) *p*-alkyl phenols used in lubricating oil formulations by separation on polyamide layers with 1*M* sodium hydroxide–methanol (70:30 v/v) as mobile phase. As the alkyl chain length increased, the R_F value approached zero, so that it was not possible to distinguish between phenols having alkyl groups longer than C_{12}. C_{12}–C_{18} alkyl phenols can, however, be separated[32] by reversed-phase chromatography on silicone oil impregnated silica gel with acetic acid–water (80:20 v/v) as mobile phase.

Additive preparation. Coates[7] used TLC to follow the preparation of alkyl phenothiazine for use as an antioxidant in aircraft engine lubricants by a Friedel–Crafts alkylation of phenothiazine with a C_7–C_9 olefin cut. The disappearance of alkenes was monitored by chromatography of their mercuric acetate derivatives, and the reaction product was shown to be a complex mixture. Similarly, the alkylation of phenols by polyisobutylene was followed and the ratio of *ortho-* to *para-* substitution determined by the use of spray reagents which distinguished the different product types.

Blending control. TLC provides a rapid and simple method of blending control. A 30% solution of the oil under test is chromatographed alongside the reference blend it is required to match in composition. A visual comparison of spot size and areas is all that is required to determine whether a component has been correctly added to within 5% of the required amount.

Additive depletion studies. TLC is particularly useful for following additive depletion rates in used oils during service or during a laboratory simulated engine test because only small amounts of sample are required, *e.g.*, a drop of oil from the end of a dipstick. Furthermore, it can be established whether the additive is actually still within the oil itself or deposited in the engine sludge. When a fresh oil is available for comparison, the chromatogram allows a semi-quantitative assessment of the decrease in additive concentration in the used oil. For example, it was shown[8] that the two major spots in a zinc dialkyl dithiophosphate antiwear additive had disappeared after 1000 miles whilst a further spot persisted right through a 5000-mile road test. Furthermore, a new spot appeared after 2000 miles and gradually increased in size as the test proceeded. The changes observed could be reproduced during thermal oxidation experiments in the laboratory. Similarly, the fate of sulphonates and phenates in motor lubricants and the depletion of oxidation inhibitors in turbine oils have also been followed by TLC.[7,8] A further important application[7] has been the detection of mineral oil contamination in synthetic hydraulic fluids, *e.g.*, brake fluids, which can lead to breakdown of the hydraulic systems owing to oil-swelling of rubber seals.

Fuel additives

Various materials, such as anti-icing compounds, antioxidants, corrosion inhibitors, metal deactivators, surfactants and dyes are added to fuels to improve their properties. Quick analytical techniques are required to check that each batch of finished product contains the correct amount of additive and to check on possible losses of additive in the distribution system. TLC has proved to be the most effective technique for those additives too involatile to be determined by gas chromatography. Since the additive levels lie in the 1–100 mg/l concentration range, a preconcentration step is generally necessary. Two general methods have been found to be most useful. The first is solvent extraction with methanol–water (95:5 v/v) and the second is to shake the fuel with activated alumina followed by desorption of the adsorbed polar additives with acetone or ethanol. In both cases, the additive extract is concentrated by removing the solvent at 40° under vacuum and the residue is examined by TLC. As an example, the author developed a routine method[33] for the determination of the antioxidant 2,4-dimethyl-6-t-butylphenol added at the 10 mg/l. level to aviation turbine fuels. Evaluation of the finished chromatogram by densitometry with the Joyce-Loebl Chromoscan gave a precision of ±5%.

TLC has been used[34] for identifying furfuraldehyde, used as a marker in gas oils and kerosenes. The oil is chromatographed on silica gel with iso-octane–chloroform (10:90 v/v) as mobile phase and the furfuraldehyde is revealed as a pink spot, in the region of $R_F = 0{\cdot}35$, by spraying with 10% v/v aniline in glacial acetic acid. As little as 20 ng of furfuraldehyde can be detected.

Crump[35] was able to recognize the crude source of different kerosenes, using a two-dimensional TLC separation of their indigeneous phenols in the form of azo dyes. The phenols were extracted from the kerosenes with aqueous sodium hydroxide solution and coupled with diazotized *p*-nitroaniline. The azo dyes were chromatographed on alkali-impregnated silica gel with acetone–chloroform (10:90 v/v) in the first direction and di-n-propylamine–benzene (1:4 v/v) in the second. Identification was achieved by comparison with the relative positions and characteristic colours of a reference chromatogram of 20 known alkyl phenols.

APPLICATIONS IN POLYMER AND PLASTICS ANALYSIS

The application of TLC to the analysis of plastics and polymers, as with petroleum, can be divided into two categories. The first deals with the examination of the polymers themselves; the second and more important application involves the detection, isolation and identification of additives in polymer formulations.

Some examples of additive types and their functions are given in Table 4. Since a polymer formulation may contain up to half a dozen different additives, chromatography is nearly always necessary before a spectroscopic identification.

Attempts to chromatograph polymer solutions directly are generally unsuccessful since a smear of the large excess of polymer over the full length of the chromatogram often masks or distorts the spots of additive. Additives are, therefore, initially separated from the polymer by solvent extraction and concentrated by removal of the solvent by evaporation. The general procedure is to disperse the polymer in a non-polar solvent such as toluene or halohydrocarbon under reflux for 1–24 hr followed by precipitation of the polymer by the addi-

Table 4. Some additive types in plastics

Antioxidants	hindered phenols hindered amines hydroquinone derivatives
Stabilizers	metal stearates urea derivatives organotin compounds
Ultraviolet absorbers	benzophenone derivatives salicylic acid esters resorcinol esters benzotriazole derivatives coumarin derivatives substituted acrylonitriles organonickel compounds
Plasticizers and lubricants	esters of dicarboxylic acids phosphate esters chlorinated hydrocarbons stearate esters
Polymerization catalysts	organic peroxides
Accelerators	thiazoles dithiocarbamates thiurams xanthates guanidines
Antistatic agents	amine derivatives sulphonates

tion of a polar solvent such as acetone or ethanol. The supernatant liquid containing additives is then reduced in bulk by evaporation under vacuum. During this process, further low molecular-weight polymer may be precipitated, which is removed by centrifugation. The concentrated extract is then examined by TLC combined with spectroscopy.

Several problems[36] can arise during the extraction procedure. First, the solubility of different polymer types in the non-polar solvent varies widely. Table 5 offers a guide for the selection of suitable solvents. Secondly, the extraction of additive by the polar solvent may be incomplete. Thirdly, decomposition of the additive by heat or light or interaction with other species may occur during the extraction procedure, and fourthly the additives may have altered in composition during the manufacture of the finished plastic, *e.g.*, during the milling stage.

As in petroleum product analysis, an elemental analysis of an unknown polymer should be done before the separation so that all elements other than carbon, hydrogen and oxygen can be accounted for subsequently. The methods used should be capable of detecting 10 ppm of each element in the polymer. This means that as little as 0·01% of an additive containing 10% of the element in question could be detected. The most useful elemental analysis techniques include ultraviolet emission, X-ray fluorescence and atomic-absorption spectroscopy together with micro-Kjeldahl or better, microcoulometry techniques, for nitrogen.

Early chromatographic separations of additive extracts were carried out[37,38,39] by classical liquid–solid adsorption chromatography using alumina, silica gel or mixtures of silica and Celite as stationary phases, on which additives were successively displaced by a series of solvent mixtures of gradually increasing eluent strength. Fractions were collected and weighed and examined by ultraviolet or infrared spectrometry or in some instances, by means of specific chromogenic reagents. Zijp[40] devised a comprehensive scheme for syste-

Table 5. Solvents for extraction of additives

Polymer type	*Extraction solvents*
Polyethylene	toluene, chloroform
Polypropylene	dichloromethane
Polyvinylchloride	ether
Rubbers	ether, acetone
Polystyrene	toluene, methyl ethyl ketone, propylene oxide

matic identification of antioxidants and accelerators by paper chromatography, using R_F values and specific colour reactions. This work was extended by Auler[41] and Williamson[42].

As a result of combining the most advantageous features of column and paper chromatography, TLC has emerged as the most useful separation technique over the past ten years for the identification of additives in plastics. TLC of each of the various additive types will now be described in turn.

Antioxidants

Methods for the determination of antioxidants in polymeric materials have been reviewed by Wheeler[43] who concluded that a general analytical scheme based on TLC showed the most promise. For example, antioxidants in polyethylene have been extracted with either 4% methanol in cyclohexane or 10% ethyl acetate in petroleum ether.[44,45] After concentration by evaporation and filtration to remove any precipitated polymer, the antioxidants were separated on layers of silica gel, with the same solvent mixtures as the mobile phase. Detection was by 3% phosphomolybdic acid or 2% 2,6-dichloroquinone-4-chloroimine in ethanol followed by a second spraying 15 min later with a 2% borax solution, which produces a wide variety of characteristic colours.

An example of a semiquantitative determination of a specific additive is given by Crompton[46] who determined Santonox R (4.4'-thio-bis-6-t-butyl-*m*-cresol) in polyethylene in amounts down to 20 ppm with an error of ± 20%. The additive was extracted with toluene for 90 min on a boiling water-bath. Dissolved polymer was precipitated by the addition of ethanol to the hot toluene solution. After cooling, the polymer was removed by filtration and the filtrate evaporated to dryness. The residue was redissolved in a small amount of chloroform and aliquots were chromatographed on a precoated Merck GF254 silica gel plate with petroleum ether (b.p. 40–60°)–ethyl acetate (5:1 v/v) as mobile phase, together with a series of Santonox R solutions in chloroform, covering a concentration range of 0·005–0·05% w/v. The intensities of standard and sample spots were compared visually by viewing under ultraviolet light (254 nm) and by comparing the purple spots produced by spraying with 2% alcoholic 2,6-dibromo-*p*-benzoquinone-4-chloroimine solution, drying the plate and spraying with 2% aqueous borax solution.

Schröder *et al.*[47] extracted antioxidants and thermal stabilizers from formaldehyde polymers with chloroform. The evaporated extract was shaken with heptane to leach out antioxidants, and the heptane-insoluble fraction was shaken with methanol to leach out stabilizers. The remaining insoluble portion was hydrolysed with hydrochloric acid. Identification of individual components was by TLC followed by infrared spectrometry.

Dobies[48] determined phenolic antioxidants down to the 0·02% level in polyethylene and polypropylene films by Soxhlet extraction of the film with a heptane–octane (4:1 v/v) mixture followed by concentration by evaporation. The antioxidants were separated by reversed-phase partition chromatography on silica gel impregnated with 5% Dow silicone oil as stationary phase, with ethanol–water (3:1 v/v) as mobile phase. Development times were 30–40 min and the spots were revealed by spraying with 3% alcoholic phosphomolybdic acid solution.

Kreiner and Warner[49] list R_F values of 36 amine antioxidants and 31 phenolic antioxidants which together represent most of the rubber-compounding materials of these types manufactured in the United States. Merck silica gel G was the stationary phase and development was carried out under standard conditions in development tanks having atmospheres saturated with solvent vapour. The mobile phase for amine antioxidants was benzene–acetone–ammonia (100:5:0·1 v/v). After the solvent front had advanced 15 cm from the origin the samples were located by spraying with a 4% solution of benzoyl peroxide in benzene, which gave a wide range of characteristic colours. Where several such antioxidants occurred in a mixture, the separation was improved by redeveloping the plate at right angles to the original development, with cyclohexane–acetone–ammonia (100:5:0·1 v/v) as mobile phase. A better separation of certain multi-component reaction mixtures such as alkylated diphenylamines and amine–acetone reaction products was obtained by using a mobile phase such as cyclohexane–benzene–acetone (100:10:1 v/v).

Benzene was found to be the most useful mobile phase for the separation of phenolic antioxidants, which were revealed by spraying with a borax buffer solution followed by 0·1% methanolic 2,6-dichloroquinone-4-chloroimine solution. Again a wide range of characteristic colours was produced, which greatly assisted in identification. A less polar mobile phase, n-hexane–benzene (8:1 v/v), is recommended for the separation of the most highly hindered phenols. Simpson and Currell,[50] however, used benzene–ethyl acetate–acetone (100:5:2 v/v) as mobile phase to measure the R_F values of 21 commercial antioxidants available in the U.K. Chromatography was carried out in sandwich-type chambers, on Merck precoated silica gel plates.

Stabilizers

These are compounds added to plastics to prevent degradation by heat or light. Crompton[46] has determined the Cyasorb UV 531 (2-hydroxy-4-n-octoxybenzophenone) content of polyethylene, down to the 20-ppm level, by TLC and ultraviolet spectroscopy. The additive was concentrated by extraction with hot toluene, any dissolved polymer being precipitated by the addition of ethanol and removed by filtration. The filtrate was evaporated to dryness and redissolved in a small, known volume of chloroform. Reference additive solutions were prepared by milling a series of blends of UV 531 in additive-free polyethylene powder (covering the concentration range 0·05–0·5% w/w) and putting them through the same extraction procedure. Aliquots of sample and reference extracts were chromatographed on Merck silica gel GF254 plates with dichloromethane as mobile phase. The zones corresponding to UV 531 were located as dark spots when viewed under short wavelength ultraviolet light, scraped off, eluted with ethanol and made up to known volumes. An area of silica gel close to the sample spots was also scraped off to use as a blank. Absorbances at 295 nm were measured, from which the concentration of additive in the sample was deduced.

Simpson and Currell[50] list the R_F values of eleven commercial ultraviolet absorbers covering the range of compound types shown in Table 4, when separated on Merck precoated silica gel plates developed in a sandwich chamber with chloroform–hexane (2:1 v/v) as mobile phase. Spots were located either by visualization under ultraviolet light or by spraying with the 2,6-dichloro-*p*-benzoquinone-4-chloroimine reagent. The same authors also successfully separated by the same technique a series of organotin compounds used as heat and light stabilizers. The mobile phase was butanol–acetic acid (97:3 v/v) and the additives were revealed as blue spots by spraying with 0·1% Catechol Violet solution in ethanol.

Uhde and Zydek[51] determined substituted 2-hydroxybenzophenones in poly(vinyl chloride) by shaking the sample with tetrahydrofuran and precipitating the polymer by dropwise addition of methanol. The ultraviolet absorbers were separated on silica gel plates with cyclohexane–ethyl acetate (4:1 v/v). Detection was by viewing under ultraviolet light (365 nm), by spraying with 2% aq. Fast Red salt AL solution, or 5% ferric chloride–5% potassium ferricyanide solution in 1*M* hydrochloric acid and heating the plate briefly at 100°.

Durisinova and Bellus[52] have studied the behavior of 38 2-hydroxybenzophenone derivatives used as ultraviolet stabilizers, in five different chromatographic systems. Polyamide layers, with chloroform–acetic acid (150:0·5 v/v) were found to be the most useful for separating polyhydroxy derivatives, whilst silica gel containing boric acid as a complexing agent gave good separations of monohydroxy derivatives with heptane–ethanol (75:25 v/v), carbon tetrachloride–ethanol (180:1·5 v/v) or chloroform–benzene (80:20 v/v) as mobile phases. The phenones were revealed as yellow–orange–brown spots on spraying with a solution of diazotized sulphanilic acid.

Dobies[53] described a specific quantitative TLC method for determining ultraviolet absorbers (hydroxybenzophenone derivatives) at the 0·005–0·01% level in paraffin wax used for paper coating. The additive was extracted from a hexane solution of the wax with alcoholic potassium hydroxide, and the acidified extract back-extracted with carbon tetrachloride (which was then removed by evaporation). The concentrate was chromatographed on silica gel plates with ethanol–water (3:1 v/v) and the separated ultraviolet absorbers were revealed by spraying with a solution of diazotized *p*-nitroaniline. Quantitative estimation was by densitometry with a Joyce-Loebl Chromoscan.

Plasticizers

Braun[54] has measured R_F values of 26 plasticizers chromatographed on silica gel G with dichloromethane as mobile phase. The compounds examined included esters of phthalic, phosphoric, adipic, sebacic and citric acids. The most useful general spray reagent was a 20% solution of antimony pentachloride in carbon tetrachloride, which produced brown spots after the plate had been heated at 120°. More specifically, phthalates were detected as orange–red spots on a yellow background by first spraying with 20% resorcinol solution containing zinc chloride and heating the plate at 150° for 10 min. The plate was then re-sprayed with 4*N* sulphuric acid and heated for a further 20 min at 120°. Finally, the plate was resprayed with 40% aqueous potassium hydroxide solution. Haase[55] carried out similar work but identified the plasticizers by infrared spectrophotometry after eluting them from the adsorbent with ether onto potassium bromide discs.

Although ester plasticizers can be positively identified by eluting the spot from the silica gel and examining the extract by mass spectrometry, they can be readily saponified and the products recognized by means of gas chromatography. Braun identified the alcohols in the form of their 3,5-dinitrobenzoates by TLC after direct *trans*-esterification of plasticizer esters with 3,5-dinitrobenzoic acid. Chromatography was carried out on layers of silica gel G with benzene–methyl acetate (150: 1 v/v) as mobile phase and the spots were located by viewing under ultraviolet light (366 nm) after spraying with 0·05% alcoholic Rhodamine B solution. C_1–C_6 esters were readily distinguishable by their R_F values, but higher alcohols were not separable from each other. Diemair *et al.*[56] also identified plasticizers by hydrolysis with hydrochloric acid and separation of the alcohols in the form of their 3,5-dinitrobenzoate esters on kieselguhr impregnated with polyoxyethylene glycol, using petroleum ether (b.p. 100–140°) as mobile phase. The esters of the C_1–C_{10} normal alcohols were separated from each other.

Plasticizers in milk pipes made from plasticized poly(vinyl chloride)[57] were determined gravimetrically after separation by preparative layer chromatography. The additives were extracted for 5 hr with dimethoxymethane and the evaporated residue, redissolved in a little benzene, was applied as a band to a plate coated with silica gel H and developed with dichloromethane. The plasticizer zone, remaining at the origin was scraped off, eluted with acetone–methanol (9:1 v/v) and chromatographed again on a second silica gel plate with di-isopropyl ether–methanol (8:2 v/v) as mobile phase. Partial identification was achieved by chromatographing known plasticizers on the same plates and revealing with 0·1% iodine solution in chloroform.

Hagen[58] identified lubricants such as stearic acid, butyl and hexyl stearates, octadecanol and dodecanol, wax and oligomeric alkyl expoxy stearate in PVC moulding powders by their R_F values after extraction with chloroform. The separated lubricants were revealed either by spraying with an alkaline iodine solution or with Rhodamine B and viewing under ultraviolet light.

Campbell *et al.*[59] determined plasticizers in poly(vinyl chloride) by dissolving the sample in tetrahydrofuran and precipitating the polymer with methanol. The evaporated extract, dissolved in ether, was separated on Merck silica gel G layers with mobile phases consisting of (*a*) ethyl acetate–2,2,4-trimethylpentane (3:17 v/v), or (*b*) dichloromethane, or (*c*) diethyl ether–petroleum ether (b.p. 40–60°) (1:4 v/v). The spots were revealed by the resorcinol or dichlorobenzoquinonechloroimide reagents previously mentioned. The R_F values of 15 plasticizers were given.

Curing agents

Several workers[49,60] have described the use of TLC for the separation of curing agents extracted from rubber. Both R_F values and the wide range of colours developed after spraying with various revealing reagents are helpful in identification. For more positive identification, the combination of spectroscopy with TLC is recommended. Kreiner and Warner have studied the chromatographic behavior of most of the commercial products used as accelerators in the United States.[49] Since only one or two accelerators are generally used in a particular rubber compound, identification is not too difficult even though many commerical products are themselves mixtures. The R_F values of 28 commercial products developed on layers of silica gel G with benzene–ethyl acetate–acetone (100:5:1 v/v) as mobile phase are listed. Those compounds containing a readily liberated amine were sprayed with 4*M* hydrochloric acid and heated in an oven at 130° for 15 min and then resprayed with a ninhydrin reagent. Thiazoles were revealed by spraying with 5% bismuth nitrate solution in 1*M* nitric acid. Benzothiazole disulphide did not react with this reagent until after reduction to 2-mercaptobenzthiazole with 0·5% ammonium sulphide solution. These reactions were carried out directly on the plate.

Amos[61] used a similar chromatographic system to study the cause of bloom formation during vulcanization of ethylene–propylene–diene terpolymers. It was shown to be due to the insolubility of certain accelerators or their derivatives formed during the vulcanization process. For example, the bloom swabbed with chloroform-soaked cotton-wool from the surface of a polymer containing the accelerators mercaptobenzthiazole, trimethyl- and triethylthiuram disulphides was shown by TLC to consist of zinc dimethyl- and diethyl-dithiocarbamates in roughly equal proportions, together with a small amount of zinc benzothiazyl sulphide. Zinc oxide was present in the original cure system.

Other additives

Davies and Thuraisingham[62] described a quantitative TLC method for free sulphur in rubber vulcanizates, from which the degree of vulcanization could be assessed. No interference from the more commonly used accelerators, antioxidants or processing oils was observed. The sulphur from milled rubber samples was Soxhlet-extracted with acetone for 16 hr and carbon disulphide solutions of the evaporated extract were separated on silica gel plates with heptane as mobile phase. Sulphur was revealed as well-defined white spots on a yellow-brown background by spraying with a 3% solution of sodium azide in $0{\cdot}1N$ iodine solution. Quantitative results were obtained by using the spot-area method of Purdy and Truter.[63] A linear relationship was obtained between the square root of the area and the logarithm of the weight of sulphur in reference solutions over the range 0–40 μg of sulphur per 5 μl of sample chromatographed. The limit of detection was 0·2 μg of sulphur, corresponding to 0·01% w/w in the original sample. The relative standard deviation was less than ± 4%.

Cornille[64] has described a scheme based on TLC and spot-tests for the identification of antistatic agents such as *N,N*-bis(hydroxyethyl)alkylamines, polyoxyethylene compounds, alkylaryl sulphonates, quaternary ammonium compounds, alkyl pyridinium chloride and Tris-2-hydroxypropylamine.

Brammer *et al.*[65] developed a method for the determination of dicumyl peroxide added to polystyrene to impart fire-resistance properties. A method was necessary to check that the additive did not deteriorate during manufacture or subsequent storage. It was extracted with acetone and separated from other additives on silica gel layers, with toluene–carbon tetrachloride mixtures as mobile phase. The silica gel in the area of the peroxide spot (located by viewing under ultraviolet light) was transferred to a small reaction flask and refluxed with a sodium iodide–glacial acetic acid mixture. The liberated iodine was then titrated with sodium thiosulphate. The reproducibility of the method is about ± 12% at the 0·25–0·50% level. Other organic peroxides commonly used in polystyrene formulations did not interfere.

Monomers

The level of unreacted volatile monomer in a polymerized product is best determined by gas chromatography. However, Braun and Vorendohre[66] describe an interesting application in which TLC was used to distinguish, by R_F value, derivatives of styrene, vinyl alcohol and acrylic acid as well as olefins. The monomers were separated, in the form of their mercuric acetate adducts on layers of silica gel G with butanone–1-propanol–ethanol–ammonia (91:9:36:64 v/v) as mobile phase. The adducts were revealed as red or yellow spots by spraying with 0·1% dithizone solution in carbon tetrachloride.

Polymers

TLC is seldom used for the examination of the polymer structures themselves, since column gel exclusion chromatography is a more powerful separation tool from which deductions about the molecular weight distribution can be made. Pyrolysis, followed by gas chromatographic, infrared or mass spectrometric examination of the degradation products has been widely used to glean information on polymer structures.

Otocka and Hellman[67] separated a $1{\cdot}03 \times 10^4$–$1{\cdot}80 \times 10^6$ molecular-weight range polystyrene into seven fractions on silica gel layers by a gradient elution technique. Scanning the chromatogram of a commerical sample by densitometry gave results in good agreement with those obtained by gel exclusion chromatography. By a similar technique a $1{\cdot}5 \times 10^3$–$2{\cdot}8 \times 10^4$ molecular-weight range poly(ethylene oxide) was separated by mixed-solvent development on silica gel or by gradient elution on alumina.

The hydrolysis products of polyamides have been identified by using TLC[68,69] on silica gel G, and polyesters[70] (*e.g.*, those of hexanediol with adipic or succinic acids) have been separated according to molecular weight, on silica gel with benzene–methanol–acetic acid (80:10:1 v/v) as mobile phase.

TLC has also been used for distinguishing between natural and synthetic rubber. The method[71] depends upon the fact that natural rubber contains about 1% of acetone-extractable lipid materials such as phospholipids, sterols, tocopherols, tocotrienols, carotenes and squalene, whilst synthetic polymers contain only acetone-extractable additives of the type we have already discussed. A characteristic spot in natural rubber was found to be due to β-sitosterol, having an R_F value of about 0·40 when developed on a silica gel plate with 40–60° petroleum ether–diethyl ether (50:50 v/v) mobile phase and revealed by phosphomolybdic acid after heating at 105° for 10 min. This component was used to detect the presence of natural rubber down to the 5% level in blends.

APPLICATIONS TO ANALYSIS FOR NON-IONIC SURFACTANTS

The most important non-ionic surfactants are the reaction products of ethylene or propylene oxide with compounds such as *p*-alkylphenols, glycols or fatty acids containing a reactive hydrogen atom. The commercial products, termed oxyalkylates, are mixtures with rather broad molecular-weight distributions. TLC has been used to produce "fingerprint" chromatograms to identify commercial products, to determine molecular-weight distribution and to produce fractions for identification of specific components by, for example, gas chromatography, gel exclusion chromatography and infrared and nuclear magnetic resonance spectroscopy.[72]

Non-ionic surfactants of the polyethylene oxide–acid, amine, alcohol or phenol type[73] can be separated by TLC according to the number of ethylene oxide units. The chromatogram can, therefore, be used to give information on the molecular-weight distribution of the condensation products. For example, Burger[74] determined the molecular-weight distribution of polyethylene oxide condensates with fatty acids, fatty alcohols and alkylphenols using silica gel as the stationary phase and the upper layer of a well-shaken mixture of methyl ethyl ketone and water (50:50 v/v) as mobile phase.

Polyglycol samples were refluxed for 1 hr with 3,5-dinitrobenzoyl chloride in benzene containing a small amount of pyridine. The separated esters were chromatographed and the number and distribution of the spots, which were revealed with a modified Dragendorff–barium chloride reagent, were found to be related to the molecular weight of the polyoxyethylene glycol. Koenig[75] described a general method for the separation of all classes of non-ionic detergents on silica gel plates impregnated with oxalic acid, using chloroform–methanol (9:1 v/v) as mobile phase. With the modified Dragendorff revealing reagent, down to 20 μg of detergent could be detected.

ANALYSIS OF CHEMICAL INTERMEDIATES

TLC has been shown to be a useful technique for the separation of fatty alcohols, used as chemical intermediates for plasticizers or synthetic detergents, obtained either from natural sources, *e.g.*, wax, whale oil or sperm oil, or from chemical synthesis, *e.g.*, by oxidation of paraffins to fatty acids, followed by high-pressure hydrogenation or *via* oxo-synthetic routes.

Kaufmann and Das[76] separated C_{16}–C_{26} alcohols on plates impregnated with tetradecane, using isopropyl alcohol–acetic acid–ethanol–water (8:4:3:2 v/v) as mobile phase, the alcohols being located by spraying with Rhodamine B solution and viewing under ultraviolet light. Hashimoto *et al.*[77,78] separated C_{10}–C_{16} alcohols from natural sources on silica gel impregnated with paraffin, using mobile phases such as hexane–diethyl ether (7:3 v/v), and unsaturated alcohols, such as mono- di- and trienoic alcohols in the form of mercuric acetate derivatives, on silica gel plates impregnated with silver nitrate, using petroleum ether–diethylether. (80:20 v/v), propanol–acetic acid–pyridine (150:1:1 v/v) or di-isobutyl ketone–acetic acid (4:1 v/v) as mobile phases. The range of alcohols separated has been extended to C_8–C_{22} alcohols, or their acetates, on kieselguhr plates impregnated with paraffin, with acetone–water (75:25 and 90:10 v/v respectively) as mobile phases.[79]

Prey *et al.*[80] separated glycerol from glycol on silica gel G layers impregnated with boric acid, using butanol–water (90:10 v/v) as mobile phase, and Seher[81] has separated the non-ionic surfactant polyglycerols from each other and from glycerine on layers of silica gel, using ethyl acetate–isopropyl alcohol–water (65:22·7:12·3 v/v) as mobile phase. Detection was achieved by first spraying with 0·1% sodium metaperiodate solution, followed by a second spray, 3-5 min later, with a benzidine solution. As little as 1% of diglycerol in glycerol could be detected in this way.

Polyethylene glycols in the 200–600 molecular weight-range can be fractionated on layers of silica gel G by using chloroform–methanol–water (6:50:24 v/v) as mobile phase.[82] However, development with aqueous alcoholic mobile phases is tediously slow by TLC standards, often taking 2–3 hr, especially with precoated plates. A range of glycols from ethylene glycol to tridecane-1,13-diol was separated on silica gel G with ethanol as the mobile phase and it was found[83] that a linear relationship existed between log R_F and the number of carbon atoms in the diol. Similarly, tetra-, penta-, hexa-, hepta-, and nona-oxyethylene glycols were separated on silica gel G impregnated with sodium acetate, with ethyl acetate–isopropyl alcohol–water (65:23:12 v/v) as mobile phase. By spraying with a modified Dragendorff reagent, red spots on a yellow background were obtained and again a relationship between R_F values and the content of oxyethylene groups was found.[84] Favretto *et al.*[85] have studied the degree of polymerization of polyethylene glycols by conversion into the dichloro-derivatives and determination of their molecular-weight distribution by TLC on silica gel by repeated development with 2-butanone–water (90:10 v/v) as mobile phase. The spots were visualized with iodine vapour and evaluated densitometrically with a Joyce Loebl Chromoscan. The method was found to be applicable for up to 21 ethylene oxide units.

APPLICATIONS TO EXPLOSIVES ANALYSIS

The role of TLC in following the course of chemical reactions is well illustrated in the control of product quality in the explosives industry. Yasuda[86] described a two-dimensional TLC method for separating and identifying 14 impurities in α-trinitrotoluene. Dinitro- and other trinitrotoluenes were found to be the most common impurities and a novel feature of the method was that zinc dust was incorporated into the stationary phase (silica gel) so that reduction to anilines could be carried out *in situ* to facilitate identification. The spots were then revealed by spraying with acidified alcoholic *p*-diethylaminobenzaldehyde solution to form coloured condensation products. The most useful mobile phase was ethyl acetate–petroleum ether (15:85 v/v). The method was extended to include the separation and identification of nineteen *N*-nitroso- and nitrodiphenylamines in a study of the reaction between diphenylamine and nitrogen oxides. Diphenylamine is used extensively as a stabilizer in explosives and propellants containing nitrocellulose, which otherwise would slowly decompose, releasing nitrogen oxides.

The production of 2-nitrodiphenylamine (used as an oxidation inhibitor in rocket propellants), starting from chlorobenzene, has been monitored by TLC,[87] and Kohlbeck *et al.*[88] used TLC for studying and improving a continuous TNT-production process by examining the effect of changes in nitrating conditions on the reaction products and thus were able to establish optimum conditions for the process.

Parihar *et al.*[89] studied the TLC of polynitrodiphenyl ethers employed as plasticizers in solid rocket propellants and used as intermediates in the synthesis of high explosives. Reversed-phase TLC utilizing cellulose–calcium sulphate plates impregnated with 5% sesame oil and 10% olive oil gave excellent separations on development with aqueous alcoholic mobile phases. They also developed TLC systems[90] for polynitrophenols, nitrosophenols, nitrohydroquinones and their esters, used in the synthesis of high energy fuels for rockets. TLC was necessary to monitor the synthesis of new explosives and for quality control work.

TLC has been combined with ultraviolet, visible and infrared spectroscopy to study the degradation of plasticizers and stabilizers, *e.g.*, nitroglycerine, triacetin, 2-nitrodiphenylamine and resorcinol in aged propellants[91] and for the determination of impurities in pentaerythritol tetranitrate[92] which affect the firing characteristics of detonators. These impurities were determined colorimetrically with a Nester–Faust Uniscan 900 after conversion into their red diazo dyes by spraying with *N*,*N*-dimethyl-1-naphthylamine in acetic acid. Relative standard deviations of better than 0·2% were obtained.

ENVIRONMENTAL CONSERVATION APPLICATIONS

Over the past ten years TLC has played an important part in providing firm data to identify possible sources of pollution. In keeping with the subject matter of this review, this discussion will be limited to air- and waterborne pollutants from industrial organic chemical sources and will exclude the study of, for example, the effect of biocides on the environment.

Polynuclear aromatics

One of the most difficult and emotive problems in recent years has involved the recognition of materials possessing carcinogenic activity, to which the human race may be exposed in the environment (food, clothing, and atmosphere). Since biological methods of measuring carcinogenicity are intolerably lengthy, recent work has been directed towards chemical or physical methods of measuring the concentration of a small number of known carcinogens. The most ubiquitous class of compound having known carcinogenic activity is that of the polynuclear aromatics (PNA) which may be formed during any hydrocarbon combustion process. Though not all polynuclear aromatics are carcinogenic, nearly half of the known carcinogens belong to this class, the most important being benz[*a*]anthracene, dibenz[*a*,*h*]anthracene, benz[*a*]pyrene and 20-methylcholanthrene. Why these structures are carcinogenic is not fully understood and the problem becomes even more confused because of the apparent existence of co-carcinogens, *e.g.*, certain straight-chain paraffins which greatly enhance carcinogenic activity though they themselves are non-carcinogenic. In the present state of knowledge, the problem is generally oversimplified by measuring benz[*a*]pyrene (BaP) concentrations and these are taken as indicators of a carcinogenic environment.

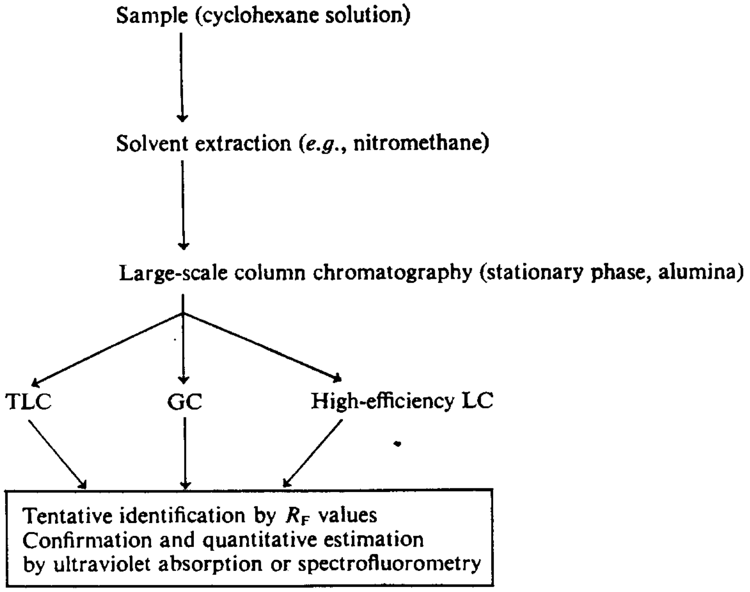

Fig. 4

From the hundreds of papers which have been written on PNA analysis, the best methods of isolation, identification and measurement of individual PNA's at the ng–μg level now fall into a recognizable pattern, summarized in Fig. 4.

The sample is generally obtained in the form of a cyclohexane, benzene or dichloromethane extract (of particulate matter, for example). Since ultraviolet absorption or, better, ultraviolet fluorescence spectroscopy are the two most powerful and sensitive identification and quantitative tools, a clean-up procedure is required, the complexity of which depends upon the complexity of the sample. For really difficult samples, *i.e.*, trace amounts of PNA in the presence of large amounts of other aromatic hydrocarbons and sulphur, oxygen and nitrogen compounds, the relevant fractions may have to be rechromatographed several times before background interferences are reduced to a sufficiently low level.

The first step, therefore, is to remove the bulk material by solvent extraction of the PNA. Dimethylsulphoxide and dimethylformamide are the most effective extractants, but unfortunately are relatively involatile and high losses are incurred on attempting to back-extract the PNA into a more volatile solvent. Extraction with acetonitrile or nitromethane is therefore preferred even though the partition coefficients of PNA between these solvents and aliphatic hydrocarbons are much less favourable. Nevertheless, recovery is virtually complete after five or six extractions.

The second step is to separate the PNA concentrate into simpler fractions. This is readily achieved on a short (20 × 1 cm) column packed with alumina deactivated with 2–4% water, with a mobile phase of dichloromethane or diethyl ether in a volatile aliphatic hydrocarbon such as pentane. The fractions of interest are located by running reference compounds under identical conditions.

The final separation, identification and concentration measurement are made by a high-efficiency chromatographic separation combined with ultraviolet absorption or fluorescence spectroscopy. At present, considerable success is being achieved by gas chromatography–ultraviolet absorption. For example, Searl *et al.*[93] used this technique to measure seven

Table 6. R_B values of polynuclear aromatic hydrocarbons (R_B of BaP = 1·00)

	System 1	System 2	System 3
Phenanthrene	1·13	3·74	1·99
Anthracene	1·14	3·33	1·99
Fluoranthene	1·09	2·92	1·89
Chrysene	1·10	—	1·75
Pyrene	1·25	3·16	1·72
Triphenylene	1·07	—	1·49
Benz[*a*]anthracene	1·03	2·70	1·47
11H-Benzo[*b*]fluorene	1·08	3·54	1·33
Benzo[*e*]pyrene	1·04	2·94	1·16
Perylene	0·91	2.86	1·14
Benzo[*k*]fluoranthene	0·98	2·40	1·03
Benzo[*a*]pyrene	1·00	1·00	1·00
Anthanthrene	0·71	2·17	0·70
Benzo[*ghi*]perylene	0·89	3·04	0·69
Dibenz[*a,h*]anthracene	0·74	2·92	0·66
Naphtho[1,2,3,4-*def*]chrysene	0·78	1·85	0·48
Benzo[*rst*]pentaphene	0·68	2·41	0·45
Coronene	0·46	2·87	0·37
Benzo[*a*]coronene	0·10	2·48	0·15
Dibenzo[*h,rst*]pentaphene	0·12	2·35	0.14

PNA's in coke-oven effluents. Difficulties are encountered because of the high operating temperatures of the columns, resulting in loss of resolution and contamination of column effluents by stationary phase. High-performance liquid chromatography in columns will probably be increasingly used for this type of separation in the future. For example, Popl *et al.*[94,95] have examined extracts from coal-tar pitch by gradient elution from a high-efficiency alumina column, and the potential of controlled surface-porosity supports has also been indicated.[96] The most popular technique in recent years has been TLC combined with ultra violet fluorescence spectroscopy, on account of its high sensitivity, high selectivity and short analysis time. Furthermore, the spots can be examined directly on the plate.[97] The application of spectrofluorimetry to this type of analysis has been the subject of a recent Talanta Review.[16]

The use of TLC for the separation of PNA's has been reviewed by several workers.[98,99,100] It can be said at the outset that no one TLC system is superior to all others, so that the choice of a particular system depends upon the complexity of the mixture to be separated and upon the particular components of interest. Consequently, where one system fails another may succeed. With a complex mixture, therefore, successive fractionations on different systems may be necessary. The three most widely used systems are as follows

Alumina with pentane–diethyl ether (19:1 v/v)	System 1
Cellulose acetate with ethanol–toluene–water (17:4:4 v/v)	System 2
Cellulose with dimethylformamide–water (1:1 v/v)	System 3

These three systems have been compared by Sawicki *et al.*[98] who obtained the data shown in Table 6. The retention values (R_B values) are the ratios of the distances travelled by the compounds to the distance travelled by benz[*a*]pyrene. Though alumina gave the best separation of PNA's from other compound types, they were poorly separated from each other.

The cellulose system gave the widest range of retention values and the separation of difficult pairs could often be improved with a slight change of water content in the mobile phase. The cellulose acetate system gave the best separation of the "benzpyrene" fraction obtained from alumina column chromatography, *i.e.*, benzo[*a*]pyrene is completely separated from benzo[*k*]fluoranthene, benzo[*e*]pyrene and perylene. Schaad *et al.*[101] however, preferred ethanol–dichloromethane–water (20:10:1 v/v) as mobile phase for the separation of the "benzpyrene" fraction.

Recoveries from cellulose and cellulose acetate are much higher (93–98%) than from alumina (50–80)%. Poor recoveries are mainly attributed to photochemical changes taking place during chromatography and these are more pronounced on silica gel and alumina than on cellulose acetate. These reactions are accelerated by ultraviolet light and by the presence of chlorinated solvents. For these reasons, chromatography should always be carried out in the dark and the use of chlorinated solvents as mobile phases avoided. Inscoe[102] identified 1,6-and 1,8-pyrenedione among the numerous photo-oxidation products formed during the chromatography of pyrene on silica.

White and Howard[103] measured the R_F values of 29 PNA's by partition chromatography between cellulose impregnated with dimethylformamide and iso-octane, which separated the PNA's into groups according to their ring structure, but they found the cellulose acetate system previously described superior in separating the 4-, 5-, and 6-ring compounds. This technique was used to separate these hydrocarbons from certain vegetable oils,[104,105] followed by ultraviolet absorption measurements after elution with methanol. They also showed that carcinogenic hydrocarbons were absent from commercial hexanes used in the extraction of edible oils from cottonseed, soya beans and peanuts.[106]

Strömberg and Widmark[107] used the two-dimensional method of Köhler[108] *et al.* to separate and identify, by ultraviolet absorption spectroscopy, thirty-five fractions from benzene extracts of air particulates taken on glass-fibre filters near gas-works retorts. The stationary phase was a 2:1 mixture of alumina–cellulose acetate, the mobile phase in the first direction being n-hexane–toluene (9:1 v/v) and diethyl ether–methanol–water (4:4:1 v/v) in the second direction. It was pointed out that while the ultraviolet spectra of isomeric PNA's are readily distinguishable, the spectra of a given PNA and its alkyl derivatives can be very similar. Such compounds are, however, readily distinguished by their mass spectra.

Several successful attempts have been made to improve the TLC separation of PNA's by using an electron-acceptor as the stationary phase. For example, Berg and Lam[109] found that the separation of PNA's on alumina or silica was improved by impregnating these adsorbents with 2,4,7-trinitrofluorenone or caffeine, which with many PNA's formed brightly-coloured fluorescent spots. The most useful mobile phases were aliphatic or acyclic hydrocarbons containing about 1% of a polar solvent such as ether, acetic acid or pyridine. Short and Young[110] achieved similar success by incorporating 30% pyromellitic dianhydride into their silica gel stationary phase.

PNA's in atmospheric dust have been determined by combining TLC with gas chromatography.[111,112] The dust itself, or a cyclohexane extract, was chromatographed on a silica gel plate, with cyclohexane–benzene (2:3 v/v) as mobile phase. This separated PNA's as a class from other types of compound (saturated compounds, heterocyclics). The PNA's (R_F = 0·65–0·75) were located by viewing under long-wave ultraviolet light, the silica gel was scraped off the plate, and the PNA's were eluted with ether. The evaporated extract was then separated by gas chromatography on a glass capillary column coated with SE52 silicone rubber. This combination of techniques provided a fast and simple procedure since the use of large volumes of solvent was avoided andre peated chromatographic separations reduced.

Benzo[a]*pyrene*

Sawicki *et al.*[113] have compared eleven procedures for the determination of BaP in particulates, for precision, accuracy, man-hours of work and total analysis time. Seven of these procedures involved TLC on alumina or cellulose acetate with a spectrofluorometric finish, usually after treatment of the eluted BaP spot with sulphuric acid to enhance selectivity. These proved to be the most sensitive methods available, with detection limits down to 0·003 μg of BaP. Analysis times ranged from 1·1 to 4·5 hr. Greatest losses occurred during the extraction procedure and dichloromethane was recommended on the basis of high solvent power and volatility. The 2-dimensional procedure (alumina and cellulose acetate) proved to be the only one in which BaP was completely separated from benzo[*e*]pyrene, benzo[*k*]fluoranthene and perylene as well as from the other known PNA's. Since benzo[*k*]-fluoranthene has a similar ultraviolet spectrum to BaP it is likely that some early data reported for BaP concentrations are erroneously high because of interference from benzo[*k*]-fluoranthene.

Scholz and Altman[114] determined the BaP content of water samples down to the 0·1 ng/l. level, with a relative error of ± 15% in the 1–10 ng/l. range. The water was shaken with cyclohexane and the concentrated extract separated on layers of silica gel impregnated with polyoxyethylene glycol 1000, with benzene–hexane (1:3 v/v) as mobile phase. The BaP spot was eluted with cyclohexane and the amount present measured by ultraviolet fluorescence.

Other organic airborne pollutants

The most powerful tool for the identification and quantitative determination of organic airborne pollutants is the combination of ultraviolet fluorescence spectroscopy with TLC. This is due to high selectivity, sensitivity and rapid analysis times. High precision is also obtainable, the main limitation being the accuracy with which representative samples for analysis can be collected. In addition to polynuclear aromatics, the technique has been used for the characterization of heterocyclics, phenols, aromatic amines, aldehydes, ketones, polynuclear ring carbonyl compounds and amino-acids in effluents. Sawicki's review[16] discusses the factors affecting the use of excitation and emission spectra under various conditions such as solvent, pH and photochemical effects arising from the use of TLC and shows how this combination of techniques has led to a better understanding and more sensible control of our environment.

Waterborne pollutants

TLC has been effectively used both to monitor trade effluents and to identify sources of contamination in sewers, rivers and in the marine environment. Berthold[115] has described a novel technique he calls "Channel Thin Layer Chromatography" for determining oil in water down to the 1–15 ppm level. A carbon tetrachloride extract of the water sample is chromatographed on precoated silica gel plates, with chloroform as mobile phase. Before the development, parallel thin lines of adsorbent are removed perpendicular to the direction of development so that the samples are confined to narrow bands of constant width. The amount of material in the spot is then calculated, after calibration by measuring the length of the spot.

The phenolic content of drinking water is monitored[116] by concentration on active carbon and extraction with diethyl ether. The separation and identification of *o*-, *m*- and *p*-cresols, phenol, 1- and 2-naphthols, 2,5-, 3,4- and 3,5-xylenols is achieved on layers of silica gel G impregnated with potassium carbonate (1:2 w/w) after coupling the phenolic concentrate with diazonium salts. Mobile phases used include dichloromethane–ethyl acetate–diethylamine (92:5:3 v/v), dichloromethane–ethyl acetate–chloroform–benzene (88:2:5:5 v/v), and dichloromethane–benzene (1:1 v/v). Polyhydric phenols were identified directly on silica gel, by using dioxan–benzene–acetic acid (25:9:4 v/v) or benzene–acetone (9:10 v/v) as mobile phases, and revealed by spraying with a solution of either diazotized sulphanilic acid or phosphomolybdic acid. These procedures have been extended to include the separation of chlorophenols.

TLC has also proved invaluable in the control of the discharge of non-ionic detergents of the alkyl phenol–polyoxyethylene type into sewage effluents and rivers.[117] Such materials are highly resistant to biological degradation and the technique enables amounts down to less than 0·1 ppm to be determined much more simply and rapidly than by any other technique. The detergent is salted-out from the effluent by addition of magnesium sulphate before extraction into chloroform and concentration by evaporation. The concentrate is chromatographed on silica gel coated plates and the detergent revealed as red-coloured spots by spraying with an acetic acid solution of bismuth oxynitrate–potassium iodide. As little as 1 μg of detergent can be detected and the colour of the spots is stabilized by inclusion of ethanol and phosphoric acid in the spray reagent. The choice of mobile phase depends on whether identification or determination is the object of the separation. For example, a solvent system consisting of ethyl acetate–water–acetic acid (70:15:16 v/v) separates the detergent Lissapol NX into a series of spots depending upon the number of ethylene oxide units in the molecule, *i.e.*, a "fingerprint" chromatogram is obtained which provides information on the commercial source of the detergent in the effluent. On increase of the polarity of the mobile phase, *e.g.*, ethyl acetate–water–acetic acid (40:30:30 v/v), the individual spots merge into a single, larger and more intense spot nearer the solvent front, which is suitable for quantitative analysis.

The varying chromatographic and fluorescence characteristics of petroleum and coal-tar

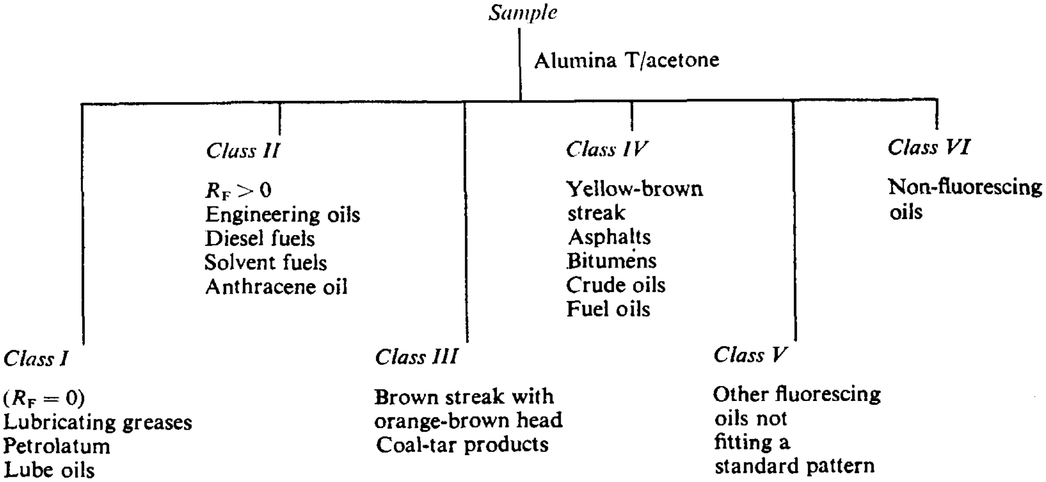

Fig. 5

derived oils, fats and greases are used to form a simple systematic approach to trace the source of these materials in trade effluents, which contribute to the blockage of sewers or of screens in pumping stations and sewage works. The scheme, proposed by Matthews,[118] is illustrated in Fig. 5. The sample (or a chloroform extract) is first chromatographed on an alumina T plate with acetone as mobile phase and the developed chromatogram is viewed under long-wave ultraviolet light. As a result the sample can usually be placed in one (or more, if the sample is derived from more than one source) of 6 classes. The choice within each class can be further narrowed down by chromatographing further portions of the sample with other chromatographic systems, *e.g.*, alumina T/petroleum ether, kieselguhr G/acetone, silica gel G/acetone. By this stage, the source of pollution can generally be narrowed down to only a few possible locations and a final positive identification can be made by comparison with reference samples. Since the introduction of this technique by the Greater London Council, the proportion of cases in which sources of oil have been successfully traced has greatly increased and it seems probable that similar methods will also be used to track down sources of pollution in the marine environment.

CONCLUSIONS

It is evident that for the past 8–10 years TLC has been, and still is being, used for a wide variety of applications within the organic chemical industry, and during this period has been the major separation technique apart from gas chromatography. Although the equipment is cheap and the technique simple to use it has provided much information quickly which would have been difficult or impossible to get in any other way.

There are, however, some limitations to this technique. Its resolving power is limited because chromatographic conditions, *e.g.*, mobile phase velocity, are difficult to control. In quantitative analysis the extra cost of ancillary equipment and the extra effort required is out of all proportion to the additional information obtained and finally, the technique is not suitable for automation. For these reasons TLC in industry is likely to be partially superseded by the newly developing technique of high-efficiency high-speed column chromatography, especially in routine quantitative analyses and for the recovery of unknown fractions for further identification. Nevertheless, the use of TLC as a rapid and simple spot-test either in the laboratory or in the field, is likely to remain with us for many years to come.

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Zusammenfassung—Die Technik der Dünnschichtchromatographie wird beschrieben, wie sie im organischen Industrielaboratorium praktiziert wird. Es wird eine Übersicht über ihre Anwendungen auf die Analyse von Petroleum-Kohlenwasserstoffen, Brennstoffen, Schmierstoffen, Polymeren, Kunststoffen und ihren Additiven, nichtionischen oberflächenaktiven Substanzen und Explosivstoffen gegeben. Die Rolle der Dünnschichtchromatographie bei der Erhaltung der Umwelt wird ebenfalls erörtert.

Résumé—On décrit la technique de la chromatographie en couche mince, telle qu'elle est pratiquée dans le laboratoire industriel organique, et passe en revue ses applications à l'analyse des hydrocarbures du pétrole, combustibles, lubrifiants, polymères, plastiques et leurs additifs, tensio-actifs non ioniques et explosifs. On considère aussi le rôle de la chromatographie en couche mince dans la conservation de l'environnement.

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TALANTA REVIEW*

PESTICIDE RESIDUE ANALYSIS†

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Summary—The review covers broadly the field of analysis for traces of pesticides and discusses the problems of separation, detection and confirmation. Clean-up procedures and GLC methods receive more detailed attention. Some 200 references are quoted.

INTRODUCTION

The detection and determination of residual traces of pesticides in foodstuffs, plant and animal tissues, *etc.*, is not a simple matter. Insecticides, fungicides, herbicides, acaricides and rodenticides together comprise several hundred compounds of widely differering chemical constitutions and properties and a pesticide residue analyst may be called upon to determine traces of any of these materials; frequently several may occur together in a single sample.

The analysis for residues of inorganic pesticides such as lead arsenate, sulphur and calomel does not differ significantly from standard trace element analysis and will not be

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discussed further. Despite the undoubted advantages of pesticide usage, concern has been expressed at the potentially harmful effects of using compounds which are very stable and which might accumulate in man and his environment. New and improved compounds are continually being sought and evaluated to avoid this difficulty. The work of the residue analyst is thus not confined to detecting and determining pesticide residues in directly treated crops and animals, but also in crops subsequently grown in treated areas, animal produce (domestic and wild), soils, water and in man himself. It will be appreciated that these analyses need to be carried out on a wide variety of commodities each with its own problems, and the most efficient methods must be used in order to determine the quantity as well as the identity of any residue present. The analysis often is further complicated by chemical changes undergone by pesticides when absorbed into living tissue, adsorbed onto the soil, or exposed to light. These changes may produce compounds which are more toxic than the original pesticides and the analyst has to be able to determine the rate of breakdown, the nature and quantity of these metabolites and end-products, as well as the residue of the parent pesticide.

The stages of analysis are usually as follows.

(1) The extraction of the residue from the sample matrix by using an efficient and selective solvent.
(2) The removal of interfering substances from the extract—usually referred to as the clean-up procedure. This often involves either chromatography or solvent partition.
(3) The estimation of the quantity of pesticide residues, together with metabolites and breakdown products, in the cleaned-up extract. These are determined at very low levels (as low as 10^{-12} g), and to obtain this sensitivity stringent requirements of selectivity are imposed on the end-method.
(4) The confirmation of the presence of the residue by, for example, using a different end-method or the formation and identification of a derivative.

There are five basic end-methods of analysis.

(*a*) *Functional group analysis*. This method involves, for example, the colorimetric assay of a particular group or element in a compound. It does not give precise identification and requires thorough clean-up and consequently is not used very frequently. However, a degree of specificity can be built into the procedure, which may be useful for confirmation purposes.

(*b*) *Biological test methods*. These can show the presence of biologically significant residues by, for example, inhibition of the enzyme cholinesterase by certain classes of pesticide, or effects on larvae. As it is possible to use these methods without clean-up they are useful as screening tests by always need additional confirmation.

(*c*) *Chromatographic methods*. These include thin-layer (TLC), paper and gas–liquid chromatography which give separation and accurate identification and estimation of a wide range of residues. High-pressure liquid chromatography is of growing importance.

(*d*) *Spectroscopic methods*. These provide evidence of identity and can in ideal conditions be used for quantitative analysis.

(*e*) *Radiochemical methods*. Included under this heading are neutron-activation analysis, direct isotope-dilution methods and the more sophisticated double-isotope derivative analysis technique.

For all methods of analysis there is a detection limit below which it is impracticable to differentiate between the noise level of the background and the analytical signal. These levels range from 10^{-6} g for chemical methods to 10^{-14} g for radiochemical procedures. The importance of modern analytical instrumentation in pesticide analysis cannot be exaggerated. The available sensitivity and versatility have made it relatively easy to solve complex problems which only a few years ago were insoluble. This progress is especially noticeable in advances in gas chromatographic detection where the electron-capture and phosphorus-sensitive flame-ionization detectors have lowered the detection limits to the nanogram (10^{-9} g) and picogram (10^{-12} g) levels. Techniques such as nuclear magnetic resonance, radioisotope labelling and mass spectrometry are proving increasingly useful for the identification of unknown metabolites and breakdown products and for confirming identification of unknown metabolites and breakdown products. In recent years there has been a need for continuous monitoring of pesticide residues and the use of automated analysis is being investigated where applicable.

Each stage of the analytical procedure is dictated both by the chemical nature of the pesticides under investigation and by the nature of the substrate. Separate discussions of the extraction, clean-up and end-method stages will follow.

EXTRACTION PROCEDURES

The extraction procedure depends on the type of pesticide and the nature of the sample under examination. It should be at least 80% efficient and sufficiently selective to require only the minimum amount of clean-up before the estimation. It is important that reagents used in the extraction and clean-up do not in any way interfere with the end detection method. A highly selective extraction procedure is desirable for pesticide residues since the concentration of residue in the substrate is normally low and it may be useful if this can be achieved, even at some loss of extraction efficiency. Because of the high sensitivity of the end-methods used, great care must be taken to avoid contamination by contact with plastics or rubber, and all solvents used must be sufficiently pure to avoid any interference problems in the end-method. Particularly when gas-liquid chromatography is to be used as an end determination method it may be necessary to redistil all solvents used. This is especially important in the case of the electron-capture detector, which, being somewhat unselective and highly sensitive, requires an almost pure solution of the pesticide in a suitable solvent.

Solvent extraction is widely used and gives great scope for choice of suitable polarity of solvent or solvent mixture, time of contact of solvent with sample and the manner of contact, so that optimum extraction conditions can be found. Many pesticides are found on the surface only of vegetables and fruit and it is possible, in some cases, to remove effectively all the pesticide residues from the sample by simply washing the sample whole with a suitable solvent. This method removes very little co-extracted material and enables the analysis to be carried out with little clean-up. However, it would be unwise to use this procedure without evidence that good recoveries are obtained by it in the particular circumstances concerned. Maceration with a solvent followed by centrifuging or filtering is particularly efficient for vegetable samples. The water in the sample may give rise to emulsions with non-polar solvents and this can be avoided by the use of a drying agent such as anhydrous sodium sulphate or propan-2-ol together with, or before, the solvent.

Meat samples may contain too much connective tissue for a macerator to deal with effectively and it is usually preferable for such samples to be comminuted before maceration. Soxhlet extraction of the finely comminuted sample is often used for meat samples. An even simpler method can often be used, namely, heating the minced sample in a beaker on a steam-bath with the solvent, possibly after grinding the sample with sodium sulphate and sharp sand which helps to break down some of the connective tissue. This technique can be used for organochlorine pesticides, for which n-hexane has been found to be a suitable solvent.

Care must be exercised however to ensure that the more volatile pesticides, *e.g.*, lindane (γ-BHC), are not lost in the process.

Water samples are normally shaken with solvent to extract any pesticide residues. Hexane is the usual solvent for organochlorine compounds and for many others chloroform is useful. It is strongly advisable to wash out the sample container with solvent since a large part of the residue may be retained in the film of grease *etc.* on the vessel walls. Extraction of pestticides from air or water samples may be affected by adsorption on to a solid such as carbon whence it can be removed by elution. This method has been used in surveys[1] and gives a means by which large samples may be taken (1000 litres or more), and is effective at the very low levels (10^{-12} g/l.) at which pesticides may be found in water. The desorption is carried out by Soxhlet extraction with a suitable solvent or combination of solvents. The adsorption of pesticides has been found to be very high[2] but the recovery on desorption may be low in some cases.[3]

The organochlorine pesticides and their initial breakdown products are fat-soluble and therefore tend to accumulate or be concentrated in the lipoid portions of food such as the cream of milk and the fat of meats. Extraction of these pesticides from foods rarely presents serious difficulties. Nevertheless careful choice of solvents and method will often minimize the amount of co-extracted material and thereby reduce the need for a more stringent clean-up procedure with its concomitant lower recovery factors. Hexane or acetone–hexane mixtures, in combination with either Soxhlet extractors, blenders of the Waring type, or simple shaking devices, are usually employed, but other solvents such as acetonitrile, benzene, dimethylformamide, dimethyl sulphoxide and propan-2-ol have also been used.

The extraction of residues of organophosphorus pesticides and their metabolites from various sample substrates poses several difficulties. Not only does the nature of the sample under examination govern the process to be applied, but the wide range of polarities encountered in these compounds makes it essential to use a general solvent for preliminary extraction if residues of unknown compounds are being sought. Such solvents also remove considerable amounts of co-extractives that are apt to complicate clean-up stages. Extraction solvents are usually chosen from benzene, chloroform, dichloromethane or acetonitrile, often in the presence of anydrous sodium sulphate to aid in the liberation of the more water-soluble compounds. The chopped or shredded sample is usually treated with the chosen solvent under vigorous agitation in a top-drive macerator or similar apparatus; frequently centrifugal action is required to break the emulsion formed and filtration of the solvent extract may also be essential. Deep-freezing of the produce followed by rapid thawing in the presence of solvent may be used to shatter the cell structure, thus giving ready release of the contents which may hold systemic pesticide residues. A more efficient clean-up technique may subsequently be required when such methods are used.

Two interesting methods of extraction are those of Grussendorf *et al.*[4] and Johnson and Starr.[5,6] The former method used a rapid sample preparation by ball grinding, extraction, freeze-out, and semimicro column clean-up. Johnson and Starr extracted insecticides from soil samples with the acid of ultrasonics and concluded that this was superior to the roller and blender methods in extraction efficiency and as efficient as an 8-hr Soxhlet extraction.

CLEAN-UP PROCEDURES

Before the quantitative determination of a pesticide residue can be carried out, the residue must be extracted and generally this extract must be purified or cleaned up. Even when a highly selective extraction procedure has been used, the extract will normally contain sufficient co-extracted matter to interfere with the end determination. Different end-methods will vary in the amounts and types of co-extractives which can be tolerated. For example, the electron-capture detector is extremely intolerant of halogenated impurities, and thin-layer chromatography tends to be intolerant of fatty material which can often grossly affect the rate of migration of a compound. Other types of co-extractives can interfere with thin-layer chromatography because of reaction with, or the masking of, the visualizing agents. Similarly, these co-extractives can affect spectrophotometric methods. Only in a few cases, such as the waters from reasonably clean rivers, can good gas chromatograms be obtained from simple hexane extracts without further treatment. The presence of co-extracted material when injections are made on to the gas chromatograph columns will not only cause non-pesticide peaks to appear on the resultant chromatograms, but constant injection of such material damages the separatory power of the columns, with the result that peaks begin to broaden, tail and ultimately to overlap. This is particularly true with extracts containing fatty material. Constant injection of small amounts of fat also leads to saturation of the first few mm of the support material with fat, which tends to act as another stationary phase and can radically alter the characteristics of the column.

The extent and nature of the co-extractives are largely governed by the nature of the sample, and apart from judicious choice of extraction procedure, the analyst must choose an appropriate clean-up procedure. Broadly, the methods available are adsorption methods (column and thin-layer chromatography), solvent partition, distillation methods (including sweep co-distillation) and gel chromatography. The type of clean-up used will obviously depend on the nature of the co-extracted material. If the extracts are low in fat content, passage through a short column of prepared alumina will often suffice; silica gel, charcoal and "Florisil" have also been recommended for this purpose. The co-extractive materials are removed from the extract solution mostly by virtue of their higher adsorption on the column. The extract solution, after concentration to a small volume, is applied to the top of the prepared column, eluted by one or more solvents and collected in fractions. Relatively large amounts of co-extractives can be tolerated by columns and very effective clean-up can be achieved, particularly when the pesticides under investigation can be collected in discrete fractions. It is important that the activity of the adsorbent used is constant and variation between different batches is often found.

The activity of adsorbents can be checked by recovery studies using a prepared column or by using standard dye materials. Adsorbents have been classified into grades of activity as weak, medium or strong, depending on their power of adsorption. It is also possible to activate or deactivate an adsorbent. Most materials may be activated by strong heating and some may be activated for a particular purpose by pretreatment with acids or bases (as with alumina) or organic solvents (as with charcoal). Deactivation of alumina has been effected by the addition of water, and the different grades of alumina thus produced are standardized according to the Brockmann activity which is based on the adsorptive capacity for various azo dyes.[7]

The Florisil clean-up procedure for pesticides is widely utilized and has been compared with a "Chrom AR" sheet clean-up for organochlorine pesticides in spinach by Beasley and Ziegler[8]. Mills[9] described a simple method for standardizing Florisil compounds, necessitated by the variation in the activity from batch to batch. Florisil columns were used by Sans[10] to fractionate insecticidal compounds which were difficult to resolve gas-chromatographically.

Fatty materials may be removed by a solvent partition method such as the dimethylformamide–hexane method of de Faubert Maunder *et al.*[11] The hexane extract of the sample is extracted three times with dimethylformamide saturated with hexane. The combined dimethylformamide phases are washed with hexane saturated with dimethylformamide and then shaken with a large volume of 2% aqueous sodium sulphate solution, On standing, the hexane previously held in solution rises to form an upper layer containing the pesticides and can then be separated.

Solvents used for partition methods include acetonitrile,[12,13] dimethylformamide (DMF)[11,14] and dimethyl sulphoxide (DMSO).[15–17] Wood[18] favoured the use of DMSO because it was a good solvent for chlorinated pesticide residues and dissolved less oil or fat than either DMF or acetonitrile. His column chromatographic method is applicable to a wide range of fatty samples. The sample is mixed with "Celite" and packed into a small column, and the chlorinated pesticides are eluted with DMSO. The eluate is then adsorbed on Florisil and the residues recovered from the DMSO by elution with hexane. This method gives a good clean-up, the author claiming that the amount of material lost in the clean-up was usually less than 0·01% of the sample. Carbon columns have been used for the clean-up of samples for the determination of both organochlorine and organophosphorus pesticides as they have a high capacity for retaining plant pigments and some waxes and oils. McLeod *et al.*[19] compared various carbon adsorbents and also proposed a mixed column of carbon ("Darco G60") and cellulose ("Solka Floc").

Thin-layer chromatography can be used for clean-up provided that there is not much fatty material present in the extract. The procedure differs from the thin-layer end detection method in that thicker adsorbent layers are used (1–5 mm) and the extract is normally applied as a streak. Standard compounds developed on the same plate are used to indicate the region of the plate on which the pesticide will be found. The band is removed by scraping and extracted to give a suitable solution for an end-method of determination.

To increase the amount of co-extractive material that can be applied to thin-layer plates, modified systems such as multiband chromatoplates and wedge-layer plates have been devised.[20,21] In wedge-layer plates the sample is applied to the thicker end of the plate, which can take heavier loading. After passing along a decreasing thickness of material it reaches the thinner layer which has a lower clean-up potential but an improved resolution. This type of plate can be used as a combined clean-up and end detection method.

The sweep co-distillation technique[22] is a useful method because it eliminates the need for specialized adsorbents and equipment, large volumes of costly purified solvents and laborious clean-up methods. The samples are extracted with a suitable solvent, for example, ethyl acetate for organophosphorus pesticides. An aliquot is then concentrated and cleaned up by injection into a long heated glass tube packed with glass wool and followed at 3-min intervals by injections of ethyl acetate. Nitrogen carrier gas sweeps the vaporized volatile components through the tube, the organic interferences remaining on the glass wool whilst the pesticides are collected for analysis. An improved version of this technique was claimed by Kim and Wilson[23] who used hexane as carrier gas in the place of nitrogen when determining organochlorine residues. A forced volatilization technique was used by Mestres and Barthes[24] to obtain vegetable tissue extracts in a suitable state for electron-capture detection.

Gel filtration or gel chromatography has been widely used in the biochemical field for a number of years but its use in the analysis of pesticides has been limited. Recently, however, fresh interest in the technique has arisen following the introduction of "Sephadex LH-20", a lipophilic modified dextran gel, which can achieve separations in non-aqueous systems.

This mode of separation, based on molecular size, offered a potential clean-up system for distinguishing organophosphorus pesticides (m.w. 200–350) from the common co-extractives chlorophyll (m.w. 906) and carotene (m.w. 536). Gel filtration using Sephadex LH-20 in ethanol was shown by Horler[25] to be a practical method for the single stage clean-up of insecticide residues from grain. Such clean-up was considered adequate for thin-layer chromatography. The possible use of the technique for the determination of organophosphorus pesticides was investigated by Ruzicka *et al.*,[26] the gel being swollen and eluted with either acetone or ethanol. Efficient separation of these pesticides from co-extractives could not be achieved, much of the pigment material eluting in the range in which pesticides were found to emerge. However, they found the observed elution volumes of the compounds examined were constant and distinctive and the sequential order differed for the two solvents. The technique is therefore useful for the identification of organophosphorus pesticides at the residue level and has been incorporated in an analytical scheme by Askew *et al.*[27] for the qualitative confirmation of the presence of these compounds in river waters. A chromatographic system using "Bio-Beads S-X2" and cyclohexane was successfully used by Stalling *et al*,[28] for the removal of lipids from fish extracts before the determination of commonly occurring pesticides and polychlorinated biphenyl residues. A useful feature of gel chromatography is that the column can be used repeatedly over long periods without any detectable change in the elution volumes or the recoveries. Application of the technique to organochlorine pesticides has not been successful as the separation is poor.

Calderbank[29] has reviewed the use of ion-exchange resins as a clean-up procedure. Cationic resins are particularly useful in the determination of "diquat" in potato tubers[30] and "paraquat" in fruit.[31]

END METHODS OF DETERMINATION

The main end determination methods used in residue analysis fall into three groups, namely, biological, spectrophotometric and chromatographic. Other methods such as electrochemical (chiefly polarographic) and radiochemical have been advocated, but their use is extremely limited.

Biological methods

Biological methods for the determination of pesticide residues include both bioassay and enzymatic techniques. They have the advantages of simplicity and sensitivity, their main disadvantage being a lack of specificity. Bioassay depends on the measurement of a physiological response of a test organism induced by exposure to the pesticide. Although the technique is relatively non-selective within the pesticide group tested for, it has been used to determine total residues of a particular group and of pesticides of known identity.[32] The insect bioassay technique has been adequately reviewed by Sun.[33]

A parallel biochemical system dependent upon the inhibition of the enzymes carboxylesterase and cholinesterase by organophosphorus and certain carbamate pesticides has been found to be particularly useful when combined with TLC. Several workers[34–36] improved the sensitivity of the combined TLC and enzyme-inhibition procedures by incorporating indoxyl acetate as the fluorogenic agent. Typical detection limits by this procedure are "carbaryl" 0·5 ng, "carbofuran" 5 ng, "propoxur" 10 ng, "parathion" 0·1 ng and "malathion" 2·5 ng.

Spectrophotometric determination

Spectrophotometric determinations of pesticide residues rarely achieve the sensitivity of thin-layer and gas chromatographic techniques. They may not be able to distinguish between the parent compound, metabolites and hydrolysis products, but can be utilized along with chromatography as a confirmatory technique. There are three types of spectrophotometric determination, based on (*a*) ultraviolet and visible (700–700 nm) (*b*) infrared (2–15 μm) and (*c*) fluorescenec and phosphorescence methods.

Ultraviolet and visible. Ultraviolet methods require a rigorous clean-up to ensure that the final solution is free from any other material that will absorb light in the region of the spectrum in which the pesticide content is to be measured. The solvent used for the initial extraction of a crop material should be chosen with care to ensure extractability of the pesticide and with consideration of its ultimate effect on the analysis in the ultraviolet region.

Since most pesticides are not coloured a chromophoric structure must be created or introduced into the pesticide molecule before it can be determined spectrophotometrically in the visible region. This colorimetric method of detection is specific to the functional group or other moiety involved in the colour-producing reaction.

Ultraviolet and visible spectrophotometry are commonly used in the determination of compounds which are difficult to separate by gas chromatography such as the acids 2,4-D[37] and 2,4,5-T,[38] and the ionic bipyridinium herbicides diquat[39] and paraquat.[40] A distinct advantage of colorimetric end detection methods is that they are readily adaptable to automated analysis.

Many of the chlorinated pesticides have been determined by colorimetric methods but with the advent of gas–liquid chromatography with its superior detection limits, they have rapidly lost favour. Fresh interest has been shown recently in the colorimetry of organophosphorus pesticides in an automated process. This method determines total phosphorus, so a suitable extraction and clean-up procedure is necessary to remove natural phosphorus-containing compounds. Direct spectrophotometric techniques can be used for water-quality monitoring or for confirmatory evidence after chromatographic separation. In many cases the sensitivity and selectivity of spectrophotometry after clean-up is sufficient for identification and quantification of organic pesticides, especially aquatic herbicides, in water.

Infrared methods. This absorption spectrophotometric technique is useful in pesticide residue analysis as it is possible to obtain qualitative identification as well as quantitative determination with one physical measurement. Generally, relatively large quantities of pure material are required to obtain suitable spectra. Good spectra can be obtained with microgram quantities of pesticide provided that background absorption due to extraneous extractives is low. The problem of obtaining a clean extract is the major disadvantage. Quantitative infrared analysis also requires scrupulously water-free solutions and thus the drying of reagents and final aliquots is necessary. Unfortunately some of the common solid drying agents may absorb or react with the pesticide and most do not remove water completely.

Pesticides can be separated and collected by gas–liquid chromatography with a fraction collector or by preparative thin-layer chromatography, and the infrared spectrum obtained by micro-infrared techniques. This procedure is particularly useful when multiple residues are present.[41]

Fluorescence and phosphorescence methods. Fluorometric methods, if applicable, are preferable to absorption methods because selectivity of measurement and sensitivity of determination are generally greater. The principal disadvantages are the limited applicability and the difficulty in obtaining suitable clean-up procedures which will remove naturally occurring fluorescent biological materials. The relationship between fluorescence and concentration is linear only up to a certain concentration.

A survey of the phosphorescence of certain pesticides and potential utility of the technique was made by Moye and Winefordner[42] who obtained the excitation and emission spectra, decay times, analytical curves and limits of detection for 32 pesticides in $10^{-2}M$ ethanolic solution. Based on the fluorescence and phosphorescence spectra obtained by Bowman and Beroza[43] for methylenedioxyphenyl synergists, fluorescence methods were developed to determine piperonyl butoxide residues in commercial fly-sprays, stored grain and milled products. Fluorescence analysis provides a rapid and sensitive method for the determination of carbonate residues, which are not readily determined by gas chromatography, and has been used for screening milk samples for carbamates. The fluorescence in methanol–tetramethylammonium hydroxide solution was measured.[44] Carbaryl and 1-naphthol have been determined in bees, pollen and honey by measurement of the fluorescence in $0{\cdot}25M$ sodium hydroxide.[45] Freed and Hughes[46] suggested the technique for the determination of low concentrations of the herbicide diquat. They found a linear relationship between the fluorescent intensity and concentration over the range 0.1–6.0 μg/ml. Unfortunately the procedure is inapplicable when small concentrations of the compound are to be determined in plant material because of interference from naturally occurring substances remaining after clean-up.

Fluorescence intensity is dependent on a number of experimental conditions, the most important being the solvent effect and the pH. These factors are discussed in the review articles by MacDougall.[47,48]

Chromatographic methods

Paper chromatography. This is the simplest method of identification and estimation. It gives a reasonable degree of sensitivity and selectivity for chlorinated and organophosphorus insecticides and chlorophenoxy acid type herbicides. Before the introduction of gas and thin-layer chromatography, paper chromatography was the only process generally applicable to the separation and indentification of many pesticide residues. Thin-layer has virtually replaced paper chromatography in pesticide residue analysis because of its increased resolution and shorter development time.

Generally when paper chromatography has been used for pesticide residue analysis, no chemical modification of the paper has been made but acetylated papers have been used for the reversed-phase separation of organophosphorus pesticides.[49] Fibre-glass papers have also been used for the reversed-phase chromatography of organophosphorus compounds.[50] Paper chromatography has been used for the determination of organochlorine herbicides in soil and water.[51] substituted urea herbicides and their trichloroacetates[52] and for the determination of organophosphorus residues in foodstuffs.[53] The use of paper chromatography in pesticide residue analysis has been reviewed by Getz[54] and Coffin.[55]

Thin-layer chromatography (TLC). This technique has grown rapidly in importance in recent years and is now widely accepted as a quick and efficient technique for the detection and determination of very small quantities of the majority of pesticides. Though lacking the precise specificity of gas-liquid chromatography, thin-layer is more precise and more sensitive than paper chromatography. TLC can be used in pesticide analysis for diagnostic work, for accurate quantitative evaluation and as a clean-up procedure for sample extracts. The adsorbent layer on the glass plate should present an even, firm and continuous surface. For most pesticide residue work a 0·25-mm layer of alumina or silica gel gives the best results, but other adsorbents such as kieselguhr and magnesium oxide are also useful in some circumstances. Recent developments have made use of polyamide layers and the microcrystalline cellulose "Avicel".[56]

After air-drying, the applied layer is completely dried and activated by heating the plate in an oven at 120° for 2 hr, and then cooled before use. The solvent in the solutions to be spotted on the plate should be volatile and care must be taken that the micro-pipettes used for spotting do not penetrate the surface layer. Standard solutions of pesticides must be developed on the same plate as the sample, preferably on both sides of the sample spot. For TLC of organochlorine compounds a number of mobile phases may be used, but it is important that the developing tank contains a saturated and stabilized atmosphere. The chromatogram is developed by the ascending technique, with the plate vertical and the start line approximately 1 cm above the solvent surface. After development the plate is air-dried and then the pesticides may be visualized by various means. One method is to spray the plate with ethanolic silver nitrate solution and irradiate with ultraviolet light, the pesticide spots appearing as dark areas against a white background. This process is not particularly sensitive, the detection limit being approximately 0·5 μg, and discolouration of large areas of the plates occurs unless precautions and care are taken. If the silver nitrate is incorporated into the adsorbent layer improvement is obtained and organochlorine pesticides in the 5–200 ng range can be detected.[57–58] Other visualizing agents that have been used are aromatic amines, bromine vapour and fluorescent indicators such as fluorescein, Rhodamine B and dichlorofluorescein.

Two-dimensional development of chromatograms with hexane and cyclohexane on silica gel chromatoplates has been used for the identification of organochlorine pesticides in blood and tissues.[59] Another development has been the use of one-dimensional chromatography but using multiple development. This technique has been used for the separation of thirteen commonly occurring organochlorine pesticides.[60] The thin-layer chromatographic behaviour of ninety pesticides on Florisil with five solvent systems has been studied.[61] A rapid screening test for detecting organochlorine pesticides present in fats and vegetables by using TLC has been published and may be useful for surveys.[58]

Carbamates which are difficult to analyse by gas chromatographic techniques have been identified and determined by TLC. Ramasamy[58] published data for seven carbamates, using a combination of two different adsorbents, three solvent systems and three chromatogenic sprays. Mendoza and Shields[63] developed a TLC–enzyme-inhibition technique which they used to detect carbamate and organophosphorus pesticides. This technique enabled carbaryl to be detected at the low level of 0·1 ng. *N*-Phenyl-, *N*-methylcarbamates and related ureas have been detected, separated and identified by thin-layer chromatography.[64] Using polyamide layers, Nagasawa and his co-workers[65] separated and determined carbamates and related compounds. They compared the detection limits on polyamide and silica gel layers and confirmed the superiority of polyamide layers. Abbott *et al.*[66] have described a TLC procedure for the separation, identification and estimation of some carbamates in soil and water.

The organophosphorus pesticides are also susceptible to treatment by TLC using adsorbents and mobile solvents similar to those used for organochlorine pesticides and carbamates. The merits of TLC in the separation of organophosphorus pesticide residues have been reviewed.[67,68] Getz and Wheeler[69] have reported the separation and selective visualization of 42 organophosphorus compounds. They used five ternary solvent systems and three selective chromatogenic sprays for the identification of the migrated spots. The use of polyamide layers has been recommended.[70,71] Watts[72] has reviewed the use of chromatogenic spray reagents for the detection of organophosphorus pesticides. The separation and identification of organophosphorus pesticides from tissues for medico-legal purposes has been achieved by the use of two-dimensional TLC.[73] Fluorescent silica gel can be used to separate and detect organophosphorus pesticides. Villeneuve *et al.*[74] have made an assessment of the applicability of these gels. Because the organophosphorus pesticides are inhibitors of esterases the combination of TLC with cholinesterase detection methods permits very rapid and sensitive procedures for separation and detection. The work done by Mendoza *et al.*,[34,75,76], Ackermann,[77,78] Winterlin *et al.*,[79] and Ernst and Schuring[80] gives examples of this technique. TLC is particularly applicable to herbicides, many of which are of a polar nature and not susceptible to gas chromatography unless first converted into a suitable ester or derivative. It has also been used for the detection and determination of phenoxyaliphatic acids[51,81] and phenylurea herbicides.[82] Cellulose layers have been used for the separation of dinitrophenols and their methyl ethers.[83] The various aspects of the detection and determination of residues of triazine herbicides by TLC have been reviewed.[84–86]

For a simple, rapid and inexpensive procedure for determining minute amounts of some herbicides Coha and Kljajic[87] have suggested a combination of TLC and ring-oven. Homans and Fuchs[88] have used direct bioautography on thin-layer chromatograms for the detection of fungitoxic substances. TLC has been used for organomercurials: Takeshita *et al.*[89] detected mercury and alkylmercury compounds by reversed-phase TLC. It has also been used for estimating methylmercury in fish, meat, liver and eggs.[90,91] The thin-layer characteristics of the dithizonates of a number of organomercurial fungicides in common use have also been studied.[92]

Gas–liquid chromatography (GLC). The most versatile and sensitive end-method for pesticide residue analysis is undoubtedly gas–liquid chromatography. Following considerable research to perfect this technique some features of the apparatus have become standard. The column tubing is usually made of glass and 1 or 2 m in length, but Crossley[93] has suggested the replacement of glass or metal by Teflon. Columns of copper and stainless steel are best avoided as both can cause decomposition of compounds on the column unless precautions are taken.

The most used stationary phases for the GCL analysis of pesticides are the organosilicones SE30, QF1 or DC200; mixtures of QF1 and DC200, "Apiezon," butane-1,4-diol succinate, "Versamid 900," "Carbowax" 20M and GE-XE60. A recent introduction is a phenylmethylsilicone, OV 17, which has been used by itself or mixed with the fluorosilicone QF1.[94] After examining five different stationary phases, Taylor[95] found the most suitable one for chlorinated pesticides was a mixture of QF1 and neo-pentylglycol succinate. The retention times and responses for 60 organophosphorus pesticides and metabolites on three different stationary phases[96] have been reported.[96]

It cannot be over-emphasized that all samples should be examined on at least two different types of column and no conclusions should be drawn unless the results agree. If necessary, injections should be made on a third type of column with a different composition from the other two. The two (or three) columns used should incorporate stationary phases of differing polarities so as to produce different sets of relative retention times for the various pesticide residues.

The electron-capture (electron-affinity) detector has become the standard detector for organochlorine compounds, with either tritiated titanium on copper foil, or a nickel-63 foil as the source of beta-radiation. The latter detector is more expensive but can be used at temperatures above 250°, which would damage the tritiated detector. The nickel-63 detector can be used up to a maximum of 400° and its use at high temperatures reduces the possibility of contamination of the source from sample impurities and from bleeding of the liquid phases from columns. In the U.S.A. the most commonly used detector for organochlorine pesticides was originally the microcoulometric detector but except for certain special purposes it has now been replaced by the electron-capture detector. The electron-capture detector responds to all electron-capturing species whereas the microcoulometric detector can be operated to be specific for halogenated compounds. The microcoulometric detector originally lacked sensitivity but modifications have lowered the detection limit for sulphur or halogen to about 10^{-9} g. This detector is still relatively expensive for residue work despite its high degree of specificity. The theory and modes of operation of electron-capture gas chromatography have been reported by many authors. Amongst these are Lovelock and Lipsky,[97] Lovelock,[98–100] Clark,[101] Dimick and Hartmann,[102] Gaston[103] and Peters and Schmidt.[104] These references should be studied for an understanding of electron-capture detection and the effect of various gas chromatographic parameters.

It is only in very recent years that GLC of organophosporus pesticides has reached a state comparable with that achieved in the organochlorine field. The electron-capture detector can be used for a few organophosphorus compounds such as "parathion" and "fenchlorphos" which contain certain electrophoric groups such as Cl and NO_2 but the sensitivity is generally rather low, requiring about 5 or 10 ng to produce a reasonable response. The flame-ionization detector is equally sensitive to organophosphorus compounds and to hydrocarbons. The need for a highly sensitive detector for these compounds was met with the introduction by Giuffrida of the sodium thermionic detector.[105] This was an important development because the detector showed a special sensitivity to phosphorus and nitrogen compounds and was comparatively insensitive to chlorine compounds. The detector consisted of a flame-ionization detector with the cathode coated with a sodium or other alkali metal salt. Unfortunately the sodium thermionic detector proved unstable in practice because its sensitivity declined rapidly and it required constant recharging with fresh sodium salt. Hartmann[106] fitted a tip made of caesium bromide and Celite prepared under high pressure. This tip was positioned on the burner so that the gas flow passed through a hole in it and the flame was produced at the exit hole; thus the flame produced contained caesium ions. The caesium tip enhanced the stability of readings and also had a reasonable working life. The sensitivity of this detector is of the order of 2 ng for full scale deflection, with no baseline noise, but for compounds with shorter retention times, such as "dichlorvos," the sensitivity is increased; full-scale deflection can be readily obtained with 0·4 ng. Conversely, the detector is less sensitive to compounds with long retention times, such as "carbophenothion," of which 5 ng are required to give full-scale deflection. The sensitivity of the instrument can be improved by re-injecting the sample extracts on shorter columns at higher temperatures. This considerably shortens the retention times with corresponding narrowing and sharpening of the chromatogram peaks, coupled with loss of resolution. A very comprehensive review of thermionic detectors used in gas chromatography has been recently published.[107] Under specific instrumental conditions the alkali-metal flame detector will give negative peaks for chlorine-containing compounds and positive peaks for bromine-, iodine-, nitrogen- and phosphorus-containing compounds. The detector has been used in the nitrogen mode for determining carbaryl direct without converting it into a derivative.[108] The negative response was used to detect chlorinated pesticides in soil at levels between 0·01 and 10 mg/kg without purification of an exhaustive hexane extract.[109]

Recent developments in detectors specific for phosporus compounds have included the flame photometric detector. Draegerwerk and Draeger[110] were granted a German patent in 1962 for the detection of sulphur and/or phosphorus compounds in air by flame photometry in a hydrogen-rich flame. Using this principle Brody and Chaney[111] produced a detector sensitive to subnanogram amounts of phosphorus compounds and/or submicrogram amounts of sulphur compounds, but relatively insensitive to all other organic compounds. The principle upon which the detector is based is the photometric detection of flame-emission of phosphorus and sulphur compounds in the hydrogen–air flame. The flame is monitored by a photomultiplier tube which has an interference filter for spectral isolation of the particular emission. The filter at 526 nm is used to sense phosphorus compounds while a second photomultiplier tube with a 394 nm interference filter for sulphur compounds provides an additional check on pesticides based on phosphorothioic acids. The usefulness of the detector for measuring organophosphorus pesticide residues in extracts of plants and animal products, with and without clean-up, has been reported.[112] The detector has been used for the determination of organophosphate pesticides in cold-pressed citrus oils[113], oranges, apples, sugar beet and potatoes.[114] Beroza and Bowman[115] concluded that GLC with flame photometric detection was a verstile, sensitive, reliable and efficient means of analysing pesticides and their metabolites containing phosphorus or sulphur. The detector also proved useful for analysing insecticides such as carbamates in the form of derivatives containing phosphorus or sulphur. By the use of two columns of differing polarity together with the flame photometric detector, Stanley and Morrison[116] identified organophosphate pesticides by comparison of the peak retention times of the unknown sample with those of a known sample. The flame detector has been improved by combining the phosphorus and sulphur detectors into a single unit.[117] Since the two detectors monitor the same burning effluent from the gas chromatographic column, precise determination of their relative response to various compounds may be made. Using twenty-one pesticides at three concentrations Bowman and Beroza[117] found that the phosphorus response was linear with concentration but the sulphur response was not. They defined the response ratio as the phosphorus response divided by the square root of the sulphur response. This ratio provided a means of estimating the atomic ratio of phosphorus to sulphur in a molecule. The operating temperature of the flame photometric detector was approximately 160° but by replacing the original air-cooled heat-sink with a water-cooled one the operating temperature could be increased to 250°.[118]

For the detection of halogenated compounds Bowman and Beroza[119] used a gas chromatographic photometric detector which responded to the green flame obtained when compounds containing chlorine, bromine and iodine burn in the presence of copper. The sensitivity of the detector to chlorinated hydrocarbons was usually 100 ng, but for the analysis of chlorinated pesticides in crops a thorough clean-up was required because the copper screen used in the detector could easily be deactivated. Unlike the normal flame-photometric detector, it was not highly selective. A recent development has been the combination of the two different flame photometric detectors to give the dual-flame photometric detector.[120] In the lower flame the compounds emerging from the column are burnt and monitored for sulphur and phosphorus. Between the upper and lower flames is a stainless-steel net holding indium pellets. The chlorine-containing compounds react with indium and the resulting emission is monitored at a wavelength of 360 nm. In this way, the simultaneous and selective determination of phosphorus-, sulphur- and chlorine-containing compounds eluted from a GLC column can be obtained.

Another specific detector is the Coulson electrolytic conductivity detector[121] which operates in the following manner. The column effluent passes into an aluminium block where it mixes with a reactant gas (either oxygen or hydrogen). The mixture passes into a pyrolysis tube containing a combustion catalyst. The pyrolysis conditions are then chosen to produce a water-soluble species containing only the desired element. Thus for halogen detection the pyrolysis unit contains a platinum gauze which gives oxidizing conditions, the products being sulphur dioxide and hydrochloric acid. The sulphur dioxide can be removed by a scrubber of calcium oxide and the hydrochloric acid can then pass into conductivity water. The change in conductivity of this water is measured and can be related to the organochlorine pesticide content. For nitrogen detection the column effluent is reduced, with a nickel catalyst, and the interfering species are removed with a strontium hydroxide scrubber. The Coulson detector can therefore be useful as a specific detector for nitrogen-containing pesticides such as the triazines. It is also useful for the determination of chlorinated pesticidal residues when the solution has not been satisfactorily cleaned up for electron capture. An evaluation of the electrolytic conductivity detector for residue analysis of nitrogen-containing pesticides has been made. The wide distribution of naturally occurring compounds did not present any serious obstacles to the use of this detector at the 0·02 mg/kg level in the analysis of crops.[122]

A highly selective detector which was reported as early as 1965 and has yet to come to the fore is the emission spectrometer detector. Bache and Lisk pioneered this type of detector and have successfully used it for determining organophosphorus pesticides,[123–126] carbamate and triazine pesticides[127] and organomercurials.[128] The detector responds to the emission from the atoms of a specific element carried in a helium or argon stream from a gas chromatograph, when passed into a microwave-sustained plasma discharge at either atmospheric or reduced pressure. Reduced pressure permits the use of helium as the carrier gas with the advantage of less background radiation and higher excitation energy than argon plasmas. All elements of organic compounds can be detected and it is possible to examine for more than one element simultaneously. Dagnall *et al.* have published several papers on the detector, including a short review article on its evaluation.[129] Attractive features of this detector are its sensitivity, range of linearity and the multi-channel examination of the various specific emission lines of the constituent atoms of compounds. Detection limits for most elements are of the order of 0·1–1·0 ng/sec; for oxygen and nitrogen they are about 3 ng/sec. Moye[130] compared the electron-capture detector and the microwave emission detector responses for celery extracts containing 10 μg per kg; of parathion. 10 ng of parathion gave the same response with the microwave instrument as 1 ng with the electron-capture instrument, but there was a complete absence of extraneous peaks with the microwave detector.

A new flameless ionization (chemi-ionization) detector has been proposed recently.[131] When phosphorus compounds from the column pass into a heated atmosphere of caesium bromide vapour and inert gas, ionization takes place and can be detected. Results from this detector for several organophosphorus pesticides were compared with results obtained with an alkali metal flame-ionization detector. Although the flameless ionization detector was less sensitive to phosphorus compounds, it was also much less sensitive to the hydrocarbon solvent. This gives the flameless ionization detector a certain degree of specificity to non-hydrocarbons, the resulting chromatograms being cleaner, with fewer interfering peaks.

Liquid–liquid chromatography. Liquid–liquid chromatography has taken its place beside

GLC as a powerful technique for the separation and analysis of complex mixtures. Separation depends on the compounds having sufficiently different partition coefficients in the selected solvent system, and by this technique an extremely wide range of compounds can be separated, since there are no limitations set by volatility requirements. Modern liquid chromatographs are characterized by small-particle column packings (down to 5 μm), narrow-bore columns (as small as 1 mm) and high inlet pressures (up to 5000 psig). Suitable column packing materials are reviewed by Kirkland[132] and Majors.[133] Important recent developments include the use of stationary phases chemically bonded to the support material and also controlled surface-porosity supports. Commercially available detectors include refractometers and those based on electrolytic conductivity, heat of adsorption, spectrophotometry, and flame ionization. Various systems have been used to transfer the sample from the liquid chromatograph column to the flame ionization column. These include a carrier wire,[134] a closed-loop[135] and a rotating circular net.[136] The last system, with its greatly increased surface area, overcomes the deposition problems of the earlier "wire collectors." Cassidy and Frei[137] have published details of a fluorescence detector with which 3 ng of 4-methylamino-7-nitrobenzo-2,1,3-oxadiazole (a fluorogenic labelling compound) could be detected consistently. Lambert and Porter[138] reported the application of liquid–liquid chromatography to the analysis of insecticides, using water–ethylene glycol as the stationary phase, adsorbed on siliconed fire-brick, and hexane–carbon tetrachloride as the mobile phase. A pressurized-flow scheme incorporating an automatic recording differential refractometer as the detector was employed.

Bombaugh *et al.*,[139] using a high-performance liquid chromatograph, determined organochlorine pesticides which were separated on a Corasil II column with n-hexane as solvent. The separated insecticides were detected with a differential refractometer and the sensitivity was of the order of 1 μg. Liquid chromatography also offers a means of carrying out a rapid and direct analysis of such compounds as the insecticidal carbamates ("carbaryl," "butacarb" *etc.*) and their hydrolysis products, with minimal interference from the biological matrix.

The logical combination of liquid chromatography and polarography was looked at initially by Kemula.[140] Separation of the components of a mixture by liquid chromatography overcomes the limitation of polarography when dealing with a mixture containing components of similar half-wave potentials and permits its use as a specific detector. The use of a carbon-impregnated silicone rubber membrane as an alternative to the dropping-mercury electrode has been examined[141] and subsequently evaluated as a detection method for high-speed liquid chromatography.[142]

Polarography

Polarography has been applied to the detection and determination of several pesticides. Although classical polarography has poor selectivity and low sensitivity, it can be used for the analysis of nitro compounds such as commercial parathion products. The fast sweep used in cathode-ray oscillographic polarography makes the instrument particularly useful in quickly finding suitable polarographic conditions and for completing rapid determinations. To yield a polarogram the compound must contain an oxidizable or reducible group such as nitro, halogen, carbonyl, *etc.* Pesticides not containing such a group can usually be determined by formation of a suitable derivative. From the published literature on polarographic behaviour, solvents and electrolytes may be selected and their suitability can be tested in the laboratory.

Gajan[143] and Allen[144] have reviewed the application of polarography to the detection and determination of pesticide residues.

Radiochemical techniques

In neutron-activation analysis, radioactivity is induced in the trace elements. The concentration of these trace elements (as low as 1 μg/kg) is determined by measuring the radiation so induced and comparing it with that of standard samples. The technique has found only limited use because expensive equipment is involved, but its potential in the analysis of pesticides has been discussed by Bogner.[145] Schmitt and his co-workers[146,147] developed a quick neutron-activation method for determining several elements, including bromine and chlorine, in milk products and fruit.

Radioactive isotopes have often been used in metabolism studies (for example[144] metabolism of "trichlorfon" by using p^{32}), and in the development of analytical methods for routine residue determinations. The technique involves the introduction of a radioactive atom into the pesticide molecule. By tracing the radioactivity emitted, the progress of the pesticide through the metabolism or analytical method may be closely followed. The method is quite sensitive (0.1 μg/kg for pesticides) and measurement is relatively independent of the chemical and physical state of the sample to be measured. The common isotopes used are ^{3}H, ^{14}C, ^{32}P, ^{35}S, ^{36}Cl, and ^{82}Br, of which ^{14}C is the most important.[149,150] A disadvantage is that most pesticide laboratories are not equipped to synthesize their own radioactive compounds.

Isotope-dilution analysis is a means of measuring the yield of a non-quantitative process and it also enables an analysis to be performed where no quantitative isolation procedure is known. A known weight of a radioactive compound is added to an unknown mixture containing that compound. They mix chemically indistinguishably. A small amount is isolated and determined chemically and radioactively. The proportion of radioactive compound to the total gives the dilution and hence the original concentration. The method has been used by Bazzi for determining "dimethoate" and "Cidial".[151]

Derivative formation

Derivatives of pesticides are prepared for two main reasons. These are (*i*) altering the structure in order to aid characterization, a technique discussed in the section covering confirmatory techniques, and (*ii*) increasing the stability of the compound to permit chromatography. Furthermore, a particular detection system is often more responsive to the conversion products. Formation of a new compound may be necessary in order to decrease the volatility of the pesticide for paper of thin-layer chromatography, increase the volatility and/or stability for gas-liquid chromatography, enhance the sensitivity of a particular detector to the pesticide, or to avoid non-Gaussian peaks.

The need for derivative formation is clearly shown by the carbamate series of compounds which are used as herbicides and, in some cases, insecticides. Few carbamate pesticides can be gas-chromatographed directly, because of thermal breakdown and poor detector response. This has led to an interest in the formation of derivatives from products of hydrolysis of the pesticide. The method of Cohen and Wheals[152] involves hydrolysis and formation of the 2,4-dinitrophenyl derivative of the amine on a silica gel thin layer. The derivative is extracted and injected into a GLC column. Frei and Lawrence[153] have investigated the formation of fluorescent carbamate derivatives. Under optimum conditions, by use of dansyl chloride and TLC separation, nanogram levels of carbamates could be determined instrumentally

Recently they published details of the use of 4-chloro-7-nitrobenzo-2,1,3-oxadiazole (NBD-Cl)[154] which was considered to be superior to dansyl chloride in that it does not form fluorescent derivatives with phenols, thiols, alcohols or anilines, and, unlike dansyl chloride, the hydrolysis product of NBD-Cl is non-fluorescent. By use of this reagent, carbamates at the μg/kg level have been determined in water and soil samples. Seiber[155] has proposed the formation of the *N*-perfluoroacyl carbamate derivatives. These are stable to gas chromatographic conditions and may be detected by electron-capture and alkali metal flame detectors. The method of forming the 2,4-dinitrophenyl ethers has been extended to phenols in general, which usually show tailing characteristics and poor detection sensitivities.[156] Herbicide acids also have poor chromatography characteristics but the problem has been overcome by the preparation of the methyl derivatives.[157,158]

CONFIRMATORY TECHNIQUES

It is important that the identity and level of pesticide residues determined should be confirmed by a different method from that used in the determination. When the end determination method is TLC, confirmation can be obtained by using alternative developing solvents or visualizing agents. Frequently the pesticide can be removed from the thin-layer plate with a suitable solvent and injected directly on to a gas chromatograph.

Interference peaks may occur on gas–liquid chromatograms even when the most selective detectors available are used. It is poor technique to run samples on only one column and in some cases two columns are insufficient. The diagnosis of BHC isomers on chromatograms is hindered at times by the presence of hexachlorobenzene (HCB). This compound is eluted along with α-BHC on silicone columns and at the same retention time as γ-BHC on Apiezon but all three compounds are resolved on a cyano-silicone column. However, despite the fact that resolution can be effected on polar columns, further proof of identity is desirable. The pentachlorophenyl propyl ether derivative prepared by Collins *et al.*[159] can be used to confirm HCB at the nanogram–microgram level by GLC. When "dieldrin" and "*pp*′-DDE" occur together in a sample extract there is no separation on a silicone column. Both the Apiezon and cyano-silicone columns will resolve the mixture but with the latter the order of emergence is reversed, *i.e.*, *pp*′-DDE appears before dieldrin.

A simple confirmation technique for GLC is afforded by TLC when the levels of residues present are high enough. An aliquot of the cleaned-up extract, calculated to contain a suitable amount of the pesticides, can be evaporated to dryness, dissolved in a suitable solvent and run on a thin-layer plate together with the appropriate standards. The identity of the residues can be confirmed and the levels substantiated within the limited quantitative nature of thin-layer chromatography.

For a limited number of pesticides GLC results obtained by using one detector can be confirmed by using another type of detector. Thus a microcoulometric detector can be used with an electron-capture detector for organochlorine compounds and the thermionic and flame photometric detectors for the organophosphorus compounds.

Nuclear magnetic resonance (NMR) spectroscopy is one of the most important tools for the structural elucidation of organic molecules and therefore finds a place in pesticide analysis. It is an extremely useful technique for structural elucidation of pesticide metabolites and degradation products, for structural confirmation of new pesticides, or for product analysis of existing ones. It has also been used for the confirmation and estimation of relative concentrations of *pp*′-DDT and *pp*′-DDE isolated from adipose and liver tissue samples.[160] Because NMR spectroscopy has low sensitivity and pesticide residues generally encountered are at low concentration, it has at present only limited use in residue work. Reference spectra of pesticides have been published and will be useful for identity confirmation. Keith *et al.*[161] have presented a description of the 100-MHz nuclear magnetic resonance spectra of forty organophosphorus pesticides. The more interesting and unusual spectral features are discussed and reproductions of some of the spectra have been included. The same authors also published reference spectra for commercially available pesticides having the diphenylmethane or substituted diphenylmethane skeleton.[162] The NMR spectrometer was used quantitatively to determine the amount of each isomer present in a mixture. The mixtures were technical DDT (containing *o,p*′-DDT and *p,p*′-DDT) and a mixture of "Bulan" [1,1-bis(4-chlorophenyl)-2-nitrobutane] and "Prolan" [1,1-bis(4-chlorophenyl)-2-nitropropane]. Keith and Alford[163] extended their work by the publication of the NMR spectra of compounds of the carbamate class of pesticide. They also reviewed the application of NMR spectroscopy to pesticide analysis.[164] Residues of *p,p*′-DDT and *p,p*′-DDE have been isolated from liver and adipose tissue and subjected to NMR and GLC using electron-capture and conductivity detectors. The results show that NMR can be used to confirm the presence and to ascertain (semi-quantitatively) the relative composition of pesticide residues isolated from tissue samples. In preparation for the application of photoelectron spectrometry to pesticide analysis, Baker *et al.*,[165] have examined five-membered aromatic heterocyclic and related molecules. This technique, which measures the binding energies of electrons in molecules, can be used to give structural information.

Mass spectrometry, because of its high sensitivity, is a useful technique in the identification of pesticides isolated from residues. It is widely used for the analysis of individual pesticides and metabolites isolated by conventional separation techniques such as TLC, GLC *etc.* When mass spectrometry is coupled to gas chromatography it enables positive identification to be made of the components of mixtures without prior separation and at a sensitivity compatible with the low level of residues encountered. Under ideal conditions, quantities as small as 10 ng will produce a useful mass spectrum. Using an extensive extraction and clean-up procedure adapted from existing analytical methods, Biros and Walker[166] separated pesticide residues from human adipose and liver tissues. Identification, quantitative determinations and confirmation of the pesticide residues were carried out with a combined gas chromatograph (with electron-capture detection) and mass spectrometer. The pesticides found were β-BHC, γ-BHC, heptachlor epoxide, dieldrin, *p,p*′-DDE, *p,p*′-TDE, *o,p*′-DDT and *p,p*′-DDT. The authors discuss the advantages and limitations and suggest modifications for improving the combined technique.

One very important use of mass spectrometry is the confirmation of pesticides in the presence of polychlorinated biphenyls (PCB's). It is difficult to separate these compounds from chlorinated pesticides because they have similar chromatographic and electron-capture characteristics. Techniques for identification of trace quantities of PCB's and chlorinated insecticides in crude natural samples and their semi-quantitative determination by mass spectrometry have been investigated.[167] Bagley *et al.*[168] have identified PBC's in the presence of organochlorine pesticides by combined GLC–mass spectrometry. From the spectral data obtained they showed that the compound extracted was identical with a particular PCB, *viz.* "Aroclor 1254."

The recent development of high-resolution mass spectrometry permits the accurate measurement of masses of ions produced in the spectrometer. The precise mass of any ion is dependent on its atomic constituents and hence the elemental composition of the pesticide molecule from which the ion was formed. Therefore, by measuring precise ionic masses, it is possible to recognize individual pesticides in complex mixtures without prior separation into the components. Lovins[169] investigated several mixtures of chlorinated pesticides and one of organophosphorus pesticides, using this technique. A mixture containing "parathion," "malathion," "carbophenothion," "diazinon," "ethion" and "OMPA" was one of those for which successful identification of the individual components was achieved. The method at present is limited to distinguishing between species of different elemental composition and cannot differentiate between two structurally isomeric pesticides of identical elemental composition such as *p,p'*-DDT and *o,p'*-DDT. The mass spectra of isomeric compounds differ in the relative intensities of the ions in the spectra and work is under way for the accurate measurement of the relative intensities of the exact masses. With these data the isomeric pesticides can be identified and it is then hoped that the method can be used in the identification of pesticide residues in extracts of food and soil samples. Damico *et al.* have published the mass spectra of some bridged polycyclic chlorinated pesticides,[170] quinquevalent organophosphorus pesticide esters,[171] and carbamates.[172,173] Zink[174] has used the mass spectrometer to identify chlorinated phenoxycarboxylic acid herbicides. Tong *et al.*[175] have used spark-source mass spectrometry for the determination of mercury in apples, the method being sensitive to 0.002 ppm.

If an individual residue is sufficiently large and enough sample is available, then an infrared spectrum of the compound can be obtained and this will confirm the identity of the compound. Modern infrared spectrophotometers with their beam condensers and microcells of as little as 3 μl capacity can produce a clear trace from 10–20 μg of most of the organochlorine pesticides. By TLC or column chromatography these amounts can be separated before the infrared spectra are obtained. The infrared spectrophotometer is more sensitive to organophosphorus pesticides than to organochlorine pesticides. Amounts as little as 0·5 μg can give a good spectrum and these quantities can be obtained from a gas chromatograph equipped with a stream splitter, 1% of the effluent stream going to the detector for monitoring purposes and the remaining 99% going to a collecting device.[41] The use of infrared spectroscopy as a confirmatory technique requires the pesticide to be isolated in a pure form in microgram quantities.

Bowman and Beroza[176] have proposed a method of identifying or confirming the identity of pesticides at levels down to a nanogram through the use of extraction *p*-values. The *p*-value is determined by the equilibration of a solute between equal volumes of two immiscible liquid phases followed by the analysis of one of the solvents for the solute. This value can be derived from a single distribution between the phases or form a multiple distribution, as in counter-current distribution. Although the general technique has many analogies with the use of several gas chromatography columns in identification by retention volumes. it has the great advantage over that procedure of being both simpler experimentally and more versatile. It is especially useful for confirming the identity of pesticide residues at levels amenable to quantitative analysis by electron-capture gas chromatography.

AUTOMATION OF PESTICIDE ANALYSIS

In the pesticide residue field, wholly automated procedures from sample to final chart record are feasible for foodstuffs and soil, when minimum detectability requirements are not too stringent. In other instances, automated procedures can be used for the extraction and clean-up of samples and preparation of a concentrate for manual or automatic injection into a gas chromatograph.

To automate gas chromatography, it is necessary to provide a means for the automatic transfer of samples onto the column. Applegate and Chittwood[177] proposed such a system, using stainless-steel gauze rings onto which the sample solution is transferred. After the solvent is driven off, the rings are inserted into a slotted Teflon wheel mounted above the column. At suitable time intervals the gauze rings are dropped into a chamber where the sample is vaporized and carried on to the column by carrier gas. The technique was developed to analyse samples from a particular area when only DDT, methyl parathion and parathion were used. Eberle *et al.*[178] used a similar system with the sample solutions being transferred to capillary glass tubes, which after evaporation of the solvent are automatically passed into a heating chamber directly connected to the gas chromatograph. The system could handle about seventy samples and was used for the automated analysis of triazine herbicides and halogenated hydrocarbons. Stockwell *et al.*[179] described a method of automated injection for gas chromatography, together with internal standards. This system has not been applied to pesticides, but the use of injection rather than the alternative application methods could prove to be a significant advantage.

One of the methods of determining certain organophosphorus and carbamate pesticides is an enzymatic method based on the inhibition of cholinesterase, When the enzyme is incubated at pH 7·4 with a thiocholine ester, enzymatic hydrolysis takes place, yielding thiocholine. This is reacted with 5,5-dithiobis-(2-nitrobenzoic acid) to give the yellow anion of 5-thio-2-nitrobenzoic acid which can be measured colorimetrically at 420 nm. In the presence of organophosphorus pesticides the cholinesterase is partially inactivated, resulting in decreased hydrolysis of the ester. This inhibition of the enzyme can be measured and readily used in an automated determination of organophosphorus pesticides. With crop samples manual clean-up to remove interfering non-pesticidal phosphorus compounds is required before the automated technique can be applied. The samples can then be wet-digested automatically and the resulting orthophosphate determined by the automated measurement of the phosphomolybdate. The combustion products have also been adapted to an automated procedure.[181] Ott[182] has extended the determination to a dual system. The stream is split and the organically-bound phosphorus determined simultaneously by a colorimetric method and by cholinesterase inhibition. This method used in a screening programme offers greater validity than either system alone, with little extra effort required, but other evidence regarding the identity of the residue will also be required.

For the determination of organophosphorus insecticides and carbamates Voss also used an automated cholinesterase inhibition method.[183] He found that by changing the type of cholinesterase, sensitivity could be improved and up to forty samples an hour could be determined with a precision equal to that of manually performed chemical methods. Many of the thiolo- and thionophosphorus pesticides are converted into much more potent cholinesterase inhibitors by selective oxidation of the sulphur atom. An automated screening procedure measuring the inhibition before and after such oxidation is useful in giving total residue information. Leegwater and van Gend[184] used an automated enzymic procedure for the detection and determination of organophosphates and carried out differential analyses on samples before and after oxidation with bromine water. The method was applied to the screening of lettuce without requiring clean-up of the extracts.

A review article on the automated analysis of pesticides and screening techniques has been published by Gunther and Ott.[185] As an example the completely automated determination of biphenyl in citrus rind is given. The rind samples were automatically homogenized in water and then steam-distilled to liberate oils, waxes and biphenyl. The steam-volatiles were trapped in cyclohexane and the oils and waxes extracted into concentrated sulphuric acid and discarded. The isolated biphenyl was then determined at a wavelength of 246 nm. This automated method takes about 10 min compared with 2 hr for the normal method.

The Technicon "Auto-Analyzer" system has been used by Friestad[186] for the determination of "linuron" (3,4-dichlorophenyl-*N*-methyl-*N*-methoxyurea) in soils. The linuron is hydrolysed to 3,4-dichloroaniline and evaluated by diazotizing and coupling with *N*-(1-napthyl)ethylenediamine, the resultant diazo dye being readily determined spectrophotometrically at 550 nm.

Recent progress in the application of computers to determine low levels of pesticides has resulted in a reduction in the time required for calculations. Modern gas chromatographic systems can be readily adapted to computers as the nature of the gas chromatographic signals permits the insertion of digitizers between the chromatograph and the computer. A system has been devised by Jennings *et al.*,[187] who used a magnetic tape analogue-to-digital conversion, in which a tape playback supplies data for the digital integrator interfaced with the computer. The recording device receives the analogue signal, converts it into a digital signal and records it on magnetic tape. The magnetic tape is replaed on the playback system to yield the results through the integrator computer system.

PRESENT PROBLEMS

The residue analyst's chief task is the identification and estimation of pesticide residues, and in carrying this out many problems are encountered. Examples of these are the disappearance of the pesticide owing to metabolism, break-down, or volatilization, and the nature of metabolites and other end-products, particularly those of toxocological significance. Unlike the persistent organochlorine pesticides, many organophosphorus pesticides breakdown or are metabolized within a few days, and in some cases a few hours, after application. For example, the P–S grouping can be readily oxidized to P–O, and sulphide groupings are oxidized to sulphoxides and sulphones. Because some of the metabolites may be more toxic than the parent compound, it is necessary to be able to establish the presence of these compounds also. As the polarity of the metabolites may differ from that of the parent, extraction and clean-up procedures may have to be modified accordingly.

Difficulties may arise from the presence in the sample of compounds having an analytical behaviour similar to that of the pesticides being sought and this may lead to erroneous conclusions. One of the problems in the analysis of material for organochlorine pesticides has been interference from polychlorinated biphenyls (PCB's). These compounds all have similar structures and are obtained on a large scale by free radical reaction between benzene and chlorine. Distillation of the product gives fractions which are graded according to carbon atom content and amount of chlorine present. These grades vary from a pale yellow mobile oil of low chlorine content, to a yellow brittle resin with a high chlorine content. The PCB compounds have been widely-used in industry as lubricants, heat-transfer media and insulators and they have been added to paints, varnishes, synthetic resins, *etc.*, to improve the product resistance to chemicals, water, *etc.* As a result of their common usage they appear to be as widely distributed as organochlorine pesticides and because they are resistant to oxidation, and to both acidic and basic hydrolysis, they tend to persist in the environment.

The presence of the multicomponent PCB's in a sample examined for pesticide residues can interfere with or prohibit identification and measurement of some chlorinated pesticides. When PCB's are present, they give a pattern of GLC peaks with retention times similar to those of dieldrin, DDT, DDE, aldrin and heptachlor epoxide. Methods for the separation of PCB's from organochlorine pesticides generally involve separation on a silica gel column although this does not separate *p,p'*-DDE from PCB's. Armour and Burke,[188] using a column of silicic acid with a controlled activity, separated PCB's from DDT and its analogues, although aldrin was eluted with the PCB's. This work was later extended to chlorinated naphthalenes[189] which may also interfere with the GLC determination of several organochlorine pesticides. Gas chromatography combined with mass spectrometry has been used for separating and identifying the PCB's in ecological samples. The technique is discussed in greater detail in the section on confirmatory techniques. Recently the individual chlorobiphenyls have been synthesized and their retention times and the response of an electron-capture detector to then have been reported.[190] Aids to the positive identification of these compounds are detailed in a recent review article.[191] In addition to gas chromatography, reversed-phase partition thin-layer chromatography has been used successfully for the separation of the components of a PCB mixture by de Vos and Peet.[192] The problem of expressing the amount of PCB's present in a sample is very real, since the pattern of PCB peaks obtained by GLC examination rarely corresponds to that of any commercial PCB preparation and also these peaks represent mixtures of PCB isomers. Collins *et al.*[193] found that the mean electron-capturing power of the highly-chlorinated biphenyls as grouped by the specified GLC conditions were similar to that of *p,p'*-DDE. PCB peaks obtained from wild-life specimens generally correspond to the highly-chlorinated biphenyls and could be equated to *p,p'*-DDE. It was shown that known weights of "Aroclors" compared favourably with results obtained by using peak height times retention time data with *p,p'*-DDE as reference standard. Chlorinated naphthalenes may interfere in PCB determinations since they give similar GLC peak patterns and are eluted in the same fraction. Holmes and Wallen[194] published a method based on the relative ease of oxidation of the chlorinated napthalenes as opposed to the non-reactivity of the PCB's, which differentiated between the two types of compounds.

Solvents or reagents used in analysis may contain contaminants such as di-n-butyl phthalate (commonly used as a plasticizer), which could be confused with BHC and aldrin in GLC with electron-capture detection. Organic solvents in contact with polythene can extract a contaminant, which reacts with the common thin-layer chromatographic reagent silver nitrate, giving a spot at an R_f value close to that of *p,p'*-DDE and having similar retention times to *o,p'*-DDE and *p,p'*-DDE. Sulphur and sulphur-containing compounds may be present in solvents, column materials (*e.g.*, carbon cellulose[195]) or in the substrate such as onion, cabbage, turnips, *etc.*[196,197] Elemental sulphur can give rise to a "pseudo-aldrin" peak in gas-liquid chromatography.[198]

One of the more difficult problems in pesticide residue analysis is the positive identification of the pesticides present in a sample. In general, chromatographic techniques can rarely give absolute indentification of a pesticide. Dieldrin and "photo-dieldrin" have similar retention times irrespective of the GLC column used and corresponding R_f values with a number of thin-layer solvent systems. *p,p'*-DDE and dieldrin provide another example of pesticides with similar retention times on certain stationary phases. There are many other examples of pesticides with similar retention times, as demonstrated in retention data given by Burke and Holswade.[195,196]

It must therefore be emphasized that confirmation of the identity of an unknown residue is essential before decisions of a legal or health nature are taken. This need for a full understanding of results is particularly important as possible alternative and misleading deductions can be made from results from the simpler non-specific residue analysis procedures.

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Zusammenfassung—Die Übersicht umfaßt weitgehend das Gebiet der Analyse nach Spuren von Pestiziden und diskutiert die Probleme der Abtrennnhg. des Nachweises und der Bestätigung. Säuberungsverfahren und GLC-Methoden werden mehr im einzelnen beachtet. Etwa 200 Literaturstellen werden zitiert.

Résumé—La revue couvre à grands traits le domaine d'analyse pour les traces de pesticides et discute des problèmes de séparation, détection et confirmation. Les techniques de purification et les méthodes CPV sont traitées avec une attention plus détaillée. On cite quelques 200 références.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—I

KOBALT

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Zusammenfassung—Zwei Verfahren zur Bestimmung von Kobalt in natürlichen Wässern werden beschrieben. Biem ersten wird die Probe mit HCl angesäuert, dann werden Ascorbinsäure und Kaliumthiocyanat zugegeben, und man läβt die Lösung durch eine Säule mit einem stark basischen Anionenaustauscher (Dowex 1-X8) laufen. Der Kobalt-Thiocyanat-Komplex wird auf der Säule festgehalten, während andere Ionen mit einem Gemisch aus organischem Lösungsmittel und wäßriger HCl ausgewaschen werden. Das Kobalt wird dann mit rein wäßriger 6M HCl eluiert und mit Nitroso-R-Salz photometrisch bestimmt. Beim zweiten Verfahren (für sehr verunreinigte Proben) wird die filtrierte Probe mehrstufig eingedampft und ann in dem Lösungsmittelgemisch auf die Säule gegeben. Für viele in Niederosterreich gesammelte Proben werden Ergebnisse mitgeteilt.

Da der Kobaltgehalt natürlicher Wässer[1–12] in der Regel sehr gering ist (im ppb-Bereich), kann dieses Element erst nach vorangehender Anreicherung quantitativ bestimmt werden, wozu sehr häufig Verfahren benützt werden, die auf flüssig-flüssig Extraktion von Komplexen des Kobalts mit organischen Reagenzien beruhen. Die dazu verwendeten Extraktionssysteme sind: 1-Nitroso-2-naphthol–Chloroform,[1] Picolinaldehyd 2-chinolylhydrazon–Isoamylalkohol oder Isobutylmethylketon,[2] 8-Hydroxychinolin–Chloroform,[4] 2-Nitroso-1-naphthol –Toluol,[6] Dithizon–Tetrachlorkohlenstoff,[7] 3-Methoxy-2-nitrosophenol–Chloroform[8] und Ammoniumtetramethylendithiocarbamat–Isobutylmethylketon.[12] Die meisten dieser Chelatbildner sind gleichzeitig auch empfindliche Farbreagenzien, so daß das Kobalt nach Extraktion in die organische Phase direkt in dieser spektrophotometrisch bestimmt werden kann.

Zur Kobaltanreicherung aus Wässern wurden weder stark saure Kationen- noch stark basische Anionenaustauscherharze herangezogen, da diese Harze keine besondere Selektivität gegenüber Kobalt aufweisen. So ist es z.B. unmöglich, das Kobalt unter Anwendung eines Kationenaustauscherharzes von dem in großen Mengen in Wässern anwesenden Calciumion und anderen zwei- und höherwertigen Ionen zu trennen, und zwar unabhängig davon, ob die Ionenaustauschoperationen in verdünnt salz-, salpeter- oder schwefelsauren Medien ausgeführt werden.[13]

Eine der sehr wenigen Möglichkeiten, um Kobalt auf einem stark basischen Anionenaustauscher anzureichern und gleichzeitig von einer größeren Anzahl von Begleitelementen (wie z.B. den Alkalimetallen, Erdalkalimetallen, Aluminium, Chrom und Nickel) abzutrennen, ist dadurch gegeben, daß das Kobalt aus stark salzsaurer Lösung (8–12 *M*) auf dem

Harz adsorbiert wird.[14,15] Diese Methode ist jedoch zur direkten Isolierung des Kobalts aus natürlichen Wässern nicht anwendbar, da das Kobalt aus verdünnt salzsauren Lösungen (kleiner als 8*M*), d.h. auch aus mit Salzsäure angesäuerten Wasserproben, praktisch überhaupt nicht von stark basischen Anionenaustauscherharzen, wie z.B. Dowex 1, festgehalten wird.

Ganz andere Verhältnisse liegen vor, wenn die Kobaltabtrennung mittels Anionenaustausches aus einem verdünnt salzsauren Medium in Gegenwart von Thiocyanation erfolgt. Es ist unter solchen Bedingungen möglich, das Kobalt direkt aus der Wasserprobe (ohne vorangehendes Eindampfen) selektiv abzutrennen und es nach Entfernung von koadsorbierten Elementen durch Nachwaschen mit einem gemischt wäßrig-organischen Lösungsmittelsystem der störungsfreien spektrophotometrischen Bestimmung mittels der Nitroso-R-Salzmethode zugängig zu machen.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustaucher Dowex 1, X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4g des Anionenaustauscherharzes in 1 ml der Vorbehandlungslösung (siehe unten) aufgeschlämmt und nach Ablauf von etwa 15 Minuten wird der Austauscher so vollständig wie möglich in die mit derselben Lösung gefüllte Ionenaustauschersäule gebracht und mit 20 bis 30 ml der Vorbehandlungslösung nachgewaschen. In jenen Fällen, bei denen die Kobaltabtrennung nach Eindampfen der Wasserproben erfolgt, wird das Harz (ebenfalls 4 g) nicht mit der Vorbehandlungslösung, sondern unter Anwendung der THF–MG–HCl-Mischung (siehe unten) in die Ionenaustauschersäule gebracht.

Kobalt-Standardlösungen. Durch Lösen von 4,411 g Kobaltchloridhexahydrat in 6*M* Salzsäure und Verdünnen der Lösung mit Säure derselben Molarität wurde eine Stammlösung hergestellt, die 1,0 mg Kobalt/ml enthielt (der Kobaltgehalt dieser Lösung wurde durch ÄDTA-Titration überprüft). Durch Verdünnen mit 6*M* Salzsäure wurden daraus Standardlösungen mit Kobaltgehalten im Konzentrationsbereich von 5 bis 500 μg Co/ml hergestellt.

Vorbehandlungslösung. Zur Herstellung der Lösung werden 100 ml dest. Wasser mit 1 ml konzentrierter Salzsäure angesäuert und darin 0,5 g Ascorbinsäure und 1 g Kaliumthiocyanat gelöst. Diese Mischung soll tunlichst immer frisch bereitet aber nicht sofort, sondern erst einige Stunden nach ihrer Herstellung, angewendet werden.

THF–MG–HCl-Mischung. Diese Mischung besteht aus 50 vol. % Tetrahydrofuran, 40 vol. % Methylglykol und 10 vol.% 6*M* Salzsäure. Um zu vermeiden, daß es in den Ionenaustauschersäulen zur Bildung von Luftblasen kommt, soll die Lösung nicht unmittelbar vor ihrer Anwendung hergestellt werden, sondern am besten schon einige Stunden vorher. Sie ist praktisch unbeschränkte Zeit haltbar und es treten selbst bei monatelangem Stehenlassen keine Zersetzungserscheinungen der organischen Lösungsmittel auf.

Phosphat-Borsäurepufferlösung. Dinatriumphosphatdihydrat(35, 6g) und Orthoborsäure (6,2 g) werden in 500 ml 1*M* Natriumhydroxydlösung gelöst, und die Lösung wird mit dest. Wasser auf 1 Liter verdünnt.

Reagenslösung. Wäßrige Lösung von Nitroso-R-Salz, 0,20 gew.%ig.

Organische Lösungsmittel. Tetrahydrofuran und Methylglykol (Monomethyläther des Äthylenglykols).

Andere Reagenzien. Ferner wurden verwendet: 0,20*M* Citronensäurelösung (4,2 g des Monohydrats in 100 ml wäßriger Lösung), Kaliumthiocyanat (*p.a.*), Ascorbinsäure, konzentrierte Perchlorsäure (70 %ig), konzentrierte Salpetersäure (65 %ig), konzentrierte Flußsäure (40 %ig), sowie 6*M* und konzentrierte Salzsäure (37 %ig) (*p.a.*).

Apparaturen

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[16] angegebenen Typs ausgeführt.

Für die photometrischen Bestimmungen des Kobalts wurde ein Beckman Spektralphotometer, Modell B und 1-cm-Küvetten verwendet.

Arbeitsvorschriften

Methode A—Direkte Abtrennung des Kobalts. Ein Liter der Wasserprobe wird sofort nach der Probenahme (mittels einer gut verschließbaren Plastikflasche) mit 10 ml konzentrierter Salzsäure angesäuert und dann im Laboratorium durch ein dichtes Filter filtriert. Dem Filtrat werden 5 g Ascorbinsäure und 10 g Kaliumthiocyanat zugesetzt, gut durchgemischt bis sich beide Reagenzien aufgelöst haben und danach wird die Mischung (Sorptionslösung) etwa 5 bis 6 Stunden stehengelassen.

Die, wie oben angegeben, hergestellte Sorptionslösung wird durch eine mit 4 g des Ionenaustauscherharzes beschickte Säule (die vorher mit etwa 20 bis 30 ml der Vorbehandlungslösung gewaschen wurde) mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 70 bis 80 ml/Stunde) fließen gelassen. Anschließend wird mit der THF–MG–HCl-Mischung so lange nachgewaschen, bis die, durch den am Harz adsorbierten Thiocyanatkomplex des Eisens während der Sorption gebildete, rote Adsorptionszone vollständig verschwunden ist (dazu sind etwa 80 ml der THF–MG–HCl-Mischung erforderlich). Hierauf wird das adsorbierte Kobalt (selbst 10 μg sind als grün-blaue Zone am Harz noch deutlich erkennbar) mit 50 ml 6*M* Salzsäure eluiert (Kobalteluat).

Methode B—Abtrennung des Kobalts nach Eindampfen der Wasserprobe. Ein Liter der mit 10 ml konzentrierter Salzsäure angesäuerten Wasserprobe wird durch ein dichtes Filter filtriert und das Filtrat zur Trockne eingedampft. Der Eindampfrückstand wird mittels 1 ml 6*M* Salzsäure in eine Platinschale gebracht, worin dann die Lösung auf dem Wasserbad zur Trockne eingedampft wird. Der Rückstand wird in m5 l konzentrierter Perchlorsäure und 1 ml konzentrierter Flußsäure aufgenommen und die Lösung auf einer Heizplatte oder auf dem Sandbad zur Trockne gebracht. Der Eindampfrückstand wird in 10 ml 6*M* Salzsäure aufgenommen und die Lösung am Wasserbad zur Trockne eingedampft. Nun wird der Rückstand in 5 ml 6*M* Salzsäure aufgenommen und die Lösung mit 25 ml Tetrahydrofuran und 20 ml Methylglykol versetzt (Sorptionslösung). Falls dabei eine trübe Lösung erhalten wird, muß diese vor der Ionenaustauschtrennung (siehe unten) durch ein trockenes Papierfilter filtriert werden. Zum Nachwaschen dienen 1 ml der THF–MG–HCl-Mischung.

Die vollkommen klare Sorptionslösung aus 50 vol.% Tetrahydrofuran, 40 vol.% Methylglykol und 10 vol.% 6*M* Salzsäure (siehe oben) wird durch eine mit 2 g des Anionenaustauschers beschickte Säule (die vorher mit etwa 20 ml der THF–MG–HCl-Mischung vorbehandelt wurde), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 1 ml/Minute), fließen gelassen. Anschließend wird mit 50 ml der THF–MG–HCl-Mischung nachgewaschen und das adsorbierte Kobalt mit 50 ml 6*M* Salzsäure eluiert (Kobalteluat).

Quantitative Bestimmung des Kobalts

Das gesamte, nach Methode A oder B erhaltene, Kobalteluat (oder nur ein Aliquot falls mehr als 10 μg Kobalt im Eluat erwartet werden) wird in einem 250-ml Becherglas auf dem Wasserbad zur Trockne eingedampft. Der Rückstand wird mit 8 bis 10 ml konzentrierter Perchlorsäure versetzt und die Lösung auf einer Heizplatte oder auf dem Sandbad zur Trockne gebracht. Der Rückstand wird in etwa 20 ml 6*M* Salzsäure aufgenommen, die Lösung auf dem Wasserbad auf etwa 10 ml eingeengt und unter Nachwaschen mit 1 ml 6*M* Salzsäure in ein 50-ml Becherglas gebracht, worin dann die Lösung auf dem Wasserbad zur Trockne eingedampft wird. Der Eindampfrückstand wird in 1 ml der 0,2*M* Citronensäurelösung aufgenommen und 1,2 ml Phosphat–Borsäurepufferlösung (wobei sich ein pH um etwa 8 einstellt), sowie 0,50 ml der Reagenslösung zugesetzt. Danach wird die Lösung genau 30 Sekunden lang gekocht (Bunsenbrenner) und sofort danach 1 ml konzentrierte Salpetersäure zugegeben und erneut 30 Sekunden lang gekocht. Nach dem Abkühlenlassen auf Raumtemperatur wird die Lösungin ein en 10-ml Meßkolben gebracht, mit Wasser zur Marke aufgefüllt und ihre Extinktion gegenüber einer Reagensleerlösung bei 420 nm gemessen. Mittels einer analog aufgestellten Eichkurve (im Konzentrationsbereich von 0 bis 12 μg Kobalt/10 ml Meßlösung) wird dann der Kobaltgehalt der Probelösung, deren Extinktion einige Tage lang konstant bleibt, ermittelt: 10 μg Kobalt entsprechen einer Extinktion von 0,575 bis 0,580.

RESULTATE UND DISKUSSION

Das Prinzip des in der Arbeitsvorschrift beschriebenen Verfahrens zur direkten Abtrennung des Kobalts aus Proben natürlicher Wässer (Methode A) beruht darauf, daß das Kobalt mit Thiocyanationen einen stabilen anionischen Komplex bildet, der aus verdünnt salzsaurer Lösung relativ stark auf dem stark basischen Anionenaustauscher Dowex 1 adsorbiert wird. Unter den angegebenen Bedingungen, d.h. in Gegenwart von 10 ml konzentrierter Salzsäure, 5 g Ascorbinsäure und 10 g Kaliumthiocyanat pro Liter Wasserprobe, wurde für Kobalt ein Verteilungskoeffizient von 980 ermittelt, d.h. die Adsorption des Kobalts aus dieser Lösung ist um etwa eine Zehnerpotenz größer als aus 8–12*M* Salzsäure. Es ist daher möglich, das Kobalt nach Zugabe der obigen Reagenzien direkt durch einfaches Durchfließenlassen der Wasserprobe durch eine kleine Säule des Anionenaustauschers quantitativ am Ionenaustauscherharz anzureichern und gleichzeitig von den in Gewässern in größeren Konzentrationen vorhandenen Calcium-, Magnesium- und Sulfationen zu trennen.

Wie aus den in Tabelle 1 gezeigten Resultaten ersichtlich ist, wird das Kobalt bis zu Konzentrationen von 100 μg pro Liter quantitativ am Austauscher adsorbiert, und zwar unabhängig davon, ob 10 oder 20 g Kaliumthiocyanat in 1 Liter der Wasserprobe anwesend sind. Erwartungsgemäß treten jedoch in Anwesenheit von nur 1 g Kaliumthiocyanat bzw. bei höheren Kobaltkonzentrationen Kobaltverluste auf, die darauf zurückzuführen sind, daß die anwesende Menge an Thiocyanation in diesen Fällen nicht mehr ausreicht, um die quantitative Bildung und Adsorption des anionischen Kobaltthiocyanatkomplexes am Harz zu ermöglichen.

Tabelle 1. Resultate von Kobaltbestimmungen im Wiener Trinkwasser*

Zugesetzte Kobaltmenge, μg/l.	Wiedergefundene Kobaltmenge, μg/l.		
	KSCN 1 g/1.	KSCN 10 g/1.	KSCN 20 g/1.
0,0	0,2	0,2	0,2
5,0	5,2	5,2	5,2
50,0	43,0	50,4	48,5
100	90,0	99,3	99,0
500	400	478,5	493,0
1000	880	954	1006

Tabelle 2. Resultate von Kobaltbestimmungen im Wiener Trinkwasser (10 g KSCN + 5 g Ascorbinsäure + variierende Mengen an konz. HCl/Liter)*

Zugesetzte Kobaltmenge, μg/l.	Wiedergefundene Kobaltmenge, μg/l.				
	1 ml HCl	5 ml HCl	10 ml HCl	50 ml HCl	100 ml HCl
0,0	0,2	0,2	0,2	0,2	0,2
5,0	5,2	5,2	5,2	5,2	5,2
50,0	49,5	48,0	50,4	49,2	51,7
100	103	97	99,3	101	98,2
500	502	494	478,5	476	467
1000	987	990	954	926	896

* Bei ähnlichen Versuchen, die mit destilliertem Wasser durchgeführt wurden, stellte man keinen meßbaren Co-Gehalt fest.

Diese Versuche, sowie auch jene, welche die in Tabelle 2 gezeigten Ergebnisse lieferten, wurden unter Verwendung von 1-Liter Proben Wiener Trinkwassers durchgeführt, in denen jeweils die in den Tabellen 1 und 2 angeführten Konzentrationsparameter, d.h. Kobalt-Thiocyanat- und Salzsäurekonzentration, variiert wurden. Nach Einstellung der gewünschten Versuchsbedingungen wurde dann das Kobalt mittels der in der Arbeitsvorschrift beschriebenen Methode A abgetrennt und quantitativ bestimmt.

Wie aus den in Tabelle 2 gezeigten Ergebnissen ersichtlich ist, treten wesentliche Kobaltverluste erst bei hohen Salzsäure- und Kobaltkonzentrationen auf.

Der Zustaz von Ascorbinsäure zu den angesäurerten Wasserproben dient dazu, um Eisen(III) weitestgehend zu zweiwertigem Eisen zu reduzieren, wodurch vermieden wird, daß der rote anionische Eisen(III)-Thiocyanatkomplex zusammen mit dem Kobalt am

Harz adsorbiert wird. In Anwesenheit größerer Eisen(III)-Mengen könnte durch diese Koadsorption das Kobalt ganz oder teilweise vom Harz verdrängt werden und so beträchtliche Kobaltverluste eintreten. Da diese Reduktion des Eisens zur zweiwertigen Oxydationsstufe nicht ganz vollständig verläuft, ist oft eine geringe Rosafärbung des Harzbettes während der Sorption des Kobalts aus den thiocyanat- und ascorbinsäurehaltigen Wasserproben zu beobachten. Dieses beeinträchtigt jedoch in keiner Weise die Adsorption des Kobalts am Harz. Wird die mit Ascorbinsäure und Thiocyanat versetzte Wasserprobe einige Stunden vor der Sorption stehen gelassen (siehe Arbeitsvorschrift), so ist die Reduktion des Eisen(III)-Ions wesentlich vollständiger als unmittelbar nach Zugabe dieser Reagenzien.

Durch das der Sorption des Kobalts nachfolgende Nachwaschen mit THF–MG–HCl-Mischung (siehe Arbeitsvorschrift) werden nicht nur die in der Ionenaustauschersäule vorhandenen Reste an Ascorbinsäure und Kaliumthiocyanat entfernt, sondern es wird auch das als Thiocyanatkomplex adsorbierte Eisen quantitativ eluiert und gleichzeitig wird dabei der Thiocyanatkomplex des Kobalts in einen anionischen Chloridkomplex übergeführt, der aus diesem salzsauren organischen Lösungsmittelsystem ebenfalls sehr stark vom Harz festgehalten wird (Verteilungskoeffizient des Kobalts = 5870).[17] Fernerhin werden auch andere Metallionen, die als anionische Thiocyanatkomplexe adsorbierbar sind[18,19], entweder zusammen mit dem Eisen eluiert oder in Chloridkomplexe übergeführt. Bei Anwendung dieses THF–MG–HCl-Systems werden zusammen mit dem Kobalt folgende Ionen vom Anionenaustauscherharz adsorbiert[17]: UO_2(II), Sn(II,IV), Pb(II), Bi(III), Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), Mn(II), Ru(IV), Rh(III), Pd(II), Os(III), Ir(IV) und Pt(IV).

Bei der Elution des Kobalts mit 6*M* Salzsäure (siehe Arbeitsvorschrift) werden von den oben genannten Metallionen (falls anwesend) nur Cu(II), Mn(II), Pb(II), Ag(I) und Rh(III) quantitativ zusammen mit dem Kobalt eluiert. Diese Ionen rufen jedoch keine Störungen bei der spektrophotometrischen Bestimmung des Kobalts hervor. Nach der Elution des Kobalts kann das Harz erneut fur eine Kobaltabtrennung benützt werden, nachdem man es zuerst mit 1*M* Salzsäure und dann mit der Vorbehandlungslösung gewaschen hat.

Da bei Anwendung des THF–MG–HCl-Systems selbst schon 10 μg Kobalt als deutlich sichtbare grünlich-blaue Zone am oberen Teil des Harzbettes erkennbar sind, ist es in allen Fällen schon vor der Elution des Kobalts mit 6*M* Salzsäure auf Grund der Intensität bzw. Breite der Adsorptionszone des Kobalts möglich, das Volumenaliquot des Eluats abzuschätzen, welches für die quantitative Kobaltbestimmung verwendet werden muß.

Da das Kobalteluat organische Substanzen enthält (stammend aus dem Anionenaustauscherharz und dem THF–MG–HCl-System), welche die Kobaltbestimmung empfindlich stören, ist es erforderlich, diese durch Abrauchen mit konzentrierter Perchlorsäure quantitativ zu zerstören (siehe Arbeitsvorschrift). Danach ist es jedoch erforderlich, das Kobaltoxid, das sich bei längerem Erhitzen auf der Heizplatte oder auf dem Sandbad bilden kann, wieder durch Eindampfen in Gegenwart überschüssiger 6*M* Salzsäure in Lösung zu bringen. Danach ist der Eindampfrückstand leicht in der Citronensäurelösung und in der Phosphat–Borsäurepufferlösung löslich (siehe Arbeitsvorschrift). Die Anwendung dieser beiden Lösungen (Grundlage der sogenannten Citratmethode[20]) ist jener Variante der spektrophotometrischen Kobaltbestimmung mittels Nitroso-R-Salz vorzuziehen, bei welcher der rotbraune Komplex des Kobalts mit Nitroso-R-Salz in stark acetathaltigem Medium gebildet wird (Acetatmethode[20]). Im Gegensatz zu dieser Acetatmethod wird die in dieser Arbeit angewendete Citratmethode durch die zusammen mit dem Kobalt miteluierten

Metallionen (siehe oben), vor allem durch Kupfer (selbst wenn dieses in großer Menge anwesend sein sollte), nicht gestört, so daß das Kobalt nach Durchführung der Ionenaustauschtrennung störungsfrei bestimmet werden kann.

Die in der Arbeitsvorschrift beschriebene Methode B wurde zur Analyse von stark mit organischen Substanzen verunreinigten Wasserproben herangezogen. Durch die dabei angewendete Naßveraschungsmethode mittels Perchlorsäure werden die organischen Verbindungen weitestgehend zerstört (auch Kieselsäure wird durch die gleichzeitig anwesende Flußsäure entfernt) und es besteht danach nicht mehr die Gefahr, daß diese die Adsorption des Kobalts am Anionenaustauscher beeinflussen können.

Aus den in Tabelle 3 gezeigten Ergebnissen von Kobaltbestimmungen in zahlreichen niederösterreichischen Gewässern geht hervor, daß mit Methode A, mit Ausnahme der Analyse einer sehr stark verunreinigten Probe (Schwechat bei Traiskirchen), dieselben Resultate erzielt wurden wie mit Methode B, deren Anwendung naturgemäß einen längeren Zeitaufwand erfordert.

Tabelle 3. Ergebnisse von Kobaltbestimmungen in Wasserproben aus Niederösterreich

		Kobaltgehalt, $\mu g/l$.		
Probenbezeichung und Datum der Probenahme		Methode A (1)	(2)[*]	Methode B
Donau[†] bei Ybbs-Persenbeug;	9.2.1973	1,4	1,6	1,5
Erlauf bei Erlauf;	„	1,6	1,5	—
Melk bei Melk;	„	1,1	1,5	1,3
Pielach bei Prinzensdorf;	„	1,5	1,8	1,7
Ybbs bei Ybbs;	„	1,3	1,2	—
Krems bei Krems;	„	1,3	1,5	1,6
Kamp bei Hadersdorf;	„	0,75	1,0	1,2
Traisen bei St. Pölten;	„	1,1	1,2	—
Ysper bei Ysperdorf;	„	0,8	1,1	1,1
Teich im Industriegebiet N.Ö.Süd;	23.2.1973	0,65	0,80	0,90
Brunnen bei Ebreichsdorf;	„	0,45	0,60	—
Mödling bei Wiener Neudorf;	„	0,90	0,80	—
Teich bei Brunn am Gebirge;	„	1,2	1,2	—
Abfluß der Metallfabrik, Möllersdorf;	„	1,6	1,7	1,7
Abflußkanal von Wr. Neustadt;	„	1,2	1,1	1,2
Abfluß der Fa. Stoll-Lack;	„	1,0	1,2	—
Schwechat bei Traiskirchen;	„	<0,4	0,35	0,8
Tristing bei Leobersdorf;	„	0,7	0,8	—
Pisting bei Miesenbach;	1.1.1973	1,6	1,5	—
Quellwasser der Schmida bei Eggenburg;	17.3.1973	0,6	0,7	—
Brunnen bei Zitternberg;	„	5,0	5,2	—
Ysperklamm bei Ysper;	„	0,7	0,6	—
Quelle bei Kotzenberg;	„	2,5	2,7	—
Weisen bei Diezheim;	„	0,75	0,8	—
Bach bei Rosenburg;	„	0,75	0,7	—
Grundwasser bei Rosenburg;	„	0,8	1,0	—
Erster Stausee der Kamp;	„	<0,4	0,20	—
Quelle bei Ottenschlag;	„	<0,3	0,25	—

[*] Kobaltgehalt nach Abzug von 5 μg Kobalt-Spike, die 1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurden.

[†] Durch spektralanalytische Messungen wurden im Jahre 1972, in mehreren an verschiedenen Stellen gezogenen Donauwasserproben, Kobaltgehalte von 0,55 bis 3,7 μg Co/Liter ermittelt.[21]

Aus Tabelle 3 ist auch ersichtlich, daß bei Analysen, die nach Abzug der als Spike zugesetzten Kobaltmenge von jeweils 5 μg, ebenso gute Ergebnisse erzielt wurden, wie bei jenen, die in Abwesenheit von Spike-Kobalt ausgeführt wurden.

Da die vorliegende Methode A auf der direkten Anwendung der weitgehend automatisierbaren Anreicherung und Abtrennung des Kobalts auf Anionenaustauschersäulen beruht, ist es möglich, viele Wasserproben gleichzeitig nach deren Ansäuern und Filtration zu analysieren, d.h. das Verfahren eignet sich vorzüglich zur serienmäßigen Bestimmung des Kobalts in Gewässern.

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Summary—Two methods are described for the determination of cobat lin natural waters. In the first the sample is acidified with HCl, then ascorbic acid and potassium thiocyanate are added, and the solution is run through a column of strongly basic anion-exchanger (Dowex 1-X8). The cobalt thiocyanate complex is retained on the column while other ions are washed through with a mixture of organic solvent and aqueous HCl. The cobalt is then eluted with purely aqueous 6*M* HCl and determined photometrically with nitroso-R salt. In the second method, (for very dirty samples) the filtered sample is taken through a multi-step evaporation procedure and then added to the column in the mixed solvent. Results are presented for many samples collected in Lower Austria.

Résumé—On décrit deux méthodes pour la détermination du cobalt dans les eaux naturelles. Dans la première l'échantillon est acidifié par HCl, puis on ajoute de l'acide ascorbique et du thiocyanate de potassium, et la solution est passée sur une colonne d'échangeur d'anions fortement basique (Dowex 1-X8). Le complexe de thiocyanate de cobalt est retenu sur la colonne tandis que les autres ions sont lavés avec un mélange de solvant organique et de HCl aqueux. Le cobalt est alors élué avec HCl 6*M* purement aqueux et dosé photométriquement avec le sel nitroso-R. Dans la seconde méthode (pour les échantillons très sales), l'échantillon filtré est soumis à une technique d'évaporation multistades puis ajouté à la colonne dans le solvant mixte. On présente des résultats pour de nombreux échantillons prélevés en Basse-Autriche.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—II

CADMIUM

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Zusammenfassung—Eine Methode wird beschrieben, die es ermöglicht ppM-Mengen Cadmium aus natürlichen Wässern zu isolieren und der spektrophotometrischen Endbestimmung zugängig zu machen. Die Wasserprobe (1 Liter) wird durch Zugabe von konzentrierter Salz- oder Bromwasserstoffsäure 1,2*M* bzw. 1,0*M* an diesen Säuren gemacht, filtriert und anschließend durch eine Säule des Anionenaustauscherharzes Dowex 1, X8 (Chloridform) fließen gelassen. Dabei wird das Cadmium nicht nur am Ionenaustauscher quantitativ angereichert, sondern auch gleichzeitig von den anderen, in der Wasserprobe anwesenden Begleitelementen getrennt. Koadsorbiertes Zink wird mittels 0,15*M* Bromwasserstoffsäure entfernt, das adsorbierte Cadmium mit 2*M* Salpetersäure eluiert und im Eluat, unter Anwendung der Dithizonmethode, spektrophotometrisch bestimmt. Die Methode wurde zur Bestimmung des Cadmiums in zahlreichen österreichischen Gewässern herangezogen, wobei Cadmiumgehalte im Konzentrationsbereich von 0,1 bis 4,0 ppM gefunden wurden.

Der Entwicklung von analytischen Methoden, die eine serienmäßige Bestimmung von Cadmium in natürlichen Wässern gestatten, wird zunehmende Beachtung geschenkt, und zwar im Zusammenhang mit dessen Toxizität und den damit eng verbundenen Problemen des Umweltschutzes.

Da die in natürlichen Wässern auftretenden Cadmiumgehalte äußerst gering sind (im ppM-Bereich), ist es häufig erforderlich, das Cadmium vor seiner quantitativen Bestimmung zu isolieren bzw. von den Begleitelementen abzutrennen.

Auf Grund von Literaturangaben[1–10] ist ersichtlich, daß die im Zusammenhang mit der Cadmiumbestimmung in natürlichen Wässern inklusive Meerwasser[1,2,9] angewendeten Abtrennungsmethoden im wesentlichen darauf beruhen, daß das Cadmium entweder durch Lösungsmittelextraktion oder durch Kationenaustausch isoliert wird. Eine der am häufigsten verwendeten Methoden benützt die Extraktion von Cadmiumdithizonat mittels Chloroform oder Tetrachlorkohlenstoff um dieses Element aus Wasserproben zu isolieren.[1–5] Auch die Extraktion des Cadmiumchelats mit 2-Merkaptobenzthiazol in Butylacetat und anschließende Bestimmung des Cadmiums mittels Atomabsorptionsspektrophotometrie wurde dazu verwendet, um den Cadmiumgehalt von Flußwässern zu ermitteln.[6] Kationenaustauschmethoden wurden zur Abtrennung des Cadmiums aus Mineralwässern[7] und anderen Süßwasserproben[8] benützt, sowie auch nach vorangehender Isolierung des Cadmiums durch Mitfällung mit Kupfersulfid zur Bestimmung dieses Elementes im Meerwasser[9] herangezogen. Aus Mineralwässern kann das Cadmium auch durch Zementierung mittels metallischen Magnesium isoliert und dann polarographisch bestimmt werden.[10]

Obwohl zur Trennung des Cadmiums von vielen Begleitelementen sehr häufig stark basische Anionenaustauscherharze verwendent werden,[11–17] hat dieses Trennungsprinzip zur Cadmiumanalyse von natürlichen Wässern bis jetzt keine Anwendung gefunden. Wie jedoch in der vorliegenden Arbeit gezeigt wird, sind Anionenaustauschverfahren sehr gut dazu geeignet, um Cadmium aus Wässern zu isolieren, wonach dieses Element, unter Anwendung der Dithizonmethode, störungsfrei spektrophotometrisch bestimmt werden kann.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1 X8 (100–200 mesh; Chloridform) verwendet. Vor dem Einfüllen in die Ionenaustauschersäule werden 4 g des Austauscherharzes in 1 ml 1,2*M* Salzsäure bzw, 1,0*M* Bromwasserstoffsäure aufgeschlämmt und nach Ablauf von etwa 10 bis 15 Minuten wird der Austauscher so vollständig als möglich in die mit derselben Lösung gefüllte Ionenaustauschersäule gebracht und mit 20 bis 30 ml 1,2*M* Salzsäure bzw. 1,0*M* Bromwasserstoffsäure nachgewaschen.

Cadmium-Standardlösungen. Durch Lösen von 2,424 g Cadmiumnitrat $[Cd(NO_3)_2.2H_2O]$ in 2*M* Salzsäure und Verdünnen der Lösung mit Säure derselben Molärität wurde eine Stammlösung hergestellt, die 1 mg Cadmium/ml enthielt (der Cadmiumgehalt dieser Lösung wurde durch ÄDTA-Titration überprüft). Durch Verdünnen mit 2*M* Salzsäure wurde daraus eine Standardlösung hergestellt, deren Gehalt 4,0 µg Cd/ml betrug.

Komplexierungslösung. Diese Lösung, die immer frisch hergestellt werden soll, wird folgendermaßen bereitet: 50 ml einer 40 % igen Natriumhydroxydlösung, die gleichzeitig 1 % ig an Kaliumcyanid ist, werden mit 10 ml 25 % iger Kalium-Natriumtartratlösung und 10 ml 20 % iger Hydroxylaminhydrochloridlösung vermischt und schließlich mit destilliertem Wasser auf 250 ml verdünnt. Mittels dieser Komplexierungslösung werden Störungen ausgeschaltet, die auf gegebenenfalls anwesende Schwermetallspuren in der zur Elution des Cadmiums verwenderen 2*M* Salpetersäure und den zur Cadmiumbestimmung verwendeten Reagenzien zurückzuführen sind.

Dithizon-Chloroformlösung. Eine 0,012 gew.%ige Lösung von Dithizon (Diphenyldithiocarbazon) in Chloroform.

Andere Reagenzien. Ferner wurden verwendet: 6 gew.%ige Natriumhydroxydlösung, 1,2*M* und konzentrierte Salzäure (37 %ig; *p.a.*) und 0,15*M*, 1,0*M* und konzentrierte Bromwasserstoffsäure sowie 2*M* und 5 %ige Salpetersäure.

Apparaturen

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[18] angegebenen Typs ausgeführt.

Vorbereitung der Wasserprobe

Ein Liter der Wasserprobe wird sofort nach der Probenahme (mittels einer gut verschließbaren Plastikflasche) mit 100 ml konz. Salzsäure bzw. 120 ml konz. Bromwasserstoffsäure angesäuert und dann im Laboratorium durch ein dichtes Filter filtriert. Das Filtrat (= Sorptionslösung) wird danach übernacht stehengelassen, wodurch, Kohlendioxyd und andere Gase, die durch Gasblasenbildung das Austauschverfahren stören würden, entfernt werden.

Ionenaustauschtrennung

Chloridmethode. Die wie oben angegeben hergestellte Sorptionslösung wird durch eine mit 4 g des Anionenaustauschers beschickte Säule (die vorher mit etwa 20 ml 1,2*M* Salzsäure gewaschen wurde) mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 50 bis 60 ml/Stunde), fließen gelassen. Anschließend wird mit 20 bis 30 ml 1,2*M* Salzäure nachgewaschen, um die das Cadmium begleitenden nicht oder nur schwach adsorbierbaren Fremdionen zu entfernen. Hierauf wird koadsorbiertes Zink mittels 100 ml 0,15*M* Bromwasserstoffsäure quantitativ entfernt und danach das Cadmium mit 50 ml 2*M* Salpetersäure eluiert (Cadmiumeluat).

Bromidmethode. Die mit Bromwasserstoffsäure angesäuerte und filtrierte Wasserprobe (siehe oben) wird durch eine mit 4 g des Anionenaustauscherharzes beschickte Säule (die vorher mit etwa 50 ml 1,0*M* Bromwasserstoffsäure gewaschen wurde), mit einer dem Gegendruck des Harzbettes entsprechenden Geschwindigkeit (etwa 50 bis 60 ml/Stunde), fließen gelassen. Anschließend wird mit 100 ml 0,15*M* Bromwasserstoffsäure nachgewaschen (Elution von koadsorbiertem Zink) und danach das Cadmium mit 50 ml 2*M* Salpetersäure eluiert (Cadmiumeluat).

Quantitative Bestimmung des Cadmiums

Das nach Anwendung der Chlorid- oder Bromidmethode (siehe oben) erhaltene Cadmiumeluat wird auf dem Wasserbad zur Trockne eingedampft, der Rückstand in 5 ml 5 %iger Salpetersäure gelöst und die Lösung, unter gleichzeitigem Nachwaschen mit weiteren 5 ml dieser Säure, in einen 50-ml Scheidetrichter gebracht. Diese Lösung wird mit 25 ml der frisch bereiteten Komplexierungslösung versetzt und danach 30 Sekunden lang mit 7 ml der Dithizon-Chloroformlösung kräftig geschüttelt. Danach wird die Chloroformschichte abgetrennt, 30 Sekunden lang mit 5 ml der 6 % igen Natriumhydroxydlösung geschüttelt (dieser Waschvorgang ist zu wiederholen, falls dabei die Natriumhydroxydlösung gelb gefärbt wird) und das organische Extrakt direkt durch ein trockenes Filter in eine 1-cm-Küvette filtriert, worin dann die Extinktion bei 490 nm gegenüber einer analog hergestellten Reagensleerlösung (ein Dithizon-Chloroformextrakt, das in Abwesenheit von Cadmium aber unter genauester Einhaltung der obigen Arbeitsvorschrift erhalten wurde) gemessen wird. Aus der gemessenen Extinktion der Meßlösung wird dann mit Hilfe einer analog aufgestellten Eichkurve (im Konzentrationsbereich von 0 bis 12 μg Cadmium/7 ml Chloroformextrakt) der Cadmiumgehalt der Probelösung ermittelt; 4 μg Cadmium entsprechen einer Extinktion von 0,26.

RESULTATE UND DISKUSSION

Stark basische Anionenaustauscherharze zeigen gegenüber Cadmium eine sehr hohe Selektivität vorausgesetzt, daß dieses Element als anionischer Chlorid- oder Bromidkomplex vorliegt. Aus Messungen der Verteilungskoeffizienten des Cadmiums an Dowex 1 X8 unter Anwendung der in dieser Arbeit verwendeten salz- und bromwasserstoffsauren Lösungen geht hervor, daß dieser Koeffizient in 1,2*M* Salzsäure einen Wert von 1646 (bei einer Beladung des Harzes mit 1 mg Cd) und in 0,15 bis 1,0 *M* Bromwasserstoffsäure einen solchen von $2{,}0 \times 10^4$ (bei Beladung des Harzes mit derselben Cadmiummenge) aufweist. Auf Grund dieser Tatsache ist es daher leicht möglich das, in natürlichen Wässern vorkommende Cadmium, nach Ansäuern mit Salz- oder Bromwasserstoffsäure und Filtration der Probe, auf einer kleinen Säule des Anionenaustauschers anzureichern. Dadurch wird nicht nur das zeitraubende Eindampfen der Wasserprobe vermieden, sondern es kann auch das Cadmium gleichzeitig aus vielen verschiedenen Proben isoliert werden.

Wie aus den in Tabelle 1 gezeigten Resultaten ersichtlich ist, wird das Cadmium bis zu Konzentrationen von 100 μg pro Liter quantitativ am Austauscher adsorbiert, und zwar unabhängig davon, ob die in der Arbeitsvorschrift beschriebene Chlorid- oder Bromidmethode zur Anwendung gelangt. Diese Versuche wurden unter Verwendung von Wiener

Tabelle 1. Resultate von Cadmiumbestimmungen im Wiener Trinkwasser

Zugesetzte Cadmiummenge, μg/l.	Wiedergefundene Cadmiummenge, μg/l. Chloridmethode	Bromidmethode
0,0	0,1	0,1*
4,0	4,1	4,1
50,0	50,2	50,1
100	102	101,5
500	489	493
1000	937	930

* Auch nach Durchfluß von 5 Litern mit Bromwasserstoffsäure entsprechend angesäuertem Trinkwasser wurde ein Cadmiumgehalt von 0,1 μg Cd/Liter gefunden. Dieser Gehalt ist um einen Faktor von etwa 7 bis 36 geringer als die Cadmiumgehalte der in den Tabellen 2 und 3 angeführten Gewässer.

Tabelle 2. Ergebnisse von Cadmiumbestimmungen in Wasserproben aus Niederösterreich

	Cadmiumgehalt μg/l			
Probenbezeichnung und Datum der Probenahme	Chloridmethode*		Bromidmethode*	
Donau† bei Klosterneuburg; 11.11.1972	0,85	0,80	—	—
Donau† bei Ybbs-Persenbeug; 9.2.1973	1,70	1,50	1,25	1,20
Pisting bei Pernitz; 2.12.1972	0,90	0,80	—	—
Pisting bei Miesenbach; 2.12.1972	1,30	1,00	—	—
March bei Marchegg; 14.2.1973	0,80	1,00	—	—
Fischa bei Ebreichsdorf; 2.1.1973	1,40	1,50	—	—
Ybbs bei Ybbs; 9.2.1973	1,10	1,25	0,85	1,00
Erlauf bei Erlauf; 9.2.1973	1,70	1,70	1,10	1,20
Pielach bei Prinzensdorf; 9.2.1973	0,90	1,00	0,70	0,60
Melk bei Melk; 9.2.1973	0,65	1,20	0,70	0,70
Kamp bei Hadersdorf; 9.2.1973	0,70	0,75	0,75	1,10
Traisen bei St. Pölten; 9.2.1973	0,75	1,20	0,60	0,50
Ysper bei Ysperdorf; 9.2.1973	1,70	1,80	1,30	1,25
Krems bei Krems; 9.2.1973	1,90	1,60	1,50	1,90
Rußbach bei Engelhartstetten; 14.1.1973	1,70	1,40	—	—
Teich im Industriegebiet N. Ö. Süd; 23.2.1973	1,30	1,20	1,15	1,25
Brunnen bei Ebreichsdorf; 23.2.1973	1,70	2,00	1,75	2,10
Mödling bei Wiener Neudorf; 23.2.1973	0,80	0,90	0,75	1,00
Teich bei Brunn am Gebirge; 23.2.1973	1,30	1,20	1,15	1,30
Abfluß der Metallfabrik Möllersdorf; 23.2.1973	0,90	1,10	0,95	0,90
Abflußkanal von Wr. Neustadt; 23.2.1973	1,10	1,25	1,15	1,20
Abfluß der Fa. Stoll-Lack; 23.2.1973	1,15	1,20	1,10	1,25
Schwechat bei Traiskirchen; 23.2.1973	1,00	1,30	1,10	1,20
Tristing bei Leobersdorf; 23.2.1973	1,90	1,70	1,70	1,90
Quellwasser der Schmida bei Eggenburg; 17.3.1973	0,60	0,65	0,80	0,70
Brunnen bei Zitternberg; 17.3.1973	3,40	3,60	3,70	3,90
Ysperklamm bei Ysper; 17.3.1973	1,10	1,20	1,30	1,20
Quelle bei Kotzenberg; 17.3.1973	1,70	1,60	1,70	1,60
Weisen bei Diezheim; 17.3.1973	1,00	0,90	0,90	0,80
Bach bei Rosenburg; 17.3.1973	0,80	0,70	0,80	0,80
Grundwasser bei Rosenburg; 17.3.1973	0,60	0,50	0,70	0,60
Erster Stausee der Kamp; 17.3.1973	0,75	0,70	0,80	0,70
Quelle bei Ottenschlag; 17.3.1973	0,60	0,80	0,80	0,70
Seitenbach der Türnitz; 3.4.1973	0,40	0,35	0,40	0,50
Traisen oberhalb Freiland; 3.4.1973	0,50	0,40	0,30	0,60
Seitenarm der Türnitz bei Türnitz; 3.4.1973	0,30	0,35	0,30	0,50
Laaberbach (Klamm) (Quelle der Gr. Tulln); 3.4.1973	0,40	0,40	0,30	0,50
Türnitz bei Moosbach; 3.4.1973	0,30	0,35	0,40	0,30
Quelle der Schwechat bei Agsbach; 3.4.1973	0,30	0,30	0,40	0,30
Quelle der Schwechat bei Lamerau; 3.4.1973	0,40	0,40	0,50	0,40
Natternbach-Nebenfluß der Pielach; 3.4.1973	0,40	0,30	0,40	0,50
Pielach bei Schwarzenbach; 3.4.1973	0,40	0,50	0,40	0,60
Gölsen bei Hainfeld-Nebenfluß der Traisen;3. 4.1973	0,60	0,70	0,60	0,80
Tradigist bei Kirchberg-Nebenfluß der Pielach; 3.4.1973	0,40	0,50	0,30	0,50
Soiserbach-Nebenfluß der Pielach; 3.4.1973	0,50	0,60	0,50	0,70

* Cadmiumgehalt in der zweite Spalte ist nach Abzug von 4,0 μg Cadmium-Spike, die 1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurden, berechnet.

† Durch spektralanalytische Messungen wurden in Jahre 1972 in mehreren, an verschiedenen Orten gezogenen, Donauwasserproben Cadmiumgehalte von 0,04 bis 2,6 μg Cd/Liter ermittelt.[20]

Tabelle 3. Ergebnisse von Cadmiumbestimmungen in Wasserproben aus dem Burgenland und der Steiermark

	Cadmiumgehalt $\mu g/l$.			
Probenbezeichnung und Datum der Probenahme	Chloridmethode*		Bromidmethode*	
Burgenland				
Leitha bei Hornstein; 3.12.1972	1,90	2,00	—	—
Neusiedlersee bei Rust, 3.12.1972	1,20	0,90	—	—
Zicksee; 2.1.1973	1,20	1,30	—	—
Wulka bei Wulkersdorf; 2.1.1973	1,00	1,20	—	—
Güns bei Landeck; 2.3.1973	0,65	0,60	0,60	0,70
Pinka bei Oberwart; 2.3.1973	0,60	0,70	0,60	0,70
Strembach bei Kemeten; 2.3.1973	0,80	0,90	0,70	0,80
Stoober bei Weppersdorf; 2.4.1973	0,50	0,60	0,40	0,60
Edlau bei Dörfl; 2.4.1973	0,80	0,90	—	—
Rabnitz bei Dörfl; 2.4.1973	1,00	1,20	1,10	1,00
Siegrabenbach bei Kalkgruben; 2.4.1973	0,70	0,60	0,80	0,70
Steiermark				
Mürz bei Kindberg; 19.11.1972	1,00	1,25	—	—
Gebirgsbach bei Afflenz; 19.11.1972	1,70	1,45	—	—
Übelbach bei Peggau; 2.3.1973	0,75	0,90	0,60	0,80
Kleinstübingerbach; 2.3.1973	0,60	0,70	0,80	0,70
Rabnitz bei Eggersdorf; 2.3.1973	0,90	1,10	1,00	1,10
Raab bei Gleisdorf; 2.3.1973	1,20	1,30	1,20	1,20
Feistritz bei Willfersdorf; 2.3.1973	0,70	0,60	0,80	0,60
Lafnitz bei Burgau; 2.3.1973	1,00	1,10	0,90	1,00
Ilz bei Gnies; 2.4.1973	1,30	1,00	0,90	1,20
Saifenbach bei Blumau; 2.4.1973	0,80	1,00	0,90	0,70

* Cadmiumgehalt in der zweite Spalte ist nach Abzug von 4,0 μg Cadmium-Spike, die 1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurden, berechnet.

Trinkwasser durchgeführt, dem pro Liter jeweils eine der in Tabelle 1 angeführten Cadmiummengen zugesetzt wurde. Danach wurde das Cadmium mittels beider in der Arbeitsvorschrift beschriebenen Methoden abgetrennt und quantitativ bestimmt.

Wie aus Tabelle 1 ersichtlich ist, sind die bei Anwesenheit von hohen Cadmiumkonzentrationen auftretenden Cadmiumverluste relativ gering, so daß die Anionenaustauschmethoden auch unter diesen Bedingungen angewendet werden könnten.

Aus 1,2*M* Salzsäure werden außer Cadmium auch die Ionen Zn(II), Hg(II), Tl(III), Bi(III), Pb(II), Ag(I), Sn(II, IV), Sb(III), Te(IV), Re(VII), Au(III), Pt(IV), Ru(IV), Pd(II), Os(III), Rh(IV) und Ir(IV) vom Anionenaustauscher adsorbiert, und zwar, mit Ausnahme von Blei und Silber, mit etwa derselben Stärke sie das Cadmium.

Da praktisch alle dieser koadsorbierten Fremdionen in natürlichen Wässern nur in Konzentrationen vorkommen, die der Cadmiumkonzentration entsprechen bzw. noch geringer sind als diese, ist eine Störung der Ionenaustauschtrennungen durch Koadsorption dieser Ionen nicht zu erwarten.

In einer wesentlich höheren Konzentration als das Cadmium tritt jedoch das Zink auf, welches außerdem ein dem Cadmium sehr ähnliches Anionenaustauschverhalten, sowohl in salzauren als auch in salpetersauren Lösungen, aufweist. Aus bromwasserstoffsauren Lösungen wird jedoch das Zink zum Unterschied vom Cadmium nur relativ schwach vom Anionenaustauscher adsorbiert (in 0,15, 0,5 und 1,0*M* Bromwasserstoffsäure weisen die

Verteilunskoeffizienten des Zinks Werte von 3, 20 und 100 auf),[19] so daß vor allem 0,15M Bromwasserstoffsäure als ein sehr wirksames Elutionsmittel für das, zusammen mit dem Cadmium aus 1,2M Salzsäure oder 1,0M Bromwasserstoffsäure, am Anionenaustauscher adsorbierte Zink benützt werden kann. Dabei reicht das in der Arbeitsvorschrift angegebene Volumen von 100 ml 0,15M Bromwasserstoffsäure dazu aus, um selbst Milligrammengen Zink quantitativ vom Cadmium zu trennen wobei, im Fall der mit Salzsäure angesäuerten Proben, das ursprünglich als Chloridkomplex adsorbierte Cadmium in den noch stärker adsorbierbaren anionischen Bromidkomplex übergeführt wird.

In Tabellen 2 und 3 werden die Ergebnisse von Cadmiumbestimmungen in Wasserproben gezeigt, die zahlreichen Gewässern einiger österreichischer Bundesländer entnommen wurden. Diese Analysen wurden unter Anwendung der in der Arbeitsvorschrift beschriebenen Anionenaustauschtrennungen und der spektrophotometrischen Endbestimmungsmethode mittels Dithizon durchgeführt. Wie daraus ersichtlich ist, werden bei den Analysen nach Abzug der als Spike zugesetzten Cadmiummenge von jeweils 4 μg, ebenso gute Ergebnisse als bei jenen erzielt, die in Abwesenheit von Spike-Cadmium durchgeführt wurden.

Erwartungsgemäß weisen die beiden untersuchten Grundwässer deutlich höhere Cadmiumgehalte auf als die meisten anderen Gewässer.

Da die vorliegenden Methoden auf der Anwendung der weitgehend automatisierbaren Anreicherung und Abtrennung des Cadmiums auf Anionenaustauschersäulen beruht, ist es möglich, viele Wasserproben gleichzeitig nach deren Ansäuern und Filtration zu analysieren d.h. das Verfahren eignet sich vorzüglich zur serienmäßigen Bestimmung des Cadmiums in Gewässern.

Danksagung—Dem Fonds zur Förderung der wissenschaftlichen Forschung wird an dieser Stelle für die Bereitstellung der zur Durchführung der beschriebenen wissenschaftlichen Arbeit erforderlichen Mittel bestens gedankt.

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Summary—A method is described for the isolation of ppM levels of cadmium from natural waters, and their spectrophotometric determination. The water sample (1 litre) is made 1·2*M* in HCl or 1·0*M* in HBr, filtered, and passed through a column of Dowex 1-X8 (chloride form) anion-exchanger. The cadmium is quantitatively sorbed and simultaneously separated from other trace metals in the sample. Co-adsorbed zinc is removed with 0·15*M* HBr, and the cadmium eluted with 2*M* HNO_3 and determined by the dithizone method. Many Austrian water samples have been analysed and found to contain 0·1–4·0 ppM of cadmium.

Résumé—On décrit une méthode pour l'isolement de teneurs de l'ordre de la ppM de cadmium d'eaux naturelles, et pour leur dosage spectrophotométrique. L'échantillon d'eau (1 litre) est rendu 1,2*M* en HCl ou 1,0*M* en HBr, filtré, et passé sur une colonne d'échangeur d'anions Dowex 1-X8 (forme chlorure). Le cadmium est sorbé quantitativement et simultanément séparé d'autres métaux à l'état de traces dans l'échantillon. Le zinc co-adsorbé est éliminé par HBr 0,15*M*, et le cadmium élué par HNO_3 2*M* et déterminé par la méthode à la dithizone. On a analysé de nombreux échantillons d'eaux autrichiennes et trouvé qu'ils contiennent 0,1–4,0 ppM de cadmium.

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ANWENDUNG VON IONENAUSTAUSCHVERFAHREN ZUR BESTIMMUNG VON SPURENELEMENTEN IN NATÜRLICHEN WÄSSERN—III

THORIUM

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Zusammenfassung—In der vorliegenden Arbeit wird eine Methode beschrieben, die es ermöglicht ppb.-Mengen Thorium aus natürlichen Wässern abzutrennen und der spektrophotometrischen Endbestimmung zugängig zu machen. Nach dem Eindampfen der mit Salpetersäure angesäuerten und filtrierten Wasserprobe (1 Liter) wird das Thorium aus $8M$ Salpetersäure durch Adsorption auf einer Säule des stark basischen Anionenaustauschers Dowex 1-X8 (Nitratform) von den Begleitementen getrennt. Das adsorbierte Thorium wird mit $6M$ Salzsäure eluiert und im Eluat, unter Anwendung der Arsenazo III-Methode, spektrophotometrisch bestimmt. Die Methode wurde zur Bestimmung des Thoriums in zahlreichen österreichischen Gewässern herangezogen, wobei Thoriumgehalte im Konzentrationsbereich von 0,4 bis 4,5 ppb. gefunden wurden.

Infolge des sehr geringen Thoriumgehaltes natürlicher Wässer (Thoriumkonzentrationen im ppb-Bereich) ist es in praktisch allen Fällen erforderlich, das Thorium vor der quantitativen Bestimmung anzureichern bzw. von den Begleitelementen abzutrennen.

Aus Literaturangaben über Thoriumbestimmungen in natürlichen Wässern[1–17] inklusive Meerwasser[1,5,8,17] geht hervor, daß die angewendeten Anreicherungsmethoden im Wesentlichen darauf beruhen, daß das Thorium entweder durch Mitfällung[1–7] mit geeigneten Kollektoren oder durch Adsorption auf Ionenaustauscherharzen[1,8,9] isoliert wird. Danach wird das Thorium entweder spektrophotometrisch bestimmt,[1,2,5,6,8–13] wie z.B. durch Anwendung der Arsenazo III-Methode[5,10,11] oder des Thoronolverfahrens,[2,6,9] oder radiochemisch nach vorangehender Neutronenaktivierung der Analysenproben.[7,14–17]

Zur Abtrennung des Thoriums aus Wässern durch Mitfällung wurden u.a. folgende Kollektoren benützt:[18] basische Phosphate des Calciums und Magnesiums,[1] Calciumoxalat,[2,6] Eisen(III)hydroxid[3,7] und Bariumsulfat.[3] Nach erfolgter Mitfällung ist es jedoch oft erforderlich, das Thorium einer weiteren Reinigungsoperation zu unterziehen, damit es störungsfrei spektrophotometrisch bestimmt werden kann. Dazu eignet sich z.B. ein System bestehend aus 40 vol.% $1M$ Salpetersäure und 60 vol.% Äthanol, aus dem das Thorium auf dem stark basischen Anionenaustauscher Dowex-1 adsorbiert und gleichzeitig von allen begleitenden Fremdionen getrennt wird.[1]

Eine Isolierung des Thoriums aus natürlichen Wässern mittels Ionenaustausches ist auch ohne dessen vorangehende Mitfällung möglich, und zwar durch Adsorption des Thoriums auf dem Chelatharz Chelex-100[8] oder auf Amberlite IRA-400 aus einer ascorbinsäurehaltigen Wasserprobe vom pH-Wert 4 bis 4,5.[9] Im letzteren Fall ist es jedoch erforderlich diese

Anionenaustauschtrennung mit einer nachfolgenden Kationenaustauschoperation auf Dowex 50 zu kombinieren, um die ebenfalls als anionische Ascorbinatkomplexe auf Amberlite IRA-400 koadsorbierten Fremdionen (vor allem Titan und Zirkonium) vom Thorium zu tennen, so daß dieses störungsfrei spektrophotometrisch bestimmt werden kann.

Obwohl sich die Adsorption des Thoriums auf stark basischen Anionenaustauscherharzen wie z.B. Dowex 1 aus 5 bis 10*M* salpetersauren, rein-wäßrigen Lösungen gut zur Abtrennung von Begleitelementen eignet,[18] hat dieses Trennungsprinzip zur Thoriumanalyse von natürlichen Wässern bis jetzt keine Anwendung gefunden. Wie jedoch in der vorliegenden Arbeit gezeigt wird, ist dieses Anionenaustauschverfahren sehr gut dazu geeignet, um Thorium aus Wässern zu isolieren, wonach dieses Element, unter Anwendung der Arsenazo III-Methode, störungsfrei spektrophotometrisch bestimmt werden kann.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Ionenaustauscher. Es wurde der stark basische Anionenaustauscher Dowex 1-X8 (100–200 mesh; Chloridform) verwendet. Zur Umwandlung in die Nitratform wurde das Harz (4 g) in die Ionenaustauschersäule gebracht und solange mit 8*M* Salpetersäure gewaschen bis im Effluenten mit Silbernitrat kein Chlorid mehr nachweisbar war. Das so hergestellte Nitratharz kann danach zur Abtrennung des Thoriums aus den Wasserproben benützt werden.

Thorium-Standardlösungen. Durch Lösen von 12,67 g Thoriumnitrathexahydrat in 8*M* Salpetersäure und Verdünnen der Lösung mit Säure derselben Molarität wurde eine Stammlösung hergestellt, die 5 mg Thorium/ml enthielt (der Thoriumgehalt dieser Lösung wurde durch ÄDTA-Titration überprüft). Die zur Aufstellung der Eichkurve nach der Arsenazo III-Methode erforderlichen Standardlösungen enthielten 1 bis 15 μg Thorium/ml konz. Salzsäure. Diese Lösungen wurden durch Eindampfen von entsprechend verdünnten aliquoten Teilen der Stammlösung in Gegenwart von konz. Salzsäure und Ameisensäure und Aufnahme der Eindampfrückstände in konz. Salzsäure hergestellt.

Arsenazo III-Lösung. Eine 0,2 gew.%ige wäßrige Lösung von Arsenazo III [2,2-(1,8-Dihydroxy-3,6-disulfo-2,7-naphthylenbisazo)-diphenylarsonsäure] (frisch bereitet oder höchstens zwei Wochen alt).

Kaliumpermanganatlösung. Eine 2 gew.%ige wäßrige Lösung von Kaliumpermanganat.

Salpetersäure 8 M. Diese Säure wurde durch Vermischen von konz. Salpetersäure (etwa 16*M*) und dest. Wasser im Verhältnis 1:1, ohne Berücksichtigung von Volumsänderungen, hergestellt. Um die Bildung von Gasblasen in den Ionenaustauschersäulen zu vermeiden, soll diese angenähert 8*M* Salpetersäure erst nach dem Abkühlenlassen auf Raumtemperatur verwendet werden.

Andere Reagenzien. Ferner wurden verwendet: konz. Ameisensäure, 1*M*, 6*M* und konz. Salzsäure (37 %ig; *p.a.*) sowie konz. Salpetersäure (65 %ig).

Apparaturen

Die Ionenaustauschtrennungen wurden in Austauschersäulen eines in einer früheren Arbeit[19] angegebenen Typs ausgeführt.

Für die photometrischen Bestimmungen des Thoriums wurde ein Beckman Spektralphotometer, Modell B und 1 cm-Küvetten verwendet.

Arbeitsvorschrift

Vorbereitung der Wasserprobe. Ein Liter der Wasserprobe wird sofort nach der Probenahme (mittels einer gut verschließbaren Plastikflasche) mit 70 ml konz. Salpetersäure angesäuert und dann im Laboratorium durch ein dichtes Filter filtriert. Das Filtrat wird in einem 2-l. Becherglas auf dem Wasserbad zur Trockne eingedampft und der Rückstand in etwa 25 ml 8*M* Salpetersäure gelöst. Sollte sich dabei der Rückstand nicht vollständig auflösen, so werden unlösliche Anteile durch ein mit 8*M* Salpetersäure gewaschenes, dichtes Filter abfiltriert und mit etwa 5 bis 10 ml 8*M* Salpetersäure nachgewaschen. Die so hergestellte Lösung stellt die für die Anionenaustauschtrennung des Thoriums erforderliche Sorptionslösung dar.

Ionenaustauschtrennung. Die, wie oben angegeben, hergestellte Sorptionslösung wird durch eine mit 4 g des Ionenaustauscherharzes beschickte Säule (die vorher mit 8*M* Salpetersäure vorbehandelt wurde), mit einer dem Gegendruck des Harbettes entsprechenden Geschwindigkeit (etwa 2 bis 3 ml/Minute), fließen gelassen. Anschließend wird mit 40 ml 8*M* Salpetersäure nachgewaschen, um die das Thorium begleitenden nicht oder nur schwach adsorbierbaren Fremdionen zu entfernen. Hierauf wird das adsorbierte Thorium mit 70 ml 6*M* Salzsäure eluiert (Thoriumeluat).

Zur Regenerierung des Harzes (Überführung in die Nitratform) wird die Säule nach Elution des Thoriums so lange mit $8M$ Salpetersäure gewaschen bis im Effluent kein Chlorid mehr nachweisbar ist. Danach ist das Harz für eine weitere Thoriumabtrennung benutzbar.

Quantitative Bestimmung des Thoriums. Das Thoriumeluat (siehe oben) wird auf dem Wasserbad zur Trockne eingedampft, und zwecks Zerstörung organischer Substanzen wird der Eindampfrückstand in 5 ml $1M$ Salzsäure und 5 ml der 2 %igen Kaliumpermanganatlösung aufgenommen, und die Lösung auf dem Wasserbad zur Trockne eingedampft. Der im Eindampfrückstand vorhandene Braunstein wird dann durch Zusatz von 10 ml konz. Salzsäure und darauffolgendes Eindampfen der Lösung zur Trockne auf dem Wasserbad in leicht lösliches Mangan(II)chlorid übergeführt. Der Eindampfrückstand wird zwecks Entfernung von gegebenenfalls anwesendem Nitration mit einigen Tropfen konz. Ameisensäure und 10 ml konz. Salzsäure versetzt, und die Lösung auf dem Wasserbad zur Trockne eigedampft. Der Rückstand wird in 5 ml konz. Salzsäure aufgenommen, die Lösung in einen 10-ml Meßkolben gebracht, 1 ml der 0,2 %igen Arsenazo III-Lösung zugesetzt und mit Wasser zur Marke aufgefüllt. Anschließend wird die Extinktion der Lösung gegenüber einer Reagensleerlösung bei 660 nm gemessen, und mittels einer analog aufgestellten Eichkurve (im Konzentrationsbereich von 0 bis 15 μg Thorium/10 ml Meßlösung) der Thoriumgehalt der Probelösung ermittelt (10 μg Thorium entsprechen einer Extinktion von 0,210). Von der gemessenen Extinktion der Probelösung muß jedoch vor Berechnung des Thoriumgehaltes ein Extinktionswert von 0,035 abgezogen werden (Reagensleerwert, den man erhält, wenn 1 Liter dest. Wasser genauso behandelt wird wie die auf Thorium zu analysierende Wasserprobe).

RESULTATE UND DISKUSSION

In rein wäßrigen salpetersauren Systemen hoher Säuremolarität bildet Thorium einen stabilen anionischen Nitratkomplex, dem die Formel $[Th(NO_3)_6]^{2-}$ zugeschrieben wird.[18] Demzufolge ist es möglich, diesen Hexanitratkomplex auf stark basischen Anionenaustauscherharzen zu adsorbieren, und so das Thorium von anderen Metallionen, die keine oder nur instabile anionische Nitratkomplexe bilden, zu trennen. Diese Trennung wird am besten in 5 bis $10M$ Salpetersäure ausgeführt, da bei diesen Säurekonzentrationen die Verteilungskoeffizienten des Thoriums z.B. auf Dowex-1 am höchsten sind. So weist der Verteilungskoeffizient des Thoriums in der in der vorliegenden Arbeit verwendeten Sorptionslösung (etwa $8M$ an Salpetersäure; siehe Arbeitsvorschrift) einen Wert von etwa 300 auf[18] während unter denselben Bedingungen Calcium, Magnesium und alle anderen in natürlichen Wässern in relativ großen Mengen auftretenden Elemente nicht adsorbiert werden. Demzufolge ist dieses Medium sehr gut dazu geeignet, um ppm—Mengen an Thorium aus den Eindampfrückständen von Wasserproben abzutrennen. Da mittels dieser Anionenaustauschtrennung auch die in Gewässern vorhandenen Spurenelemente wie z.B. Uran, Titan, Zirkonium und die seltenen Erdmetalle, sowie Anionen, wie Phosphat, Fluorid und Sulfat quantitativ vom Thorium trennbar sind (sie werden ebenfalls nicht vom Austauscher adsorbiert) ist es möglich, das Thorium nach dessen Elution vom Austauscher störungsfrei, spektrophotometrisch unter Anwendung der Arsenazo III-Methode zu bestimmen. Eine wesentliche Vorausssetzung für die Anwendung von Arsenazo III zur Thoriumbestimmung ist nämlich die weitgehende Abwesenheit von störenden Fremdionen, vor allem Zirkonium, Titan, Uran und der seltenen Erdmetalle.

Das nach Elution des Thoriums erhaltene $6M$ salzsaure Thoriumeluat enthält keines der oben angeführten Elemente, dagegen aber immer wechselnde Mengen von aus dem Anionenaustauscher stammenden, organischen Substanzen, die unbedingt vor der spektrophotometrischen Bestimmung des Thoriums zerstört werden müssen.[20] Dazu eignet sich vorzüglich die in der Arbeitsvorschrift angegebene oxydative Methode. Da selbst nach Zerstörung der organischen Substanzen und dem darauffolgendem Eindampfen mit konz. Salzsäure der manganchloridhaltige Rückstand noch immer Nitration enthalten kann, so muß dieses vor Anwendung der Arsenazo III-Methode zerstört werden (siehe Arbeitsvorschrift). Anderenfalls tritt eine oxydative Zerstörung des Farbstoffes ein, wodurch verursacht wird, daß die angewendete Farbstoffmenge nicht mehr dazu ausreicht, um mit dem anwesenden Thorium quantitativ den für die Messung erforderlichen Komplex zu bilden.

Tabelle 1. Resultate von Thoriumbestimmungen im Wiener Trinkwasser

Probenbezeichnung und Datum der Probenahme	Thoriumgehalt ($\mu g/l.$)	
Leitungswasser, Analytisches Institut der Universität, Wien 1090; 19.1.1973	3,75	4,10*
Leitungswasser, Analytisches Institut der Universität, Wien 1090; 24.1.1973	3,35	—
Leitungswasser, Analytisches Institut der Universität, Wien 1090; 12.3.1973	3,13†	—
Erste Wiener Hochquellenwasserleitung (Rosenhügel); 7.4.1973	3,50	3,40*
Zweite Wiener Hochquellenwasserleitung (Mauer); 7.4.1973	3,90	4,00*
Pumpenwasser aus der Lobau; 7.4.1973	0,60	0,70*
Grundwasser aus Nußdorf; 7.4.1973	0,50	0,40*

* Thoriumgehalt nach Abzug von 5 μg. Thorium-Spike, die 1 Liter Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurde.

† Thoriumgehalt nach Abtrennung des Thoriums aus einer 3 Liter Wasserprobe.

Bei Anwendung der Arsenazo III-Methode ist ferner zu beachten, daß alte Lösungen dieses Farbstoffes nach längerem Stehenlassen (länger als etwa 2 Wochen) niedrigere Extinktionswerte für Thorium ergeben und auch oft, infolge Bildung eines Niederschlags in der Farbstofflösung, trübe Meßlösungen erhalten werden. Es ist daher erforderlich die Messungen von unbekannten Thoriumgehalten unter Benützung einer erst kürzlich hergestellten Farbstofflösung auszuführen und die Extinktionswerte mit jenen von gleichzeitig hergestellten Standard-Meßlösungen von bekannten Thoriumgehalten zu vergleichen, d.h. die Aufstellung der Eichkurve soll zur selben Zeit erfolgen.

Tabelle 2. Ergebnisse von Thoriumbestimmungen in Wasserproben aus Niederösterreich, dem Burgenland und der Steiermark

Probenbezeichnung und Datum der Probenahme	Thoriumgehalt ($\mu g/l.$)*	
Niederösterreich		
Donau bei Ybbs-Persenbeug; 9.2.1973	1,4	1,2
Erlauf bei Erlauf; 9.2.1973	1,9	2,0
Melk bei Melk; 9.2.1973	3,0	2,9
Pielach bei Prinzensdorf; 9.2.1973	1,4	1,3
Pielach bei Schwarzenbach; 3.4.1973	1,6	2,0
Natternbach-Seitenarm der Pielach; 3.4.1973	1,7	1,9
Ybbs bei Ybbs; 9.2.1973	1,1	0,9
Krems bei Krems; 9.2.1973	1,5	1,3
Kamp bei Hadersdorf; 9.2.1973	1,7	1,5
Traisen bei St. Pölten; 9.2.1973	4,0	4,0
Traisen, oberhalb Freiland; 3.4.1973	2,3	2,1
Gölsen bei Hainfeld-Nebenfluß der Traisen; 3.4.1973	1,4	1,6
Ysper bei Ysperdorf; 9.2.1973	3,1	2,8
Tradigistbach bei Kirchberg, Nebenfluß der Pielach; 3.4.1973	1,8	2,1
Soiserbach bei Kirchberg; 3.4.1973 Nebenfluß der Pielach	2,0	2,4
Teich im Industriegebiet N.Ö.Süd; 23.2.1973	1,5	1,6
Brunnenwasser bei Ebreichsdorf; 23.2.1973	1,7	1,9
Mödling bei Wiener Neudorf; 23.2.1973	2,8	2,9
Teich bei Brunn am Gebirge; 23.2.1973	2,4	2,1
Abfluß der Metallfabrik Möllersdorf; 23.2.1973	1,2	1,3
Abflußkanal von Wr. Neustadt; 23.2.1973	1,5	1,4
Abfluß der Fa. Stoll-Lack; 23.2.1973	0,7	0,7

Fortsetzung von Tabelle II

Probenbezeichnung und Datum der Probenahme	Thoriumgehalt* (µg/l.)	
Schwechat bei Traiskirchen; 23.2.1973	4,5	4,3
Quellwasser der Schwechat bei Agsbach; 3.4.1973	3,4	3,6
Quellwasser der Schwechat bei Lamerau; 3.4.1973	3,2	3,0
Tristing bei Leobersdorf; 23.2.1973	1,4	1,2
Schmida bei Eggenburg; 17.3.1973	1,6	1,7
Brunnen bei Zitternberg; 17.3.1973	1,7	1,5
Ysperklamm bei Ysper; 17.3.1973	2,8	2,6
Quelle bei Kotzenberg; 17.3.1973	1,8	1,5
Weisen bei Diezheim; 17.3.1973	1,5	1,4
Bach bei Rosenburg; 17.3.1973	1,8	1,7
Grundwasser bei Rosenburg; 17.3.1973	1,6	1,7
Erster Stausee der Kamp; 17.3.1973	1,8	1,9
Quelle bei Ottenschlag; 17.3.1973	1,4	1,3
Seitenarm der Türnitz bei Schwarzenbach; 3.4.1973	1,8	1,5
Seitenarm der Türnitz bei Türnitz; 3.4.1973	1,4	1,7
Türnitz bei Moosbach; 3.4.1973	1,5	1,8
Laaberbach (Klamm), Quellfluß der Großen Tuln; 3.4.1973	1,6	1,9
Kalter-Gang bei Klostertal, Quellwasser der Piesting; 24.4.1973	3,4	3,1
Quellwasser der Schwarza	3,5	3,6
Trinkwasser-Pernitz (bei Schallhof); 24.4.1973	3,2	3,2
Burgenland		
Güns bei Landeck; 2.3.1973	1,4	1,2
Pinka bei Oberwart; 2.3.1973	1,7	1,5
Strembach bei Kemeten; 2.3.1973	2,6	2,5
Stoober bei Weppersdorf; 2.4.1973	2,8	3,1
Edlau bei Dörfl; 2.4.1973	3,0	3,0
Rabnitz bei Dörfl; 2.4.1973	1,4	1,3
Siegrabenbach bei Kalkgruben; 2.4.1973	2,5	2,8
Steiermark		
Übelbach bei Peggau; 2.3.1973	1,8	1,9
Kleinstübingerbach; 2.3.1973	1,8	1,7
Rabnitz bei Eggersdorf; 2.3.1973	1,4	1,4
Raab bei Gleisdorf; 2.3.1973	2,8	3,2
Feistritz bei Wilfersdorf; 2.3.1973	1,5	1,4
Lafnitz bei Burgau; 2.3.1973	1,5	1,4
Ilz bei Gnies; 2.4.1973	1,8	1,5
Saifenbach bei Blumau; 2.4.1973	3,6	3,6

* Die Resultate der zweiten Spalte wurden nach Abzug von 5 µg Thorium-Spike, die 1 Liter der Wasserprobe vor der Ionenaustauschtrennung zugesetzt wurden, erhalten.

In Tabellen I und II werden die Ergebnisse von Thoriumbestimmungen in Wasserproben gezeigt, die zahlreichen Gewässern einiger österreichischer Bundesländer und dem Wiener Trinkwasser entnommen wurden. Diese Analysen wurden unter Anwendung der in der Arbeitsvorschrift beschriebenen Anionenaustauschtrennung und der spektrophotometrischen Endbestimmungsmethode mittels Arsenazo III durchgeführt. Wie daraus ersichtlich ist, werden bei den Analysen oder mit Spike versehenen Proben, nach Abzug der als Spike zugesetzten Thoriummenge von jeweils 5 µg, ebenso gute Ergebnisse als bei jenen erzielt, die in Abwesenheit von Spike-Thorium durchgeführt wurden.

Aus den in Tabellen I und II gezeigten Resultaten ist auch ein allgemeiner Trend ablesbar, und zwar weisen Trink- und Quellwässer meist beträchlich höhere Thoriumgehalte auf als Grund- oder Abflußwässer und auch Wässer stammend aus Flüssen oder größeren Bächen.

Der Grund hierfür dürfte darin liegen, daß in allen Gewässern mit Ausnahme der Trink- und Quellwässer eine starke Abreicherung durch Mitfällung des Thoriums eintritt, die umso größer ist, je verunreinigter das betreffende Wasser ist.

Da die vorliegende Methode auf der Anwendung der weitgehend automatisierbaren Anreicherung und Abtrennung des Thoriums auf Anionenaustauschersäulen beruht, ist es möglich, viele Wasserproben gleichzeitig nach deren Eindampfen zu analysieren, d.h. das Verfahren eignet sich vorzüglich zur serienmäßigen Bestimmung des Thoriums in Gewässern.

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Summary—A method is described for separation of ppb levels of thorium from natural waters and a spectrophotometric finish. A 1-litre water sample is acidified with nitric acid and filtered, then evaporated, and the thorium adsorbed on Dowex 1-X8 strongly basic anion-exchanger (nitrate form) from 8*M* nitric acid to separate it from accompanying elements. The thorium is eluted with 6*M* hydrochloric acid and determined spectrophotometrically by the Arsenazo III method. The method has been applied to determination of thorium at the 0.4–4.5 ppb level in Austrian natural waters.

Résumé—On décrit une méthode pour la séparation de teneurs de l'ordre de la ppb. de thorium des eaux naturelles et le dosage spectrophotométrique final. Un échantillon d'eau de 1 litre est acidifié à l'acide nitrique et filtré, puis évaporé, et le thorium absorbé sur l'échangeur d'anions for tement basique Dowex 1-X8 (forme nitrate) à partir 'dacide nitrique 8*M* pour le séparer des éléments qui l'accompagnent. Le thorium est élué par l'acide chlorhydrique 6*M* et dosé spectrophotométriquement par la méthode à l'Arsenazo III. On a appliqué la méthode au dosage du thorium au niveau de 0,4–4,5 p.p.M. dans des eaux naturelles autrichiennes.

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COULOMETRIC MICRODETERMINATION OF PEROXIDES—II*

ORGANIC PEROXIDES

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Summary—An iodometric method for the rapid microdetermination of organic peroxides, utilizing electrochemical reduction in the iodine–iodide system, has been developed. After complete reaction between peroxide and iodide in an acidic semi-aqueous medium the iodine produced is reduced at a rotating platinum electrode, at constant potential. Electronic integration is used. Organic peroxides of different reactivities have been analysed by making use of the increased rate of reaction at elevated temperatures. Accurate and precise results were obtained for samples at the 1-mg level and the total time of analysis varied from 8 to 20 min, depending on reactivity.

Organic peroxides are of importance because of their use in industry and their occurrence in many industrial products. The problem of the analytical chemist is to select the most appropriate method of analysis; this is particularly important for organic peroxides where reactivity varies widely and the compounds have to be determined in very diverse materials. The purpose of the present work was to develop a simple and general method for the microdetermination of pure organic peroxides and for application to some problems concerning industrial products.

The choice of a suitable method for the determination of organic peroxides depends on several factors, such as concentration, reactivity and solubility of the peroxide and the nature of the matrix. An excellent survey of present analytical methods for organic peroxides has been given in a book by Johnson and Siddiqi.[1] Titrimetric, colorimetric, polarographic, spectroscopic and chromatographic techniques are discussed. For the determination of pure organic peroxides iodometric procedures are the most generally applicable. Besides, the simple iodometric methods are often adequate for the non-selective determination of total peroxide content, as in most routine analyses of peroxides in industry, such as determination of the peroxide value of fats and oils. Finally, the iodometric technique may be used as a sensitive analytical method for the determination of traces of peroxides in petrochemicals.

Iodometric methods for the determination of organic peroxides are based on quantitative reduction by iodide ions in acid solution:

$$\mathrm{ROOR'} + 2\mathrm{H}^+ + 2\mathrm{I}^- \rightleftharpoons \mathrm{I}_2 + \mathrm{ROH} + \mathrm{R'OH}$$

where R and R′ denote hydrogen, alkyl, acyl or aralkyl groups. The determination of hydrogen peroxide (R = R′ = H) has been discussed in an earlier paper.[2] The reaction above, carried out in the absence of oxygen, proceeds at various rates depending on the reactivity

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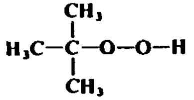
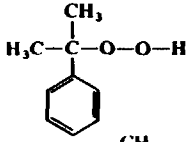
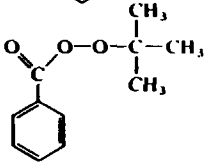
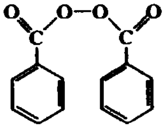
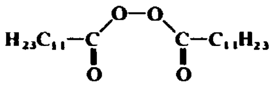
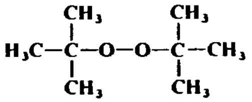
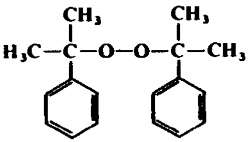
* Part I—*Talanta*, 1973, **20**, 1097.

Table 1. Coulometric determination of organic peroxides.

Name	Formula	Reaction conditions	Sample size, *mg*	Apparent purity, %	Number of determinations	Precision at a confidence limit of 95%, %
t-Butyl hydroperoxide	 $H_3C{-}C(CH_3)_2{-}O{-}O{-}H$	60°C, 3 min	0·1–0·7	77·94	25	±0·09
Cumene hydroperoxide		60°C, 2 min	0·2–1·0	78·28	28	±0·09
t-Butyl perbenzoate		60°C, 3 min	0·6–1·3	70·96	25	±0·14
Benzoyl peroxide		25°C, 30 sec	0·3–1·4	99·83* 100·08†	71 10	±0·04 ±0·05
Lauroyl peroxide		50°C, 2 min	0·5–1·5	99·05* 99·63†	15 9	±0·12 ±0·16
t-Butyl peroxide	 $H_3C{-}C(CH_3)_2{-}O{-}O{-}C(CH_3)_2{-}CH_3$	60°C, 3 min 90°C, 5 min	0·4 0·4	0·57‡ 1·11‡	3 2	— —
Cumyl peroxide		90°C, 5 min	0·7	91·74	6	±0·25

* Commercial product. † Purified product. ‡ Total recovery obtained.

of the peroxide. After complete reaction the liberated iodine is usually determined by titration with standard thiosulphate solution. Provided no other oxidizing agents or unsaturated compounds are present, the iodometric method is simple and relatively quick and can give reliable and reproducible results. However, one of the limiting factors in this procedure is the titration end-point determination for small samples. Electrometric methods have been reported as possible alternatives to visual methods in the titration of very dilute solutions. In the newly developed method presented here, this difficulty has been completely eliminated, by replacing the titrimetric iodine determination by a coulometric iodine reduction.

An electroanalytical method, based on controlled-potential coulometry in the iodine–iodide system, has been investigated for the microdetermination of organic peroxides of different reactivities. In the working electrolyte, consisting of an acidic semi-aqueous iodide solution, the organic peroxide added reacts quantitatively, producing an equivalent amount of iodine. When reaction is complete, the iodine is reduced at the working electrode, maintained at a controlled potential. The number of coulombs consumed in this reaction, which is a measure of the amount of iodine, is determined by electronic integration of the decaying current–time curve. By keeping the reaction mixture at thermostatically controlled elevated temperatures this method has been made applicable to a wide range of organic peroxides, and samples in the range 0·1–1·5 mg have been determined with good accuracy and a precision around ±0·2% (Table 1).

EXPERIMENTAL

Electrolysis cell

The electrolysis cell used is of the same basic construction as described previously.[2] To allow analysis of peroxides of different reactivities, the sample compartment has been furnished with a glass jacket for circulation of water, thereby allowing the reaction mixture to be kept at different constant temperatures below 100°.

Electrodes

A three-electrode system, consisting of a platinum gauze working electrode, a saturated calomel reference electrode and a platinum-spiral counter-electrode, has been used as described earlier.[2]

Apparatus

The electronic circuitry was identical to that described in Part I.[2] For the calculation of *p*-values, current–time curves were registered by means of a recorder.

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized, freshly distilled water.

The supporting electrolyte, used for filling the connecting chamber and auxiliary compartment of the cell, was $1M$ aqueous sodium perchlorate. The working electrolyte consisted of $1M$ sodium perchlorate–$1M$ sodium iodide in a medium of glacial acetic acid–water (1:1).

Nitrogen, used for continuous deaeration of the working electrolyte, was of a high purity (>99·9%), and passed over copper at 500° for removal of any oxygen.

As a test substance for the coulometric cell potassium iodate (KIO_3; Merck) was used. After drying at 150° for 8 hr, a purity of 99·95–100·05% was obtained according to the manufacturer.

Organic peroxides. The following classes of peroxides are listed in order of decreasing oxidative reactivity (*e.g.*, towards iodide ions):

(1) hydroperoxides
(2) peroxy esters
(3) diacyl and diaroyl peroxides
(4) dialkyl and diaralkyl peroxides

From these groups the following peroxides have been tested:

t-butyl hydroperoxide (Schuchardt); technical, ≥79·5%
cumene hydroperoxide (Schuchardt); ~70%

t-butyl perbenzoate (BDH)
benzoyl peroxide (BDH)
lauroyl peroxide (BDH)
t-butyl peroxide (Schuchardt); ≥98%
cumyl peroxide (Schuchardt); 96–99%

As benzoyl peroxide is one of the most frequently analysed organic peroxides mentioned in the literature, it was the first tested in this work. The analysis was performed on the commercial product, both untreated and after purification by precipitation from a chloroform solution with an excess of cold absolute methanol, followed by drying in vacuum over concentrated sulphuric acid.[3] Lauroyl peroxide was also purified by this method. All other compounds tested in this work were analysed for peroxide content without further purification.

Glacial acetic acid and chloroform were used as solvents for the peroxides.

Procedure

The three compartments of the electrolysis cell were filled with the appropriate electrolytes. The semi-aqueous working electrolyte, consisting of acetic acid and water, was at about pH 2. This solution was continuously deaerated with nitrogen, passing at a flow-rate of 10 ml/min. The glass jacket, surrounding the working compartment of the cell, was provided with circulating water, thermostatically controlled at the desired temperature. All iodine present in the reaction mixture was reduced at the rotating platinum gauze working electrode until the current reached a stable residual value ($< 10\ \mu A$).

After this start-up, the analysis was performed according to the same sequence of operations as described earlier for large samples of H_2O_2.[2] The pre-reaction time, necessary for complete iodine formation, varied for the different peroxides and also with the reaction temperature. Whenever the pre-reaction time was superfluous, the simplified procedure[2] described for small samples of H_2O_2 was adopted.

The integrator reading obtained was converted into mg of organic peroxide as follows:

$$M \cdot \frac{10^3 \cdot A \cdot U_c}{F} = \text{mg of organic peroxide}$$

where M = equivalent weight of the peroxide and A, F and U_c have the same meaning as before.[2]

Sample volumes ranging from 50 to 250 μl of acetic acid or chloroform solutions of peroxides were added from a glass syringe microburette (Agla) with an accuracy of $\pm 0{\cdot}02\ \mu l$. The analysis time varied from 8 to 20 min over the sample range investigated (0·1–1·5 mg) for the different peroxides.

RESULTS AND DISCUSSION

Reactivity

Organic peroxides are characterized by an oxygen–oxygen bond (ROOR′) and may be classified according to the functional groups R and R′ attached to the central oxygen atoms. The electron density on the peroxy bond has a marked influence on the oxidizing power of the compound. Thus, peroxides having a low electron density are more reactive towards iodide ions. The electron density on the peroxy bond is affected by the character of adjacent functional groups. Peroxides containing strongly electron-releasing groups, such as dialkyl peroxides, have least oxidizing power. Bulky alkyl groups, such as t-butyl, may also exert steric hindrance to reaction with large ions or molecules. These effects will be much less pronounced in the case of the hydroperoxides where only one alkyl group is present, and in fact hydroperoxides are far more reactive than the dialkyl peroxides. One would expect that most of the other classes of peroxides would have a reactivity somewhere in between, and this is generally true.

Johnson and Siddiqi[1] have described earlier investigations of iodometric peroxide determinations. Summarizing these results, it has been found that peroxy acids are the most reactive peroxides. Alkyl hydroperoxides are also very reactive. These peroxides have been determined iodometrically although reaction times of 10–20 min are required at room temperature. In some cases elevated temperatures are necessary for complete reaction. Per-esters also react with iodide ions in, *e.g.*, aqueous acetic acid. However, in the absence of a catalyst the reaction requires prolonged reaction times (1–4 hr at room temperature). Aqueous acetic acid or chloroform–acetic acid has been used as a solvent for diacyl or diaroyl peroxides, which react somewhat slowly with iodide ions. The reaction time and temperature required depend on the particular peroxide and the solvents used. Finally, dialkyl peroxides dissolved in the above-mentioned solvents react very slowly with iodide ions and need to be heated at 60 or 120° for 45 min to ensure complete reaction. Thus, the majority of organic peroxides can be reduced by iodide ions in acid solution.

Choice of solvent and working electrolyte

The choice of solvent depends on the sample and on the peroxide to be determined. Water is only suitable for the low molecular weight per-acids. Acetic acid has proved a useful solvent for many organic peroxides and was subsequently used for dissolving most of the peroxides tested. Whatever solvent mixture is chosen, each component must be free of peroxides and dissolved oxygen must be removed. The absence of peroxides is confirmed by a low blank value. The matrix-correction for pure acetic acid corresponded to about 0·002 μeq of peroxide per 100 μl of acetic acid at 25° but amounted to 0·015 μeq/100 μl at 60°, traces of peroxides in the solvent then being more readily reduced. Thus, this method can be used for the determination of traces of peroxides in solvents such as ether and dioxan (see *Applications*).

The working electrolyte has to meet at least two requirements: the peroxide has to dissolve and furthermore react rapidly, *i.e.*, in a few minutes, with the iodide ions in the usable temperature range 25–90°C. The organic peroxide does not dissolve in a purely aqueous acidic medium. In that respect an acetic acid medium would be more suitable. However, a semi-aqueous acetic acid medium containing iodide ions was selected as the most appropriate working electrolyte. This medium readily dissolves most organic peroxides and reduces them quantitatively, forming iodine. The cell resistance was reduced to a reasonable level by addition of a supporting electrolyte, sodium perchlorate. However, it has been stated that the presence of water in the acetic acid medium retards the reaction between peroxide and iodide ions.[4] This effect, although small, can be compensated for by increasing the reaction time or the temperature. The main advantage in using a semi-aqueous medium as electrolyte in the coulometric determination is that the following reduction of iodine can be carried out with a high initial electrolysis current due to low cell resistance. Furthermore, the diffusion coefficient for iodine is larger, giving a more rapid determination (high p-value) and a low residual current.

For the analysis of strongly lipophilic peroxides, such as lauroyl peroxide and for the determination of peroxides in lipids, such as oils and fats, water has to be absent during the reaction with iodide ions. Chloroform and acetic acid–chloroform were two of the possible solvents. After complete reaction, water (containing supporting electrolyte) was added to the reaction mixture in order to facilitate rapid electrochemical reduction of the iodine produced. Thus, the simple procedure of making successive analyses in the same reaction mixture was not applicable to this group of peroxides. However, results proved that the method used was quite feasible.

The iodide ions of the working electrolyte were provided by sodium iodide, which has a high solubility in organic solvents. There are two main advantages in using a liberal excess of iodide.[5] First, losses of iodine either from heating or purging the reaction mixture with a stream of inert gas are prevented, since non-volatile I_3^- is formed.[2] Secondly, since tri-iodide ion will not add to olefinic double bonds, errors due to absorption of liberated iodine by unsaturated compounds in the sample are eliminated.

Choice of reaction conditions

As with the choice of solvent, the reaction conditions selected depend upon the nature of the sample and the class of peroxides present. In the coulometric method described here, complete reaction with iodide in the reaction mixture selected was established by means of varying the temperature and time of reaction. As a rule lower temperature and/or shorter time of reaction could be used with this method than with iodometric methods earlier described, and the sample size was essentially smaller.

A helpful guide in selecting the most suitable reaction conditions was the *p*-value of the cell, defined according to:

$$i = i_0 \cdot e^{-p \cdot t}$$

As mentioned earlier the *p*-value increases with the diffusion coefficient (*D*). If the other parameters determining *p* (electrode area, solution volume and rate of stirring) are kept constant, an elevated reaction temperature influences *p* by increasing *D*. Thus, favourable conditions are obtained *both* for reaction between peroxide and iodide *and* for reduction of the iodine produced. It was found that *p* increased linearly with the temperature in blank tests, the gradient being 0·032 min^{-1}. deg^{-1}, and the value of *p* about 1·2 min^{-1} at 25°. By studying the *p*-value for reduction of the iodine produced by an organic peroxide, the most suitable temperature and reaction time can be chosen. If the temperature is too low or the reaction time too short, the *p*-value will be smaller and the linear range of log *i* *vs.* time will be less than for the corresponding blank test, owing to incomplete formation of iodine before starting the reduction. As a rule reaction times longer than 3 min were undesirable; the use of a higher temperature was preferred, to obtain a rapid determination.

The working electrolyte of pH = 1·9 was studied by means of current–voltage measurements[2] in order to choose the most suitable working potentials. Thus, the iodine produced was reduced at 0 mV *vs.* SCE in all experiments, and the electrolytically generated iodine for blank tests was produced at +300 mV *vs.* SCE.

The loss of iodine from the sample compartment was studied by means of blank tests. In addition to the previously mentioned parameters,[2] the temperature of the reaction mixture influenced the total loss, as the aerial oxidation of iodide increases with temperature, giving an efficiency larger than 100%. However, the effect was small and the results obtained for a given temperature were reproducible. For oxidation and reduction of about 2·5 μmole of iodine with a pre-reaction time of 1 min, the efficiency was 100·0% at 25° and 100·4% at 60° (*cf.* Fig. 4 in ref. 2).

Applications

In order to test the accuracy of the coulometric method a suitable test substance of a high and specified purity was analysed, using the working electrolyte selected. The method was then used for the determination of the purity of some organic peroxides of different reactivities (Table 1). Furthermore, it was applied for analysing traces of peroxides in some solvents and for the determination of low peroxide values of fats and oils.

Test substance. Potassium iodate reacts instantaneously with iodide ions in an acid medium

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$

Samples containing 0·1–0·3 mg of KIO_3 were analysed at 25° according to two methods. The simplified procedure with no pre-reaction time resulted in a purity of 100·02 ± 0·05% with a confidence limit of 95%. After a pre-reaction time of 30 sec, the result, corrected for the blank test, was 99·98 ± 0·04% with the same confidence limit.

Benzoyl peroxide. Many iodometric methods for the determination of benzoyl peroxide have been described in the literature. They have all been developed for relatively large sample sizes (> 10 mg) and require at least 5 min reaction time at room temperature. In the coulometric method complete reaction is established within 30 sec. The purity of the commercial product after drying over phosphorus pentoxide was determined to be 99·83%. After suitable purification (see *Reagents*) the increased melting point (103·5–103·9°) indicated a higher purity. A value of 100·08% was now obtained with the coulometric method. Samples containing 0·3–1·4 mg of peroxide were thus analysed with a high precision.

As benzoyl peroxide has often been used as a test substance in *e.g.*, standard addition methods, an examination was made with this peroxide over a wider range of sample size. For triple determinations of samples containing from 10 μg to 10 mg, the relative standard deviation never exceeded 0·3% and the accuracy relative to the value determined earlier was within ±0·2%.

The kinetics of the decomposition of benzoyl peroxide in various solvents have been extensively studied.[6] For a 0·050*M* solution of benzoyl peroxide in acetic acid the calculated decrease in concentration is about 0·1% in 10 hr. Thus, all sample solutions had to be freshly prepared daily.

Lauroyl peroxide. Lauroyl peroxide reacts much more slowly than does benzoyl peroxide. Complete reaction was established after 2 min in a non-aqueous solution of iodide in acetic acid, maintained at 50°. Aqueous sodium perchlorate solution was added before electrolytic reduction. In this case the blank test was performed according to the same procedure, on pure solvent (chloroform). In spite of careful deaeration of the solutions, this method gave higher blank values but still with good reproducibility (corresponding to 0·127 ± 0·002 mg lauroyl peroxide with 95% confidence).

t-Butyl perbenzoate. With ferric chloride being used as a catalyst, reaction times of 10–15 min have been reported for peroxy-esters;[7,8] without any catalyst the reaction has proved to be very slow. In the coulometric method it was found that a reaction time of at least 10 min was necessary for complete reaction at room temperature when ferric ions were present. To decrease the total time of analysis, the reaction temperature was increased to 60°, whereby use of catalyst was made superfluous, and the reaction time was reduced to 2–3 min.

t-Butyl hydroperoxide. To get a rapid reaction between peroxide and iodide a relatively high reaction temperature had to be chosen. At 60° reaction was complete within 3 min.

Cumene hydroperoxide. This peroxide, being slightly more reactive than t-butyl hydroperoxide, required 2 min reaction time at 60°.

t-Butyl peroxide. This peroxide is one of the least reactive organic peroxides. As it often occurs as an impurity in the corresponding hydroperoxide, it was first determined under the same conditions as t-butyl hydroperoxide, *i.e.*, 3 min reaction at 60°. The total recovery obtained was 0·57%, assuming a 100% pure dialkyl peroxide. Thus, on the assumption that the impurity of the hydroperoxide is mainly dialkylperoxide, the maximum error in the calculated purity is 0·13% (see Table 1).

By investigating different reaction conditions it was found that complete reaction between this peroxide and iodide ions could not be obtained in the working electrolyte used. Even at 90° a reaction time of 5 min yielded a recovery of only about 1 %.

Cumyl peroxide. Experiments proved that this peroxide really is more reactive than the bulky t-butyl peroxide. Reaction was complete after 5 min at 90°.

It has been reported[5] that the determination of cumyl peroxide in solutions containing water gives somewhat low results. However, this is considered as a minor drawback since all interferences from any cumyl alcohols present disappeared.

Peroxides in solvents. The determination of traces of peroxides in some ethers was investigated.

It has been stated in the literature that ultraviolet light produces peroxides in ethers.[4] Pure diethyl ether was analysed, and showed no peroxide content whatsoever. After 30 min exposure to ultraviolet light (254 nm) the peroxide content, determined after 30 sec of reaction at 25°, was $4{\cdot}24 \pm 0{\cdot}16$ ppm active oxygen with a 95 % confidence limit.

Pure dioxan was analysed according to two methods. Direct determination of the peroxide content yielded $77{\cdot}6 \pm 0{\cdot}3$ ppm active oxygen. Determination by means of standard addition of pure benzoyl peroxide (of known purity) yielded $78{\cdot}7 \pm 1{\cdot}7$ ppm active oxygen, both precisions referring to a confidence limit of 95 %.

Peroxide values of fats and oils. This coulometric method was finally applied to a practical problem of great interest. Low peroxide values of fats and oils are almost impossible to determine by the usual titrimetric methods, especially when coloured samples have to be analysed. However, successful results were obtained by the coulometric method, where peroxide values down to 0·06 were determined with reasonable precision. The results of this investigation will be reported elsewhere.[9]

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Zusammenfassung—Eine jodometrische Methode zur raschen Mikrobestimmung von organiscchen Peroxiden mit Hilfe elektrochemischer Reduktion im Jod–Jodid-System wurde entwickelt. Nach Beendigung der Reaktion zwischen Peroxid und Jodid in saurem halbwäßrigem System wird das gebildete Jod bei knostantem Potential an einer rotierenden Platinelektrode reduziert. Die Integration wird elektronisch ausgeführt. Organische Peroxide verschiedener Reactivität wurden analysiert, indem die höhere Reaktionsgeschwindigkeit bei höherer Temperatur ausgenutzt wurde. Genaue und richtige Ergebnisse wurden bei Proben von etwa 1 mg erhalten; die gesamte Analysenzeit lag je nech der Reaktivität zwischen 8 und 20 min.

Résumé—On a mis au point une méthode iodométrique pour le microdosage rapide de peroxydes organiques, utilisant le réduction électrochimique dans le système iode-iodure. Après réaction complète entre le peroxyde et l'iodure dans un milieu semi-aqueux acide, l'iode produit est réduit à l'électrode tournente de platine, à potentiel constant. On utilise l'intêgration électronique. On a analysé des peroxydes organiques de différentes réactivités en utilisant la vitesse accrue de réaction aux températures élevées. On a obtenu des résultats précis et justes pour des échantillons à l'échelle de 1 mg et le temps total d'analyse a varié de 8 à 20 mn, dépendant de la réactivité.

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CONTROLLED-POTENTIAL BACK-TITRATION WITH ELECTROGENERATED IODINE AS AN INTERMEDIATE

APPLICATION TO THE DETERMINATION OF THIOLS

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Summary—A controlled-potential electroanalytical method has been devised for the accurate determination of small amounts of thiols. An adequate excess of iodine is generated, the sample is added and the unreacted iodine is then electrolytically reduced. The iodine consumed is calculated from the measured number of coulombs. Amounts of thiols in the range 0·2–5 mg may be determined with an error of ±0·05%. A coulometric cell has been constructed which permits very high electrolysis rates, owing to efficient stirring by a large rotating platinum electrode combined with a high electrode-area to solution-volume ratio. A constant of 0·11 sec^{-1} is found for the reduction of iodine. The necessity of careful control of background currents and current efficiency in coulometric determinations is discussed.

Controlled-potential coulometry is a well-established technique for precise and accurate analysis. Its usefulness is, however, limited to systems with fast and well-defined electrode reactions. In cases where efficient electrode reactions are difficult to obtain, the introduction of a chemical intermediate and use of constant-current coulometry is often used as an alternative. While the end-point in controlled-potential coulometry is obtained directly when the electrolysis current has reached a low, nearly constant value, the constant-current coulometric method requires a suitable end-point indicating system. A combination of these methods whereby controlled-potential coulometry is applied to an intermediate system seems attractive.

In this investigation a method is developed in which a chemical intermediate is generated in a controlled-potential back-titration (CPBT). The following procedure is adopted. An excess of an intermediate is generated at a rotating platinum electrode. The sample is then added and after complete reaction the remainder of the intermediate is re-electrolysed at controlled potential. The electrolysis currents are electronically integrated and the quantity of intermediate consumed by the sample is calculated from the difference in the quantity of electricity used in the generating and re-electrolysis steps. The method is applied to the determination of thiols with iodine as the intermediate.

It is well known that thiols are rapidly and quantitatively oxidized by iodine to the corresponding disulphides [1–4] according to the reaction

$$2RSH + I_2 \longrightarrow RSSR + 2HI \qquad (1)$$

More recently, Danehy[5] has investigated the reaction mechanism for the oxidation of thiols by iodine. He has shown that there is a tendency for further oxidation to higher oxidation states of sulphur. The thiols investigated here are not problematic in this respect. In other cases, especially for cystein and other β-mercaptocarboxylic acids, precautions must be taken in the choice of experimental conditions in order to avoid errors caused by over-oxidation. Furthermore, many thiols are unstable in solution and sensitive to aerial oxidation. Therefore it is necessary to control carefully the sample preparation and handling. Much effort was spent on preparing pure thiols in order to facilitate testing of the accuracy of the determination.

From a practical viewpoint, fast electrolysis is desirable and it is important to shorten the electrolysis time in order to minimize the error introduced in the correction for the background current. A cell with small volume and a rapidly rotating platinum gauze electrode was constructed. Because of the high ratio of working-electrode area to solution volume and the efficient stirring, very high electrolysis rates could be used. The constant for the reduction of iodine was 0·06–0·11 sec^{-1}. When iodine was used as the intermediate in the 1–25 μmole range the electrolysis time was 2–5 min. The initial current was 100 mA for reduction of more than 8μmole of iodine and the background current was smaller than 5 μA.

EXPERIMENTAL

Electrolysis cell

The coulometric cell shown in Fig. 1 is made in two parts, the lower consisting of a plate with a filter system connecting to the auxiliary electrode, and the upper where a depression facing the lower part constitutes the working compartment. The lower part is made of glass. It consists of a plate (11), 60 mm in diameter, sealed to the bridge (20) and auxiliary electrode (18) compartments which are of conventional design, including a glass frit (19) of porosity 4. The surface of the plate is carefully ground with carborundum No. 800. A 6-mm hole (13) through the glass plate provides connection to the bridge compartment. From the surface to a depth of 3 mm the bore is 10 mm. This provides room for a filter (12) between the bridge compartment and the working compartment. The filter used is a Haldenwanger clay filter with a pore size smaller than that of glass frits of porosity 4 but giving higher conductivity. The clay filter cannot be heat-sealed to glass, but a special cement supplied by Haldenwanger is used instead. When the filter is put in position it is polished with emery paper to the level of the glass surface.

The upper part is a Teflon disc, 80 mm in diameter and 30 mm thick. In the lower surface of the disc a circular depression, 45 mm in diameter and 4mm deep, is machined. The axis of the depression is displaced 2·5 mm with respect to the axis of the disc. When the disc is placed on the glass plate the depression constitutes the working-electrode compartment (17). Sealing against the ground-glass surface is effected with an O-ring (9). The working electrode (10) is positioned centrically with respect to the Teflon disc and eccentrically with respect to the working-electrode compartment. The shaft of the electrode is placed in two stainless-steel ball-bearings mounted in the support (4) protruding 20 mm above the upper surface of the Teflon disc. The shaft of the electrode is guided in a narrow tube which is enlarged to 10 mm for a length of 5 mm at the lower end in order to prevent electrolyte from creeping up the shaft. Two 3-mm holes (6, 7) ending in the enlarged part of the shaft tube are used as sample and nitrogen inlets respectively. The nitrogen inlet is threaded in the upper end for attachment of a Teflon tubing connector. Holes for reference electrode and glass electrode are positioned near the circumference of the working compartment in such a manner that the electrodes are placed completely outside the area covered by the working electrode. This prevents disturbances caused by mechanical scraping.

The upper and lower parts of the cell are placed together and secured with the aid of six winged screws and a ring-formed PVC holder (14) pressed against the glass part.

Electrodes

The rotating circular working electrode is made from 36-mesh platinum gauze. It is 40 mm in diameter and has an effective area of about 25 cm^2. The electrode is attached to a 15 mm long, 3-mm platinum rod which is soldered to a stainless-steel shaft of the same diameter. The shaft is mounted in the Teflon disc with two stainless-steel ball-bearings. The entire length of the shaft is Teflon-covered to prevent contact between steel and the solution. Electrical contact to the potentiostat is made by a mercury pool contact (1 in Fig. 1). The gauze is rotated by a stirring motor (Radiometer Type M22) *via* a transmission system permitting choice of speed in the range 150–1500 rpm. The reference electrode is a saturated calomel electrode (Radiometer K 401) with a potential of 0·244 V *vs.* the standard hydrogen electrode. The glass electrode is a combination electrode including a saturated calomel electrode (Radiometer GK 2321 C). Both

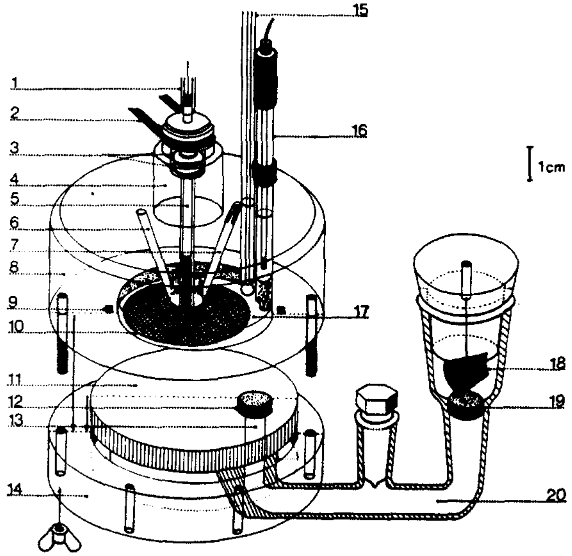

Fig. 1. Electrolysis cell.

1. Mercury contact
2. Drive belt
3. Stainless-steel ball-bearings
4. Teflon support
5. Working-electrode shaft
6. Sample inlet
7. Nitrogen inlet
8. Teflon disc
9. O-ring
10. Working electrode
11. Glass plate
12. Clay filter
13. Connection to bridge compartment
14. PVC holder
15. Glass electrode
16. Reference electrode
17. Working compartment
18. Auxiliary electrode
19. Glass frit
20. Bridge compartment

electrodes are held tight against the Teflon disc with Teflon tape. The auxiliary electrode (18) is 36-mesh platinum gauze with an area of about 10 cm^2 mounted in a Teflon plug containing a narrow bore for ventilation.

Electronics

The coulometric circuit is shown in Fig. 2. In addition to the electrolysis cell the coulometric apparatus consists of a potentiostat and an integrator. The potentiostat, which is constructed around an operational amplifier (Burr-Brown 3312/12C) and a booster, controls the working-electrode potential at a constant preselected value *vs.* the saturated calomel electrode. The quantity of electricity consumed is measured by time–current integration with an integrator consisting of a chopper-stabilized operational amplifier (SP 65A) with a 10-μF feedback capacitor. The output of the integrator is measured with a digital voltmeter (Eldorado Model 1820) and the electrolysis time with an electric timer. The value of the integrating resistor R_i can be selected from 6 resistors with values between 0·05 and 10 MΩ, giving a broad working range to the integrator. The integrator was calibrated for each resistor R_i by application of known voltages for measured times. The integration error was determined to be smaller than ±0,02% with 95% confidence. The number of moles of iodine is determined from the output of the integrator according to

$$\text{moles } I_2 = \frac{U \cdot A}{2 \cdot F} \qquad (2)$$

where U = integrator read-out (V), A = factor for integrating components (sec/ohm), F = Faraday's constant (96487 coulomb/mole).

An ordinary pH-meter (Radiometer pH-meter 26) was used for pH measurement with the glass electrode.

Chemicals

All chemicals used were of *pro analysi* quality. The distilled water used was boiled and cooled under nitrogen. The electrolyte was thoroughly bubbled with a rapid stream of nitrogen to remove any dissolved

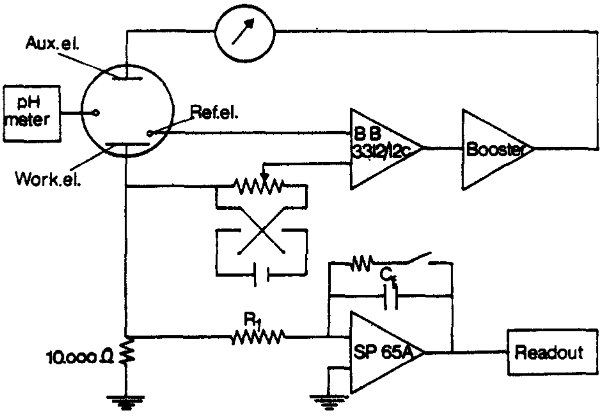

Fig. 2. Coulometric circuit.

oxygen before introduction into the cell. A stream of nitrogen through the coulometric cell was purified by passage over copper at 500° then over "Ascarite" and "Dehydrite". Commercially available buffer solutions were used.

Purification of thiols. Heptanethiol was purchased from American Petroleum Institute (API-USBM standard sample 30-5S) with a guarantee of less than 0·04 ± 0·02 mole per cent impurity. *Benzthiazolin-2-thione of pro analysi* quality was purchased from Merck (Darmstadt). These two thiols were not further purified. *2-Mercaptoethanol, mercaptoacetic acid* and *thiophenol* were purified by repeated vacuum distillations under nitrogen. p-*Thiocresol* was subjected to zone melting at 44° and then dried over phosphorus pentoxide in a vacuum. Samples were taken after different numbers of oven passages and analysed coulometrically. The iodine consumption successively increased. After fifteen oven passages the iodine consumption became constant. *α-Toluenethiol* was purified by means of preparative gas-liquid chromatography on an "Apiezon" column. The product was chromatographed on an analytical column, and gave only the thiol peak. *Pyrid-2-thione* was recrystallized from a chloroform–hexane mixture to a constant melting point of 129°.

Sampling of thiols

After purification the thiols were stored under nitrogen in darkness. For non-volatile thiols a special sampling technique was adopted in which the thiols were weighed in glass capillaries on a Sartorius electronic ultramicrobalance 4125. The balance was first tared with one clean glass capillary on each pan. For liquid thiols one of the glass capillaries was connected to a syringe by a silicone rubber tube and an adequate amount of thiol was sucked up. The glass capillary was again placed on the pan and weighed. The capillary was then connected with a silicone rubber tube to an Agla syringe microburette containing the same medium as the cell with the exception of iodide. The Agla microburette with micrometer was mounted on a rigid steel stand which could be adjusted so that the glass capillary dipped precisely into the solution in the working compartment. The thiol in the glass capillary was rinsed out with about 100 μl of solution from the Agla syringe.

Solid thiols were transferred to the glass capillary in a way similar to the filling of a melting-point glass capillary. After weighing, the thiol was rinsed down into the cell in the same manner as for the liquid thiols. Some of the thiols were difficult to keep in the glass capillary during handling of the sample. In those cases one end of the glass capillary was closed by introduction of a small column of electrolyte immediately after the weighing.

One thiol, benzthiazolin-2-thione, was not rapidly dissolved in methanol and therefore it was not feasible to add the pure thiol directly to the coulometric cell. A standard solution of benzthiazoline-2-thione in methanol was prepared in a calibrated-volume vessel and known volumes of this solution were added with an Agla microburette syringe.

The ultramicrobalance was calibrated against a set of three 1-mg weights which had been compared with a 1-mg mass standard calibrated by the National Bureau of Standards. The weighing error was less than 0·05% from 0·2 to 5 mg. The mass standard was recently compared with a newly calibrated set of mass standards (NBS), the earlier calibration being confirmed.

RESULTS AND DISCUSSION

Current–time behaviour and background current

For controlled-potential coulometry to be an attractive and accurate analytical technique, the electrolysis time must be short and the background current low. The relationship between current and time in controlled-potential coulometric determinations carried out at a potential where the rate of reaction is limited by the rate of mass transfer of the electroactive species to the working electrode is given by the equation:[6]

$$i_t = i_0 \cdot e^{-p \cdot t} \tag{3}$$

where i_0 = initial current, i_t = the current at time t, p = electrolysis rate constant.

A coulometric system with a high, constant p-value indicates a high electrolysis rate and good cell design.[7] The relationship between the electrolysis rate constant and experimental parameters is

$$p = \frac{D \cdot A}{V \cdot \delta} \tag{4}$$

where D = diffusion coefficient of the electroactive species, A = working-electrode area, V = volume of working-compartment solution, δ = thickness of the Nernst diffusion layer.

Thus the rate of electrolysis is highly influenced by the ratio of electrode area to electrolyte volume and the stirring efficiency. Different approaches have been made in order to optimize these factors. Bard[8] used a stationary platinum electrode made from platinum gauze wound in a spiral to fill the working compartment and the stirring was attained by an ultrasonic generator in combination with a rapid nitrogen flow through the electrolyte. Another high-speed controlled-potential coulometric cell was devised by Goode and Herrington.[9] They used a stationary annular platinum gauze combined with magnetic stirring. Recently, Clem[10] has constructed a rotating platinum cell where the electrolyte solution is kept against the cell wall by rotation and is stirred by its motion against a special stationary reference–counter electrode probe. The cell in the present investigation (see Fig. 1) is provided with a rotating platinum electrode in very effective contact with the working-compartment solution, resulting in a very high electrolysis rate. The ratio of the working-electrode area to the working-compartment volume is very high, and since the solution is strictly confined to a small closed volume, effective stirring can be obtained by rapidly rotating the platinum gauze. The stationary reference electrode contributes to the efficiency by giving turbulence in the solution. From log i–time curves for reduction of iodine in water and water–methanol (1:1), electrolysis rate constants were found, from equation (3), to be 0·11 and 0·06 sec^{-1} respectively. The curves were linear over the whole range except for a tendency to deviate from linearity at currents below 10–20 μA, depending on influence from the background current. The solution volume in the cell was 5 ml and the rotational speed of the working electrode 1000 rpm.

In discussing residual currents it is essential to differentiate between background current and current caused by the remaining portion of the electroactive species to be determined. A generally accepted approach is to consider the electrolysis completed when the current has decreased to 0·1% of the initial value.[8] According to equation (3) this will give 99·9% electrolysis. This, however, assumes ideal behaviour with a negligible background current. When the background current cannot be neglected it is of interest to find a suitable method for correction of its influence. If the background current is considered to be constant the electrolysis current finally decays to this background value rather than to zero. This means that the background current contributes with a constant increment to the current caused by the electroactive species and the observed current will not satisfy equation (3). If 99·9% completeness of electrolysis is desired the measured current is not a reliable indication of the end-point. A better approach is to use the electrolysis time. Laitinen[11] has used the term half-time of electrolysis. The half-time $t_{1/2} = 2{\cdot}3 \log 2/p$, where p is the electrolysis rate constant for the species to be determined. Thus, for instance, if 99·9% electrolysis is desired the electrolysis is to be terminated after a time period equal to 10 half-times.

A correction can be applied in the case of constant background current by subtracting this from the current caused by the species to be determined. The fact that the background current in reality varies means that the best result is obtained when its influence is as small as possible, *i.e.*, background currents in the μA range combined with a high p-value. In the present investigation the background current never exceeded 5 μA and the p-value was 0·06–0·11 $\sec^{-1}$. An error of 10% in the estimation of the quantity of electricity caused by the background current will then result in an error smaller than 0·01% in the determination.

Controlled-potential back-titration of thiols

Iodine is a relatively weak oxidizing agent with good selectivity, widely used in volumetric analysis.

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\circ = 0{\cdot}5355 \text{ V}$$

The system is reversible with well-defined electrode reactions and is therefore very useful in electroanalytical applications. Many coulometric determinations involving iodine have been described[12,13]. Generally iodine is used as an intermediate in controlled-current coulometry. An alternative technique has been devised whereby iodine is used as an intermediate but the coulometric determination is performed at controlled potential.

In this investigation controlled-potential back-titration (CPBT) has been developed and applied for the determination of thiols. The basic procedure is that iodine is generated in excess relative to the thiol to be determined. After addition of the sample the remainder of the iodine is determined at controlled potential.

The electrolyte was 1*M* sodium iodide and 1*M* sodium perchlorate in water. For thiols only slightly soluble in water, methanol–water (1:1) was used as solvent. From the current-voltage curves in Fig. 3 the potential of the working electrode for oxidation of iodide to iodine and the potential for reduction of iodine to iodide were chosen as 300 and 0 mV respectively *vs.* SCE. The procedure adopted for the determination of thiols was (1) oxidation of an adequate amount of iodide to iodine at 300 mV *vs.* SCE, (2) addition of the sample, (3) reduction of the unreacted iodine to iodide at 0 mV *vs.* SCE.

In step (1) iodine is generated at virtually constant current, owing to the high concentration of iodide in the solution. This means that the oxidation is very rapid. The quantity of electricity consumed is monitored on the integrator read-out and the electrolysis is interrupted when the preselected amount of iodine has been formed. Upon addition of the thiol [step (2)] an equivalent amount of iodine is consumed. Generally the reaction is instantaneous but for some thiols 2 or 3 min must be allowed to pass before step (3) is started. In this step the unreacted iodine is reduced at 0 mV. The ordinary exponential current–time relationship holds unless the quantity of iodine exceeds about 5 μmole, in which case the current at the beginning is limited to 0·1 A by the booster. Since the current is reversed

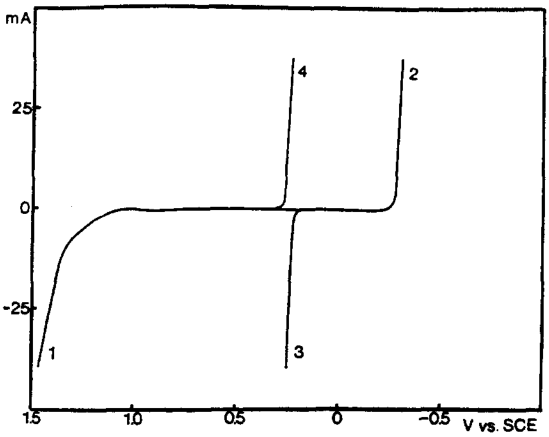

Fig. 3. Current-voltage curves.
1. Oxidation of supporting electrolyte (1*M* $NaClO_4$, pH 7).
2. Reduction of supporting electrolyte (1*M* $NaClO_4$, pH 1).
3. Oxidation of iodide (1*M* NaI).
4. Reduction of iodine (1*M* NaI, 0·005*M* I_2).

compared to step (1) the integration is now performed with opposite sign, resulting in subtraction from the integral stored in the integrator. Thus the read-out on the integrator is a direct measure of the thiol when the reduction step is completed.

The determination is preceded by a check procedure in which an amount of iodine in the same range as the excess used in the determination is generated and immediately re-electrolysed. This check procedure is repeated directly after the determination. Under ideal conditions the read-out on the integrator is zero at the end of a check procedure. Thus any deviation from zero indicates non-ideal behaviour and can be used as a correction. In the experiments described in this investigation the correction never exceeded a value corresponding to 0·1 % of the amount of thiol and was often considerably smaller. The fact that the check procedure after the determination gave the same correction as before the determination indicates that the reaction between thiol and iodine was completed during the determination and also that the disulphide was not slowly consuming iodine.

Table 1. Coulometric determination of thiols.

Thiol	Thiol found‡ *mg*	Number of determinations	Standard deviation, *μg*	pH
Heptanethiol*	1·0001	5	0·6	self-pH†
2-Mercaptoethanol	0·9999	7	0·7	5–7
Mercaptoacetic acid	0·9997	6	0·8	5–7
Thiophenol*	1·0002	9	0·9	3–8
p-Thiocresol*	0·9994	5	0·6	self-pH†
a-Toluenethiol*	1·0004	7	0·7	self-pH†
Pyrid-2-thione	0·9998	6	0·8	6–8
Benzthiazolin-2-thione*	0·9999	6	1·3	self-pH†

* Solvent water–methanol (1 :1)
† pH not controlled with buffer
‡ Data recalculated as for exactly 1·0000 mg of sample.

The results from the coulometric determination of 1-mg samples of eight different thiols are presented in Table 1. The actual sample size varied between 0·9 and 1·1 mg because of the weighing technique but is recalculated to 1·0000 mg in order to facilitate the comparison of the accuracies. The thiols were determined in the range 0·2–5 mg. The accuracies in this range show no significant deviation from those illustrated in Table 1 for 1 mg. In the last column the pH interval is given where the iodine consumption is in agreement with reaction (1).

The results in Table 2 for the determination of different amounts of 2-mercaptoethanol show that the precision in the range 0·2–5 mg is about ±1 μg (95% confidence). The time for generating an excess of iodine, addition of the thiol and reduction of the unreacted iodine was 2–4 min. The check procedures described above take 2 min each, giving a total analysis time of 6–8 min. In the cases where the solvent was water–methanol (1:1) these times were increased by 20%, because of the smaller *p*-value for the reduction of iodine. The lower limit of 0·2 mg for the sample size is set by the working range of the ultramicrobalance. Smaller amounts of thiol can be analysed if known volumes of standard solutions are used. In this case, however, the result is less precise than if the pure thiols are used.

Table 2. Precision of 2-mercaptoethanol determination.

2-Mercaptoethanol taken, *mg*	Precision at a confidence limit of 95%, *μg*	Number of determinations
0·2–1	±0·6	6
1–2	±0·9	8
2–5	±1·2	5

Current efficiency

For coulometric determinations with good precision and accuracy, high current efficiency is a necessity. The oxidation of iodide to iodine at a platinum electrode is generally considered to take place with satisfactory current efficiency.[14,15] The reduction of iodine to iodide has not been so extensively studied but there is no reason to expect greater errors in this case. In order to determine the current efficiency in the reduction step in the system investigated, the reaction

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

was employed. A measured amount of potassium iodate was added to an acidified iodide solution and the iodine formed was electrolysed. The current efficiency for reduction of iodine in amounts corresponding to more than 1 mg of thiol was 100·1 ± 0·1%. Measurement of the background current before and after the analysis gives a correction of −0·1%.

A pure electrochemical current efficiency can be obtained as described by Marinenko and Taylor.[15] They evaluated from current–voltage curves a current efficiency for generation of iodine at a platinum electrode by subtracting the current in pure phosphate buffer of pH 7 from the current for solutions which in addition contained potassium iodide in different concentrations. Current efficiencies of 99·99999% were obtained at background currents smaller than 10^{-2} μA. These values are found under very ideal conditions since they are evaluated with the assumption that the generating current is due only to the oxidation of iodide to iodine, except for a negligible background current. A more relevant method for practical use is to determine a titration efficiency by measuring the amount of iodine formed and comparing this with the number of coulombs consumed in the electrode reaction. In the case of constant-current coulometry the titration efficiency can be obtained chemically by titration of standard materials, for example arsenious oxide and thiosulphate.

In the controlled-potential back-titration a corresponding efficiency is obtained electrically by performing the check procedure described above. This gives an overall titration efficiency including, for example, losses of iodine in the clay filter, in side-reactions and in non-electroactive adsorption[16] at the platinum electrode as well as background currents. A small deviation from 100% efficiency can be accepted and applied as a correction to the analytical result.

CONCLUSION

Controlled-potential back-titration as applied to the determination of thiols with iodine in this investigation renders possible the coulometric determination at controlled-potential of substances not themselves readily electrolysed at an electrode. With a suitable choice of intermediate very good accuracy and precision can be obtained. The check procedure involving generation and re-electrolysis of the intermediate without sample addition gives an opportunity for close control over the coulometric efficiency.

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Zusammenfassung—Zur genauen Bestimmung kleiner Mengen von Thiolen wurde ein elektroanalytisches Verfahren bei geregeltem Potential entworfen. Es wird ein passender Überschuß an Jod erzeugt, die Probe zugegeben und dann das nicht verbrauchte Jod elektrolytisch reduziert. Der Jodverbrauch wird aus der gemessenen Anzahl Coulomb berechnet. Thiolmengen von 0,2–5 mg können mit einem Fehler von ±0,05% bestimmt werden. Es wurde eine coulometrische Zelle konstruiert, die sehr hohe Elektrolysegeschwindigkeiten erlaubt: dies beruht auf wirksamem Rühren mit einer großen rotierenden Platinelektrode, verbunden mit einem hohen Verhaltnis von Elektrodenfläche zu Lösungsvolumen. Für die Reduktion von Jod wird eine Konstante von 0.11 sec^{-1} gefunden. Die Notwendigkeit, bei coulometrischen Bestimmungen die Untergrundströme und die Stromausbeute sorgfältig zu kontrollieren, wird diskutiert.

Résumé—On a établi une méthode électroanalytique à potentiel contrôlé pour la détermination précise de petites quantités de thiols. Un excès convenable d'iode est engendré, l'échantillon est ajouté et l'iode non réagi est alors réduit électrolytiquement. L'iode consommé est calculé à partir du nombre mesuré de coulombs. On peut déterminer des quantités de thiols comprises entre 0,2 et 5 mg avec une erreour de ±0,05%. On a construit une cellule coulométrique qui permet de très hautes vitesses d'électrolyse, du fait d'une agitation efficace par une grande électrode tournante de platine combinée avec un rapport élevé de la surface d'électrode au volume de solution. On trouve une constante de 0,11 sec^{-1} pour la réduction de l'iode. On discute de la nécessité d'un contrôle rigoureux des courants de fond et de l'efficacité de courant dans les dosages coulométriques.

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SHORT COMMUNICATIONS

β-DITHIOCARBAMINOPROPIONIC ACID AS A NEW MASKING AGENT

COMPLEXOMETRIC DETERMINATION OF ZINC IN THE PRESENCE OF CADMIUM

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Masking by means of complex formation is the most convenient method for eliminating interferences in complexometric titrations. It is very difficult to find a specific masking agent for cadmium, which is why only a few methods for determination of zinc in the presence of cadmium without previous separation are known. Mekada *et al.*[1] have examined dimercaptosuccinic acid as a masking agent for cadmium in the EDTA titration of zinc. At pH 6 it is possible to determine zinc in the presence of cadmium if the amount of the latter does not exceed that of the zinc. Přibil and Veselý[2] have proposed a method for the determination of zinc, based on the masking of cadmium with β-mercaptopropionic acid (MPA). The masking is effective if triethylenetetraminehexa-acetic acid (TTHA) is used as titrant, as the Cd–MPA complex is not stable enough to mask cadmium completely in the titration of zinc with EDTA. Good results for zinc are obtained if the Cd : Zn ratio does not exceed 40 : 1. Dithiocarbaminoacetic acid (TCA)[3] is another masking agent which can be used successfully in complexometry. It masks cadmium at pH 5–6, thus making possible the complexometric determination of zinc in the presence of cadmium in amounts up to 60 mg. Flaschka and Butcher[4] have proposed an EDTA titration of zinc in the presence of cadmium at pH 5, in which cadmium is first masked with iodide. Good end-points are obtained for Cd : Zn mole ratios up to 300 : 1. Cadmium is also masked with iodide in the photometric titration of zinc at pH 5 with diethylenetrinitrilopenta-acetic acid (DTPA) as titrant.[5] Correct results have been obtained with Cd/Zn mole ratios up to 3300 : 1. Fabregas *et al.*[6] masked cadmium with lead–EDTA complex. The results are satisfactory up to a weight ratio Cd : Zn = 17 : 1. The pyridinium salt of hydroxyethyldithiocarbamic acid[7] was used as a masking reagent for lead and cadmium in a photometric titration of microgram amounts of zinc. About 100 μg of the interfering metals could be masked with this reagent. A rapid method for successive complexometric determination of zinc and cadmium was proposed,[8] in which cadmium was masked as the ethyl xanthate complex. Good results were obtained with Cd : Zn ratio 24 : 1.

In the course of our investigations on the properties of new selective dithiocarbamic derivatives of aminocarboxylic acids which form stable water-soluble complexes with metal ions, β-dithiocarbaminopropionic acid (β-DTCPA) has now been studied. It has one more methylene group than TCA.[3] The stability constants of the complexes of β-DTCPA with cadmium, lead and zinc have been determined[9] and show that β-DTCPA may be useful as a masking agent in complexometric determinations (see Table 1).

Table 1. Values of the concentration stability constants

	β-DTCPA	TCA
Cd	$\log \beta_1 = 6{\cdot}35 \pm 0{\cdot}16$	$\log \beta_1 = 5{\cdot}4 \pm 0{\cdot}4$
	$\log \beta_2 = 12{\cdot}10 \pm 0{\cdot}22$	$\log \beta_2 = 9{\cdot}3 \pm 0{\cdot}3$
	$\log \beta_3 = 16{\cdot}96 \pm 0{\cdot}22$	$\log \beta_3 = 13{\cdot}7 \pm 0{\cdot}5$
Pb	$\log \beta_1 = 8{\cdot}20 \pm 0{\cdot}26$	$\log \beta_1 = 7{\cdot}30 \pm 0{\cdot}1$
	$\log \beta_2 = 15.59 \pm 0{\cdot}08$	$\log \beta_2 = 13{\cdot}00 \pm 0{\cdot}2$
Zn	$\log \beta_1 = 3{\cdot}55 \pm 0{\cdot}12$	$\log \beta_1 = 3{\cdot}4 \pm 0{\cdot}3$
	$\log \beta_2 = 6{\cdot}47 \pm 0{\cdot}08$	$\log \beta_2 = 6{\cdot}6 \pm 0{\cdot}2$
		$\log \beta_3 \pm 8{\cdot}9 \pm 0{\cdot}3$

EXPERIMENTAL

The diammonium salt of β-DTCPA was prepared from β-alanine and carbon disulphide in ammoniacal medium in the same way as TCA.[3] β-Alanine, 4 g (0·05 mole), was dissolved in 20 ml of concentrated ammonia (0·6 mole), 12 ml of carbon disulphide were added (0·2 mole) and the mixture in the reaction flask was stirred for 3 hr (magnetic stirrer) at room temperature. The unreacted carbon disulphide was discarded and the diammonium salt of β-DCTPA precipitated with ethanol. It forms white crystals of composition $NH_4SCSNHCH_2CH_2COONH_4$, calculated: C 24·12%, H 6·55%, N 21·09%, S 32·19%; found: C 24·2%, H 6·4%, N 21·4%, S 31·7%. The diammonium salt of β-DTCPA is stable in air and needs no special storage, while TCA is stable only when kept in a desiccator.[3] The stability of aqueous solutions of β-DTCPA was examined and established to be like that of TCA[10]; β-DTCPA is not very stable in acidic solutions, but stable enough above pH 4.

Preliminary investigations

In acidic medium (pH 2–3) β-DTCPA masks bismuth, indium, thallium(III), lead, cadmium, mercury(I), mercury(II), iron(III). Aluminium, gallium and thorium are not masked. In the pH range 5–6 the lead, cadmium, mercury(I), mercury(II), copper(II), iron(III), nickel and cobalt(II) are masked. The complexes of mercury, copper, iron, nickel and cobalt are coloured. The complexes of nickel and cobalt are of interest, since the colour is intense and stable. The stability of these complexes is close to that of the corresponding EDTA complexes. The Cu–β-DTCPA complex is more stable than the Cu–EDTA complex but the solution becomes turbid on standing. In the pH range 9–10 lead, cadmium and copper(II) are masked with β-DTCPA, but zinc, manganese(II) and alkaline earth metals are not.

Applications of β-DTCPA in complexometry

On the basis of the qualitative examination, quantitative determinations of various pairs of ions were made, namely: Zn–Cd, Zn–Pb, Ni–Pb, Mn–Pb, Mn–Cd, Co–Pb and Co–Cd. It appeared that β-DTCPA could be used most successfully as a masking agent in complexometric determinations of zinc in the presence of cadmium.

Zinc was determined in the following manner. To a solution containing appropriate amounts of zinc and cadmium, 40 ml of pH 5·5 buffer solution (potassium phthalate–sodium hydroxide), solid diammonium salt of β-DTCPA (6-fold excess with respect to Cd content) and a few drops of Xylenol Orange indicator solution were added. After dilution to about 70 ml the solution was titrated with 0·01*M* EDTA. The results of titrations are summarized in Table 2. The results of complexometric determinations of other pairs of ions are shown in Table 3.

Table 2. Titration of zinc in the presence of cadmium

Zn taken, *mg*	Cd present, *mg*	β-DTCPA added, *mg*	Zn found, *mg*	Difference *mg*
4·24	1·1	50	4·26	+0·02
4·24	11·0	100	4·28	+0·04
9·40	49·7	300	9·43	+0·03
9·40	99·3	600	9·39	−0·01
9·40	198·6	1100	9·41	+0·01
1·26	100·3	650	1·28	+0·02
1.26	159·3	1000	1·25	−0·01
1·26	212·4	1300	1·28	+0·02
1·26	265·5	1600	1·19	−0·07
0·85	275	1650	0·83	−0·02

RESULTS AND DISCUSSION

β-DTCPA can be used successfully as a masking agent for cadmium and lead in complexometric determinations of elements which do not form stable complexes with it. Zinc can be titrated selectively in the presence of large amounts of cadmium. Correct results have been obtained with Zn : Cd ratios from 10 : 1 up to 1 : 300, but with more than 280 mg of cadmium the end-point is not very sharp because of the high concentration of β-DTCPA. It is also possible to determine zinc and cadmium in one sample by titration of both ions with EDTA followed by addition of β-DTCPA, which liberates an equivalent amount of EDTA from the cadmium complex. The EDTA liberated is titrated with a suitable titrant under the same conditions (*e.g.*, a zinc solution). In this way zinc and cadmium in weight ratio Zn : Cd = 1 : 5 can be determined. β-DTCPA can be used successfully for masking lead in EDTA titrations of zinc at pH 5–6 if the amount of lead does not exceed 10 times the amount of zinc. At pH 5–6 Pb–β-DTCPA complex is precipitated but in the course of titration the precipitate dissolves and it is possible to see the end-point clearly. β-DTCPA can also be used to mask cadmium and lead in EDTA titrations of nickel and manganese. Cadmium and lead cannot be masked in EDTA titrations of cobalt, however, owing to the higher stability of the Co–β-DTCPA complex and its intense colour.

Table 3. Complexometric determinations of various ions, with β-DTCPA as a masking agent

Metal (1) taken, *mg*	Metal (2) taken, *mg*	β-DTCPA added, *mg*	Metal (1) found, *mg*	Difference, *mg*
Zn 9·89	Pb 9·76	50	9·87	−0·02*
Zn 9·40	Pb 99·50	500	9·41	+0·01*
Ni 11·12	Cd 29·91	150	11·16	+0·04†
Ni 11·12	Pb 30·45	150	11·18	+0·06†
Mn 9·85	Cd 49·75	250	9·90	+0·05§
Mn 9·85	Pb 50·75	250	9·91	+0·06§

* pH 5·5, buffer hexamine, indicator Xylenol Orange;

† pH 5·5, buffer hexamine, indicator Xylenol Orange, back-titrated with $ZnSO_4$;

§ pH 5·5, buffer hexamine, indicator Xylenol Orange, back-titrated with $ZnSO_4$.

The main advantage of β-DTCPA over TCA[3] is its stronger masking ability for cadmium. The extra CH_2-group in the β-DTCPA molecule causes changes in the stability constants and in the composition of some of its metal complexes. Zinc forms two comparatively weak complexes with β-DTCPA, unlike TCA which forms three (see Table 1). Probably the β-DTCPA molecule provides steric difficulties for co-ordination of the third ligand. On the other hand, the Cd- and Pb–β-DTCPA complexes are more stable than the corresponding TCA complexes (see Table 1). A drawback of β-DTCPA is its unsatisfactory masking efficiency at pH 9–10.

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Summary—A new masking agent in complexometry, β-dithiocarbaminopropionic acid (β-DTCPA) is proposed. β-DTCPA forms very stable water-soluble complexes with a number of metal ions. Zinc can be titrated selectively with EDTA at pH 5–6 in the presence of large amounts of cadmium, which is masked effectively as a cadmium–β-DTCPA complex. Correct results have been obtained with Cd/Zn ratios up to 300 : 1.

Zusammenfassung—Ein neues Maskierungsmittel für die Komplexometrie wird vorgeschlagen: β-Dithiocarbaminopropionsäure (β-DCTPA). β-DTCPA bildet mit einer Anzahl von Metallionen sehr stabile wasserlösliche Komplexe. Zink kann mit EDTA bei pH 5–6 selektiv in Gegenwart großer Mengen Cadmium titriert werden; Cadmium wird wirkungsvoll als Cadmium-β-DTCPA-Komplex maskiert. Es wurden mit Cd/Zn-Verhältnissen bis höchstens 300 : 1 korrekte Ergebnisse erzielt.

Résumé—On propose un nouvel agent de dissimulation en complexométrie, l'acide β-dithiocarbaminopropionique (β-DTCPA). Le β-DTCPA forme des complexes solubles dans l'eau très stables avec un certain nombre d'ions métalliques. On peut titrer le zinc sélectivement à l'EDTA à pH 5–6 en la présence de grandes quantités de cadmium, qui est efficacement dissimulé en tant qu'un complexe cadmium-β-DTCPA. On a obtenu des résultats corrects avec des rapports Cd/Zn jusqu'à 300:1.

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INDIVIDUAL MICRODETERMINATION OF CHLORINE, BROMINE AND IODINE IN HALOGENATED ORGANIC COMPOUNDS BY THE OXYGEN-FLASK METHOD

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The growing interest in the synthesis of halogenated organic compounds containing more than one halogen necessitated the development of an accurate and rapid method for estimation of the individual halogens. Methods are already known, based on use of aliquots of a solution obtained from a single sample.[1,2] The present work was undertaken to develop a micro-method for the individual determination of chlorine, bromine and iodine in all possible combinations, by oxygen-flask combustion. In the combustion of chlorinated organic compounds containing less than about 30% of chlorine the oxygen-combustion reaction gives only hydrogen chloride.[3,4] On the other hand, in the combustion of brominated and iodinated organic compounds, some free halogen is always formed, especially with the latter.[3] It is now found that bromide and iodide can be oxidized to the elements by addition of potassion bromate or hydrogen peroxide respectively, and the elements removed by boiling, facilitating determination of the remaining halide(s) by standard mathods.

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

$$H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$$

It is found that addition of potassium bromate (0·2–4 ml of 0·5% solution) has no effect on chloride, the analytical results being correct within experimental error (±1% relative).

EXPERIMENTAL

Reagents

Bromine–glacial acetic acid–sodium acetate solution.[5]

Sodium hypochlorite solution. Absorb chlorine in $1{\cdot}1M$ sodium hydroxide until the solution is about $1N$ in chlorine.

Procedures

(*i*) *Determination of chlorine or bromine in presence of iodine.* Burn the sample (3–5 mg) as usual by the oxygen-flask method. Absorb the combustion products in 5 ml of distilled water and 3 drops of 30% hydrogen peroxide. Shake thoroughly, then leave for 15 min. Rinse the stopper and the walls of the flask with 20 ml of distilled water. Boil gently for a few min then evaporate the mixture to about 5 ml with intermittent swirling. Cool to room temperature. For chlorine, rinse down with 20 ml of 95% ethanol, add 0.5 ml of $0{\cdot}5M$ nitric acid and titrate with $0.005M$ mercuric perchlorate, using 1% ethanolic diphenylcarbazone solution as indicator.[5] For bromine, place in the mixture during evaporation a 25-mm square of platinum foil (held in a glass rod and electrolytically coated with a rough surface of platinum black) to destroy the excess of hydrogen peroxide. Warm the solution, and when the evolution of oxygen ceases (*ca.* 10 min) remove the rod,

Zusammenfassung—Ein neues Maskierungsmittel für die Komplexometrie wird vorgeschlagen: β-Dithiocarbaminopropionsäure (β-DCTPA). β-DTCPA bildet mit einer Anzahl von Metallionen sehr stabile wasserlösliche Komplexe. Zink kann mit EDTA bei pH 5–6 selektiv in Gegenwart großer Mengen Cadmium titriert werden; Cadmium wird wirkungsvoll als Cadmium-β-DTCPA-Komplex maskiert. Es wurden mit Cd/Zn-Verhältnissen bis höchstens 300 : 1 korrekte Ergebnisse erzielt.

Résumé—On propose un nouvel agent de dissimulation en complexométrie, l'acide β-dithiocarbaminopropionique (β-DTCPA). Le β-DTCPA forme des complexes solubles dans l'eau très stables avec un certain nombre d'ions métalliques. On peut titrer le zinc sélectivement à l'EDTA à pH 5–6 en la présence de grandes quantités de cadmium, qui est efficacement dissimulé en tant qu'un complexe cadmium-β-DTCPA. On a obtenu des résultats corrects avec des rapports Cd/Zn jusqu'à 300:1.

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INDIVIDUAL MICRODETERMINATION OF CHLORINE, BROMINE AND IODINE IN HALOGENATED ORGANIC COMPOUNDS BY THE OXYGEN-FLASK METHOD

(*Received* 11 *April* 1973. *Accepted* 26 *June* 1973)

The growing interest in the synthesis of halogenated organic compounds containing more than one halogen necessitated the development of an accurate and rapid method for estimation of the individual halogens. Methods are already known, based on use of aliquots of a solution obtained from a single sample.[1,2] The present work was undertaken to develop a micro-method for the individual determination of chlorine, bromine and iodine in all possible combinations, by oxygen-flask combustion. In the combustion of chlorinated organic compounds containing less than about 30% of chlorine the oxygen-combustion reaction gives only hydrogen chloride.[3,4] On the other hand, in the combustion of brominated and iodinated organic compounds, some free halogen is always formed, especially with the latter.[3] It is now found that bromide and iodide can be oxidized to the elements by addition of potassion bromate or hydrogen peroxide respectively, and the elements removed by boiling, facilitating determination of the remaining halide(s) by standard mathods.

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$$H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$$

It is found that addition of potassium bromate (0·2–4 ml of 0·5% solution) has no effect on chloride, the analytical results being correct within experimental error (±1% relative).

EXPERIMENTAL

Reagents

Bromine–glacial acetic acid–sodium acetate solution.[5]

Sodium hypochlorite solution. Absorb chlorine in 1·1*M* sodium hydroxide until the solution is about 1*N* in chlorine.

Procedures

(*i*) *Determination of chlorine or bromine in presence of iodine.* Burn the sample (3–5 mg) as usual by the oxygen-flask method. Absorb the combustion products in 5 ml of distilled water and 3 drops of 30% hydrogen peroxide. Shake thoroughly, then leave for 15 min. Rinse the stopper and the walls of the flask with 20 ml of distilled water. Boil gently for a few min then evaporate the mixture to about 5 ml with intermittent swirling. Cool to room temperature. For chlorine, rinse down with 20 ml of 95% ethanol, add 0.5 ml of 0·5*M* nitric acid and titrate with 0.005*M* mercuric perchlorate, using 1% ethanolic diphenylcarbazone solution as indicator.[5] For bromine, place in the mixture during evaporation a 25-mm square of platinum foil (held in a glass rod and electrolytically coated with a rough surface of platinum black) to destroy the excess of hydrogen peroxide. Warm the solution, and when the evolution of oxygen ceases (*ca.* 10 min) remove the rod, rinsing it and the foil with distilled water into the flask.[1] Cool, add 5 ml of sodium hypochlorite solution and 5 ml of 20% sodium dihydrogen phosphate solution, cover the flask with a watch-glass and heat almost to boiling during 10 min, with shaking. Add 5 ml of 50% sodium formate solution, and cool to room temperature with swirling. Add 20 ml of 3*M* sulphuric acid and 0·5 g of potassium iodide. Titrate with 0·02*M* sodium thiosulphate solution.[6]

(*ii*) *Determination of iodine in the presence of chlorine or bromine.* Burn another sample (3–5 mg), using 10 ml of 0·05*M* sodium hydroxide as absorbent. Shake thoroughly, leave for 15 min, rinse down with 15 ml of distilled water and then add 10 ml of bromine solution. Leave for 2–3 min, add a few drops of 98% formic acid, with shaking, to destroy the excess of bromine. Add 5 ml of 1*M* sulphuric acid and 0·5 g of potassium iodide. Titrate the liberated iodine with standard sodium thiosulphate solution.[7]

(*iii*) *Determination of chlorine in presence of bromine.* Burn a sample as in (*i*) but use only distilled water as absorbent. Rinse with 20 ml of distilled water, add 0·2 ml of 0·5% potassium bromate solution, 0·5 ml of 0·5*M* nitric acid and evaporate to about 5 ml, then determine the chloride by Cheng's method.[8]

(*iv*) *Determination of bromine in presence of chlorine.* Burn another sample, using 5 ml of sodium hypochlorite solution and 10 ml of sodium dihydrogen phosphate solution as absorbent, then determine bromine iodometrically.[5]

(*v*) *Determination of chlorine in presence of bromine and iodine.* Burn a sample and proceed as in (*iii*).

(*vi*) *Determination of bromine in presence of chlorine and iodine.* Burn a sample and apply procedure (*i*).

(*vii*) *Determination of iodine in presence of chlorine and bromine.* Burn a sample and apply procedure (*ii*).

For all procedures do a blank determination under the same experimental conditions.

RESULTS AND DISCUSSION

Potassium bromate and hydrogen peroxide are used as selective oxidants for bromide and iodide, the peroxide to oxidize iodide but not chloride or bromide, and the bromate to oxidize bromide and iodide but not chloride. Cheng's method[8] is recommended for the chlorine determination, but has a poor conversion factor for determination of bromine and iodine.[9] The hypochlorite and Leipert methods are superior for determining bromine and iodine because of the six-fold amplification. Large numbers of samples have been analysed under routine conditions with good results. The mean absolute error is <0·2% for all three elements (see Table 1).

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Table. 1. Results obtained for microdetermination of individual halogens in organic compounds

Compound	Cl, % Calc.	Cl, % Found	Br, % Calc.	Br, % Found	I, % Calc.	I, % Found
2-Chloro-4-iodoaniline	14·01	14·2 14·1 14·3			50·08	50·1 50·2 50·0
4-Bromo-2-iodoaniline			26·83	26·6 27·1 26·8	42·61	42·4 42·6 42·7
1,1,1-Tribromo-2,2-bis-*p*-chlorophenylethane	14·54	14·6 14·4 14·2	49·16	49·1 49·5 49·5		
1,1-Dibromo-2,2-bis-*p*-chlorophenylethylene	17·44	17·6 17·4 17·4	39·29	39·3 39·0 39·4		
2-Bromo-1,1-di-*p*-chlorophenyl-3,3-diphenylprop-1-ene	14·36	14·6 14·6 14·4	16.18	16·0 16·2 16·3		
4-Bromo-2-iodoaniline hydrochloride	10·62	10·7 10·7 10·8	23·91	24·0 24·1 24·0	37·96	37·9 38·0 37·8

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Summary—A simple and accurate micro-method for the individual determination of Cl, Br and I in halogenated organic compounds by the oxygen-flask method is described. Addition of potassium bromate to oxidize bromide, and of hydrogen peroxide to oxidize iodide, followed by boiling, is used to eliminate these two halides in mixtures with chloride or each other.

Zusammenfassung—Eine einfache und ganaue Mikromethode zur Einzelbestimmung von Cl, Br und J in halogenierten organischen Verbindungen mit der Sauerstoffkolbenmethode wird beschrieben. Die Zugabe von Kaliumbromat zur Oxidation von Bromid und von Wasserstoffperoxid zur Oxidation von Jodid mif nachfolgendem Kochen dient dazu, diese beiden Halogenide in Gemischen mit Chlorid oder untereinander zu eliminieren.

Résumé—On décrit une microméthode simple et précise par la détermination individuelle de Cl, Br et I dans les composés organiques halogénés par la méthode à la fiole d'oxygène. On utilise l'addition de bromate de potassium pour oxyder le bromure, et de peroxyde d'hydrogène pour oxyder l'iodure, suivies d'ébullition, pour éliminer ces deux halogenures en mélanges avec le chlorure ou l'un avec l'autre.

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POLAROGRAPHIC DETERMINATION OF NITRAMIDE

(*Received* 22 *March* 1973. *Accepted* 3 *July* 1973)

Nitramide is a weak acid with equilibrium constant for

$$NH_2NO_2 \rightleftharpoons NHNO_2^- + H^+$$

$K = 2{\cdot}55 \times 10^{-7}$ at 15°.[1] It is thus weaker than the isomeric hyponitrous acid $(NOH)_2$ which has $K_1 = 9 \times 10^{-3}$ and $K_2 = 10^{-11}$ at 25°, and is also weaker than acetic acid. The decomposition kinetics have been studied by La Mer and Greenspan[3] and the effect of catalysis on its decomposition has been looked at by Liotta and La Mer.[4] In these studies the course of the reaction was followed by measuring the volume of N_2O liberated. The object of the present work was development of a direct method for determination of nitramide.

EXPERIMENTAL

Nitramide was prepared by the method of Thiele and Lachmann as improved by La Mer and Greenspan.[5] The curves were recorded with a polarograph LP 55, and a Kalousek cell with SCE was used. The capillary constants were $m = 2{\cdot}73$ mg/sec, $t = 3$ sec at a column height h of 85 cm (open circuit).

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RESULTS

Stability of aqueous solutions of nitramide

Solutions of nitramide in water ($3 \times 10^{-3}M$) are stable for some 5 hr at 0–2°. In buffered solutions, as reported by other workers,[3,4] the stability is strongly dependent on the pH. Some results are presented in Fig. 1. At pH 2·5 and at 2°, the solutions are stable for about 100 min; at pH 4·5 the half-life is about 200 min, and at pH 6·8, 15 min (both at 2°). It is clearly necessary to work rather quickly at higher pH values in order to obtain reproducible results.

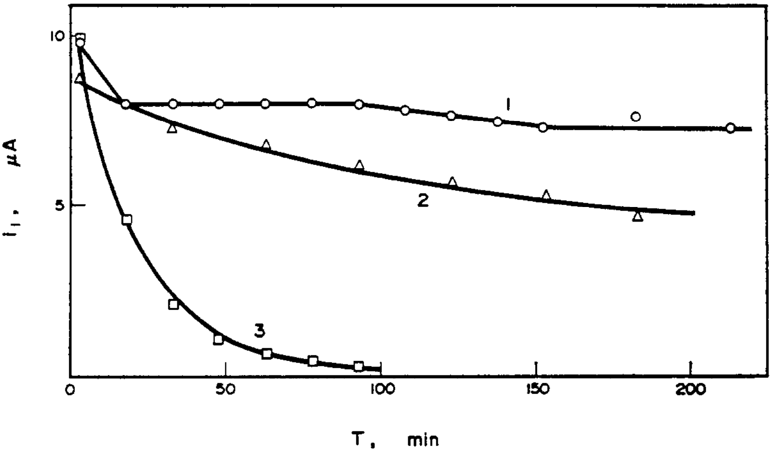

Fig. 1. Nitramide decomposition expressed as height of first wave *vs.* time. Nitramide, $10^{-3}M$ in Britton–Robinson buffer. pH: 1—2·56; 2—4·56; 3—6·80. Temperature 2°C.

Polarographic waves

Figure 2 shows the two waves found at pH 7·24. For neutral solutions they are of about the same height, but for more acidic solutions the second wave is higher. Comparison with thallium waves for similar concentrations indicates that these waves represent two-electron reductions.

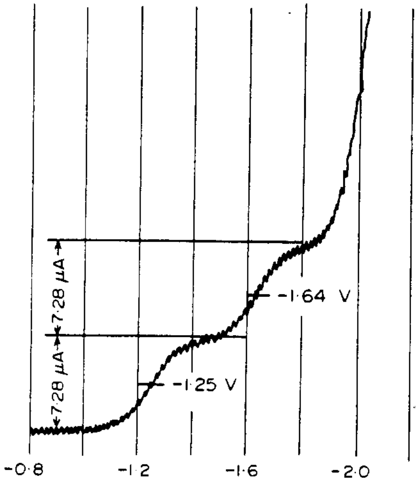

Fig. 2. Reduction waves of nitramide. Britton–Robinson buffer, 0·026*M*, pH = 7·24. NH_2NO_2, $10^{-3}M$; temperature, 1°C; anode, SCE.

Reversibility

The wave-height is a linear function of $\sqrt{h_{cor}}$ for both waves for pH < 4·56 (h_{cor} is the corrected reservoir height). The extrapolated plot passes through the origin only for the first wave—the second gives an intercept on the abscissa; this anomaly has been reported previously only for the catalytic hydrogen wave of the nitrohydroxylamine complex of cobalt in ammoniacal buffer.[6] It is likely that in both cases there is a secondary reaction at the electrode. Both nitramide waves are therefore diffusion-controlled at pH 4·5. but only the first is purely diffusion-controlled.

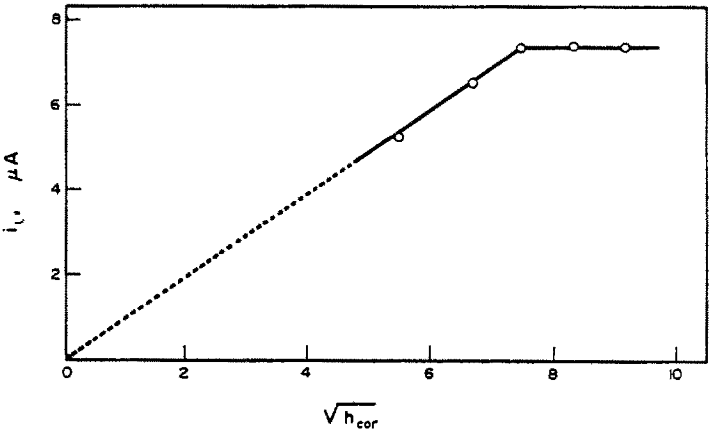

Fig. 3. Wave-height *vs.* square root of corrected mercury reservoir height. NH_2NO_2 $10^{-3}M$, in Britton–Robinson buffer, pH = 7·24, at 1°C.

Figure 3 shows the variation of wave-height with $\sqrt{h_{cor}}$ at pH 7·24. The wave-height is seen to remain constant at higher values of $\sqrt{h_{cor}}$. This may be due to a secondary reaction between the initial reduction product and the excess of nitramide. At larger values of $\sqrt{h_{cor}}$ the higher rate of mass transfer increases the concentration of both species but favours the secondary reaction.

Two further approaches have been used to investigate the reversibility of the electrode reactions: logarithmic plots, and the Kalousek commutator technique. Plots of $\log[i/(i_d - i)]$ *vs.* ΔE gave straight lines from which apparent transfer coefficients were calculated to be $\alpha_1 = 1{\cdot}06$ and $\alpha_2 = 1{\cdot}035$. These values would suggest that the waves are quasi-reversible, though the criterion is not a decisive one. In the Kalousek commutator technique, occurrence of an anodic wave when the applied potential is rapidly switched between an oxidizing and a reducing potential, indicates a reversible wave. Neither the first nor the second wave gave an anodic wave with this technique. However, it should be remembered that if the reduction products are highly unstable, there will be no anodic wave under these conditions even for reversible reactions.

Variation of pH and ionic strength

Owing to the poor stability of nitramide at higher pH values, it was not possible to make a thorough study of the variation of wave-height with pH. In acid solutions the wave-height is constant.The half-wave potentials, however, do change with pH, and are well separated below pH 8 but overlap at pH > 9. The experimental values shown are in Fig. 4. The relationship between half-wave potential and pH is appreciably modified in the presence of a supporting electrolyte such as potassium or lanthanum chloride. Small quantities of supporting electrolyte improve the separation of the waves, though with larger amounts of lanthanum chloride the second wave becomes less well-defined as it tends to merge with the discharge potential for the electrolyte, which becomes more positive as the pH is lowered by the increased concentration of lanthanum. However, the half-wave potentials are not affected over a wide range of potassium or lanthanum chloride concentrations. Variation in the ionic strength (concentration of added buffer) results in maximum wave-height in 0·013*M* electrolyte. This is difficult to explain, but at low concentrations migration may occur to some extent, and at higher concentrations the electrolyte may catalyse the nitramide decomposition. No polarographic catalytic effect, has, however, been found in the reduction of nitramide.

Catalytic waves

Unlike the nitrohydroxylamine ion[6,7] nitramide has no effect on the cobalt polarographic wave. Its effect on the hydrogen catalytic wave produced by the cobalt–nitrohydroxylamine complex has been studied previously.[8] Hyponitrous acid has no effect on the polarographic reduction of nitramide.

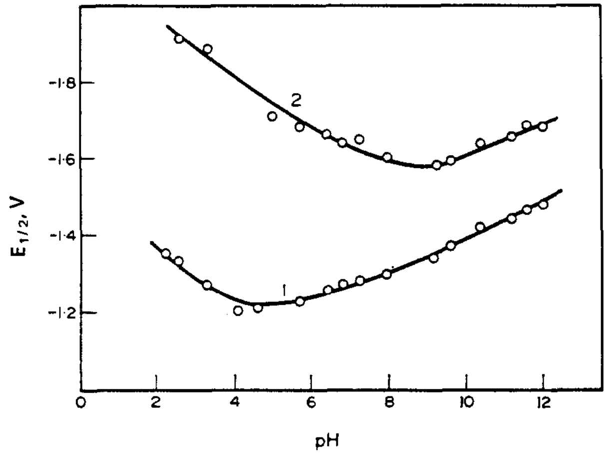

Fig. 4. Half-wave potential of the first (1) and second (2) waves as a function if pH. Britton–Robinson buffer, 0·013*M*; nitramide, $10^{-3}M$; SCE.; temperature, 1°C.

DISCUSSION

From the waves in Fig. 2 the reduction of nitramide in neutral media can be represented as follows:

$$NH_2NO_2 + 2H^+ + 2e^- = NH_2NO + H_2O \qquad (1)$$

$$NH_2NO + 2H^+ + 2e^- = NH_2NHOH \qquad (2)$$

where nitrosamine (NH_2NO) is formed in the first step and hydroxylhydrazine in the second. This second compound has not so far been isolated.[1]

The explanation of the reaction mechanism becomes more difficult for acidic media. If the spontaneous decomposition of nitrosamine in water is considered

$$2\,NH_2NO = N_2 + NH_4NO_2 \qquad (3)$$

the second wave should be smaller than the first one, not larger as is found experimentally. It is possible that more than two electrons are consumed in the second step, *e.g.*,

$$NH_2NO + 4H^+ + 4e^- = NH_2NH_2 + H_2O \qquad (4)$$

The reduction of nitramide to hydrazine has already been postulated.[1] In this case the four-electron wave is diminished owing to the decomposition reaction (3).

We have already suggested that the anomalous variation of the wave-height with $\sqrt{h_{cor}}$ (Fig. 3) and the similarity in behaviour of the two waves may be ascribed to some reaction between nitramide and nitrosamine produced from it. This reaction is not known, and cannot be determined from the polarographic data alone, but together with equation (4) it might explain the decreased four-electron wave.

Another problem is the variation of half-wave potential with pH, and the existence of a minimum in the curve (Fig. 4). It is likely that protonation plays an important role in this effect. It has been suggested[1] that an ammonium-type ion $NH_3NO_2{}^+$ may be produced in more acidic media. If the minimum half-wave potential corresponds to the neutral species NH_2NO_2, the maximum concentration of this form should be present at pH 4·5 (Fig. 4). It follows that the dissociation constant of the hypothetical $NH_3NO_2{}^+$ should be about 3×10^{-3}. Similar considerations apply to nitrosamine, and a protonated species NH_3NO^+ may be formed.

Analytical procedure

Nitramide can conveniently be determined in the range 10^{-4}–$10^{-3}M$ in a solution containing Britton–Robinson buffer at pH 5, and with added potassium chloride (0·05–0·1M), and at low temperature (0–2°) to slow down the decomposition. The first wave should be used, as its height is not dependent on the pH, and is a linear function of nitramide concentration. The precision is improved by using freshly prepared solutions and working to a strict time schedule.

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Summary—Nitramide gives two cathodic polarographic waves with half-wave potentials varying with pH, and having minimum values −1·22 V at pH 4·5 and −1·58 V at pH 8·8. Nitramide is first reduced to nitrosamine in a two-electron reduction. In the second step, hydroxyhydrazine may be formed in a two-electron reduction, or hydrazine itself in a four-electron step. For the polarographic determination of nitramide the first wave is used, and the supporting electrolyte is a Britton–Robinson buffer 0·1 M in KCl, at pH < 5 and at 0–2°.

Zusammenfassung—Nitramid gibt zwei kathodische polarographische Stufen mit pH-abhängigem Halbstufenpotential; Minimalwerte sind −1,22 V bei pH 4,5 und −1,58 V bei pH 8,8. Nitramid wird zuerst in einem Zweielektronen-Prozeß zu Nitrosamin reduziert. In der zweiten Stufe kann durch Zweielektronen-Reduktion Hydroxyhydrazin oder durch einen Vierelektronenschritt Hydrazin selbst gebildet werden. Zur polarographischen Bestimmung bon Nitramid wird die erste Stufe verwendet; der Tragerelektrolyt ist ein Britton–Robinson-Puffer, der 0,1 M an KCl ist, bei pH < 5 und bei 0–2°.

Résumé—La nitramide donne deux vagues polarographiques cathodiques avec des potentiels de demi-vague variant avec le pH, et ayant des valeurs minimales −1,22 V à pH 4,5 et −1,58 V à pH 8,8. La nitramide est d'abord réduite en nitrosamine dans une réduction à deux électrons. Dans le second stade, l'hydroxyhydrazine peut être formée dans une réduction à deux électrons, ou l'hydrizane elle-même dans un stade à quatre électrons. Pour le dosage polarographique de la nitramide on utilise la première vague, et l'électrolyte support est un tampon Britton-Robinson 0,1M en KCl, à pH < 5 à 0–2°.

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EXTRACTION WITH LONG CHAIN AMINES—VII
POLAROGRAPHIC DETERMINATION OF URANIUM

(*Received* 30 *November*, 1971. *Revised* 8 *June* 1973. *Accepted* 28 *June* 1973)

Many polarographic determinations of uranium have been proposed. Their common disadvantage is the interference of many cations. To increase the selectivity of the determination, preliminary isolation of uranium as uranyl ammonium phosphate has often been recommended.[1–4] Ion-exchange has also been

Analytical procedure

Nitramide can conveniently be determined in the range 10^{-4}–$10^{-3}M$ in a solution containing Britton-Robinson buffer at pH 5, and with added potassium chloride (0·05–0·1M), and at low temperature (0–2°) to slow down the decomposition. The first wave should be used, as its height is not dependent on the pH, and is a linear function of nitramide concentration. The precision is improved by using freshly prepared solutions and working to a strict time schedule.

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Summary—Nitramide gives two cathodic polarographic waves with half-wave potentials varying with pH, and having minimum values −1·22 V at pH 4·5 and −1·58 V at pH 8·8. Nitramide is first reduced to nitrosamine in a two-electron reduction. In the second step, hydroxyhydrazine may be formed in a two-electron reduction, or hydrazine itself in a four-electron step. For the polarographic determination of nitramide the first wave is used, and the supporting electrolyte is a Britton–Robinson buffer 0·1 M in KCl, at pH < 5 and at 0–2°.

Zusammenfassung—Nitramid gibt zwei kathodische polarographische Stufen mit pH-abhängigem Halbstufenpotential; Minimalwerte sind −1,22 V bei pH 4,5 und −1,58 V bei pH 8,8. Nitramid wird zuerst in einem Zweielektronen-Prozeß zu Nitrosamin reduziert. In der zweiten Stufe kann durch Zweielektronen-Reduktion Hydroxyhydrazin oder durch einen Vierelektronenschritt Hydrazin selbst gebildet werden. Zur polarographischen Bestimmung bon Nitramid wird die erste Stufe verwendet; der Tragerelektrolyt ist ein Britton–Robinson-Puffer, der 0,1 M an KCl ist, bei pH < 5 und bei 0–2°.

Résumé—La nitramide donne deux vagues polarographiques cathodiques avec des potentiels de demi-vague variant avec le pH, et ayant des valeurs minimales −1,22 V à pH 4,5 et −1,58 V à pH 8,8. La nitramide est d'abord réduite en nitrosamine dans une réduction à deux électrons. Dans le second stade, l'hydroxyhydrazine peut être formée dans une réduction à deux électrons, ou l'hydrizane elle-même dans un stade à quatre électrons. Pour le dosage polarographique de la nitramide on utilise la première vague, et l'électrolyte support est un tampon Britton-Robinson 0,1M en KCl, à pH < 5 à 0–2°.

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EXTRACTION WITH LONG CHAIN AMINES—VII
POLAROGRAPHIC DETERMINATION OF URANIUM

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Many polarographic determinations of uranium have been proposed. Their common disadvantage is the interference of many cations. To increase the selectivity of the determination, preliminary isolation of uranium as uranyl ammonium phosphate has often been recommended.[1–4] Ion-exchange has also been used.[5] Marshall and Kendler[6] avoided interference from iron(III), molybdenum(VI) and cerium(IV) by reducing them with ascorbic acid to lower oxidation states that do not interfere. Fluoride medium was reported to be suitable for the determination of uranium in the presence of iron,[7] but traces of titanium and lead interfere. The polarographic determination of uranium in the presence of organic complexing agents such as oxalic acid,[8–9] EDTA,[10–13] tiron[14] and 8-hydroxyquinoline derivatives[15–16] does not satisfactorily solve the problem of selectivity. More advantageous seems to be preliminary separation of uranium by extraction with tributyl phosphate.[17,18] Adam and Přibil[19] recently suggested extraction with trioctylamine (TOA, Alamine S-336) and colorimetric determination with oxine or dibenzoylmethane. This extraction is rather selective, only chromium(VI), molybdenum(VI), vanadium(V), gold and the platinum metals being co-extracted.[20–22] In the present paper, trioctylmethylammonium chloride (TOMA) was used for the extraction of uranium before its polarographic determination.

EXPERIMENTAL

Reagents

Uranyl sulphate solution, 0.05*M*. Prepared by evaporation of 5·319 g of $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ with dilute sulphuric acid, followed by dissolution of the residue in 250 ml of water to give a solution which was standardized gravimetrically.

Trioctylmethylammonium chloride solution, 5%. Prepared by dissolving 50 g of Aliquat S-336 (General Mills Inc., Kankakee, Illinois) in 1 litre of chloroform.

Other metal solutions were prepared from reagent grade chemicals.

Polarographic determination of uranium

Uranium(VI) in 0·5*M* HCl–0·5*M* KCl medium gives two waves that correspond to the reductions U(VI)→ U(V) → U(IV). The first wave is well developed with $E_{1/2} = -0{\cdot}15$ V *vs.* SCE. The diffusion character of the limiting current was proved by its dependence on the square root of the height of the mercury head. The reversibility of the electrode reaction was confirmed by means of the Kalousek commutator. The concentration dependence of the limiting current is linear in the range 40–2400 μg/ml.

The supporting electrolyte used is also a very suitable medium for the stripping of uranium from the chloroform extract into aqueous solution.

Extraction and stripping of uranium

It has been found that the conditions for the extraction of uranium with TOMA are similar to those for TOA.[9] Uranium is extracted quantitatively from sulphuric acid solutions (pH 1–3·5). With a single extraction at least 24 mg of uranium can be separated with 5 ml of 5% TOMA. Uranium is very easily stripped into acid solutions of sodium or potassium chloride. Uranium was determined as follows: A 0·5–20 ml portion of $5 \times 10^{-3}M$ uranium sulphate solution was placed in a 150-ml separatory funnel, diluted to 40–50 ml with water and adjusted to pH 1·0–3·5 with dilute sulphuric acid. Uranium was then extracted by shaking for 1 min with 5 ml of 5% TOMA solution in chloroform; 2 ml of saturated sodium sulphate solution were added to accelerate separation of the phases. After transfer of the organic phase into another 150-ml separatory funnel, the aqueous phase was washed with 5 ml of pure chloroform, which was then added to the first chloroform extract. Uranium was stripped by shaking for 1 min with 10 ml of supporting electrolyte, which was then transferred into a Kalousek cell and deaerated with pure nitrogen; the polarographic wave was recorded from +0.1 V *vs.* SCE.

This procedure was employed in the investigation of the completeness of the extraction. It was found that a single extraction with 5 ml of TOMA solution is quantitative over the pH range 1·0–3·5 for up to 24 mg of uranium.

Influence of anions

It has been found that the extraction is not quantitative in the presence of chloride, nitrate, acetate or fluoride, and that phosphate precipitates uranium. Low concentrations of chloride (0.003*M*) or nitrate (0.02*M*) are tolerable, decreasing the extraction by about 1%. Fluoride hinders the extraction even in very low concentrations.

Influence of other metals

Attention has been paid to elements that are frequently present in rocks and minerals. It was found that the determination of uranium is not affected by the presence of 400 mg of iron, 240 mg of zinc, 200 mg of manganese, 500 mg of copper and cobalt, 250 mg of rare earths, 50 mg of cerium, 200 mg of thorium or 300 mg of arsenic. Chromium(VI), which is extracted together with uranium, does not interfere in amounts up to 250 mg, if reduced with ascorbic acid before the polarography. Interference is caused by molybdenum(VI), gold and the platinum metals, which are extracted with uranium and are reduced at the dropping mercury electrode.

Applications

The proposed method was checked by analysing monazite sand to which various amounts of uranium were added and by replicate analysis of a standard reference sample of river deposit containing 0.104% of uranium. The samples were decomposed by using the following procedure.

Approximately 1 g of the sample was fused with a mixture of potassium and sodium carbonates and the fused mass was treated with dilute sulphuric acid; the resulting solution was filtered into a 100-ml volumetric flask. Various amounts of 0.005*M* uranyl sulphate solution were then added in the case of monazite sand samples, and the solution was made up to the mark with distilled water. This solution was used, after pH adjustment, for uranium determination according to the procedure described above. The results of replicate determinations are shown in Table 1.

Table 1. The determination of uranium

Sample		U present, μg	U found,* μg	Standard deviation, μg
Monazite	1	476	475	6·9
sand	2	952	956	8·4
	3	2142	2130	21·3
River	1	232†	236	7·2
sediment	2	464†	458	9·3
	3	929†	919	12·0

* Average of five determinations.
† Corresponds to the given value of 0·104% uranium.

The proposed method is applicable for the rapid determination of uranium in rocks, minerals and silicates, as well as in uranium concentrates, with sufficient accuracy and precision (see Table).

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Summary—A polarographic determination of uranium is described, based on the highly selective extraction of uranium(VI) with a chloroform solution of trioctylammonium chloride, followed by re-extraction of uranium into an aqueous 0·5*M* KCl–0·5*M* HCl solution, which also serves as the polarographic supporting electrolyte. In this medium, uranium(VI) is reduced at the dropping mercury electrode to give two polarographic waves, the first of which is of analytical significance. In this way it is possible to determine 50–2400 μg of uranium in 1 ml of supporting electrolyte and in the presence of large amounts of accompanying elements.

Zusammenfassung—Es wird eine polarographische Uranbestimmung beschrieben, die auf der hochselektiven Extraktion von Uran(VI) mit einer Chloroformlösung von Trioctylammoniumchlorid und nachfolgender Rückextraktion des Urans in eine wäßrige 0,5M KCl–0,5M HCl-Lösung beruht; diese dient auch als polarographischer Tragerelektrolyt. In diesem Medium wird Uran(VI) an der Quecksilbertropfelektrode reduziert: es ergeben sich zwei polarographische Stufen, von denen die erste von analytischer Bedeutung ist. Auf diese Weise kann man 50–2400 μg Uran in 1 ml Trägerelektrolyt in Gegenwart großer Mengen von Begleitelementen bestimmen.

Résumé—On décrit un doage polarographique de l'uranium, basé sur l'extraction hautement sélective de l'uranium (VI) par une solution chloroformique de chlorure de trioctylammonium, suivie de la reextraction de l'uranium dans une solution aqueuse 0,5*M* KCl–0,5*M* HCl qui sert aussi comme électrolyte support polarographique. Dans ce milieu, l'uranium (VI) est réduit à l'électrode à goutte de mercure pour donner deux vagues polarographiques, dont la première est de signification analytique. De cette façon, il est possible de doser 50–2400 μg d'uranium dans 1 ml d'électrolyte support et en la présence de grandes quantités d'éléments accompagnants.

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ION-EXCHANGE ISOLATION OF CHROMATE FROM ALKALINE PEROXIDE SOLUTIONS

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The sexivalent state of chromium plays a significant role in the analytical chemistry of the element. Two very well known volumetric methods are based on the reduction of dichromate, with iron(II),[1] and with iodide followed by a thiosulphate titration.[2] Gravimetric procedures involving barium[3] and lead[4,5] chromate are also often employed. Solutions of chromate have been used directly in colorimetric and spectrophotometric methods,[6,7] and for greater sensitivity the colour reaction with diphenylcarbazide can be used.[8–10] Solutions of chromium(VI) are employed in determination of the element by atomic absorption.[11–13] Kinetic methods employing chromium(VI) for microdetermination of chromium have been reported.[14] Recently ion-exchange separation methods for chromium, employing solutions of sexivalent chromium, have appeared in the literature.[15–18]

The element is usually present in its lower oxidation states, and there is therefore a need for a reliable method of effecting its rapid oxidation. Oxidation with peroxide in alkaline solution or by fusion with the sodium salt qualifies well for the purpose. At present however, there is a scarcity of satisfactory ways of removing excess of peroxide once the oxidation is completed, so on acidifying (a necessary step in most of the determinations) there is partial decomposition of the chromium peroxide formed to chromium(III). Some of the procedures presently available for removal of the peroxide interference are either cumbersome[19] or have

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The element is usually present in its lower oxidation states, and there is therefore a need for a reliable method of effecting its rapid oxidation. Oxidation with peroxide in alkaline solution or by fusion with the sodium salt qualifies well for the purpose. At present however, there is a scarcity of satisfactory ways of removing excess of peroxide once the oxidation is completed, so on acidifying (a necessary step in most of the determinations) there is partial decomposition of the chromium peroxide formed to chromium(III). Some of the procedures presently available for removal of the peroxide interference are either cumbersome[19] or have been exposed to even more serious criticisms.[20,21] Excess of peroxide may be destroyed by boiling. This technique has often been employed in analysis of chrome iron ores.[22] However, there is no reliable indication as to when peroxide has been completely eliminated, so that one must be prepared to carry out several determinations and select those which give consistent results. The results of the present work indicate that the presence of peroxide does not interfere with the absorption of chromate from alkaline solution on strongly basic anion-exchange resins, provided suitable precautions are taken. Further, complete removal of peroxide from the resin may be achieved by washing with 2% sodium hydroxide solution. The chromate may be quantitatively eluted with sodium hydrogen carbonate solution.[17]

EXPERIMENTAL

Reagents

Analytical grade reagents were used throughout.

Procedure

A small ion-exchange column with dimensions 1 $cm^2 \times 8$ cm and a bigger column 1·5 $cm^2 \times 20$ cm, packed with 7 and 20 ml of the wet resin (Amberlite IRA 400, chloride form) were used for chromium amounts in the ranges 5–50 and 50–200 mg respectively. To ensure reproducibility of experimental conditions, constant flow-rate ion-exchange columns were used as previously described.[23] Stock solutions of potassium dichromate and potassium chromic sulphate were prepared from accurately weighed amounts of the reagents. If the usual precautions[24] were taken, there was no need for standardization of the dichromate solution. The dichromate solution was used to standardize the sodium thiosulphate and ferrous ammonium sulphate solutions used. Potassium chromic sulphate solution was standardized according to two independent procedures.[2,25] Each of the stock solutions contained 10 mg of Cr/ml. Suitable aliquots of potassium dichromate were taken and diluted to 50 ml, and reduction was carried out with hydrazine sulphate solution. The mixture was warmed, and when necessary more hydrazine sulphate was added to achieve complete reduction. The chromic hydroxide obtained was green and there were no signs of any yellow colour of chromate. Sodium hydroxide solution (10 ml of 20% solution) was added. After heating to just boiling, 29% hydrogen peroxide solution was added drop by drop with constant shaking. An equally effective peroxide solution may be prepared by dissolving 1 g of sodium peroxide in 10 ml of 2% sodium hydroxide solution. With solutions containing up to 200 mg of chromium, the oxidation is complete in 5 min with less than 2 ml of hydrogen peroxide. Under those conditions there is still an excess of peroxide, as is easily indicated by the frothing when the reaction vessel is swirled. The solution was immediately allowed to cool to room temperature and after dilution with distilled water to 400 ml, it was passed through the ion-exchange column at the rate of 20 drops/min. The ion-exchange column had previously been treated with 50 ml of 2% sodium hydroxide solution. The dilution step is essential for prevention of the build-up of too many bubbles in the resin bed, which would interfere with the flow and the sorption of chromate by the resin. When all the solution had passed through the column, the bubbles in the resin bed were removed with the aid of a glass rod, and then 200 ml of 2% aqueous sodium hydroxide were passed through the column. A saturated solution of sodium hydrogen carbonate in 10% sodium carbonate decahydrate solution was used to remove chromate from the resin. The removal is regarded as complete when the effluent becomes colourless and on acidification no longer gives a blue colour with starch–iodide paper. All the chromium is removed by about 400 ml of the eluent solution. Aliquots of chromium(III) solutions were treated in the same way.

RESULTS AND DISCUSSIONS

Table 1 gives a summary of the results. There is good agreement between the amount of chromium taken and that recovered. The errors are within the range expected from the accuracy of the titrations. The results were obtained from 10 samples of dichromate solution and 8 aliquots of potassium chromic sulphate solution. For half of the determinations from each solution the alkaline peroxide solutions were diluted to 400 ml before passage through the column. With the other aliquots, the peroxide content was reduced by additional boiling for 10 min, and the solutions were then diluted to only 150 ml. In the second case, the flow of the solution through the column was smoother and easier to regulate. It is therefore recommended that the solution should be boiled to reduce the peroxide concentration before passage through the column. The results demonstrate that peroxide oxidation can be used for accurate determination of chromium, and standardization of chromium solutions, if the interference of peroxide is eliminated according to this procedure.

Recommended procedure

Take a neutral solution containing chromium(III) and make it alkaline with 10 ml of 10% aqueous sodium hydroxide solution. Heat the solution nearly to boiling and add hydrogen peroxide (30% w/v) or 10% sodium peroxide solution in 2% sodium hydroxide drop by drop with constant shaking. In about 5 min, when 1 ml of the peroxide solution has been added, the solution loses its green colour, and is yellow. Now boil the solution gently for an additional 5 min. Allow the solution to cool, dilute it to 150 ml, and pass it through

Table 1. Recovery of chromium in the ion-exchange removal of peroxide

Chromium(III) from hydrazine reduction of chromate, *mg*		Chromium in potassium chromic sulphate solution, *mg*	
Added	Recovered	Added	Recovered
25·0	25·0	15·0	15·1
30·0	30·2	20·0	20·0
41·0	40·9	40·5	40·4
53·0	53·1		
60·0	60·0	59·0	58·8
85·0	84·9	80·1	80·1
100·0	100·0	95·0	95·1
122·0	122·1	104·5	104·9
150·0	149·8		
200·0	200·2	200·5	200·4

the ion-exchange column. Use 250 ml of 2% aqueous sodium hydroxide solution to wash away any peroxide still in the resin bed. Then elute the chromate with a saturated solution of sodium hydrogen carbonate in 10% sodium carbonate decahydrate solution. Determine the chromate in the usual way.

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Summary—The interference by excess of peroxide seriously affects the reliability of chromium determination procedures involving prior oxidation of the element with sodium or hydrogen peroxide. Some of the methods used to overcome this problem are either cumbersome or unreliable. A method for quantitative and rapid isolation of chromate from alkaline peroxide solutions is now presented. This involves sorption of chromate on a strongly basic anion-exchange resin. The interfering peroxide is washed away with 2% aqueous sodium hydroxide solution.

Zusammenfassung—Es wird über eine potentiometrische und spektrophotometrische Untersuchung der Bilding von Zink(II)-Komplexen mit Semi-Xylenolorange (SXO oder H_4L) berichtet. In einer wäßrigen Lösung ($\mu = 0,1$) existieren anscheinend drei 1:1-Komplexspezies MH_2L, MHL^- und ML^{2-} sowie ein 1:2-Komplex ML_2^{6-}. In stark alkalischem Medium (pH über 12.5) konnen die Komplexe zu Zinkhydroxid und L^{4-} dissoziieren. Die Bilding eines Hydroxykomplexes wird nicht beobachtet. Die Absorptionsmaxima liegen bei 445 nm (MH_2L), 466 nm (MHL^-) und 561 nm (ML^{2-}), die molaren Extinktionskoeffizienten betragen $2,34 \times 10^4$, $2,42 \times 10^4$ bzw. $3,13 \times 10^4$ $1\ mol^{-1}\ cm^{-1}$. Die Bildungskonstanten sind (bei $25 \pm 0.1°$) log $K^M_{ML} = 11,84$, log $K^M_{MHL} = 7,13$, log $K^M_{MH_2L} = 2,70$ und log $K^M_{ML_2} = 16,60$.

Résumé—L'interférence par un excès de peroxyde affecte sérieusement l'exactitude des techniques de dosage du chrome mettant en jeu une oxydation préliminaire de l'élément par le peroxyde de sodium ou d'hydrogène. Quelques-unes des méthodes utilisées pour surmonter ce problème sont pénibles ou incertaines. On présente maintenant une méthode pour l'isolement quantitatif et rapide du chromate à partir de solutions alcalines de peroxyde. Elle comprend la sorption du chromate sur une résine échangeuse d'anions fortement basique. Le peroxyde gênant est éliminé par lavage avec une solution aqueuse à 2 % de soude.

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DETERMINATION OF URANIUM AFTER ITS SELECTIVE EXTRACTION AS PHENYLACETATE

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Of the many methods for the complexometric determination of uranium[1] the best is that proposed by Kinnunen and Wennestrand.[2] It is based on the reduction of uranium by boiling with ascorbic acid in the presence of an excess of EDTA at pH 3–4. The U(IV)–EDTA complex so formed is very stable (log $K_{UY} = 25$) and allows the determination of the excess of EDTA by titration at pH 2–3 with thorium nitrate solution, Xylenol Orange being used as indicator. A similar method has been proposed by Buděšínský,[3] who reduced uranium with dithionite and titrated the excess of EDTA with thorium nitrate, using Methylthymol Blue as indicator.

The determination of uranium in this way cannot be performed in the presence of thorium, hafnium, zirconium, tervalent iron, gallium and indium, and separation of the uranium from interfering elements is necessary. Many extraction methods[4] are not selective enough and in many cases are useful only for trace amounts of uranium.

In a previous communication[5] describing the extraction properties of metal phenylacetates, we mentioned that in the presence of EDTA the extraction of uranium is highly selective. During further study we found that such extractions were not entirely quantitative and the results for uranium were a little low. Very good results were obtained with extraction of uranium from solutions containing nitrilotriacetic acid (NTA), which is capable of masking all the interfering metals. Because the extraction with phenylacetic acid (PAA) itself is highly selective and practically limited to only a few elements (Fe, Cu, Pb, In, Ga)[5,6] it was obvious that with the use of NTA it would be possible to work out very simple conditions for specific extraction of uranium.

EXPERIMENTAL

Reagents

A $1M$ solution of PAA was prepared by dissolution of 136 g of phenylacetic acid in one litre of pure chloroform. A $0{\cdot}5M$ solution of NTA was prepared by dissolution of 9·55 g of NTA in 500 ml of $2M$ sodium hydroxide and dilution to one litre with distilled water. A $0{\cdot}05M$ solution of uranyl chloride was prepared by dissolving 4·711 g of $UO_2Cl_2 . 2H_2O$ in 250 ml of redistilled water, and standardized complexometrically.[1] A $0{\cdot}05M$ solution of thorium nitrate was prepared by dissolving 28·507 g of $Th(NO_3)_4.5H_2O$ in 1 of water. Further reagents include $0{\cdot}05M$ EDTA, saturated hexamine solution, solid ascorbic acid, $1M$ acetic acid, $1M$ hydrochloric acid and 0·5% Xylenol Orange solution.

Zusammenfassung—Es wird über eine potentiometrische und spektrophotometrische Untersuchung der Bilding von Zink(II)-Komplexen mit Semi-Xylenolorange (SXO oder H_4L) berichtet. In einer wäßrigen Lösung ($\mu = 0,1$) existieren anscheinend drei 1:1-Komplexspezies MH_2L, MHL^- und ML^{2-} sowie ein 1:2-Komplex ML_2^{6-}. In stark alkalischem Medium (pH über 12.5) konnen die Komplexe zu Zinkhydroxid und L^{4-} dissoziieren. Die Bilding eines Hydroxykomplexes wird nicht beobachtet. Die Absorptionsmaxima liegen bei 445 nm (MH_2L), 466 nm (MHL^-) und 561 nm (ML^{2-}), die molaren Extinktionskoeffizienten betragen $2,34 \times 10^4$, $2,42 \times 10^4$ bzw. $3,13 \times 10^4$ l mol^{-1} cm^{-1}. Die Bildungskonstanten sind (bei 25 ± 0.1°) log $K^M_{ML} = 11,84$, log $K^M_{MHL} = 7,13$, log $K^M_{MH_2L} = 2,70$ und log $K^M_{ML_2} = 16,60$.

Résumé—L'interférence par un excès de peroxyde affecte sérieusement l'exactitude des techniques de dosage du chrome mettant en jeu une oxydation préliminaire de l'élément par le peroxyde de sodium ou d'hydrogène. Quelques-unes des méthodes utilisées pour surmonter ce problème sont pénibles ou incertaines. On présente maintenant une méthode pour l'isolement quantitatif et rapide du chromate à partir de solutions alcalines de peroxyde. Elle comprend la sorption du chromate sur une résine échangeuse d'anions fortement basique. Le peroxyde gênant est éliminé par lavage avec une solution aqueuse à 2 % de soude.

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Extraction and determination of uranium

In preliminary experiments we found that uranium can be quantitatively removed from its aqueous solutions buffered with hexamine, by double extraction with a chloroform solution of PAA. In the aqueous phase (after double washing with pure chloroform) uranium cannot be detected with either potassium ferrocyanide or dibenzoylmethane. We have obtained the same result for the extraction of uranium from solutions containing excess of NTA.

Procedure. A slightly acidic solution containing 10–80 mg of uranium was taken in a 200-ml separatory funnel and diluted to 70 ml with water, and 10 ml of 1*M* PAA were added. The mixture was gently stirred for a while and 3 ml of saturated hexamine solution were added, then the mixture was shaken for 1 min. The yellow extract was transferred into another separatory funnel and the extraction repeated with 10 ml of 1*M* PAA and the extract added to the first one. The aqueous phase was twice washed with 5 ml of pure chloroform, and the washings were also added to the second separatory funnel. The combined chloroform extract was stripped twice with 20 ml of water and 3 ml of 1*M* hydrochloric acid, the strippings being transfered into a 500-ml titration flask. After the addition of an excess of 0·05*M* EDTA and 1 g of ascorbic acid, the pH was adjusted to 3–4 with 1*M* sodium hydroxide. Then the solution was gently boiled for at least 10 min, cooled and diluted to 200–250 ml. The pH was adjusted to 2–3 by addition of 10–20 ml of 1*M* acetic acid and the excess of EDTA was back-titrated with 0·05*M* thorium nitrate solution, with Xylenol Orange as indicator.

When other metals were also present, 10–25 ml of 0·5*M* NTA—or more if necessary—were added before the PAA, and then the procedure described above was followed.

RESULTS

Table 1 summarizes results for determination of uranium in the presence of large concentrations of zirconium, thorium, bismuth, iron and some rare earths. Table 2 includes results of uranium determination in the presence of bivalent metals, iron and aluminium.

Table 1. Determination of uranium in the presence of Zr, Th, La, Bi, Fe, *etc*

Metals, *mg*								0·05*M* EDTA required for uranium, *ml*	
Zr	Th	La	Pr	Dy	Bi	Fe	Cu	Calculated	Found
23	—	—	—	—	—	—	—	3·86	3·88
46	—	—	—	—	—	—	—	3·86	3·86
137	—	—	—	—	—	—	—	1·93	1·90
137	—	—	—	—	—	—	—	3·86	3·86
137	—	—	—	—	—	—	—	7·72	7·70
—	116	—	—	—	—	—	—	3·86	3·87
—	116	—	—	—	—	—	—	1·93	1·90
—	—	35	35	40	—	—	—	3·86	3·87
—	—	70	70	80	—	—	—	3·86	3·87
—	116	70	70	80	—	—	—	1·93	1·90
—	116	70	70	80	—	—	—	3·86	3·86
—	116	70	70	80	—	—	—	7·72	7·69
—	—	35	35	40	104	28	32	3·86	3·90
—	—	35	35	40	104	28	32	1·93	1·91
—	—	35	35	40	104	28	32	7·72	7.70
—	—	—	—	—	—	—	—	3·86	3·90
—	—	—	—	—	—	—	—	1·93	1·90
—	—	—	—	—	—	—	—	7·72	7·69

Similar results were obtained in the presence of molybdenum(VI) and vanadium(V), which are not extracted with PAA at all. Tungsten, together with silicic acid, has to be separated by evaporation. Smaller amounts of titanium are masked with NTA. Masking of large amounts of titanium with hydrogen peroxide failed, because uranium in its presence is precipitated with PAA and is not properly extracted. Scandium is reliably masked with NTA and does not interfere.

Table 2. Determination of uranium in the presence of bivalent metals, iron and aluminium

Metals, *mg*										0·05M EDTA required for uranium, *ml*	
Fe	Cu	Co	Ni	Mn	Zn	Pb	Al	Ca	Mg	Calculated	Found
28	16	—	—	—	—	—	—	—	—	3·88	3·98
14	32	—	—	—	—	—	—	—	—	3·88	3·90
—	—	15	15	8	10	51	4	—	—	3·88	3·86
—	—	15	15	27	16	103	7	—	—	3·88	4·00
—	—	30	15	14	16	103	13	—	—	3·88	3·92
—	—	30	15	14	16	103	13	—	—	7·76	7·78
28	16	15	15	28	16	51	7	—	—	7·76	7·78
28	32	—	—	28	—	—	—	20	6	3·88	3·92
14	16	—	—	28	—	51	7	10	12	7·76	7·88
28	—	—	—	14	—	—	7	20	12	7·76	7·76
14	—	15	15	14	16	51	7	—	—	7·76	7·74
14	—	15	15	14	16	51	7	—	—	3·88	3·86

DISCUSSION

The proposed method for uranium extraction is highly selective, without any interference from at least twenty elements. It is suitable for large amounts of uranium up to 80 mg and applicable for the analysis of uranium alloys, minerals and uranium concentrates. Because of the high sensitivity of the extraction, it should be possible to use it for separation of uranium before its polarographic or colorimetric determination in trace amounts. It should be more suitable than the recently described extraction of uranium with a chloroform solution of trioctylmethylammonium chloride (Aliquat 336-S), where molybdenum(VI), vanadium(V) and chromium(VI) are also quantitatively extracted.[7]

Elements such as nickel and cobalt are not extracted if present in concentrations $<10^{-3}M$, even in the absence of NTA,[5] and in some circumstances the NTA might be omitted if low concentrations of these species were to be determined in the aqueous phase after the extraction.

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Summary—The method described is based on the extraction of uranium with a chloroform solution of phenylacetic acid from slightly acidic solution containing nitrilotriacetic acid, which masks all interfering metals. After stripping into very dilute hydrochloric acid, uranium is reduced with ascorbic acid and determined complexometrically. The method permits reliable determination of uranium in the presence of all quadri-, ter- and bivalent metals investigated, molybdenum(VI), tungsten(VI), and vanadium(V).

Zusammenfassung—Das beschriebene Verfahren beruht auf der Extraktion von Uran mit einer Chloroformlösung von Phenylessigsaure aus schwach saurer Lösung, die Nitrilotriessigsäure enthält, durch die alle störenden Metalle maskiert werden. Nach Rückextraktion in sehr verdünnte Salzsäure wird Uran mit Ascorbinsäure reduziert und komplexometrisch bestimmt. Das Verfahren erlaubt die zuverlässige Bestimmung von Uran in Gegenwart aller untersuchten vier-, drei- und zweiwertigen Metalle sowie von Molybdän(VI), Wolfram(VI) und Vanadium(V).

Résumé—La méthode décrite est basée sur l'extraction de l'uranium par une solution chloroformique d'acide phénylacétique à partir d'une solution légèrement acide contenant de l'acide nitrilotriacétique, qui dissimule tous les métaux gênants. Après extraction dans une solution très diluée d'acide chlorhydrique, l'uranium réduit par l'acide ascorbique et dosé complexométriquement. La méthode permet le dosage exact de l'uranium en la présence de tous les métaux tétra-, tri- et divalents étudiés, des molybdène (VI), tungstène (VI) et vanadium (V).

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Among the spectrophotometric methods for the determination of manganese, those based on the permanganate reaction are undoubtedly the most widely used. The methods are specific but not sensitive ($\varepsilon = 2{\cdot}42 \times 10^3$ l. mole^{-1}. cm^{-1} at 546 nm).[1] On the other hand, many of the more sensitive reagents such as 4,4′-tetramethyldiaminotriphenylmethane[2] (tetrabase) are not selective and give strongly coloured oxidation products which are not stable. Thus, a search for a more suitable reagent led us to the application of the very sensitive reaction between manganese(II) and PAR for determining minute amounts of the metal.

Yotsuyanagi *et al.*[3] described the use of PAR in the analysis of water and gave the molar absorptivity as $\varepsilon = 7{\cdot}80 \times 10^4$ l.mole^{-1}. cm^{-1}. Tataev and Anisimova[4] found $\varepsilon = 3{\cdot}83 \times 10^4$, $K_{\text{instab.}} = 3{\cdot}9 \times 10^{-12}$ and M:L = 1:2. Corsini *et al.*[5] established the stability constant of the complex potentiometrically and found $\log K_1 = 9{\cdot}7$ and $\log K_2 = 9{\cdot}2$, *i.e.*, $\log \beta_2 = 18{\cdot}9$ in 50% aqueous dioxan solution. Ueda *et al.*[6] reported the formation of a manganese(II)–PAR complex with a molar ratio 1:3, finding $\varepsilon = 8{\cdot}50 \times 10^4$ and $\lambda_{\max} = 500$ nm.

The present paper attempts to resolve these discrepancies, reporting a detailed investigation of the reaction between manganese(II) and PAR and its application for the spectrophotometric determination of this metal.

EXPERIMENTAL

Reagents

4-(2-Pyridylazo)resorcinol monosodium salt. A $10^{-4}M$ solution was standardized by spectrophotometric titration with copper(II) nitrate solution at pH 5 and 520 nm.[7]

Manganese(II) nitrate solution. A $10^{-2}M$ solution was standardized complexometrically.[8] The working solutions were prepared by appropriate dilution.

Buffer solution. Disodium phosphate ($0{\cdot}1M$) and sodium hydroxide solutions were used to prepare a buffer solution of pH 11·2, a pH-meter being used to check the pH.

Sodium nitrate solution, $1M$. Used to maintain the ionic strength constant at 0·1.

All chemicals were analytical-reagent grade.

Properties of the complex

Composition. The metal to ligand molar ratio of 1:2 at pH > 9 was confirmed by the Job, Harvey–Manning and isosbestic point[9] methods.

Optimum pH value. The dependence of the absorbance spectrum on pH was recorded at different pH values for equimolar solutions (Fig. 1), then absorbance measurements at pH > 10 were performed. These experiments revealed a maximum sensitivity at pH 11·2–11·7 and $\lambda_{\max}$ of the complex at 496 nm. The curves in Fig. 1 pass through one isosbestic point, thus proving a simple complex-forming equilibrium in solution and only one complex formed under the various conditions.

Zusammenfassung—Das beschriebene Verfahren beruht auf der Extraktion von Uran mit einer Chloroformlösung von Phenylessigsaure aus schwach saurer Lösung, die Nitrilotriessigsäure enthält, durch die alle störenden Metalle maskiert werden. Nach Rückextraktion in sehr verdünnte Salzsäure wird Uran mit Ascorbinsäure reduziert und komplexometrisch bestimmt. Das Verfahren erlaubt die zuverlässige Bestimmung von Uran in Gegenwart aller untersuchten vier-, drei- und zweiwertigen Metalle sowie von Molybdän(VI), Wolfram(VI) und Vanadium(V).

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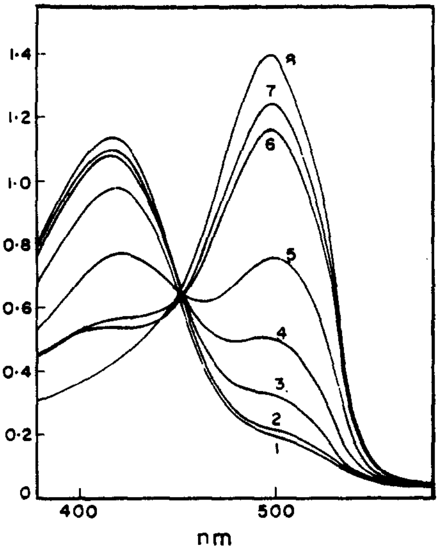

Fig. 1. Dependence of absorbance spectra on pH
$C_{Mn} = 0{\cdot}8 \times 10^{-5}M$; $C_{PAR} = 1{\cdot}6 \times 10^{-5}M$; 2-cm cells.
pH: (1) 6·10; (2) 7·00; (3) 8·50; (4) 9·15;
(5) 9·80; (6) 10·70; (7) 11·00; (8) 11·70.

Reagent excess. Investigation of solutions containing a constant amount of manganese(II) showed that the minimum molar excess of PAR necessary in solutions buffered at pH 11·2–11·7 is from 4- to 5-fold.

Development time. Full colour development occurs immediately, and the absorbance remains constant for half an hour, then slowly decreases. When potassium cyanide is added as masking agent, the solution requires 10–15 min for full colour development.

Beer's law. Under the optimum conditions described, a calibration graph over the range 0·02–0·5 μg of Mn per ml is linear (2-cm cells).

Molar absorptivity. The molar absorptivity of the complex was determined at the optimum pH value and λ_{max} 496 nm in the presence of an approximately 10-fold excess of PAR, the least-squares procedure being applied to the calibration curve. Fourteen points were used and a value $\varepsilon = 7{\cdot}91 \pm 0{\cdot}06 \times 10^4$ l.mole^{-1}.cm^{-1} was obtained. To determine the true value of ε, the absorbances of a series of solutions containing an exactly known and constant amount of PAR and a 2- to 200-fold excess of manganese(II) were measured, thus eliminating the effect of the absorbance of the free reagent. The molar absorptivity $\varepsilon = 8{\cdot}65 \pm 0{\cdot}04 \times 10^4$ was found (95% confidence limits, 36 variates).

The sensitivity according to Sandell was calculated to be 0·63 ng/cm^2. A comparison of the sensitivity of various methods is given in Table 1.

Table 1. Sensitivities of some methods for spectrophotometric determination of manganese[2]

Method	Mn, μg/cm^2 for $A = 0{\cdot}001$
$KMnO_4$	0·027
Diethyldithiocarbamate	0·025
Formaldoxime	0·005
Tetrabase	0·0001
PAR	0·00063

Investigation of the reaction and determination of the stability constant

Methods based on the relationship $A = f(\text{pH})$ were used (A = absorbance). Because of the considerable absorption by the reagent at higher pH values and the working wavelength, complex-formation was investigated only with equimolar solutions and solutions containing a small excess of metal ion. The straight-line portions of the absorbance–pH plots were used for calculations. The number of protons n split off during complexation, as well as the equilibrium constants, were established graphically. The graphs for equimolar solutions:[10]

$$\log \frac{A}{(A_0 - A)^3} = \log K_{eq} - \log \frac{A_0^2}{4C_M^2} + n\,\text{pH} \qquad (1)$$

and for solutions with a slight metal-ion excess:

$$\log \frac{A}{(2A_0 - mA)(A_0 - A)^2} = \log K_{eq} - \log \frac{A_0^2}{mC_M^2} + n\,\text{pH} \qquad (2)$$

gave straight lines with slopes of 2·0, *i.e.*, two protons are released during complexation (A is the absorbance at a given pH value, A_0 is the maximum absorbance, C_M is the total metal concentration, and $m = C_L/C_M < 1$ where C_L is the total ligand concentration). Assuming that the HL^- species of PAR predominates at the pH used,[10] the following reaction should take place:*

$$Mn^{2+} + 2HL^- = MnL_2^{2-} + 2H^+$$

The equilibrium constants were determined from the intercepts of the straight lines on the pH axis and the corresponding stability constants were calculated from the equation $\beta_2 = K_{eq}/K_3^2$ where K_3 is the third dissociation constant of PAR. The value $pK_3 = 12{\cdot}31$ was used.[11,12] The results obtained are summarized in Table 2.

Table 2. Constants for manganese(II)-PAR complex

	Slope	Intercept	$\log K_{eq}$	$\log \beta_2$
Equimolar solutions	2·0	9·10	−8·99	15·6
Excess of manganese(II)				
$m = 0{\cdot}506$	2·0	9·15	−8·97	15·3
$m = 0{\cdot}651$	2·0	8·85	−8·61	16·0

In order to verify the value of the stability constant obtained, we used it for calculation of the optimum pH range within which the reaction is practically complete,[13] *i.e.*, $[MnPAR_2]/[Mn'] > 10^3$. According to literature data[14] there is no evidence for complex-formation of manganese(II) with phosphate, so to determine the conditional stability constant $K_{ML'_2}$ only the side-reaction coefficient $\alpha_{PAR(H)}$ was taken into account. The results are presented in Table 3, which shows that complex-formation is complete at pH > 11, which is in accord with the experimental results.

Table 3.

pH	$\log \alpha_{PAR(H)}$	$\log K_{ML'_2} = 15{\cdot}6 - 2 \log \alpha_{PAR(H)}$	$\log[MnPAR_2]/[Mn]$ at $C_{PAR} = 10^{-5}M$
1	17·5	−19·4	−29·4
2	14·6	−13·6	−23·6
3	12·0	−8·4	−18·4
4	9·8	−4·0	−14·0
5	7·9	−0·2	−10·2
6	6·4	2·8	−7·2
7	5·3	5·0	−5·0
8	4·3	7·0	−3·0
9	3·3	9·0	−1·0
10	2·3	11·0	1·0
11	1·3	13·0	3·0
12	0·5	14·6	4·6

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* The anionic nature of the complex was confirmed by electrophoresis.

Interfering ions

The effect of several interfering metal ions on the determination of manganese(II) with PAR was investigated. Potassium cyanide was used as masking agent in a solution containing 2 ml of $10^{-4}M$ manganese(II), 0·5 ml of 5% ascorbic acid solution (as reducing agent), 3 ml of $0{\cdot}1M$ sodium hydroxide, 5–20 drops of 5% potassium cyanide solution, 0·5 ml of 0·05% PAR solution and 2 ml of buffer solution in a 25-ml volumetric flask (preliminary tests showed that the amount of potassium cyanide does not affect the absorbance). The following results were obtained: up to 200-fold amounts of Ni(II), Cu(II), Hg(II) and Al(III), 5-fold amounts of Zn(II) and Cd(II), and 50-fold amounts of Co(II) do not interfere. Iron(III) interferes when present in concentration equal to or greater than that of the manganese. In this case the order of adding the reagents is important: the solution containing Fe(III) must be introduced after the potassium cyanide, sodium hydroxide and ascorbic acid. In all experiments using potassium cyanide as masking agent, the PAR was added 10–15 min after the potassium cyanide, and a development period of 10–15 min was allowed.

Application of the method

As an extension of this work, attempts were made to apply the reaction for determining manganese in a standard steel (C 0·56; Mn 0·77; S 0·007; Ni 1·52; Al 0·024; Si 0·28; P 0·027; Cr 1·22; Ti 0·16%), a standard ARMCO iron (C 0·014; Si 0·005; Mn 0·05; P 0·010; S 0·030; Ni 0·05; Co 0·012; Cu 0·09; As 0·016; Sn 0·014; Sb 0·006; N 0·0027; and Fe 99·64%) and a pure ferrous sulphate certified to contain not more than 0·025 % Mn.

The bulk of the iron was removed by extraction with diethyl ether from $6M$ hydrochloric acid solution.[15] The results are shown in Table 4.

Table 4. Determination of manganese

Sample	Certificate Mn, %	Number of determinations	Mn found, mean value, %	Standard deviation	Relative standard deviation %
Standard steel	0·77	8	0·77	0·046	6
ARMCO iron	0·05	12	0·046	0·0014	3
Ferrous sulphate	0·025	10	0·026	0·0012	5

Method

Dissolve 0·05–0·1 g of steel (0·5 g of ferrous sulphate) in 2–3 ml of $6M$ hydrochloric acid. Oxidize the iron(II) with 1 ml of concentrated nitric acid. Evaporate almost to dryness, add a little $6M$ hydrochloric acid and digest to dissolve the salts. Cool, and transfer the solution to a 100-ml separatory funnel with the aid of several ml of $6M$ hydrochloric acid. Add about 10 ml of diethyl ether and extract the bulk of the iron(III). Separate the two phases. Repeat 5 or 6 times with fresh solvent until the organic phase is colourless. Run the aqueous phase into a 150-ml tall-form beaker and evaporate the solution to dryness to remove the acid. Dissolve the residue in distilled water, transfer to a 50- or 100-ml volumetric flask and dilute to the mark. Pipette an appropriate fraction (1–5 ml) into a 25-ml volumetric flask containing 0·5 ml of 5% ascorbic acid solution, 2–3 ml of $0{\cdot}1M$ sodium hydroxide, 2–5 ml of buffer and 4–6 drops of 5% potassium cyanide solution. Mix well and stand for 10–15 min, then add 1 ml of 0·05% PAR solution, make up to the mark and stand for a further 10–15 min. Measure the absorbance of the solution in a 1-cm cell at 496 nm against a reagent blank.

Prepare a calibration graph by applying the procedure to 70-mg samples of high-purity iron and suitable quantities of a standard manganese(II) solution.

Acknowledgement—The assistance of N. Lihareva and A. Kurktchieva with the experimental work is greatly appreciated.

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Summary—A highly sensitive method for spectrophotometric determination of manganese(II) with 4-(2-pyridylazo)resorcinol (PAR) as reagent is described. The molar absorptivity of the complex was found to be $8{\cdot}65 \pm 0{\cdot}04 \times 10^4$. The stability constant of the ML_2 complex was found to be $\log \beta_2 = 1\,5{\cdot}6$. Beer's law is obeyed within the range 0·02–0·5 μg of Mn/ml. An application of this reaction for analytical purposes is described.

Zusammenfassung—Eine hochempfindliche Methode zur spektrophotometrischen Bestimmung von Mangan(II) mit 4-(2-Pyridylazo)resorcin (PAR) als Reagens wird beschrieben. Der molare Extinktionskoeffizient des Komplexes wurde als $8{,}65 \pm 0{,}04 \times 10^4$ l $mol^{-1}cm^{-1}$ bestimmt, die Stabilitätskonstante des ML_2-Komplexes als $\log \beta_2 = 15{,}6$. Das Beersche Gesetz wird bei 0,02–0,5 μg Mn im ml befolgt. Es wird eine Anwendung dieser Reaktion für analytische Zwecke angegeben.

Résumé—On décrit une méthode hautement sensible pour le dosage spectrophotométrique du manganèse (II) par le 4-(2-pyridylazo) résorcinol (PAR) comme réactif. On a trouvé que le coefficient d'absorption molaire du complexe est $8{,}65 \pm 0{,}04 \times 10^4$ $1.mole^{-1}.cm^{-1}$. On a trouvé que la constante de stabilité du complexe ML_2 est $\log \beta_2 = 15{,}6$. La loi de Beer est suivie dans le domaine 0,02–0,5 μg de Mn/ml. On décrit une application de cette réaction à des fins analytiques.

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ANALYTICAL DATA

STABILITY CONSTANTS OF SOME BIVALENT METAL COMPLEXES OF *N*-PHENYL-*o*-TOLYLBENZOHYDROXAMIC ACID

(*Received* 30 *May* 1973. *Accepted* 16 *June* 1973)

The thermodynamic stability constants of the Mn^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} chelates of *N*-phenyl-*o*-methylbenzohydroxamic acid have been determined by the procedure described earlier.[1] The results given in Table 1 were reproducible within ± 0·05.

There was no evidence of polynuclear protonated complexes, or metal ion hydrolysis. Nitrate, chloride, perchlorate, sodium and potassium ions have no effect on the formation constants under the experimental conditions used. The maximum $\bar{n}$ values of about 2 suggest 1:2 complex formation in solution.

The log K values are in the Irving–Williams[2] order. The value for zinc is higher than that for nickel, as for other hydroxamic acids[3–5] and other chelates[6,7] where steric hindrance prevents formation of a square planar structure for the nickel complex.

The log K_1 values were a linear function of the ionization potential of Mn(II), Ni(II) and Zn(II) but not for Cu(II). The extra stability of the copper complex may be attributed to the tetragonal distortion of octahedral symmetry as a result of the Jahn–Teller effect.

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Table 1. Stability constants of *o*-MBHA metal complexes in 50% v/v aqueous dioxan media at 30°C.

Ion	log K_1 (±0·05)	log K_2 (±0·05)	Ionization potential, *kcal/mole*
Cu^{2+}	10·45	8·90	647
Zn^{2+}	8·16	6·70	632
Ni^{2+}	7·52	6·01	590
Mn^{2+}	6·33	5·59	532

The values of log K_1 and log K_2 are the averages of six titration points.

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Summary—The stability constants of the Cu^{2+}, Zn^{2+}, Ni^{2+} and Mu^{2+} complexes of *N*-phenyl-*o*-methoxybenzohydroxamic acid at 30° in 50% v/v aqueous dioxan are: log K_1 10·45, 8·16, 7·52, 6·33; log K_2 8·90, 6·70, 6·01, 5·59 (for the ions in the order given).

Zusammenfassung—Die Stabilitätskonstanten der Komplexe von Cu^{2+}, Zn^{2+}, Ni^{2+} und Mn^{2+} mit N-Phenyl-o-methoxybenzhydroxamsäure betragen bei 30° in 50% V/V wäßrigem Dioxan: log K_1 10,45, 8,16, 7,52, 6,33; log K_2 8,90, 6,70, 6,01, 5,59 (für die Ionen in der angegebenen Reihenfolge).

Résumé—Les constants de stabilité des complexes de Cu^{2+}, Zn^{2+}, Ni^{2+} et Mn^{2+} avec l'acide N-phényl-*o*-méthoxybenzohydroxamique à 30° en dioxane aqueux à 50 % v/v sont: long K_1 10,45; 8,16; 7,52; 6,33: log K_2 8,90; 6,70; 6,01; 5,59 (pour les ions dans l'ordre donné).

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CORRECTION FACTORS FOR THE GLASS ELECTRODE IN AQUEOUS DIOXAN

(*Received* 25 *May* 1973. *Accepted* 3 *June* 1973)

Van Uitert and Hass[1] have discussed the conversion of pH measurements in aqueous dioxan media into hydrogen ion concentrations and given the necessary data.[2,3] Irving and Mahnot[4] have pointed out anomalies in these data and published revised values. The data published so far refer only to 25 and 30°. The present work has re-examined these values and extended the temperature range to 35°. Van Uitert's method[2] was used for mixtures of dioxan and water (both purified as indicated earlier[5]), and the result (Table 1) evaluated according to the van Uitert method.

The values found for log U_{H}^{0} at 30° are similar to these found by van Uitert[2], but the values at 25 and 30° are lower than those reported by Irving and Mahnot,[4] possibly because of the different methods of calculation.

Acknowledgement—The author is indebted to Prof. A. B. Biswas, Professor of Chemistry, Indian Institute of Technology, Bombay, for his inspiring guidance. Grateful acknowledgement is made to C.S.I.R., New Delhi for the award of a Senior Research Fellowship.

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Zusammenfassung—Die Stabilitätskonstanten der Komplexe von Cu^{2+}, Zn^{2+}, Ni^{2+} und Mn^{2+} mit N-Phenyl-o-methoxybenzhydroxamsäure betragen bei 30° in 50% V/V wäßrigem Dioxan: log K_1 10,45, 8,16, 7,52, 6,33; log K_2 8,90, 6,70, 6,01, 5,59 (für die Ionen in der angegebenen Reihenfolge).

Résumé—Les constants de stabilité des complexes de Cu^{2+}, Zn^{2+}, Ni^{2+} et Mn^{2+} avec l'acide N-phényl-*o*-méthoxybenzohydroxamique à 30° en dioxane aqueux à 50 % v/v sont: long K_1 10,45; 8,16; 7,52; 6,33: log K_2 8,90; 6,70; 6,01; 5,59 (pour les ions dans l'ordre donné).

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Table 1. Determination of log U_H and log U_H^0.* [$HClO_4$] = 0·0016*M*; [$NaClO_4$] = 0·0300*M*

		At 25°C				At 30°C					At 35°C		
				log U_H^0				log U_H^0					log U_H^0
Dioxan, % v/v	Mole fraction of dioxan	log U_H	log $1/\gamma_\pm$	This study	Ref. 4	log U_H	log $1/\gamma_\pm$	This study	Ref. 2	Ref. 4	log U_H	log $1/\gamma_\pm$	This study
0	0	−0·075	0·075	0·00	0·00	−0·090	0·087	0·00	—	—	−0·070	0·072	0·00
10	0·023	−0·070	0·080	0·01	0·01	−0·080	0·090	0·01	—	0·03	−0·065	0·076	0·01
20	0·050	−0·080	0·100	0·02	0·04	−0·085	0·104	0·02	0·02	0·06	−0·070	0·090	0·02
30	0·083	−0·090	0·130	0·04	0·06	−0·080	0·131	0·05	0·05	0·10	−0·075	0·134	0·06
40	0·123	−0·090	0·170	0·08	0·11	−0·080	0·169	0·09	0·09	0·16	−0·070	0·171	0·10
45	0·147	−0·070	0·190	0·12	0·16	−0·065	0·195	0·13	0·13	0·20	−0·060	0·201	0·14
50	0·174	−0·010	0·210	0·20	0·22	−0·010	0·229	0·22	0·22	0·26	+0·010	0·229	0·24
60	0·240	+0·100	0·300	0·40	0·44	+0·060	0·328	0·39	0·40	—	+0·105	0·320	0·42
70	0·330	+0·250	0·550	0·80	0·85	+0·250	0·553	0·80	0·80	—	+0·290	0·537	0·83

* $-\log[H^+] = B + \log U_H$ where B is the pH, and $\log U_H = \log U_H^0 - \log 1/\gamma_\pm$ ($\gamma_\pm$ is the mean activity coefficient of hydrochloric acid under the conditions in which U_H is determined). The values of B were the average of at least 5 independent measurements on solutions of the same nominal composition. Log $1/\gamma_\pm$ values were calculated by interpolation from data given by Harned and Owen.[6] The value $-\log[H^+] = 2·90$ was taken as pH − log $1/\gamma_\pm$ for aqueous solution.

Summary—The conversion factors for obtaining the hydrogen ion concentration from pH measurements at different mole fractions of dioxan in water at 25, 30 and 35° are reported.

Zusammenfassung—Die Umrechnungsfaktoren zur Bestimmung der Wasserstoffionenkonzentration aus pH-Messungen bei verschiedenen Molenbrüchen von Dioxan in Wasser bei 25°, 30° und 35° werden mitgeteilt.

Résumé—On rapporte les facteurs de conversion pour obtenir la concentration en ion hydrogène à partir de mesures de pH pour différentes fractions molaries de diozane dans l'eau à 20, 30 et 35°.

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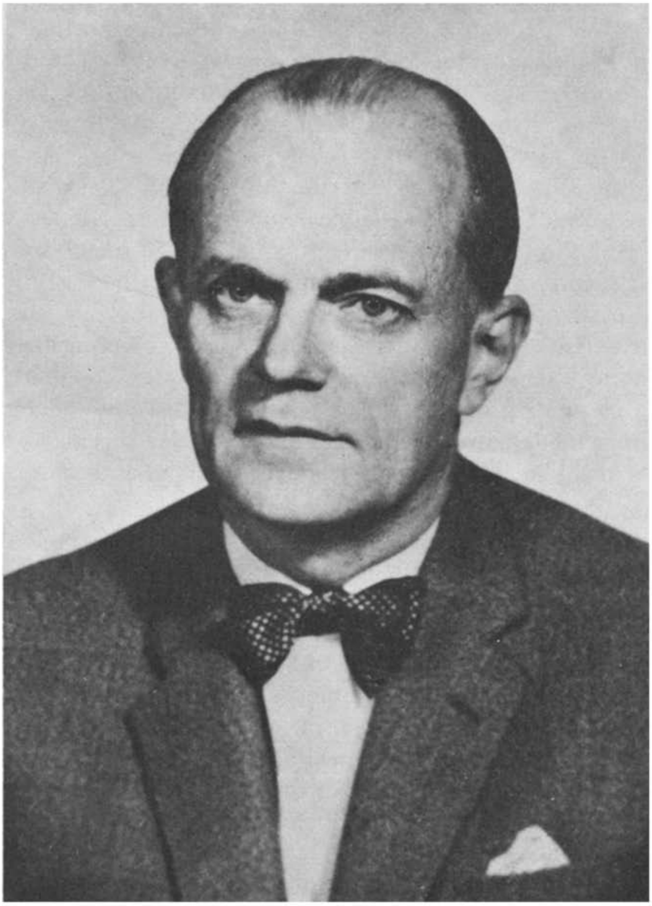


ANDERS RINGBOM

Professor Anders Ringbom passed away in Åbo, Finland, on 21 December 1972. Anders Ringbom was born in Åbo in 1903. After going to school in the same city, he entered the Faculty of Chemical Engineering at Åbo Akademi where he became M.Sc. in 1925 and Dr.Sc. in 1936. When he retired on January 1, 1969 he could look back on 42 active years at Åbo Akademi, first as research and teaching assistant, later as lecturer and finally as professor of analytical and inorganic chemistry.

His scientific contributions bear witness of deep knowledge and outstanding ability. His papers are characterized by clarity of thought and presentation and by a rare ability to find elegant solutions to complicated problems. The treatment is always based on theoretical calculations. It is therefore not surprising that his papers have been highly appreciated among analytical chemists. Several of his contributions may now be considered classics.

The greatest achievement of Anders Ringbom is his contribution to the development of the theory of complexometric analysis of metal ions in solution. He began his research work in this field about 1950 and was soon able to show how the mathematical problems could be solved in a simple and elegant way. He presented his method in the form of a paper and later as a chapter in a large compilatory work. Both received much favourable attention, and Professor Ringbom was invited to several countries to give lectures about the new technique.

In 1963 Professor Ringbom published the monograph *Complexation in Analytical Chemistry* where different types of chemical analysis were treated according to the principles developed for the complexometric analysis of metal ions. The book has greatly influenced theoretical analytical chemistry all over the world. Its importance is further evidenced by the translations into French and Japanese.

In 1966 Finska Vetenskapssocieteten selected Anders Ringbom for the E. J. Nyström award for outstanding scientific contributions. The same year Åbo Akademi awarded him the Harry Elving teacher's grant. In 1969 Svenska Kemistsamfundet honored him with the Torbern Bergman medal for excellent scientific work. He was also a honorary member of the Finnish Chemical Societies, Finska Kemistsamfundet and Suomalaisten Kemistien Seura.

After his retirement in 1969 Anders Ringbom remained active in research. He was particularly interested in the determination of equilibrium constants for complexation reactions and was also working on a new edition of his monograph. Professor Ringbom's ability was also utilized by international organizations. As a member of the Analytical Section of the International Union of Pure and Applied Chemistry he took an active part in the compilation of solubility product tables for metal sulphides.

At Åbo Akademi Professor Ringbom took an active part in the administration as vice president 1954–57 and as dean of the Faculty of Chemical Engineering 1962–66. During the period 1961–65 he was a member of the State Commission for Technological Research and in 1965 The Ministry of Education appointed him a permanent adviser on technical education for the period 1965–67. Professor Ringbom also took an active interest in student organizations. He was president of the student corporation at Åbo Akademi 1953–57 and was elected honorary member of the corporation in 1957.

Anders Ringbom was highly regarded as friend and colleague. His pleasant and cheerful personality made everybody enjoy his company. His memory shall live among those who had the privilege of being his friends.

ERKKI WÄNNINEN

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

R. GIJBELS	D. JAGNER
L. KOSTA	H. B. MARK, JR.
J. M. OTTAWAY	S. SIGGIA
J. D. WINEFORDNER	I. A. VOINOVITCH

They also wish to record their sincere thanks for the help given by

E. CERRAI	H. MALISSA
L. C. PASZTOR	J. E. REIN

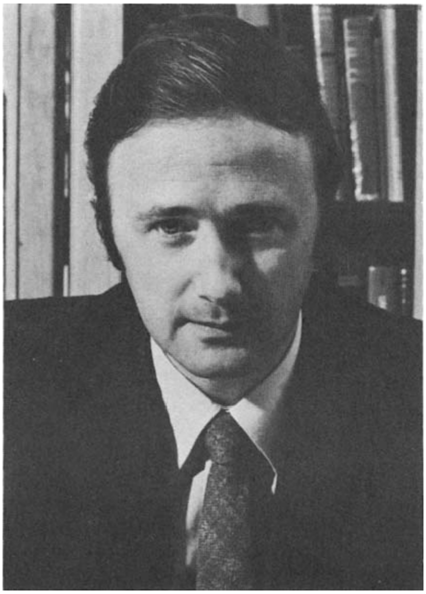
E. SAWICKI

who retire from the Advisory Board.

DR. DANIEL JAGNER, born in 1940, has been working as research assistant and lecturer with Professor D. Dyrssen at the University of Göteborg, Sweden, since 1965. His research interests include high-precision photometric and potentiometric titrations, and in particular, their application to the analytical chemistry of sea-water. Emphasis has been placed on the use of computer calculations to study the theoretical aspects of titration procedures. Latterly, his research work has also included the automation of analytical instruments and procedures, using easily programmable mini-computers, in connection with, *e.g.*, ion-selective electrodes and atomic-absorption spectroscopy. He is co-author of "Computer Calculation of Ionic Equilibria and Titration Procedures" and joint editor of "The Changing Chemistry of the Oceans." Dr. Jagner's British wife is an inorganic chemist and they have three sons.

DR. R. GIJBELS was born in 1939 and graduated Ph.D. at Ghent (Belgium) in 1965. After a stay at the Laboratory for Nuclear Sciences of M.I.T. Cambridge, Mass. and at the U.S. Geological Survey, Denver, Colo., he is now working in the Institute for Nuclear Sciences of the University of Ghent as a research associate of the Interuniversity Institute for Nuclear Sciences. He is also lector in geochemistry at the same University, and teaches physical chemistry at the University of Antwerp.

His scientific interests include activation analysis with reactor and 14-MeV neutrons (applied to geological samples and industrial products, including high-purity materials), nuclear chemistry (cross-section measurements of fission neutron-induced threshold reactions) and geochemistry (trace-element analysis related to the differentiation of volcanic rocks and layered intrusions). He has written 40 papers and is co-author of two monographs (on neutron-activation analysis). Dr. Gijbels is married and has one child.



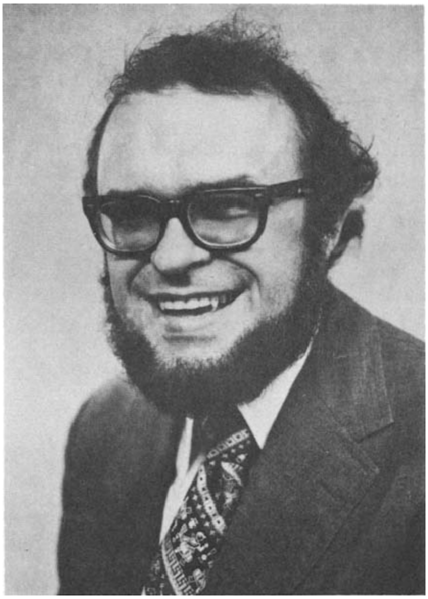
Dr. John M. Ottaway has been a lecturer in Analytical Chemistry at the University of Strathclyde since September 1966 and was previously, for three years, assistant lecturer at the University of Exeter where he obtained the degrees of B.Sc. (1961) and Ph.D. (1965). A major research interest is in the application of kinetics in analytical chemistry, particularly to the determination of traces of metals and non-metals by catalytic analysis. Dr. Ottaway also has a strong interest in atomic spectroscopy, related particularly to mechanisms of atom formation and interferences in flame and non-flame atom cells. Dr. Ottaway has been Honorary Secretary of the Scottish Region of the Society for Analytical Chemistry for a number of years and currently serves on the Council, *The Analyst* Executive Committee and Advisory Board, The Programmes Committee and The Analytical Methods Committee of the Society. He is also a member of the committee of the Glasgow and West of Scotland Section of the Chemical Society.

Professor Sidney Siggia was born in New York City in 1920. He attended Queens College in New York, receiving a B.S. degree in 1942. He was then employed as research fellow at the Polytechnic Institute of Brooklyn, where he received an M.S. degree in 1943 and a Ph.D. in 1944. Dr. Siggia had his first contact with analytical research while at Queens College, where he worked with Dr. A. A. Benedetti-Pichler. At Brooklyn Poly he was connected with Dr. H. Mark, and his work was on kinetic studies in polymer chemistry and analysis of polymeric materials. From Brooklyn Poly, Dr. Siggia went to General Aniline and Film's Central Research Laboratory in Easton, Pennsylvania, where he was employed as a research analyst. He became manager of GAF's Analytical Department in 1955. In 1958 he joined Olin Mathieson's New Haven Research Lab to set up and direct their Central Analytical Services—Research group. In 1966 he joined the faculty of the University of Massachusetts as professor of chemistry.

Dr. Siggia specializes in organic analysis with emphasis on the handling of mixtures of organic compounds. He has published over 80 papers in the field and also four books: "Quantitative Organic Analysis Via Functional Groups" (now in its 3rd edition); "An Introduction to Modern Organic Analysis"; "Continuous Analysis of Chemical Process Systems," and "Survey of Analytical Chemistry." He has also contributed sections to eight textbooks.

Dr. Siggia is a member of the American Chemical Society, American Association for the Advancement of Science, American Society for Testing Materials, Sigma Xi, and Phi-Lambda Upsilon. He has been advisory board member to Analytical Chemistry; chairman of the ASTM committee on Functional Group Analysis; chairman of the Gordon Conference on Analytical Chemistry; President of the Olin Chapter, Research Society of America. He was chairman of the Division of Analytical Chemistry of the American Chemical Society for the years 1969–1970. He has served on the Advisory panel to the National Bureau of Standards and is serving on the advisory panel to the Oak Ridge National Laboratory. Dr. Siggia is winner of the 1969 Anachem Award. He has also been appointed to the Editorial Board of *Analytical Chimica Acta.*

James D. Winefordner received his B.S., M.S., and Ph.D. degrees in Chemistry from the University of Illinois in 1954, 1955, and 1958 respectively. His research advisor was Professor H. V. Malmstadt. He is married to Laura Whitney of Galva, Illinois and has three children, Philip, Carl, and Anne. From September 1958 to September 1959 he served as a postdoctoral fellow at the University of Illinois. In September 1959, he was appointed Assistant Professor of Chemistry at the University of Florida. In September 1965, he was promoted to Associate Professor of Chemistry and in July 1967, he was promoted to Full Professor at the University of Florida. He is currently Chairman of the Analytical Division of the Department of Chemistry. His research interests include: atomic and molecular emission, absorption and fluorescence in flames and other hot gases; molecular fluorescence and phosphorescence of species in the condensed phase; development of sensitive, selective, accurate methods of trace analysis of metals and molecules in materials based on the above spectroscopic methods; development of sensitive, selective gas and liquid chromatographic detectors; and development of spectroscopic instrumentation for analysis. He has published nearly 200 scientific papers and chapters on these topics and given over 80 invited talks and seminars at international and national conferences and symposia and in universities, colleges, and industries. Since his coming to the University of Florida, 30 of his graduate students have received Ph.D. degrees and 10 M.S. degrees. He has also had 16 postdoctorate fellows work with him. He is a member of the American Chemical Society, Society of Applied Spectroscopy, Phi Lambda Phi, Alpha Chi Sigma, and American Association for Advancement of Sciences. He is a member of the Advisory Boards of *Spectrochimica Acta B*, *Chemical Instrumentation*, *Analytical Letters*, *Talanta*, and the Wiley's Chemical Analysis Series, and has been a member of the advisory board of *Analytical Chemistry*. Dr. Winefordner is a titular member of IUPAC Commission V-4 (Spectrochemical and Other Optical Procedures for Analysis). He received the 1971 Sigma Xi University of Florida Research Award, the 1968 Meggers Award, the 1973 ACS Award in Analytical Chemistry (Fisher Award), and the 1973 Pittsburgh Society of Applied Spectroscopy Award.



Professor L. Kosta was born in 1921, graduated as B.Sc.(Eng.) in chemistry at the University of Ljubljana in 1944, and started his career as toxicologist at the Medical Faculty, Institute for Legal Medicine. In 1952 he joined the "Jožef Stefan" Institute as head of the Analytical Section. He obtained his Ph.D. in 1957. From 1963 to 1967 he was on the Staff of the IAEA, Laboratory Seibersdorf, his main responsibilities being activation analysis and preparation of standard reference materials. At present he is Professor of Analytical Chemistry, University of Ljubljana and head of the Nuclear Chemistry Section of the IJS. He has been a member of the IUPAC Commission on Analytical Radiochemistry and Nuclear Materials since 1965.

Harry B. Mark, Jr., Professor of Chemistry and Chairman of the Analytical Chemistry Division, Department of Chemistry, University of Cincinnati, received his B.A. degree from the University of Virginia in 1956 and his Ph.D. degree from Duke University in 1960. He was a postdoctoral research associate at the University of North Carolina (with C. N. Reilley) from 1960 to 1962 and at the California Institute of Technology (with F. C. Anson) from 1962 to 1963. He was a member of the staff of the Department of Chemistry at the University of Michigan from 1963 to 1970, Visiting Professor of Chemistry at the Université Libre de Bruxelles, 1970, and joined the staff at the University of Cincinnati in 1970. His research interests are in electrochemistry, surface chemistry, kinetic methods of analysis, environmental analytical problems, and instrumentation. In addition to research papers, he is the coauthor of the books "Kinetics in Analytical Chemistry," "Activated Carbon," "Surface Chemistry and Adsorption from Solution," and "Simplified Circuit Analysis; Digital-Analog Logic." He is also a coeditor of the monograph series "Computers in Chemistry and Instrumentation" and a member of the Editorial Boards of *Analytical Letters* and *Chemical Instrumentation*.

I. A. Voinovitch studied at the Lyceum and University in Paris, and from 1945 to 1950 worked on enzymology and microanalysis, discovering (with Prof. Kahane and Dr. Grabar) the antioxidant and bacteriostatic effect of thiamine. After four years in industry he became chief of the analytical laboratory of the French Ceramic Society, and in 1962 published his book on analysis of silicates (English edition 1966). In the same year he became head of the Chemical Department, Central Laboratory of Roads and Bridges, and has remained there since. In 1971 he published books on mineralogical analysis of clay soils and on atomic-absorption spectrometry. Dr. Voinovitch is President of the Analytical Group of the French Industrial Chemistry Society.

ANNOUNCEMENT

Professor T. **Fujinaga** has been awarded the new appointment on the Editorial Board as Regional Editor for Japan.

EDITORIAL

Readers will observe that with this issue we have a new format for *Talanta*, as a result of a change of printer and printing process. The new style allows us to use a lighter paper and to print about 5% more per page. We hope that this will enable us to withstand the ever-increasing cost of printing without having to increase the subscription price. We are sure that readers will find the new style as pleasing as the old, and that contributors will note the few changes in overall house style and make the necessary adjustments to their manuscripts.

Talanta, Vol. 20, pp. i. Pergamon Press, 1973. Printed in Great Britain

PAPERS RECEIVED

1,2,3-Phenyloxyamidine—A new type of analytical reagent Solvent extraction and spectrophotometric determination of vanadium(V): K. Satyanarayana and Rajendra Kumar Mishra. (13 June 1973)

Interference of aluminium in the chelation-extraction of cadmium, with sodium diethyldithiocarbamate as chelating agent: E. E. Kaminski. (13 June 1973)

Benzoylsalicylal hydrazone as a chromogenic reagent for copper(II) and palladium(II): D. K. Rastogi, S. K. Dua, Shri Prakash and R. P. Singh. (13 June 1973)

Sulphur species reaction in (K–Na)SCN eutectic melt: Paolo Cescon, Filippo Pucciarelli, Vito Bartocci and Roberto Marassi. (15 June 1973)

A study of the solvent extraction separation of rhodium from iridium with tri-n-octylamine as a liquid anion-exchanger: G. A. Kanert and A. Chow. (15 June 1973)

Extraction-spectrophotometric determination of thallium in high-purity indium: Z. Marczenko, H. Kałowska and M. Mojski. (19 June 1973)

New applications of thiosemicarbazones for the gravimetric estimation of palladium. Study of thiophen-2-aldehyde and benzaldehyde thiosemicarbazones: J. M. Cano Pavon, M. T. Martinez Aguilar and F. Pino. (19 June 1973)

Extraction of metals into chloroform with some derivatives of phenylacetic acid: J. Adam and R. Pribil. (8 June 1973)

Trace analysis by microwave excitation of sealed samples: A. Van Sandwijk and J. Agterdenbos. (21 June 1973)

Coulometric microdetermination of peroxides: Ulla Fiedler. (22 June 1973)

Untersuchungen an Reagenzien zur photometrischen Zinnbestimmung: Gerhard Ackermann and Hanspeter Heegn. (22 June 1973)

Einflüsse dritter Partner bei der Lösungsspektralanalyse nach dem Zerstäuberverfahren—I. Einflüsse anorganischer Fremdionen: Gerhard Ackermann and Manfred Münx. (22 June 1973)

Carboxylic acids as metal extractants: F. Miller. (25 June 1973)

Extractive separation of molybdenum as Mo(V) xanthate from iron, vanadium, tungsten, copper and uranium: V. Yatirajam and Jaswant Ram. (26 June 1973)

Adsorption of chlorinated pesticides from river water, on XAD-2 resin: John J. Richard and James S. Fritz. (26 June 1973)

Bromine cyanide as titrimetric oxidant in non-aqueous media: Ram Chand Paul, Raj Kumar Chauhan and Ram Parkash. (26 June 1973)

The fluorimetric determination of triphenyltin compounds: F. Vernon. (26 June 1973)

Talanta. Vol. 20. p. i. Pergamon Press. 1973. Printed in Great Britain

PAPERS RECEIVED

Trien and tetren as titrants in potentiometry with a silver indicator-electrode: Adam Hulanicki, Marke Trojanowicz and Joanna Domanska. (19 *February* 1973)

Formation constants of cobalt(II) and nickel(II) complexes with Semi-Methylthymol Blue: Takashi Yoshino, Sadaaki Murakami and Megumi Kagawa. (20 *February* 1973)

Formation constants of cobalt(II), copper(II) and zinc(II) complexes with Methylthymol Blue: Takashi Yoshino, Sadaaki Murakami and Megumi Kagawa. (20 *February* 1973)

Determination of Hg(II) in acidic media by stripping voltammetry with collection: Robert E. Allen and Dennis C. Johnson. (21 *February* 1973)

Spectrophotometric study of the reaction between uranium(VI) and salicylanilide: B. S. Pannu, B. S. Sekhon and S. L. Chopra. (21 *February* 1973)

Polarographic procedures without removal of oxygen, and other approaches to decreasing the time-scale of the experiment: A. M. Bond. (22 *February* 1973)

Synergistic solvent extraction of bivalent cations with decafluoroheptanedione and di-n-butylsulphoxide: Charles A. Burgett. (26 *February* 1973)

Precise determination of oxygen and silicon in rocks by 14-MeV neutron-activation analysis: K. Huysmans, R. Gijbels and J. Hoste. (26 *February* 1973)

Forced-flow liquid chromatography using a coulometric detector: Dennis C. Johnson and John Larochelle. (27 *February* 1973)

NMR determination of the microscopic constants of diprotonated diamines in aqueous solution: H. S. Creyf, L. C. van Poucke and Z. Eeckhaut. (27 *February* 1973)

Analytical application of organic reagents in hydrophobic gel media—1. General principle and the use of dithizone gel: Yukio Sekizuka, Takehiro Kojimo, Tairoku Yano and Keithei Ueno. (28 *February* 1973)

Rapid EDTA determination of lead–tin alloys: Melvin J. Tschetter and Robert Z. Bachman. (16 *February* 1973)

Metal complexes of 2-hydroxyacetophenone: G. D. Tiwari and V. S. Bajpai. (2 *March* 1973)

New method for colorimetric estimation of guanine: Raina Vijay. (5 *March* 1973)

Quantitative phosphorescence study of interactions of cytoside and cytidine and its nucleotides in frozen aqueous solution. Evidence for anomalous heavy-atom effect: J. J. Aaron, W. J. Spann and J. D. Winefordner. (5 *March* 1973)

The oxidation of organic substances by compounds of tervalent manganese—I. The oxidation of mandelic acid, ethylene glycol, glycerol and D-mannitol by the pyrophosphate complex of tervalent manganese and by manganese(III) sulphate: J. Barek, A. Berka and I. Procházková. (6 *March* 1973)

A twinned mercury-filled glass electrode system for acid-base titrations in a number of non-aqueous solvents: M. Bréant and J. Georges. (6 *March* 1973)

Studies of the quantitative oxidation of carbonyl compounds with alkaline permanganate—III. Oxidation and determination of chloral hydrate: I. M. Issa, M. N. H. Moussa, R. M. Issa and M. A. A. Ghandour. (8 *March* 1973)

Potentiometric determination of autoprotolysis constants of solvents: G. Velinov, P. Zikolov, P. Tchakarova and O. Budevsky. (9 *March* 1973)

Solvent extraction–spectrophotometric determination of rare earths with chlorophosphonazo III: Tomitsugu Taketatsu, Masami Kaneko and Noriko Kono. (12 *March* 1973)

The interpretation of mass spectra: J. D. Lee. (12 *March* 1973)

Investigations of polymerization of sodium molybdate by thermometric titration: Nobutoshi Kiba and Tsugio Takeuchi. (13 *March* 1973)

Talanta, Vol. 20, pp. i Pergamon Press, 1973. Printed in Great Britain

PAPERS RECEIVED

Determination of copper in ammonium fluoride solutions by extraction and atomic-absorption spectrophotometry: M. BRISKA and W. HOFFMEISTER. (19 *January* 1973)

Analytical chemistry of sulphur acids: LASZLO SZEKERES (23 *January* 1973)

Fluorimetric determination of submicrogram amounts of cyanide with phenylfluorone: L S. BARK and S. MEHDI HUSSAIN. (24 *January* 1973)

Indirect spectrophotometric determination of thiocyanate by extraction as dithiocyanatodiquinolinemercury(II) complex and ligand substitution with dithizone: H. EINAGA, H ISHII and I. IWASAKI. (29 *January* 1973)

Determination of boron in silicon for semiconductors: M. TADDIA and M. T LIPPOLIS. (2 *February* 1973)

Determination of hydrogen peroxide by thallium(III) in the presence of iron(II): P. D. SHARMA and Y. K. GUPTA. (6 *February* 1973)

Thin-layer chromatography in industrial organic analysis: R. AMOS. (7 *February* 1973)

Determination of calcium oxide in calcined phosphate ores: R. S. YOUNG. (15 *February* 1973)

Determination of lithium stearate in sebacate-base lubricants by atomic absorption: GEORGE NORWITZ and HERMAN GORDON (16 *February* 1973)

LOUIS GORDON MEMORIAL AWARD

The Editorial Board and Publishers of *Talanta* have great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper appearing in *Talanta* during 1972 has been made to Ludmila Huderová and Karel Štulík, of the Department of Analytical Chemistry, Charles University, Prague, for their paper "A contribution to increasing the sensitivity of anodic-stripping voltammetry," which appeared in the November issue of Volume 19, p. 1285.

Talanta, Vol. 20, pp. i. Pergamon Press, 1973. Printed in Great Britain

PAPERS RECEIVED

How to write a paper on atomic-absorption spectrometry: J. Ramírez-Muñoz. (18 *December* 1972)

Dosage microanalytique du deuterium dans les composés organiques: Daniel Fraisse, Denise Girard and Roger Levy. (5 *December* 1972)

Results of an interlaboratory programme for the determination of tin in a standard reference ore: A caveat: G. H. Faye, W. S. Bowman and Sutarno. (18 *December* 1972)

Acid equilibria of semi-Methylthymol Blue and formation constants of zinc(II) and copper(II) complexes with semi-Methylthymol Blue: Takashi Yoshino, Sadaaki Murakami, Megumi Kagawa, Hidenori Sogabe and Shigeki Suetomi. (20 *December* 1972)

The formation constants of zinc(II) complexes with semi-Xylenol Orange: Takashi Yoshino, Sadaaki Murakami, Megumi Kogawa and Takashi Araragi. (20 *December* 1972)

On the anion-exchange separation of small quantities of gold from base metals. Determination of gold in anodic copper: L. L. Kocheva and R. Gecheva. (29 *December* 1972)

Precipitation of magnesium ammonium phosphate from homogeneous solution by means of hydrolysis of *p*-nitrophenylphosphate with an alkaline phosphatase: Seiichiro Hikime, Hitoshi Yoshida, Mitsuo Taga and Shigeru Taguchi. (8 *January* 1973)

Quantitative determination of some organic azides: L. S. Bark and A. F. M. Fahmy. (8 *January* 1973)

Solvent extraction equilibria in vanadium(V)-2-thenoyl-trifluoroacetone system: C. R. Sahu. (8 *January* 1973)

Non-aqueous cerimetric determination of thioureas: Balbir Chand Verma and Swatantar Kumar. (8 *January* 1973)

Acid equilibria of Methylthymol Blue and formation constants of nickel complexes with Methylthymol Blue: Takashi Yoshino, Harumi Imada, Sadaaki Murakami and Megumi Kagawa. (8 *January* 1973)

Spectrophotometric and chelatometric determination of iron(III) with 5-chloro-2,3-pyridinediol: Veena Kushwaha and Mohan Katyal. (9 *January* 1973)

***N*-Benzoylphenylhydroxylamine as an analytical reagent: A review:** R. A. Nadkarni. (9 *January* 1973)

Analytical application of *p*-methoxyphenylpyruvic acid oxime. A quick and simple method for the separation and determination of copper and zinc in brass: A. Ahmad, Q. Haider, V. N. Mehrotra and E. B. Singh. (10 *January* 1973)

Chelating properties of α-oximinocarboxamides-II. Syn-α-oximinophenylacetamide: copper(II) complexes: Hamed M. Fatatry, Alfred W. von Smolinski, Cecilio E. Gracias and Dominick A. Coviello. (16 *January* 1973)

The graphical analysis of the formation function-I. The real cross-over point: L. C. van Poucke and H. F. de Brabander. (16 *January* 1973)

Determination of trace amounts of copper: L. S. Bark and P. R. Wood. (17 *January* 1973)

Effects of auxiliary complex-forming agents on the rate of indicator colour change: Genkichi Nakagawa and Hiroko Wada. (18 *January* 1973)

Native fluorescence of analgesics derived from *N*-phenylanthranilic acid: Anil C. Mehta and Stephen G. Schulman. (18 *January* 1973)

LOUIS GORDON MEMORIAL AWARD

Professor A. Corsini presenting the Louis Gordon Memorial Award for 1971 to **Mrs. Elsie M. Donaldson**, joint winner with Dr. Humphries and Dr. Briscoe.

Talanta Vol 20 p 1 Pergamon Press 1973 Printed in Great Britain

ERRATA

In the paper by A Barańskei and Z Galus, *Talanta*, 1972, **19**, 761, the following changes should be made

1 On p 762, equation (15) should be

$$[\mathrm{HgX}_n^{2-n}] = \beta_n[\mathrm{Hg}^{2+}][\mathrm{X}^-]^n$$

instead of

$$[\mathrm{HgX}_n^{2-n}] = \beta n[\mathrm{Hg}^{2+}][\mathrm{X}^-]^n$$

2 On p 765, equation (27) should be

$$f(\theta_{\mathrm{max}}) = \frac{C_{\mathrm{X}0}}{2\beta_2 K K_{\mathrm{S}0}}\left[\sqrt{\frac{L_2(E)}{C_{\mathrm{X}0}} + 1} - \sqrt{\frac{L_2(E)}{C_{\mathrm{X}0}}}\right]^2$$

instead of

$$f(\theta_{\mathrm{max}}) = \frac{C_{\mathrm{X}0}}{2\beta_2 K K_{\mathrm{S}0}}\left[\sqrt{\frac{L_2(E)}{C_{\mathrm{X}0}}} + 1 - \sqrt{\frac{L_2(E)}{C_{\mathrm{X}0}}}\right]^2$$

3 The captions to Fig 1 and Fig 2(*b*) should be interchanged

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In the article "Moglichkeiten und Grenzen bei der Verwendung von Filterpapier als Träger beider Rontgenspektrometrischen Analyse" by G. Ackermann, R.-K Koch, H. Ehrhardt and G Sanner, *Talanta*, 1971, **18**, 293, the paragraph on p. 294, starting "Durch Vergleich mit den Meßwerten . " should be replaced by the following text

Durch Vergleich mit dem Meßwert für die reinen Lösungen kann dann auf den Einfluß der Matrix-Elemente geschlossen werden Dabei ergab sich, daß der Anstieg der Eichgeraden auch in den untersuchten Elementgemischen von den noch vorhandenen Komponenten beeinflußt wird. Um Schwankungen durch die Meßanordnung zu beseitigen, sind die Messungen mit äußerem Standard vergenommen worden.

Talanta, Vol. 20, pp. i. Pergamon Press, 1973. Printed in Great Britain

PAPERS RECEIVED

An electroanalytical study of the catalytic enhancement by antimony(III) of the anodic wave for bromide in acidic media: LARRY R. TAYLOR, RONALD J. DAVENPORT and DENNIS C. JOHNSON. (16 *September* 1972)

Anion-exchange behaviour of various metals on DEAE-cellulose in mixed acetic acid–nitric acid media: ROKURO KURODA, TAKAAKI KONDO and KOICHI OGUMA. (4 *October* 1972)

Computer program for calculation of electric dipole moments from measurements in solution: C. W. N. CUMPER. (25 *October* 1972)

Indirect flame-photometric determination of silicon: IVAN GABROVSKY, IONCA TCHEHLAROVA and ANTOANETA DELYISKA. (27 *October* 1972)

Analysis of precision of activation-analysis methods: K. HEYDORN and KIRSTA NØRGÅRD. (31 *October* 1972)

Spectrophotometric determination of the stability constants of $HgCl_3^-$ and $HgCl_4^{2-}$ in aqueous ethanol: R. ANANTARAMAN, A. BALASUBRAMANIAN and K. SARAMMA. (1 *November* 1972)

Use of vitreous carbon as a working electrode in a coulometric acid titration: V. J. JENNINGS, A. DODSON and G. TEDDS. (6 *November* 1972)

Talanta, Vol. 20, pp. i–ii. Pergamon Press. 1973. Printed in Great Britain

PAPERS RECEIVED

Automated wet chemical analysers and their applications: J. T. van Gemert. (7 *May* 1973)

Properties and analytical application of chlorpromazine picrate: Mikołaj Tarasiewicz and Halina Basińska. (7 *May* 1973)

Quantitative measurement of mixtures of hallucinogens by fluorometry and phosphorimetry: D. M. Fabrick and J. D. Winefordner. (8 *May* 1973)

Selective separation of uranium from other elements by cation-exchange chromatography in HBr– and HCl–acetone mixtures: F. W. E. Strelow and C. H. S. W. Weinert. (8 *May* 1973)

Anwendung von Ionenaustauschverfahren zur Bestimmung von Spurenelementen in natürlichen Wässern—II. Cadmium: J. Korkisch and D. Dimitriadis. (9 *May* 1973)

Oxidation with permanganate in acid medium containing fluoride ions—II. Potentiometric and visual determination of bisulphite: I. M. Issa, K. A. Idriss, M. M. Ghoneim and A. El-Farra. (9 *May* 1973)

The error in absorption measurements, caused by the use of non-monochromatic light—II. Gaussian functions and experiments: J. Agterdenbos, J. Vlogtman and L. van Broekhoven. (9 *May* 1973)

Controlled-potential back-titration with electrogenerated iodine as an intermediate. Application to the determination of thiols: Lars-Gunnar Torstensson. (9 *May* 1973)

The error in absorption measurements, caused by the use of non-monochromatic light—III. Application to linear calibration curves: J. Agterdenbos and J. Vlogtman. (9 *May* 1973)

Detection and spectrophotometric determination of cobalt with dimedone dioxime: R. Belcher, S. Ghonaim and A. Townshend. (14 *May* 1973)

Anwendung von Ionenaustauschverfahren zur Bestimmung von Spurenelementen in natürlichen Wässern—III. Thorium: J. Korkisch and D. Dimitriadis. (14 *May* 1973)

Distinguishing polyfunctional from monofunctional acids and bases by acid–base titrimetry, multiparametric curve-fitting, and deviation-pattern recognition: Louis Meites and Dana M. Barry. (15 *May* 1973)

Evaluation of 1-(2-thiazolylazo)-2-hydroxy-3-naphthoic acid as a metallochromic indicator: Hiroko Wada, Osamu Nakazawa find Genkichi Nakagawa. (15 *May* 1973)

Stability of ascorbic acid solutions: M. Ashraf and H. D. C. Rapson. (16 *May* 1973)

Spectrophotometric determination of mixtures of vitamins B_1 and B_6: M. Ashraf and H. D. C. Rapson. (16 *May* 1973)

Two-phase titration of organic ammonium ions with lauryl sulphate: Sven Olof Jansson, Rolf Modin and Göran Schill. (16 *May* 1973)

Separation and study of some aromatic amines, nitriles and hydrocarbons by GLC—I: Sabri M. Farroha and Samir S. Emeish. (21 *May* 1973)

Separation and study of some aromatic amines, nitriles and hydrocarbons by GLC—II. Viscosity of the solute and its specific retention volume: Sabri M. Farroha and Samir S. Emeish. (21 *May* 1973)

Separation and study of some aromatic amines, nitriles and hydrocarbons by GLC—III. Classification of stationary liquid phases: Sabri M. Farroha and Samir S. Emeish. (21 *May* 1973)

Verfahren und Methoden zur Analytik dünner Schichten—I. Bestimmung von Sulfid: Eberhard Than and Hartmut König. (21 *May* 1973)

Contribution to the basic problems of complexometry—XXV. Determination of uranium after its selective extraction as phenylacetate: Jiří Adam and Rudolf Přibil. (22 *May* 1973)

Estimation of cysteine separately and in the presence of other amino-acids by different titrimetric methods: Krishna Bahadur and Padam Sen. (22 *May* 1973)

Some aspects of the spectrophotometric determination of vanadium with aromatic hydroxylamine derivatives: B. C. Bhattacharyya and S. K. Bhowal. (22 *May* 1973)

Rapid extraction and spectrophotometric determination of vanadium(IV) with thiothenoyltrifluoroacetone: K. R. Solanke and S. M. Khopkar. (23 *May* 1973)

Correction factor for glass electrode in mixed aqueous media: Y. K. Agrawal. (23 *May* 1973)

Reaction rates between water and the Karl Fischer reagent: A. CEDERGREN. (30 *May* 1973)

Stability constants of some bivalent metal ions with *N*-phenyl-*o*-tolylbenzohydroxamic acid: Y. K. AGRAWAL and J. P. SHUKLA. (30 *May* 1973)

Non-isothermal thermal analysis: A critical examination of some recent theories: G. GYULAI and E. J. GREENHOW. (31 *May* 1973)

The chloro and nitro derivatives of 2,3-quinoxalinedithiol: A. M. DENNY and A. K. SLAWINSKI. (4 *June* 1973)

The reaction of cobalt with 2-nitroso-5-diethylaminophenol and the solvent extraction of its cobalt complex: SHOJI MOTOMIZU. (5 *June* 1973)

Ion-exchange removal of interfering excess of peroxide in the determination of chromium after oxidation with sodium peroxide: ADOLF M. MULOKOZI. (6 *June* 1973)

The oxygen shielded air–acetylene flame in emission analysis: K. E. CURTIS, R. G. STEVENSON JR., and R. STEPHENS. (7 *June* 1973)

Complex formation with and hydrolysis of *N,N'*-ethylene-bis-[2-(*o*-hydroxyphenyl)]glycine: KNUT HENNING SCHRØDER and MAHER YOUSEF EL-SHEIK. (7 *June* 1973)

Potentiometric estimation of metal ions, with membranes as indicator electrodes: M. ADHIKARI, D. GANGOPADHYAY and G. SEN. (8 *June* 1973)

The effect of HNO_3, HCl and HBr on the fluorescence of the aluminium complex of 1-(2-pyridylazo)-2-naphthol, and an improved fluorometric procedure for determination of aluminium: P. R. HADDAD, P. W. ALEXANDER and L. E. SMYTHE. (11 *June* 1973)

Talanta. Vol. 20, pp. i–ii. Pergamon Press. 1973. Printed in Great Britain

PAPERS RECEIVED

The determination of chromium in steel by atomic-absorption spectrometry with an air–acetylene flame: J. M. Ottaway and N. K. Pradhan. (15 *March* 1973)

Analytical properties of 3-hydroxypicolinaldehyde azine: A. Garcia de Torres, M. Valcarcel and F. Pino. (20 *March* 1973)

A note on the determination of thorium in the presence of some bivalent metals: R. Přibil and V. Veselý. (20 *March* 1973)

Thiotropolone as a chromogenic reagent for the simultaneous determination of cobalt(II) and nickel(II): J. N. Srivastava and R. P. Singh. (20 *March* 1973)

Spectrophotometric estimation of molybdenum(VI) with potassium ethyl xanthate and ammonium thiocyanate: M. K. Arunachalam and M. K. Kumaran. (20 *March* 1973)

Addition compounds of lanthanum and cerium trichlorides with phosphorus oxychloride: M. K. Arunachalam. (20 *March* 1973)

Polarographic study and determination of nitramide: A. Călușaru. (22 *March* 1973)

Application of the Davidon–Fletcher–Powell method to the calculation of stability constants: P. Gans and A. Vacca. (23 *March* 1973)

Miniquad—A general computer programme for the computation of formation constants from potentiometric data: A. Sabatini, A. Vacca and P. Gans. (23 *March* 1973)

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o-(2-Hydroxy-5-dodecylphenylazo)benzosäure und -arsonsäure als Chelatnildner flüssiger Ionenaustauscher: E. Blasius and H.-J. Finkenauer. (26 *October* 1972)

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Effects of quaternary ammonium base on a valence-saturated but co-ordination-unsaturated chelate—I. Extraction of GHA and SAPH chelates: MASAKICHI NISHIMURA, SHINICHIRO NORIKI and SEIJI MURAMOTO. (14 *December* 1972)

Analysis of the species in the cobalt(II) chloride-2-nitroso-1-naphthol system in benzene–ethanol mixtures: VINCENZO CARUNCHIO, ROBERTO BEDETTI and GIUSEPPE DE CECCO. (14 *December* 1972)

SUMMARIES FOR CARD INDEXES

Determination of chromium in steel by atomic-absorption spectrometry with an air–acetylene flame: J. M. Ottaway and N. K. Pradhan, *Talanta*, 1973, **20**, 927. (Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow, G1 1XL, U.K.)

Summary—A new atomic-absorption procedure is described for the determination of chromium, at levels up to 1%, in steel. The method involves the use of the air–acetylene flame and incorporates 8-hydroxyquinoline as a releasing agent to suppress metallic interferences. Chemical operations have been reduced to a minimum in order to provide a simple, rapid and accurate procedure.

Photometric complex-formation titrations of submicromole amounts of metals—III. Back-titrations: J. Kragten, *Talanta*, 1973, **20**, 937. (Natuurkundig Laboratorium, University of Amsterdam, Valckenierstraat 65, Amsterdam, The Netherlands).

Summary—In this paper the theoretical considerations on photometric complex-formation titrations of submicromole amounts of metals in the presence of an approximately equivalent amount of indicator are completed by considering the back-titration of a metal in the presence of another metal which is displaced by the titrant. The simultaneous formation of different metal–indicator complexes M_pI_q is taken into account. Titration conditions have been derived, with which optimal experimental conditions can be selected. Optimum conditions for the analysis of an indium–ytterbium alloy are deduced from the theory.

Electroanalytical study of the catalytic enhancement by antimony(III) of the anodic wave for bromide in acidic media: Larry R. Taylor, Ronald J. Davenport, and Dennis C. Johnson, *Talanta*, 1973, **20**, 947. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—The results are given of a study using a rotating disk electrode to develop an amperometric method for the determination of Sb(III) in acidic media, based on the catalytic increase of the limiting anodic current for Br^-. Analytical application was successful provided the bulk concentration of antimony(III) was less than that of bromide. The enhancement technique was also applied to the determination of Sb(III) injected into a stream of electrolyte passing through a platinum coulometric detector.

Forced-flow liquid chromatography, with a coulometric detector: Dennis C. Johnson and John Larochelle: *Talanta*, 1973, **20**, 959. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—A tubular platinum electrode packed with small chips of platinum is described which was shown to function with 100% electrolytic efficiency. Application of the electrode is described for the coulometric determination of electroactive species in the effluent from a liquid chromatograph. Cu and Fe were determined in a series of standards. An average relative deviation of less than 2 ppt was obtained for analysis of samples containing 5 μg of Cu(II) and 5 μg of Fe(III).

Определение хрома в стали методом атомно-абсорбционной спектрометрии с использованием пламени воздух-ацетилен: J. M. Ottaway and N. K. Pradhan, *Talanta* 1973, **20**, 927.

Безюме — Описана новая методика атомно-абсорбционной спектрофотометрии для определении хрома в стали вплоть 1%. Метод использует пламя воздух-ацетилен и включает 8-оксихинолин в качестве выпускающего агента для подавления влияния металлов. Химические операции приведены к минимуму с целью обеспечивания несложного, быстрого и аккуратного метода.

Фотометрические титрации субмикромолевых количеств металлов(III) на основе комплексообразования: III. Обратные титрования: J. Kragten, *Talanta*, 1973, **20**, 937.

Резюме — В настоящей статье обсуждено обратное тнтрование одного металла в присутствии другого металла замещенного титрованным раствором, в заключении теоретических обсуждений фотометрических титраций субмикромолевых количеств металлов на основе комплексообразования, в присутствии приблизительно эквивалентного количества индикатора. Принято во внимание одновременное образование различных комплексов металл-индикатор M_pI_q. Определены условия титрования при помощи которых можно отбрать оптимальные экспериментальные условия. Оптимальные условия для анализа сплава индия-иттербия выведены из теоретических рассмотрений.

Изучение электроаналитическим методом каталитического усиления анодной волны бромида сурьмой(III) в кислых средах: Larry R. Taylor, Ronald J. Davenport and Dennis C. Johnson, *Talanta* 1973, **20**, 947.

Резюме — Приведены результаты изучения амперометрического метода для определения Sb(III) в кислых средах с использованием вращающегося дискового электрода, основывающегося на каталитическом усилении предельного анодного тока для Br^-. Метод можно применять в анализе если объемная концентрация сурьмы(III) меньше чем концентрация бромида. Метод усиления также применен в определении Sb(III) впрыснутого в струю электролита, проходящего через платиновый кулонометрический детектор.

Жидкофазная хроматография с принудительным протоком пользующаяся кулонометрическим детектором: Dennis C. Johnson and John Larochelle, *Talanta*, 1973, **20**, 959.

Резюме — Описан трубчатый, заполненный кусочками платины платнновый электрод, электролитическая эффективность которого была 100%. Описаны применения электрода в кулонометрическом определении электроактивных соединений в элюате жидкофазного хроматографа. Определены Cu и Fe в ряде эталонов. Получена средная относительная ошибка не больше чем 2 частей на тысячу в анализе проб содержащих 5 мкг Cu(II) и 5 мкг Fe(III).

NMR determination of the microscopic constants of diprotonated diamines in aqueous solution: H. S. CREYF, L. C. VAN POUCKE and Z. EECKHAUT, *Talanta*, 1973, **20**, 973. (Department of General and Inorganic Chemistry, University of Ghent, Ghent, Belgium).

Summary—The microscopic acidity constants of the diprotonated asymmetric *N*-methyl-substituted ethylenediamines and *N*-methylpiperazine were determined by using the change of the chemical shift of the methyl protons with varying acidity. The determination was carried out at 25° in aqueous solution and in an ionic medium of $1M$ KNO_3. The basicity of the amino-functions follows the expected sequence: secondary > primary ≫ tertiary. The influence of the substituent on the basicity of the end-group is primary > secondary ≫ tertiary.

Analytical application of organic reagents in hydrophobic gel media—I. General principle and the use of dithizone gel: YUKIO SEKIZUKA, TAKEHIRO KOJIMA, TAIROKU YANO and KEIHEI UENO, *Talanta*, 1973, **20**, 979. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan).

Summary—Two types of hydrophobic gel particles containing dithizone were prepared, either by the swelling of low cross-linkage polystyrene beads with a dithizone solution in chlorobenzene, or by the gelatinization of a dithizone solution with dibenzalsorbitol. The extraction capacity of the gel particles for metal ions such as mercury, cadmium, zinc and lead from dilute aqueous solution, was investigated at various dithizone concentrations and pH values. A column packed with such gel particles is found to be useful for the selective preconcentration or the selective trapping of specific metal ions at low concentration levels.

Fluorimetric method for the determination of long-chain amines in water: G. E. BATLEY, T. M. FLORENCE and J. R. KENNEDY, *Talanta*, 1973, **20**, 987. (Australian Atomic Energy Commission, Research Establishment, Lucas Heights, N.S.W., Australia.)

Summary—A method is presented for the determination of long-chain quaternary ammonium salts, tertiary amines and secondary amines in water or aqueous raffinates, based on their extraction and fluorimetric determination as amine salts with Eosine Yellowish in toluene–hexanol (4 : 1) as solvent. No interferences were obtained from metal ions, or chloride, nitrate or phosphate ions when a back-washing method was applied to the sample extract. The method allows the determination of long-chain tertiary amines down to 4 ppM.

Calculation of stability constants from photometric data: FOLKE INGMAN, *Talanta*, 1973, **20**, 993. (Department of Inorganic and Analytical Chemistry, Åbo Akademi, Åbo, Finland).

Summary—A method originally designed for the determination of stability constants by using a wedge colorimeter has been adapted to normal photometric measuring techniques. The calculations are simple and the method is especially suitable for use when the absorptivities of the absorbing species are unavailable because these species cannot be obtained alone in solution. Results of some determinations are given.

Определение микроскопических констант дипротонированных диаминов в водном растворе методом ЯМР: H. S. Creyf, L. C. van Poucke and Z. Eeckhaut, *Talanta*, 1973, **20**, 973.

Резюме — Микроскопические константы кислотности дипротонированных асимметрических *N*-метилзамещенных этилендиаминов и *N*-метилпиперазина определены на основе перемены химического сдвига протонов метила с изменением кислотности. Определение проведено при 25° в водном растворе и в ионной среде 1 *M* KNO_3. Основность аминофункций снижается в ожиданном порядке: вторичный > первичный ≫ третичный. Влияние заместителя на основность конечной группы — первичный > вторичный ≫ третичный.

Применение в анализе органических реагентов в гидрофобных гелях: — I. Общие принципы и применение дитизон-геля: Yukio Sekizuka, Takehiro Kojma, Tairoku Yano and Keihei Ueno, *Talanta*, 1973, **20**, 979.

Резюме — Приготовлены два типа частиц гидрофобного геля содержащего дитизон: набуханием шариков полистирола с небольшим числом поперечных связей, или желатинизацией раствора дитизона дибензалсорбитодом. Способность частиц геля экстрагировать ионы металлов, как на пример ртуть, кадмий, цинк и свинец из разбавленных водных растворов изучена с использованием различных концентраций дитизона и при различных pH. Колонка заполненная такими частицами геля оказалась полезной для селективного предварительного концентрирования или селективного задерживания известных ионов металлов при низких концентрациях.

Флуорометрический метод определения аминов с длинной цепью в воде: G. E. Batley, T. M. Florence and J. R. Kennedy, *Talanta*, 1973, **20**, 987.

Резюме — Предложен метод определения солей четвертичного аммония, третичных аминов и вторичных аминов с длинной цепью в воде или водных раффинатах, основывающийся на их извлечении и флуорометрическом определении в форме аминовых солей с использованием эозинового желтоватого в растворе толуола-гексанола (4 : 1). Ионы металлов, хлорид-, нитрат- или фосфатионы не влияли на определение если метод обратной промывки применен на экстракт пробы. Метод позволяет определять третичные амины с длинной цепью при концентрациях вплоть до 4 ч. на миллион.

Расчет констант устойчивости на основе фотометрических данных: Folke Ingman, *Talanta*, 1973, **20**, 993.

Резюме — Метод, первоначально назначенный для определения констант устойчивости с применением клинового колориметра, использован в связи с нормальной методикой фотометрических измерений. Расчет несложен, а метод оказался полезным особенно в случаях когда не имеются экстинкции поглощающих веществ, потому что они не могут приготовиться в растворах содержащих только это вещество. Приведены результаты некоторых определений.

Photometric determination of aluminium with Alizarin Fluorine Blue: Folke Ingman, *Talanta*, 1973, **20**, 999. (Department of Inorganic and Analytical Chemistry, Åbo Akademi, Åbo, Finland).

Summary—In order to decide whether Alizarin Fluorine Blue (alizarin complexan, 3-aminomethylalizarin-*N*,*N*-diacetic acid) is a suitable reagent for the spectrophotometric determination of aluminium, values of the stability constants for some reactions of this reagent with aluminium(III) and iron(III) have been determined spectrophotometrically in a medium containing 20% dioxan and 80% water at ionic strength 0·1. The values of the constants that were determined are $\log K^{\mathrm{Al}}_{\mathrm{AlHL}} = 14{\cdot}3$, $\log K^{2\mathrm{Al}}_{\mathrm{Al_2L}} = 25{\cdot}3$ and $\log K^{\mathrm{Fe}}_{\mathrm{FeHL}} = 19{\cdot}6$. These results were employed in the design of a method for the spectrophotometric determination of aluminium in the presence of iron and titanium. The Sandell sensitivity is 0·01 μg/cm^2 and the coefficient of variation for 34 determinations was 0·9%.

Calculation of equilibrium concentrations: G. A. Cumme, *Talanta*, 1973, **20**, 1009. (Institut für Physiologische Chemie, Friedrich-Schiller-Universität, Jena, G.D.R.)

Summary—Metal complexes often act as substrates in enzymic reactions. Because their concentrations cannot be measured directly, they must be calculated from the formation constants and the total concentrations of the different metal and ligand species. An iteration algorithm devised by Sayce has been used to formulate a FORTRAN (ICT 1900) programme, which meets the following requirements. (1) The programme may be made to calculate the total concentrations for the parent species, if the *free* concentration of any metal or ligand species is known or to calculate the free concentrations of all species for which the total concentrations are known. This feature of the programme is useful for calculation of the total amounts which must be put into a solution in order to achieve prescribed free concentrations. (2) To allow for the uncertainty in the formation constants of the complex species the programme permits the input values of the formation constants to be varied automatically and the resulting variation of the calculated concentrations to be evaluated.

Indirect spectrophotometric determination of thiocyanate by extraction as bisthiocyanatbiosquinolinemercury(II) complex and its ligand substitution reaction with dithizone: Hisahiko Einaga and Hajime Ishii, *Talanta*, 1973, **20**, 1017. (National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki-ken, Japan).

Summary—Thiocyanate forms with mercury(II) in the presence of quinoline a mixed-ligand mercury(II) complex, bisthiocyanatobisquinolinemercury(II), and is extracted into chloroform. This mixed-ligand complex is treated with dithizone and forms the bisdithizonatomercury(II) complex. Maximum and constant absorbance of the dithizone complex is obtained when thiocyanate is extracted at pH 5·1–6·5, and Beer's law is obeyed at 498 nm, where the difference in absorbance between the dithizone complex and dithizone is largest. Chloride, bromide, iodide, cyanide and large amounts of ammonium and copper(II) ions interfere.

Фотометрическое определение алюминия с использованием ализаринфтористого синего: Folke Ingman, *Talanta*, 1973, **20**, 999.

Резюме — Для оценки ализаринфтористого синего (ализарин-комплексан, 3-аминометилализарин-*N*,*N*-диуксусная кислота) в качестве реагента для спектрофотометрического определения алюминия, определены спектрофотометрическим путем константы устойчивости некоторых реакций этого реагента с алюминием(III) и железом(III) в растворе содержащем 20% диоксана и 80% воды, при ионной силе 0,1. Определенные константы равны $\lg K^{\mathrm{Al}}_{\mathrm{AlHL}} = 14{,}3$, $\lg K^{2\mathrm{Al}}_{\mathrm{Al_2L}} = 25{,}3$ и $\lg K^{\mathrm{Fe}}_{\mathrm{FeHL}} = 19{,}6$. Эти результаты представляют собой основу метода для спектрофотометрического определения алюминия в присутствии железа и титана. Чувствительность Санделла равна 0,01 мкг/см², а коэффициент вариации для 34 определений — 0,9%.

Расчет равновесных концентраций: G. A. Cumme, *Talanta*, 1973, **20**, 1009.

Резюме — Комплексы металлов часто служат в качестве субстратов в энзимных реакциях. Непосредственное измерение их концентраций не возможно, поэтому их надо расчитать на основе констант образования и общих концентраций разных родов металлов и лигандов. Разработанный Сайсом итеративный алгоритм использован для установления программы FORTRAN (ICT 1900), удовлетворящей следующим требованиям. (1) Программа позволяет расчитать общие концентрации родственных веществ если знакома *свободная* концентрация любого рода металла или лиганда, или расчитать свободные концентрации всех родов, общие концентрации которых знакомы. Эта характеристика программы полезна для расчета общего количества, растворимого в растворе для получения предписанных свободных концентраций. (2) Для учета неизвестности констант образования комплексов, программа позволяет автоматические вариации входа констант образования и оценку проистекающей вариации расчитанных концентраций.

Косвенное спектрофотометрическое определение тиоцианата путем экстракции в форме комплекса бистиоцианато-бисхинолинртути(II) и его реакция замещения лиганда дитизоном: Hisahiko Einaga and Hajime Ishii, *Talanta*, 1973, **20**, 1017.

Резюме — Тиоцианат образует с ртутью(II) в присутствии хинолина комплекс ртути(II) с смешанными лигандами — бистиоцианато-бисхинолинртуть(II) — который экстрагируется хлороформом. Этот комплекс при обработке с дитизоном образует комплекс бисдитизонатортуть(II). Максимальное и постоянное светопоглощение дитизонового комплекса получается экстрагированием тиоцианата при pH 5,1–6,5 а закон Бера почитается при 498 нм, где разница между светополощением дитизонового комплекса и дитизона является самой большой. Хлорид, бромид, иодид, цианид и большие количества аммоиня и меди(II) мешают определеиию.

Interpretation of mass spectra: J. D. LEE, *Talanta*, 1973, **20**, 1029 (Department of Chemistry, Loughborough University of Technology, Loughborough, Leics., LE11 3TU, England.)

Summary—A computer programme is described which calculates the mass numbers and the relative intensities of each of the lines in the cluster formed in a mass spectrometer from a single type of fragment ion which contains one or more polyisotopic elements. Many elements such as B, C, S, Cl and Br possess more than one naturally occurring isotope, and the relative abundances of the various isotopes are known. A whole series of possible fragment ions may be calculated quite readily, and the results, which are printed numerically and in the form of a histogram, facilitate the interpretation of mass spectra. Trial data, a FORTRAN listing of the programme, and a sample of the output are given. The programme requires approximately 17K of fast core, and should be implemented without difficulty on any computer with a FORTRAN IV compiler.

Indirect complexometric determination of chromium: ARTHUR DE SOUSA, *Talanta*, 1973, **20**, 1039. (Research Laboratories, Alpha Materials Technology, P.O. Box 816, Pottstown, Pa. 19464, U.S.A.)

Summary—Chromate is determined indirectly, by precipitation as silver chromate, dissolution of the precipitate in potassium tetracyanonickelate, and titration of the liberated nickel with EDTA, with Murexide as indicator.

Indirect flame-photometric determination of silicon: IVAN GABROVSKY, IONCA TCHEHLAROVA and ANTOANETA DELYISKA, *Talanta*, 1973, **20**, 1040. (Department of Analytical Chemistry, Institute of Ferrous Metallurgy, Botunetz, Sofia, Bulgaria).

Summary—An indirect flame-photometric method for the determination of silicon in terms of the potassium in precipitated K_2SiF_6 has been developed. Optimum conditions have been found for the precipitation and the washing of the precipitate with aqueous ethanol. Satisfactory results have been obtained for silicon contents $>1\%$ in ores and alloys.

Интерпретация масс-спектров: J. D. Lee, *Talanta*, 1973, **20**, 1029.

Резюме — Описана программа ЭВМ для вычисления массовых чисел и относительных интенсивностей каждой линии в группе пиков образованных в масс-спектрометре из одного типа фрагментных ионов содержащих один или больше полиизотопных элементов. Ряд элементов, в том числе B, C, S, Cl и Br содержают больше чем один природный изотоп, а относительные концентрации разных изотопов известны. Легко провести расчет серии возможных фрагментных ионов, а результаты, приказанные в цифровой форме или в форме гистограмм, облегчают интерпретацию масс-спектров. Приведены опытные данные, FORTRAN программа и пример выхода. Программа изыскует приблизительно 17 K быстрого ядра и ее можно пользоваться на каждой электронновычислительной машине снабженной компилатором FORTRAN IV.

Косвенное комплексонометрическое определение хрома: Arthur de Sousa, *Talanta*, 1973, **20**, 1039.

Резюме — Хромат определяют косвенным методом, осаждением в форме хромата серебра, растворением осадка в тетрациано-никеляте калия и титрованием выделенного никеля с ЭДТА с использованием мурексида в качестве индикатора.

Косвенное определение кремния методом пламенной спектрофотометрии: Ivan Gabrovsky, Ionca Tchehlarova and Antoaneta Delyiska, *Talanta*, 1973, **20**, 1040.

Резюме — Разработан косвенный метод пламенной спектрофотометрии для определения кремния на основе определения калия в осажденном K_2SiF_6. Определены оптимальные условия для осаждения и промывки осадка водным раствором этилового спирта. Получены удовлетворительные результаты в рудах и сплавах содержащих $>1\%$ кремния.

Volume 20, 1973
July–December, Nos, 7–12

SUBJECT INDEX

PRINTED IN GREAT BRITAIN BY A. WHEATON & CO., EXETER

Talanta, Vol. 20, p. ii. Pergamon Press, 1973. Printed in Great Britain

PUBLICATIONS RECEIVED

Aufschlußmethoden der anorganischen und organischen Chemie: RUDOLF BOCK, Verlag Chemie, Weinheim/Bergstr. 1972. Pp. 232. DM 64.

Here in one book is an attempt to cover what has been divided between two in the English language, dealing with all types of samples, organic and inorganic, though listed according to procedure and reagent used. The index lists many sample types. This is a thorough and critical survey of the literature, is up to date, and presents much of the information in some 75 tables (of particular help to non-German-speaking readers). In addition to the three major sections on decomposition by oxidation, by reduction, or by neither, shorter chapters on materials, solvents, and thermal decomposition complete this very useful and welcome compilation.

Quantitative measurements and chemical equilibria: E. H. SWIFT and E. H. BUTLER, Freeman, San Francisco, 1972. Pp. xviii + 719. $14.50.

The emphasis in this book seems curiously unbalanced. It is intended for freshman students—but certainly in British universities there is unlikely to be time to devote to so much practical chemistry at this level. Precipitation methods are discussed in detail—but not thermodynamically—and most of the interesting material is in the footnotes. Redox reactions are treated to an extensive discussion, particularly of practical details (though the use of electron-dot chemical formulae is not to be recommended). There are numerous problems involving stoichiometry, but very few on equilibria. Complexometry is sadly neglected in spite of its practical importance and its usefulness as a basis for the study of ionic equilibria in solution. There is much material in this book—too much for an elementary book, but not treated with sufficient rigour for it to be useful at a later stage.

EDITORIAL

In this issue we present the fifth paper in our series on the ideal format for a paper describing a piece of research based on a particular technique such as spectrophotometry or titrimetry. These articles are intended to show research workers what information is regarded as essential for other workers in the field to use the work to full advantage, and include explanations of why the information is regarded as important. The articles therefore constitute a guide to research and investigational procedures, and should prove most useful to students besides reminding others of what they might otherwise forget. The series has attracted the interest of IUPAC, which has established a working party (Analytical Chemistry Division, Commission V3, Project 3.9) to consider the presentation of papers for publication. It is expected that our series will provide at least the basis for any IUPAC publications on the subject. Further articles in the series are in preparation and will appear from time to time.

Talanta, Vol. 20, pp. ii–iii. Pergamon Press, 1973. Printed in Great Britain

PUBLICATIONS RECEIVED

Ion-Selective Electrodes: edited E. PUNGOR and I. BUZÁS, Akadémiai Kiadó, Budapest, 1973. Pp. 283. £3.50.

This work contains the text of 7 plenary lectures and 10 discussion lectures which were delivered and a summary of discussions which took place at a Symposium held in Mátrafüred in October 1972. The rapid publication endows the work with a topicality to which publishers aspire but rarely attain. The plenary lectures were given by B. Fleet, A. Liberti, C. Liteanu, J. D. R. Thomas, G. Milazzo, W. Simon and K. Toth. They, and the discussion lectures, fairly reflect the state of the art. They include up-to-date work, predictions and controversial statements. It is unfortunate that there are no contributions from the U.S.A. and Denmark, but all in the field will wish to acquire a copy and general readers will also find it a convenient source book. The editing and production are particularly noteworthy and at £3.50 it must be rated a good buy.

Proceedings of the 3rd Symposium on Co-ordination Chemistry, Vol. 2: editor MIHÁLY T. BECK, Akadémiai Kiadó, Budapest, 1971. Pp. 287.

This second volume of the "Proceedings of the 3rd Symposium on Co-ordination Chemistry" contains the Plenary Lectures and the discussion of contributed papers. The lectures by J. Bjerrum and by H. Diebler are concerned with the detailed mechanism of the formation of complexes. The former deals with the relation between outer and inner sphere complexes while the latter is a general survey of the field. Ya. D. Fridman's lecture is a detailed survey of mixed-ligand complexes while A. E. Martell's is concerned with the reaction of certain ligands in metal ligand complexes. The remaining plenary lecture by D. N. Hume describes the use of computers in evaluating mixed-ligand stability complexes. These five papers are all useful surveys of their fields as plenary lectures should be and are certainly worthy of preservation in the literature. The same does not seem to apply to the remainder of the volume (some 40%). This consists of supplements to the contributed papers which appear in Vol. 1 of the Proceedings: a considerable number of corrections to contributed papers and an account of the discussion of papers. From the number of errata associated with some papers it would appear that in their uncorrected form in Vol. 1 they could be misleading. Now it is true that both volumes appeared within a short time of the actual conference but how much better it would have been to have published both together and properly proof-read at the expense of a short delay in publication.

It has become fashionable to publish detailed proceedings of conferences in recent years but as most of the material has either been published in the journals or will be published at a later date the desirability of this practice is open to question. There are undoubtedly times, when a subject is in a seminal stage, when publication of proceedings is justified, but these are few and far between.

The value of the volume certainly lies in the plenary lectures from which many chemists will gain an enhanced insight into reactions of co-ordinated metal ions.

High-precision Titrimetry: C. WOODWARD and H. N. REDMAN, Society for Analytical Chemistry, London, 1973. Pp. viii + 63. £2.50.

This little volume on high-precision titrimetry is full of hints and tips for achieving the precision that is well-known by older analysts to be attainable in titrimetry, and is so seldom achieved by analysts who have not undergone the rigorous training of an older generation. It is therefore all the more the pity that the publishers should have set the price at about twice what might have been thought a fair market price. The book is recommended to all who like to read shrewd and informed comment on the analytical scene.

Modern Inorganic Chemistry: J. J. LAGOWSKI, Dekker, New York, 1973. Pp. xii + 806. $13.75.

It will probably never be possible to produce a textbook of inorganic chemistry that will please everybody. This one does as good a job as most, but likewise has similar shortcomings to those of other texts. The Born-Haber cycle has proved a pitfall for many a student in the past, largely because it was enunciated before thermochemical sign conventions became established, and because most texts reproduce the original form without bothering to point out the consequences of ignoring sign conventions. The main stumbling block is the sign to be used for the electron affinity, and this text does not appear to help the reader as much as it might. Redox reactions get very short shrift, and the Nernst equation does not seem to have been heard of (it is not mentioned in the index at any rate). Crystal field theory is mentioned, but the reader will look in vain for ligand field theory in the index. Nevertheless, the book contains a vast amount of up to date treatment of inorganic chemistry, and at the price represents a bargain for students.

Talanta, Vol. 20, p. iii. Pergamon Press, 1973. Printed in Great Britain

NOTICE

HUNGARIAN CHEMICAL SOCIETY 3rd SYMPOSIUM ON ION EXCHANGE LAKE BALATON, 28–31 May 1974

The topics for this symposium will be ion-exchange materials, theory, applications to analysis, and technology. There will be about 6 main lectures and a limited number of papers covering original unpublished work (those wishing to submit papers should send a 250–300 word synopsis in English as soon as possible but not later than end of July). Further details can be obtained from The Hungarian Chemical Society, Organizing Committee, 3rd Synposium on Ion Exchange, H-1368 Budapest, P.O.B. 240, Hungary.

Talanta, Vol **20** pp. iii Pergamon Press, 1973 Printed in Great Britain

PUBLICATIONS RECEIVED

Symmetry—A Stereoscopic Guide for Chemists: IVAN BERNAL, WALTER C. HAMILTON and JOHN S. RICCI. Freeman, San Francisco, 1972. pp. viii–180. $9·50.

The usual applications of symmetry arguments to chemistry, involving the relevance to wavefunctions, selection rules, *etc.*, are not included in this book. However, the title in no way implies that they should be, and the prime objective of the book is to instruct the reader so that he is able to classify molecules according to their symmetry. Symmetry operations are explained and related to groups, but this is done at a very elementary level and representations of groups, characters, *etc.* are not dealt with. The Schoenflies and Hermann-Mauguin symbols are both used, and one molecule is given as an example for each point group. Each molecule is drawn as a stereoscopic pair, and with the aid of the stereoscopic viewer which accompanies the book, a realistic three-dimensional effect is obtained. It will come as a surprise to inorganic chemists that the point group O_h is not exemplified by an octahedral six-co-ordinate complex. The easiest way to learn about the symmetry of molecules is to receive personal instruction with the aid of models. If this is not possible, then this book will prove useful.

Talanta, Vol. 20. pp. iii. Pergamon Press. 1973. Printed in Great Britain

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Symmetry—A Stereoscopic Guide for Chemists: Ivan Bernal, Walter C. Hamilton and John S. Ricci. Freeman, San Francisco, 1972. pp. viii–180. $9·50.

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Talanta, Vol. 20, pp. iii–iv. Pergamon Press, 1973. Printed in Great Britain

PUBLICATIONS RECEIVED

The Determination of Sulphur-Containing Groups: M R. F. ASHWORTH. Academic Press, London, 1972. Pp. viii + 149. £3.20.

This book constitutes the first volume in the second topic in the series of monographs on the analysis of organic materials, which is concerned with the determination of sulphur-containing groups. The classes of compounds which are dealt with here include sulphones, sulphoxides, sulphonyl halides, thiocyanates, isothiocyanates and, unexpectedly, isocyanates. There are full experimental details for carrying out both qualitative and quantitative analyses and very full lists of references are given at the end of each section dealing with a particular class of sulphur compound.

Handbook of Commerical Scientific Instruments; Volume 1. Atomic Absorption: CLAUDE VEILLON. Dekker, New York, 1972. Pp. xvi + 174. $11.75.

This is a compendium of information about atomic-absorption instrumentation. There is a brief introductory chapter which outlines the technique and gives short descriptions of essential components of atomic-absorption spectrophotometers The remainder of the book is a series of sections, each dealing with an instrument or instruments marketed by specific manufacturers, and based on information supplied by the individual companies. The list is not exhaustive, including mainly those instruments which are readily available in the United States. Spectrophotometers manufactured by British Companies are not included. The purpose of the book is to provide a survey of existing equipment with relative prices and performance, to assist a potential customer to make an intelligent choice.

An Experimental Contribution to the Knowledge of Average Cross-Sections in a Fission Neutron Spectrum (in Flemish). J. P. FRANÇOIS. Paleis der Academiën, Hertogstraat 1, Brussels, 1972. Pp. 104. B.F. 330.

This work is rather specialized and deals mainly with the determination of some average cross-sections in a fission neutron spectrum. The reaction ^{55}Mn(n, 2n)^{54}Mn is shown to be of interest for monitoring the hard part of the fission spectrum, especially for long irradiations. The (n, p) and (n, 2n) reactions upon ruthenium-free monoisotopic ^{103}Rh are also useful for fast neutron dosimetry, but post-activation chemical separations of ^{103}Ru and ^{102} ^{102m}Rh are required. The gamma-ray spectra and yields of ^{102}Rh and ^{102m}Rh are described for sources prepared by the nuclear reactions ^{103}Rh(n, 2n), ^{103}Rh(γ, xn), ^{104}Pd(d, α) and Ru(d, xn). The preparation of carrier-free long-lived rhodium tracer from deuteron-irradiated ruthenium may be of interest for developing an isotope dilution method for rhodium. This element is, indeed, difficult to determine by thermal-neutron activation analysis because of the short half-lives produced. This monograph contains useful information for those faced with fast neutron dosimetry and absolute countings in general. Some parts contain analytical information, *e.g.*, for the separation Rh/Ir. It is the reviewer's hope that the Royal Academy of Belgium will encourage its authors to publish in a more universally used language.

Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—I: General Atomic Emission Spectroscopy: IUPAC. Butterworths, London, 1972. Pp. 30. $1.20 or £0.40 (post free if cash with order). Available as a reprint from: IUPAC Secretariat, Bank Court Chambers, 2-3 Pound Way, Cowley Centre, Oxford OX4 3YF, UK.

The purpose of this document is to propose a consistent nomenclature for workers in spectrochemical analysis Many of the terms have already been defined in several nomenclature documents, especially those developed by IUPAC, IUPAP, and ASTM. The fact that many of the symbols, units, nomenclature and definitions previously recommended are repeated in this document demonstrates that the nomenclature of a specific field, i.e., spectrochemical analysis, is deeply rooted in the general nomenclature of chemistry and physics However, the adaptation of a general system to a specialized field required a careful selection of general terms and the addition of new ones. The tentative version of Part I was published as *Tentative Nomenclature Appendix* No. 1 (December 1969) to the *Information Bulletin*. After careful revision the Commission on Spectrochemical and other Optical Procedures for Analysis of the Analytical Chemistry Division has now produced a definitive version for IUPAC. Included in Part I are the following: General Recommendations and Practices: Terms and Symbols for Physical Quantities in General Use; Terms, Symbols, and Units Related to Radiant Energy, Terms and Symbols for Description of Spectrographic Instruments; Terms and Symbols Related to Analytical Procedures: Terms and Symbols Related to Fundamental Processes Occurring in Light (Excitation) Sources; Photographic Intensity Measurements (Photographic Photometry). A statement by ASTM on General Principles of Nomenclature Standardization is reprinted as an Appendix. A second Appendix deals with Application of the Concept of Optical Conductance.

Die Chemische Industrie und ihre Helfer: KURT R. SELKA (Ed.) Industrieschau Verlagsgesellschaft mbH., Darmstadt, 1972 73. Pp. 612, DM 30.00.

As this year sees another ACHEMA exhibition, this guide to the German chemical industry could well prove to be more than usually useful. The section on new machines and devices will be studied beforehand, and the comprehensive buyers' guide to manufacturers and agents will certainly remain within easy reach of the chemical engineer's hand at his desk.

Handbuch der analytischen Chemie. Teil 3, Band 6bβ—Uran: J. KORKISCH and F. HECHT. Springer-Verlag, Berlin, 1972. Pp. 524. DM 168. US $53.30.

The detailed and somewhat formidable list of contents of this volume suggests that the authors have simply made a very thorough search of the literature, as one comes to expect from this series, but the seemingly endless chain of procedures is liberally interspersed with general discussions of the usefulness of the approaches, and with observations which are of considerable help to the non-specialist reader in pointing out possible sources of trouble, other related procedures, or perhaps also more useful ones. It is in these additions that the expertise of the authors becomes evident. Fluorimetry—openly admitted as a technique much preferred by the authors—gets an admirable discussion, but electrochemical methods, in particular coulometry, come off very poorly (the latter dealt with in 3 pages). In addition to chapters on methods of determination are those on chromatography, solvent extraction, spectroscopic methods (in particular mass spectrometry) and radiochemical analysis. A final chapter by H. Sorantin deals with the problem of analysis of irradiated fuel elements.

Workbook in Organic Chemistry: T. A. GEISSMAN, Freeman, San Francisco, 1972. Pp. xii + 245. $4.95.

While the primary purpose of this book is "to provide the student in the introductory course in organic chemistry with the opportunity to review and reinforce his understanding of the fundamental modes of behavior of organic compounds," it is the reviewer's opinion that its greatest value will be to the advanced student and to the industrially oriented organic chemist. The book fills a number of deficiencies of the ordinary textbook, mainly the use and interpretation of simple analytical data. Also included are sections on molecular bonding, stereochemistry, the mechanisms involved in organic synthesis, a novel treatment of organic oxidation equations, and many problems and examples of the elucidation of structure and identity from functional and elemental analytical data. The book is extremely well illustrated, printed on good paper, and contains many worked problems to illustrate procedures. This book can be recommended, without reservation, to the student and practising organic chemist. The price is much lower than one would expect for such a valuable and well done publication.

Talanta, Vol. 20, pp. iii–iv. Pergamon Press, 1973. Printed in Great Britain

PUBLICATIONS RECEIVED

Pharmaceutical Applications of Thin-Layer and Paper Chromatography: KAREL MACEK (editor), Elsevier, Amsterdam, 1972. Pp. XVI + 743. Dfl. 250 (*ca* $73.50).

Whenever one is confronted with a volume of this nature, one's first reaction is one of wonder and admiration at the industry and expertise of the authors. The name of the editor is a household word in chromatographic circles and by itself a guarantee of authenticity and thoroughness. Any analyst in the pharmaceutical industry will want to have a copy of this volume for laboratory use. One's second reaction, however, is to consider the economics and mechanics of the operation, and to ask whether something cheaper could have been contrived without loss of essential information. A quick look at the illustrations in the first part of the book (the part which discusses apparatus and techniques) shows that something like twenty photographic reproductions are of commercial equipment or laboratory apparatus and convey little or nothing to the reader that is not already in the text. In any case, the manufacturers will gladly send an illustrated brochure on receipt of a postcard. Then the manner of presenting references is the Harvard system, which inevitably wastes space on the repetition of authors' names. At the end there is a 20-page author index which repeats all the names yet again. The layout in some sections also seems rather wasteful of paper—surely the sections in the chapter on detection reagents need not have been so widely spaced, for example. The 'meat' of the book is in the sections dealing with specific classes of compound, and much of the first 150 pages or so is already available in some form or other in books likely to be at the reader's disposal. At the rule-of-thumb costing rate of £2 per 100 pages the book would cost about £15; its length could have been reduced by at least 40 pages by elimination of material on the lines suggested above, and by much more if the 'apparatus and techniques' section had been omitted or curtailed. The conclusion is that a very limited market is expected; the resultant price may limit it even more.

Analytical Chemistry of Phosphorus Compounds: M. HALMANN (editor), Wiley, New York, 1972. Pp. x + 850. $39.95.

With literature coverage up to 1970 (in some chapters) this book gives a survey of the analytical methods for phosphorus and its compounds, and for determination of phosphate species in various types of natural and synthetic samples. The division of the writing between a number of experts has led to a certain amount of repetition of material, and it might have been better to use fewer authors. In some parts the coverage is less complete than would be expected in a book of this nature, but in general the volume is to be welcomed as a useful tool in the analyst's library, and the price is reasonable in view of the length of the book.

Separation and Purification Methods, Vol. 1: EDMOND S. PERRY and CAREL J. VAN OSS (editors), Dekker, New York, 1972. $19.50 per volume (2 issues) plus $1.50 postage outside U.S.A. and Canada.

According to the preface this new journal is the successor of the same editors' earlier series *Progress in Separation and Purification* (Wiley). The price quoted is for the soft-bound version. A hard-cover version (price not specified) will also be available. A reduced combined subscription ($59.50) is offered for *Separation Science* taken along with this new journal.

Khimiya protsessov ekstraktsii: YU. A. ZOLOTOV and B. YA. SPIVAKOV (editors), Izdat. Nauka, Moscow, 1972. Pp. 288. 1 R. 91 K.

Readers of Russian will welcome this new contribution to the literature of extraction chemistry, prepared under the able editorship of two well-known Russian workers in the field. It is, in fact, a collection of research papers on the chemistry of extraction processes. It ends with a tear-out section of card-index summaries, a good idea that is slightly spoiled by the fact that both sides of the pages are used. However, a photocopying machine would soon deal with that problem.

Actualités de Chimie Analytique: J. A. GAUTIER, P. MALANGEAU and F. PELLERIN (editors), Masson, Paris, 1972. Pp. 186. 98 F.

This volume, the 21st in the series, contains a number of review-type articles, on applications to various organic or biological systems, of a.c. polarography, thin-layer chromatography, vanadium(V) as an oxidant, GLC, ion-exchange, and nmr.

Modern Analytical Methods: D. BETTERIDGE and H. E. HALLAM, Chemical Society, London, 1972. Pp. vii + 227. £2.00.

This is No. 21 in the "Monographs for Teachers" series, intended for use at GCE A level and above. Even a quick glance at the contents shows that it is 'above' that is the operative word. Those who deal with entrants to university know only too well that exposure to 'advanced' topics at school level results in a very patchy knowledge of the material, and a woeful ignorance of many of the essentials, since time spent on being 'modern' is then not available for the traditional. Taken as a text for students at say second year university level or above the book does an admirable job as far as it goes. Some, however, will regret that gravimetric analysis is ignored and will feel that the 300 words or so on sample dissolution might as well have been left out too. It may be argued that gravimetry has no place in modern analysis, but that is highly debatable. What is certain is that the decomposition techniques used correlate large areas of factual chemistry with theoretical considerations, and provide innumerable object lessons in the logic of development of an analytical procedure. The important topic of sampling is also not discussed. An extra 30 pages (and 10 shillings on the price) would have transformed a valuable book into an invaluable one.

Spot Tests in Inorganic Analysis, 6th English Edition: FRITZ FEIGL and VINZENZ ANGER (translated by RALPH E. OESPER), Elsevier, Amsterdam, 1972. Pp. XXIX + 669. Dfl. 125 (ca. $39.00).

The long-awaited new edition of "Feigl" will be a lasting memorial to the work of the senior author. The treatment is as wide-ranging and authoritative as ever, and the number of tests has been expanded by over 30%. The accumulated experience of the last 14 years has been sifted and documented, and laid out in orderly manner for general use. Dr. Anger is to be warmly congratulated in his preservation of the flavour of the original, so that the blend is as smooth as could be desired. The extensive applications of spot tests amply illustrate the power and utility of the technique, and all who need to investigate small samples will be glad to have this book as guide. Professor Oesper's translation has that easy flow that disguises the fact that the original language was not English.

SUMMARIES FOR CARD INDEXES

Oxidation with permanganate in presence of fluoride: Potentiometric determination of manganese(II): I. M. ISSA and M. M. GHONEIM, *Talanta*, 1973, **20**, 517. (Chemistry Department, Assiut University, Assiut, Egypt.)

Summary—The effects of acidity, fluoride concentration, temperature and concentration of manganese in the reaction between $KMnO_4$ and Mn(II) were studied potentiometrically. The rate of reaction is increased by increasing the fluoride concentration and/or decreasing the acidity of the solution. The formal redox potentials of the MnO_4^-/Mn(III) and the Mn(III)/Mn(II) systems were determined at different pH values. The E° values obtained by extrapolation to pH = 0 were 1·58 and 1·52 V respectively. The amount of Mn(II) determined was varied from 5 to 56 mg. The net reaction can be represented as $MnO_4^- + 10HF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O$.

Simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroazoles and criteria for their identification—I. Nitroimidazoles and nitropyrazoles—Polarographic determination: DRAGICA DUMANOVIĆ and JANKA ĆIRIĆ, *Talanta*, 1973, **20**, 525. (Research Laboratory "Galenika," Zemun, Yugoslavia.)

Summary—The *N*-unsubstituted nitroazoles have an imino hydrogen atom in contrast to the *N*-substituted derivatives, and react with hydroxide to give nitroazole anions. The strongly negative shift of $E_{1/2}$ for these anions makes possible simultaneous polarographic determination of any pair of compounds, one of which is an *N*-unsubstituted nitroazole and the other a corresponding *N*-substituted derivative. Simultaneous polarographic determination of three compounds [4(5)- 4- and 5-nitroimidazole] is also possible from alkaline medium, but only when $\Delta E_{1/2}$ between the *N*-substituted isomers is at least 100 mV. Chromatographically, and/or by some other criteria it is possible to distinguish between the *N*-unsubstituted nitroazole and the *N*-substituted derivatives. These compounds appear together in reaction mixtures arising during substitution of the hydrogen atom.

Anion-exchange behaviour of various metals on DEAE-cellulose in mixed acetic acid–nitric acid media: ROKURO KURODA, TAKAAKI KONDO and KOICHI OGUMA, *Talanta*, 1973, **20**, 533. (Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba, Japan.)

Summary—A number of nitrato complexes of metals have been found to be adsorbed on DEAE-cellulose from mixed acetic acid-nitric acid media, although none can be adsorbed from aqueous nitric acid solutions. The distribution coefficients of Sc, Mo, La, Sm, W, Re, Bi, Th and U are given as functions of acetic acid and nitric acid concentrations (sometimes in the presence of hydrogen peroxide to prevent hydrolytic precipitation). For 25 other metals column adsorption behaviour is described for a 90% acetic acid–10% 7·6*M* nitric acid mixture. Favourable differences in the distribution coefficients allow useful separation such as Fe–Mo–W and U–Sm–Mo–Bi–Th, to be achieved.

Complexation of polyvinyl acetate with iodine: J. G. PRITCHARD and F. T. SERRA, *Talanta*, 1973, **20**, 541. (North East London Polytechnic, London, E.15, U.K.).

Summary—Polyvinyl acetate and iodine form a characteristic red complex in the presence of potassium iodide. Spectrophotometry of the complex at 510 nm in a methanol water-system at 20° yields linear calibration curves over the range 25–100 mg of polyvinyl acetate per l. of final solution. The limit of detection is 0·1 mg of polyvinyl acetate in 0·5 ml of initial sample. Replacement of acetate groups by inert groups reduces the sensitivity of the method, and other details of the system are discussed.

Окисление перманганатом в присутствии фторида: Определение марганца потенциометрическим методом: I. M. Issa and M. M. Ghoneim, *Talanta* 1973, **20**, 517.

Резюме — Изучено потенциометрическим методом влияние кислотности, концентрации фторида, температуры и концентрации марганца на реакцию $KMnO_4$ с Mn(II). Скорость реакции повышается с повышением концентрации фторида и/или снижением кислотности раствора. Определены формальные окислительно-восстановительные потенциалы систем MnO_4^-/Mn(III) и Mn(III)/Mn(II) при различных величинах pH. Величины E^0, полученные экстраполяцией до $pH = 0$ составляли 1,58 и 1,52 в, соответственно. Количество определяемого Mn(II) изменяли в диапазоне 5–56 мг. Общую реакцию можно приказать формулой $MnO_4^- + IOHF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O$.

Одновременное определение *N*-незамещенных и *N*-замещенных нитразолов и критерии их идентификации — I. Нитроимидазолы и нитропиразолы — определение полярографическим методом: Dragica Dumanović and Janka Ćirić, *Talanta* 1973, **20**, 525.

Резюме — В отличии от *N*-замещенных производных, *N*-незамещенные нитроазолы имеют имино-атом водорода и реагируют с гидроокисью с образованием нитразоланионов. Сильноотрицательное перемещение $E_{1/2}$ для этих анионов позволяет одновременное полярографическое определение либой пары соединений, если одно из них *N*-незамещенный нитроазол а другое — соответствующее *N*-замещенное производное. Одновременное полярографическое определение трех соединений (4(5)-, 4-, и 5-нитроимидазола) также возможно из щелочной среды, но только если $\Delta E_{1/2}$ между *N*-замещенными изомерами превышает 100 мв. Возможно различать хроматографическим путем и/или использованием некоторых других критериев между *N*-незамещенным нитразолом и *N*-замещенными производными. Эти соединения появляются одновременно в реакционных смесях существующих при замещении атома водорода.

Анионообменные характеристики разных металлов на ДЕАЕ целлюлозе в средах содержащих уксусную и азотную кислоты: Rokuro kuroda, Takaaki Kondoand and Koichi Oguma, *Talanta* 1973, **20**, 533.

Резюме — Установлено что ряд нитратокомплексов металлов адсорбируются на ДЕАЕ целлюлозе из сред содержащих уксусную и азотную кислоты, хотя они не адсорбируются из водных растворов азотной кислоты. Приведены коэффициенты распределения Sc, Mo, La, Sm, W, Re, Bi, Th, и U в зависимости от концентраций уксусной и азотной кислотах (в некоторых случаях в присутствии перекиси водорода для предупреждения гидролитического осаждения). Описаны адсорбционные характеристики 25 других металлов с использованием смеси 90% уксусной кислоты и 10% 7,6*M* азотной кислоты. Подходящие разницы между коэффициентами распределения позволяют провести разделение Fe — Mo — W и U — Sm — Mo — Bi — Th.

Образование комплекса поливинилацетата с иодом: J. G. Pritchard and F. T. Serra, *Talanta* 1973, **20**, 541.

Резюме — Поливинилацетат образует с иодом характеристический комплекс в присутствии иодида калия. Спектрофотометрией комплекса при 510 нм в системе метанол-вода при 20° получаются линейные калибровочные кривые в диапазоне концентраций 25–100 мг/л поливинилацетата в конечном растворе. Чувствительность метода равна 0,1 мг поливинилацетата в 0,5 мл начальной пробы. Замещение ацетатгрупп инертными группами сиижает чувствительность метода; также обсуждены другие детали метода.

A proposed sampling constant for use in geochemical analysis: C. O. INGAMELLS and P. SWITZER, *Talanta*, 1973, **20**, 547. (Climax Molybdenum Company, Golden, Colorado and Departments of Statistics and Geology, Stanford University, Stanford, California, U.S.A.).

Summary—The error in a determination of an element in a rock or mineral sample depends on the analytical error, the weight of sample analysed, and the nature and history of the laboratory sample. The most probable result is not independent of the weight of sample analysed. This is due to the fact that trace constituents often reside in isolated mineral grains. The chance of such mineral grains appearing in any one analysed sample becomes more remote as the sample weight decreases, even when rock or mineral samples are reduced to fine powders. Such subsampling errors can be controlled through the use of sampling constants. These may be estimated by several procedures, including repetitive determination of a constituent and physical measurement of relevant sample characteristics. Sampling constants can be usefully employed during the establishment and certification of reference samples or standards. When subsampling is deficient, analytical results may yield erroneously low values, sometimes with high precision. High precision never implies high accuracy; it may be a symptom of gross error.

Use of non-selective reagents in direct thermometry: P. MARIK-KORDA, L. BUZÁSI and T. CSERFALVI, *Talanta*, 1973, **20**, 569. (Institute of General and Analytical Chemistry, Technical University, Gellért tér 4, Budapest XI, Hungary).

Summary—A method has been developed for the simultaneous determination of sulphide and thiosulphate with non-selective reagents on the basis of the difference in their heats of reaction. Iodine solution was used as one reagent and bromine water as the other. An error diagram has been calculated and the theoretical errors compared with those obtained in practice.

Relative sensitivity coefficients for rare earths in spark-source mass spectrometry: R. J. CONZEMIUS and H. J. SVEC, *Talanta*, 1973, **20**, 575. (Ames Laboratory-USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.).

Summary—Relative sensitivity coefficients have been computed for rare earth elements according to empirical models which have been proposed in the literature. Explanations concerning differences between the computed and observed values are based upon possible instrumental discrimination effects which negate some processes occurring in the ion source. Computations relating elemental physical constants to observed results in a semi-random manner are shown which support this contention.

Synthesis and ion-exchange properties of ceric tungstate: S. N. TANDON and J. S. GILL, *Talanta*, 1973, **20**, 585. (Department of Chemistry, University of Roorkee, Roorkee (U.P.), India.)

Summary—Ceric tungstate has been prepared under varying conditions of precipitation. Its properties and ion-exchange behaviour have been studied. Separations of Hg^{2+} from Zn^{2+}, Cd^{2+} and Pb^{2+}; Co^{2+} from Mn^{2+} and Fe^{3+}; and Al^{3+} from Cr^{3+} and Fe^{3+} have been carried out on ceric tungstate columns.

Предложенная константа опробования для использования в геохимическом анализе: C. O. Ingamells and P. Switzer, *Talanta* 1973, **20**, 547.

Резюме — Ошибка в определении одного элемента в горной породе или минерале зависит от аналитической ошибки, веса анализируемой пробы и природы и истории лабораторной пробы. Наиболее вероятный результат зависит от веса анализируемой пробы. Это появляется в результате того что чаше всего следовые компоненты существуют в изолированных минеральных зернах. Вероятность появления этих минеральных зерн в анализируемой пробе снижается с уменьшением веса пробы, даже если пробы горных пород или минералов измельчаются в мелкозернистые порошки. Такие ошибки опробования можно контролировать с использованием констант опробования. Эти константы можно определять разными методамн, включая повторное определение одного компонента и физическое измерение касающихся характеристик пробы. Константами опробования можно пользоваться при определении и удостоверении эталонов или стандартов. В случае недостаточного вторичного отбора проб могут получаться ошибочные низкие результаты, иногда с высокой воспроизводимостью. Высокая воспроизводимость никогда не заключает в себе высокую точность; она может представлять собой симптом большой ошибки.

Использование неселективных реагентов в непосредственной термометрии: P. Marik-Korda, L. Búzasiand and T. Cserfalvi, *Talanta* 1973, **20**, 569.

Резюме — Разработан метод одновременного определения сульфида и тиосульфата с использованием неселективных реагентов на основе разницы между их теплотами реакции. Раствор иода использовали в качестве одного реагента а в качестве другого — бромную воду. Вычислена диаграмма ошибок, а теоретические ошибки сравнены с ошибками, полученными в практике.

Относительные коэффициенты чувствительности для редкоземельных элементов в масс-спектрометрии с искровым источником: R. J. Conzemius and H. J. Svec, *Talanta* 1973, **20**, 575.

Резюме — Вычислены относительные коэффициенты чувствительности для редкоземельных элементов на основе эмпирических моделей предложенных в литературе. Объяснения разниц между вычисленными и обнаруженными величинами основаны на возможными эффектами дискриминации прибора, которые отрицают некоторые процессы появляющиеся в источнике ионов. Приведены расчеты связывающие элементарные физические константы с обнаруженными результатами в полуслучайном способе, подкрепляющие этот спор.

Синтез и ионообменные характеристики вольфрамата церия: S. N. Tandon and J. S. Gill, *Talanta* 1973, **20**, 585.

Резюме — Вольфрамат церия приготовлен при различных условиях осаждения. Изучены его свойствия и ионообменные характеристики. Удалось отделить Hg^{2+} от Zn^{2+}, Cd^{2+} и Pb^{2+}, Co^{2+} от Mn^{2+} и Fe^{2+}, и Al^{3+} от Cr^{3+} и Fe^{3+} на колонках вольфрамата церия.

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SUMMARIES FOR CARD INDEXES

How to write a paper on atomic-absorption spectrometry: J. RAMÍREZ-MUÑOZ, *Talanta*, 1973, **20**, 705. (Beckman Instruments Inc., Fullerton, California 92634, U.S.A.).

Summary—The present situation in the preparation of new papers on atomic-absorption spectrometry is discussed. The different types of papers published in this field are reviewed and details given of topics that *must* be dealt with in writing such papers. Particular attention is given to experimental papers dealing with new instrumentation, study of the analytical behaviour of analytes, and new procedures for specific analytical applications.

The performance characteristics of analytical methods—III: A. L. WILSON, *Talanta*, 1973, **20**, 725. (The Water Research Association, Medmenham, Bucks., U.K.)

Summary—The range of concentrations covered by an analytical method is an important performance-characteristic, and suggestions are made for definition of this range. The ability to detect small concentrations are also considered, and it is suggested that the standard deviation of blank determinations be quoted as the performance-characteristic relevant to the power of detection.

Graphical analysis of the formation function—I. The real cross-over point: L. C. VAN POUCKE and H. F. DE BRABANDER, *Talanta*, 1973, **20**, 733. (Department of General and Inorganic Chemistry, University of Ghent, Ghent, Belgium).

Summary—From a mathematical treatment, it has been proved that a family of formation curves shows a real cross-over point in the following cases: (*a*) a mixture of mononuclear complexes BA, $BA_2 \ldots BA_N$ and polynuclear complexes of general formula $(B_q A_p)_n$, provided that $p/q < N$; (*b*) a mixture of homonuclear complexes $B_Q A_P$, where Q is constant, and mononuclear complexes shows at least one cross-over point if the maximum value for P is smaller than NQ and at least two cross-over points if NQ lies between the minimum value and the maximum value for P. Curves calculated for three different examples are in perfect agreement with the theory.

Determination of traces of zinc by fluorimetrically indicated complexometric titrations: R. VAN SLAGEREN, G. DEN BOEF and W. E. VAN DER LINDEN, *Talanta*, 1973, **20**, 739. (Laboratorium voor Analytische Scheikunde, Universiteit van Amsterdam, Amsterdam, The Netherlands.)

Summary—Zinc forms fluorescent complexes with 8-hydroxyquinoline-5-sulphonic acid (HQS) in the pH region 7–10. The stability of these complexes is such that two different titration procedures are possible: the titration of zinc with HQS and the titration of zinc with EDTA in the presence of HQS. For both procedures the choice of the titration conditions is described. Also two separation procedures for zinc are described, especially suitable in connection with the EDTA titration. The practical results show that zinc in concentrations larger than $10^{-6}M$ (0·05 μg/ml) can be titrated with good precision.

A study of the composition and properties of the ion-association complex of Rhodamine B with silicomolybdic acid, with a view to its analytical application: A. GOŁKOWSKA and L. PSZONICKI, *Talanta*, 1973, **20**, 749. (Department of Analytical Chemistry, Institute of Nuclear Research, Dorodna 16, 03-195 Warsaw, Poland).

Summary—The composition of the ion-association complex of Rhodamine B with silicomolybdate has been examined by Job's method and spectrophotometric titration. The ratio of Rhodamine B to silicon in the complex is 4 : 1. The same ratio is obtained by analysis of the crystalline complex. The composition of the complex is identical in aqueous medium, an organic solvent (ethanol) and in the crystalline state $(C_{28}H_{30}N_2O_3)_4SiMo_{12}O_{40}$). The complex is stable in the organic solvent and has its absorption maximum at 555 nm and a molar absorptivity of 5×10^5 l.mole^{-1}cm^{-1}. The complex can be advantageously used for the determination of silicon.

Как написать статью о атомно-абсорбционной спектрометрии: J. Ramírez-Muñoz, *Talanta* 1973, **20**, 705.

Резюме — Рассмотрена настоящая ситуация в составлении новых статей о атомно-абсорбционной спектрометрии. Обсуждены различные типы статей опубликованных в этой области и приведени детали тем, которые *надо* рассматривать в такой стате. Особенное внимание уделено экспериментальным статьям, касающимся новых приборах, изучения аналитических характеристик анализируемых веществ и новых методик специфического применения в анализе.

Характеристические параметры аналитических методов — III: A. L. Wilson, *Talanta* 1973, **20**, 725.

Резюме — Область концентраций, в которой можно пользоваться данным аналитическим методом представляет собой важную характеристику метода; предложены дефиниции этой области. Также считана возможность обнаружения небольших концентраций и предложено взять стандартную ошибку навески слепых проб в качестве характеристического параметра, характеризирующего чувствительность обнаружения.

Графический анализ функции образования — I. Действительная точка пересечения: L. C. van Poucke and H. F. de Brabander, *Talanta* 1973, 20, 733.

Резюме — Математическая обработка показала что род кривых образования показывает действительную точку пересечения в следующих случаях: а) в смеси одноядерных комплексов BA, BA_2 … BA_N и многоядерных комплексов общей формулы $(B_qA_p)_n$, если ${}_p/{}_q < N$; б) в смеси гомоядерных комплексов B_QA_P, где Q константно, а одноядерные комплексы показывают не менее чем одную точку пересечения если максимальная величина P меньше чем NQ, а не менее чем две точки пересечения если NQ между минимальной и максимальной величиной P. Кривые, вычисленные для три различных случая хорошо соглашаются с теорией.

Определение следов цинка с использованием комплексонометрического титрования и флуориметрической индикации: R. van Slageren, G. den Boef and W. E. van der Linden, *Talanta* 1973, **20**, 739.

Резюме — Цинк образует флуоресцирующие комплексы с 8-оксихинолин-5-сульфоновой кислотой (ОХС) в области pH 7–10. Стабильность этих комплексов позволяет проводить две различных титрационных процедуры: титрование цинка с ОХС и титрование цинка с ЭДТА в присутствии ОХС. Отбор оптимальных условий титрования приведен для обоих методов. Описаны также два разделительных метода для цинка, специально подходящих в связы с титрованием с ЭДТА. Результаты показывают что метод позволяет определять цинк при концентрациях больше чем 10^{-6} *M* (0,05 мкг/мл) с хорошой воспроизводимостью.

Изучение состава и характеристики ионного комплекса родамина Б с кремнемолибденовой кислотой с целью его применения в анализе: A. Golkowska and L. Pszonicki, *Talanta* 1973, **20**, 749.

Резюме — Состав ионоассоциационного комплекса родамина Б с силикомолибденовой кислотой изучен с использованием метода Джоба и спектрофотометрическим титрованием. Отношение родамина Б и кремния в комплексе равно 4 : 1. Это же отношение получено в анализе кристаллического комплекса. Состав комплекса идентичный в водном растворе, в растворе органического растворителя (этанола) и в кристаллической форме $(C_{28}H_{30}N_2O_3)_4SiMo_{12}O_{40}$. Комплекс является устойчивым в органическом растворителе, его максимум светопоглощения при 555 нм, а молярное светопоглощение равно 5×10^5 л.моль$^{-1}$.см$^{-1}$. Комплексом можно успешно пользоваться для определения кремния.

Evaluation of a carbon-rod atomizer for routine determination of trace metals by atomic-absorption spectroscopy. Applications to analysis of lubricating oil and crude oil: G. HALL, M. P. BRATZEL, JR. and C. L. CHAKRABARTI, *Talanta*, 1973, **20**, 755, (Department of Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada).

Summary—A carbon-rod atomizer (CRA) fitted with a 'mini-Massmann' carbon rod was evaluated for routine analysis of petroleum and petroleum products for trace metal content by atomic-absorption spectroscopy. Aspects investigated included sensitivity, detection limit, effect of solvent type, and interferences. The results of analysis of oil samples with this technique were compared with those obtained by other techniques. Metals studied were silver, copper, iron, nickel, and lead. Sensitivity and detection limit values obtained with the CRA were similar to those obtained with the carbon-filament atomizer. Strong 'solvent effects' were observed as well as interference by cations. On the basis of this study, design changes for the CRA are suggested, with the object of minimizing 'solvent effects' and interferences, increasing the atomization efficiency, and increasing the residence time of the atomic vapour in the optical path of the instrumental system.

Application of an oxygen-shielded air–acetylene flame to atomic spectroscopy: R. STEPHENS, *Talanta*, 1973, **20**, 765. (Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, N.S., Canada.)

Summary—A burner has been designed which provides an oxygen-shielded air–acetylene flame for atomic-absorption work. The chemical reducing properties of the oxygen-shielded flame operated under fuel-rich conditions are enhanced by the higher C : O ratio obtainable in the flame and by the higher flame temperature just above the reaction zone. The flame is inherently essentially free from the risk of flashback, and is offered as an alternative to the nitrous oxide–acetylene flame for use with certain types of equipment and for particular applications.

Computer programme for calculation of electric dipole moments from measurements in solution: C. W. N. CUMPER, *Talanta*, 1973, **20**, 775. (School of Chemistry, Thames Polytechnic, London, S.E.18, U.K.).

Summary—An ALGOL computer programme is described for the calculation of an electric dipole moment from measurements made on dilute solutions in a non-polar solvent.

Determination of copper and molybdenum in the hard dental tissues of rats by atomic-absorption spectrophotometry: CHRISTINE A. HELSBY, *Talanta*, 1973, **20**, 779. (Department of Conservative Dentistry, University of Manchester, Manchester 15, U.K.).

Summary—The measurement of uptake of copper and molybdenum from the diet into rat's teeth required the use of an accurate but rapid method of analysis. The simultaneous extraction of copper and molybdenum with APDC from the sample, combined with atomic absorption, proved to be both accurate and reliable. Interference from other elements present in the sample was easily overcome by the use of standards with a matrix equivalent to that of the teeth.

Spectrophotometric determination of ascorbic acid with potassium hexacyanoferrate(III): NICOLETTA BURGER and VINKA KARAS-GAŠPAREC, *Talanta*, 1973, **20**, 782. (Department of Chemistry and Biochemistry, Faculty of Medicine, University of Zagreb, 41000 Zagreb, Croatia, Šalata 3, Yugoslavia).

Summary—A new, simple and rapid method of determination of ascorbic acid in amounts of 45–360 μg is described. The ascorbic acid is determined spectrophotometrically at 420 nm from the decrease in absorbance it causes in $1 \times 10^{-3}M$ hexacyanoferrate(III) in McIlvaine buffer at pH 5·2. The proposed method is suitable for the determination of ascorbic acid in pharmaceutical preparations and probably in natural products.

Оценка графитовой кюветы для серийного определения следов металлов методом атомно-абсорбционной спектроскопии: Применение метода в анализе смазочных масел и сырой нефты: G. Hall, M. P. Bratzel, Jr. and C. L. Chakrabarti, *Talanta* 1973, 20, 755.

Резюме — Проведена оценка графитовой кюветы типа «Мини-Массман» для серийного анализа следов металлов в сырой нефти и нефтяных продуктах методом атомно-абсорбционной спектроскопии. Изучены чувствительность метода, влияние типа растворителя и мешающие действия. Результаты, полученные в анализе масел этим методом сравнены с результатами полученными другими методами. Изученные металлы включают серебро, медь, железо, никель и свинец. Этим способом получены чувствительности, похожие чувствительностями полученными с использованием кюветы на основе углеродной нити. Обнаружены сильные «эффекты растворителей» и мешающие действия катионов. На основе этого исследования предложены измененные кюветы, с целью уменьшать «эффекты растворителей» и мешающие действия, путем повышения эффективности атомизации и продолжением времени пребывания пара атомов в оптической пути прибора.

Использование защищенного кислородом пламени воздуха-ацетилена для атомно-абсорбционной спектроскопии: R. Stephens, *Talanta* 1973, 20, 765.

Резюме — Сконструирована горелка дающая защищенное кислородом пламя воздуха-ацетилена для атомно-абсорбционной спектроскопии. Химические восстанавливающие характеристики защищенного кислородом пламени при избытке топлива еще усилены повышенным отношением C:O получаемым в пламени и повышенной температурой пламени над реакционной зоной.´Пламя существенно свободное от риска вспышки и предложено для использования вместо пламени закисиазота-ацетилена в некоторых приборах и для некоторых особенных применений.

Программа для вычисления электрических дипольных моментов на основе измерений в растворе с использованием электронно-вычислительной машины: C. W. N. Cumper, *Talanta* 1973, 20, 775.

Резюме — Описана программа ALGOL для ЭВМ для вычисления электрического дипольного момента на основе измерений проведенных в разбавленных растворах в неполярном растворителе.

Определение меди и молибдена в твердих зубных тканях крыс методом атомно-абсорбционной спектрометрии: Christine A. Helsby, *Talanta* 1973, 20, 779.

Резюме — Определение количества меди и молибдена, переходящего из пищи в зубы крыс изыскивало использование точного но быстрого аналитического метода. Одновременное экстрагирование меди и молибдена из пробы с помощью АПДЦ связанное с методом атомно-абсорбционной спектрофотометрии оказалось точным и надёжным. Влияние присутствующих в пробе других элементов избегнуто использованием стандартов, матрица которых соответствовала матрицы зубей.

Спектрофотометрическое определение аскорбиновой кислоты гексацианоферратом(III) калия: Nicoletta Burger and Vinka Karas-Gašparac, *Talanta* 1973, 20, 782.

Резюме — Описан новый несложный и быстрый метод определения аскорбиновой кислоты в количествах 45–360 мкг. Аскорбиновую кислоту определяют спектрофотометрическим методом при 420 нм на основе снижения светопоглощения в 1×20^{-3} *M* растворе гексацианоферрата(III) калия в буффере Мак Ильвейна при pH 5,2. Преложенным методом можно пользоваться для определения аскорбиновой кислоты в фармацевтических препаратах и вероятно в природных веществах.

Species in the cobalt(II) chloride-2-nitroso-1-naphthol system in benzene-ethanol mixtures: VINCENZO CARUNCHIO, ROBERTO BEDETTI and GIUSEPPE DE CECCO, *Talanta*, 1973, **20**, 787. (Instituto Chimico della Università di Roma, 00185, Rome, Italy).

Summary—The cobalt(II) chloride-2-nitroso-1-naphthol system in mixtures of benzene and ethanol has been investigated spectrophotometrically. The complexation ratios of the species present have been determined and the values of the respective concentration quotients at equilibrium at 25° have been calculated. These values seem to be dependent to only a small extent on the variation of the mixture composition; the most considerable aspect is the decrease of the complexation ratios with increasing benzene concentration.

Polarography of cadmium malate complexes: S. C. KHURANA and C. M. GUPTA, *Talanta*, 1973, **20**, 789. (Chemical Laboratories, Universities of Rajasthan, Jaipur-4, India).

Summary—The electrode reduction reaction of cadmium malate complexes at various pH values and ligand concentrations has been studied. At $\text{pH} < \text{p}K_1$ the complex $\text{Cd(H}_2\text{A)}$, $\log K = 0{\cdot}57$, exists. At $\text{pH} > \text{p}K_2$ $\text{Cd(A}^{2-})_n$ species exist, $\log \beta_1 = 1{\cdot}9$, $\log \beta_2 = 2{\cdot}8$, $\log \beta_3 = 3{\cdot}4$. At intermediate pH the complex Cd(HA) exists.

Комплексы присутствующие в системе хлорид кобальта(II) — 2-нитрозо-1-нафтол в смесях бензола-этанола: Vincenzo Carunchio, Roberto Bedetti and Giuseppe de Cecco, *Talanta* 1973, **20**, 787.

Резюме — Изучена спектрофотометрическим методом система хлорид кобальта(II) — 2-нитрозо-1-нафтол в смесях бензола и эталона. Определен состав присутствующих комплексов и частные концентраций при равновесии при 25°. Эти величины зависят только в незначительиой мере от состава смеси. Найзначительное обнаружение — снижение отношений комплексообразования с растущей концентрацией бензола.

Полярография комплексов малеата кадмия: S. C. Khurana and C. M. Gupta, *Talanta* 1973, **20**, 789.

Резюме — Изучена реакция восстановления на электроде комплексов малеата кадмия при разных величинах pH и концентрациях лиганда. При $pH < pK_1$ существует комплекс $Cd(H_2A)$, $\lg K = 0{,}57$. При $pH > pK_2$ существует род $Cd(A^{2-})_n$, $\lg \beta_1 = 1{,}9$, $\lg \beta_2 = 2{,}8$, $\lg \beta_3 = 3{,}4$. При промежуточных pH существует комплекс Cd(HA).

Talanta, Vol. 20, pp. iv. Pergamon Press, 1973. Printed in Great Britain

NOTICE

THE PITTSBURGH CONFERENCE 1974

The Twenty-fifth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Ohio, USA, March 4–8, 1974. An estimated 350 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. Symposia on the following subjects are now being arranged.

1. RECENT DEVELOPMENTS AND TRENDS IN CLINICAL CHEMISTRY
2. GREAT MOMENTS IN ANALYTICAL CHEMISTRY AND SPECTROSCOPY
3. REMOTE SENSING OF ENVIRONMENTAL AIR POLLUTANTS
4. THE ROLE OF ANALYSIS IN CONSUMER CHEMISTRY
5. RECENT ADVANCES IN SELECTIVE ION ELECTRODES
6. SYMPOSIUM ON APPLIED LIQUID CHROMATOGRAPHY
7. MONITORING OF WATER POLLUTANTS: FOR ABATEMENT, FOR PREVENTION, FOR ECONOMICS
8. SYMPOSIUM ON COMPUTERIZED LABORATORY SYSTEMS (ASTM)
9. SYMPOSIUM ON MATRIX ISOLATION SPECTROSCOPY
10. COBLENTZ SOCIETY AWARD SYMPOSIUM

Papers are *not* restricted to the symposium topics and original papers on *all* phases of Analytical Chemistry and Spectroscopy are invited.

Authors wishing to present papers at the 1974 Pittsburgh Conference should submit three copies of a 150-word abstract to:

Richard S. Danchik, Program Chairman
1974 Pittsburgh Conference
Alcoa Laboratories
Alcoa Center, Pennsylvania 15069 USA

Abstract forms are available from the Program Chairman.

The names and *complete* addresses of all authors should be included with all abstracts submitted and the name of the person who will present the paper should be underlined.

The final date for receipt of abstracts is *October 1, 1973.*

In addition to the programme of techical papers, more than 275 companies, both foreign and domestic, will be represented at the Exposition of Modern Laboratory Equipment, the largest exposition of analytical instrumentation and related materials in the world. Reservations for exhibit space should be directed to:

Robert W. Baudoux, Exposition Chairman
U.S. Steel Corporation
Research Laboratory, M.S. 57
Monroeville, Pennsylvania 15146 USA

NOTICE

IV-th POLISH CONFERENCE ON ANALYTICAL CHEMISTRY WARSAW, 26–31 AUGUST 1974

The Commission of Analytical Chemistry of the Polish Academy of Sciences is organizing in Warsaw on 26–31 August 1974 the IV-th Polish Conference on Analytical Chemistry.

The Conference will cover the broad field of analytical chemistry with preference given to trace analysis and organic analysis. Papers may be presented in Polish, English, Russian, French or German. The deadline for sending the Preliminary Registration Form is 15 October, 1973. The deadline for sending a summary of a paper is 1 January 1974.

All correspondence should be directed to the Secretary of the Organizing Committee, Dr hab. Rajmund Dybczyński, Institute of Nuclear Research, ul. Dorodna 16, 03–195 Warszawa, Poland.

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NOTES FOR AUTHORS

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Scripts should be submitted in duplicate; they should be typewritten and the lines double-spaced. Where possible, papers should follow the pattern: *Introduction, Experimental, Results, Discussions, Conclusions* (or such of these headings as apply).

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Tables should be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarize results by an accepted method of expression (*e.g.* standard deviation). The same information should not be produced in both tables and figures.

The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

References

References should be indicated in the text by consecutive superior numbers placed outside any punctuation marks; the full references should be given in a list at the end of the paper in the following form:

1. J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
2. S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon Press, Oxford, 1956.
3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strength of Metals.* A.E.R.E., M/R 6329, 1962.
5. W. Jones, *Brit. Pat.* 654321, 1959.

Journal-name abbreviations should be those used in *Chemical Abstracts* (see *Chem. Abstr.*, 1961, *et seq.*).

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Because of the international character of the journal, authors should follow the recommendations of the *International Union of Pure and Applied Chemistry* as regards nomenclature and symbols. In the editing of papers for publication, English spelling will be used for all matter in the English language. Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript. Attention is particularly drawn to the importance of correctness of grammar and clarity of expression.

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SUMMARIES FOR CARD INDEXES

Simultaneous determination of arsenic, manganese and selenium in biological materials by neutron-activation analysis: Kaj Heydorn and Else Damsgaard, *Talanta*, 1973, **20**, 1 (Isotope Division, Research Establishment Risø, Roskilde, Denmark.)

Summary—A new method was developed for the simultaneous determination of arsenic, manganese and selenium in biological material by thermal-neutron activation analysis. The use of ^{81m}Se as indicator for selenium permitted a reduction of activation time to 1 hr for a 1-g sample, and the possibility of loss of volatile compounds during irradiation could be dismissed. No pretreatment of the sample is required, and the radiochemical separation scheme is based on simple chemical operations, completed in less than 3 hr. A systematic experimental investigation of the performance characteristics of the method was carried out, including studies of the accuracy of the results. The actual precision achieved in routine application of the method in the analytical laboratory was in good agreement with the calculated precision, and the results are therefore well suited for statistical evaluation of differences at the ppM level in samples of biological tissue.

Spectrophotometric determination of vanadium with 1,10-phenanthroline: Amal Kanti Bhadra, *Talanta*, 1973, **20**, 13. (Central Chemical Laboratories, Geological Survey of India, Calcutta-13, India).

Summary—A simple and sensitive spectrophotometric method for the determination of vanadium based upon the reaction of vanadate with 1,10-phenanthroline in the presence of sodium dithionite in ammoniacal solution is described. The absorbance of the complex measured at 645 nm follows Beer's law for solutions containing 30–400 μg of vanadium in 100 ml of solution. A 10-fold excess of molybdenum, tungsten, phosphorus or chromium does not interfere. The molar absorptivity has been found to be $8{\cdot}0 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. The complex is shown to be tris-1,10-phenanthroline vanadium(II). The method has been applied successfully to the determination of vanadium in bauxite.

Use of the titanium(IV) chelate of salicylic acid for a selective absorptiometric determination of titanium: R. S. Ramakrishna and H. D. Gunawardena, *Talanta*, 1973, **20**, 21. (Department of Chemistry, University of Ceylon, Colombo 3, Ceylon).

Summary—Titanium(IV) forms a 1:1 chelate with salicylic acid in 40% aqueous ethanolic solution. The chelate is extractable into chloroform. A selective extraction method for the estimation of titanium in the presence of a variety of commonly interfering species is described. The addition of pyridine is found to increase the sensitivity and selectivity and makes it unnecessary to use alcohol in the extraction. The extracted species is a pyridine adduct of the titanium–salicylic acid chelate.

Application of flow microcalorimetry to analytical problems—1. Determination of organophosphorus pesticides by inhibition of cholinesterase: A. E. Beezer and C. D. Stubbs, *Talanta*, 1973, **20**, 27. (Chemistry Department, Chelsea College of Science and Technology, Manresa Road, London S.W.3).

Summary—Flow microcalorimetry has been applied to the determination of organophosphorus pesticides by inhibition of cholinesterase. One direct inhibitor (TEPP) and one latent inhibitor (parathion) were investigated. The former is determinable at concentrations of about $10^{-6}M$ and the latter at about $10^{-4}M$. The inhibitory power of parathion is increased if methanol is used as solvent.

Одновременное определение мышьяка, марганца и селена в биологических веществах метолом нейтроноактивационного анализа:
Kaj Heydorn and Else Domegaard, *Talanta* 1973, **20**, 1.

Резюме — Разработан новый метод одновременного определения мышьяка, марганца и селена в биологических веществах методом нейтроноактивационного анализа с использованием термических нейтронов. Использование ^{91m}Se в качестве индикатора позволило сократить продолжительность активации до 1 ч. в случае пробы 1 г, и избегнуть потерю летучих соединений в течение иррадиации. Метод не изыскует предварительную обработку пробы, а радиохимическая схема разделения основана на несложных химических операциях, проведимых в меньше чем 3 ч. Проведено систематическое экспериментальное исследование характеристик метода, включая изучение точности результатов. Воспроизводимость полученная при применении метода в серийном анализе в лаборатории хорошо соглашается с вычисленной воспроизводимостью; результаты потому поддаются статистической оценки разниц на уровне частей на миллион в образцах биологической ткани.

Спектрофотометрическое определение ванадия 1,10-фенантролином: Amal Khanti Badra, *Talanta* 1973, **20**, 13

Резюме — Описан несложный и чувствительный спектрофотометрический метод определения ванадия, основанный на реакции ванадата с 1,10-фенантролином в присутствии дитионита натрия в аммиачном растворе. Светопоглощение комплекса, измеренное при 645 нм повинуется закону Бера в случае растворов содержащих 30–400 мкг ванадия в 100 мл раствора. 10-кратный избыток молибдена, вольфрама, фосфора или хрома не мешает определению. Молярное поглощение равно $8{,}0 \times 10^3$ л.моль$^{-1}$.см$^{-1}$. Структура комплекса — трис-1,10-фенантролин-ванадий(II). Метод успешно применен в определении ванадия в боксите.

Использование хелата титана (IV) с салициловой кислотой для селективного определения титана: R. S. Ramakrishna and H. D. Gunawardena, *Talanta* 1973, **20**, 21

Резюме — Титан (IV) образует хелат 1:1 с салициловой кислотой в растворе 40%тного водного спирта. Хелат экстрагируется хлороформом. Описан селективный экстракционный метод для определения титана в присутствии ряда ионов, которые обыкновенно мешают определению титана. Прибавление раствору пиридина повыщает чувствительность и селективность метода, а позволяет избежать использование спирта в экстракции. Экстрагированный комплекс является пиридиновым аддуктом хелата титана с салициловой кислотой.

Применение метода проточной микрокалориметрии в анализе — I. Определение фосфорорганических пестицидов путем ингибирования холинэстеразы: A. E. Beezer and C. D. Stubbs, *Talanta* 1973, **20**, 27

Резюме — Метод проточной микрокалориметрии применен в определении фосфорорганических пестицидов путем ингибирования холинэстеразы. Изучены один из непосредственных ингибиторов (ТЭПП) и один из латентных ингибиторов (паратион). Первый можно определять при концентрациях 10^{-6} *M*, а второй — при 10^{-4} *M*. Ингибирующее действие паратиона повышается с использованием метилового спирта в качестве растворителя.

Electronic absorption and fluorescence of cinchopen, cinchoninic acid and their methyl esters; Biprotonic phototautomerism of the singly-protonated species: B. Zalis, A. C. Capomacchia, D. Jackman and S. G. Schulman, *Talanta*, 1973, **20**, 33. (College of Pharmacy, University of Florida, Gainesville, Florida 32601, U.S.A.).

Summary—The pH and Hammett acidity dependences of the absorption and fluorescence spectra of cinchoninic acid (quinoline-4-carboxylic acid), cinchophen (2-phenylquinoline-4-carboxylic acid) and their methyl esters, were studied. The predominant uncharged ground-state species derived from the free acids are zwitterions. Prototropic equilibria are too slow to compete with fluorescence for deactivation of the excited state at hydrogen ion concentrations represented by the pH scale. However, fluorescence shifts accompanying protonation indicate that the carboxyl group is more basic than the ring nitrogen atom in the excited state. In the Hammett acidity range the singly-charged cations of all the compounds studied undergo phototautomerism in the lowest excited singlet state. The rate of this process is acidity dependent. In very concentrated sulphuric acid solutions doubly-charged cations are formed in the excited state but not in the ground state. The intense emissions of these compounds in moderately concentrated sulphuric acid may be suitable for quantitative analysis if great care is taken to control solution acidity.

Bestimmung ^{35}S-Markurter Polythionate nach Hochspannungsionophoretischer trennung: E. Blassius und H. Wagner, *Talanta*, 1973, **20**, 43. (Insitut für Analytische Chemie und Radio-chemie der Universität des Saarlandes, 6600 Saarbrücken, B.R.D.).

Summary—The activity of ^{35}S-labelled polythionates has been measured on electrophoretograms by elution followed by precipitation as Ba^{35}SO$_4$ and, end-window GM-tube counting, and directly on the support material by liquid-scintillation counting. The results obtained by the two methods are presented and compared. The count-rate yield is only 0·25% for the first method, but 55% for the second, though this does suffer from a slight dependence on the nature of the ion present.

Extraction with long-chain amines—VI. Separation of manganese ASMn(CNS)$_6^{4-}$ complex and its complexometric determination in calcareous material: Rudolf Přibil and Jiří Adam, *Talanta*, 1973, **20**, 49. (J. Heyrovský Instute for Physical Chemistry and Electrochemistry, Analytical Laboratory, Prague 1, Jilská 16 and Analytical Laboratory, Institute for Geological Sciences, Charles University, Prague 2, Albertov 6, Czechoslovakia).

Summary—Manganese is quantitatively extracted into benzene solution of trioctylmethylammonium chloride (TOMA) from a solution at least 0·25*M* in potassium thiocyanate and at pH 2·5–7. After stripping into dilute ammonia containing triethanolamine (TEA) and hydroxylamine hydrochloride, manganese is determined by EDTA titration. Calcium and magnesium are not extracted even in traces. Iron is co-extracted with manganese and is masked with TEA during the stripping. Aluminium also does not interfere. In the aqueous phase, after the extraction of manganese, calcium or magnesium can be determined by the usual EDTA titration. The method described permits highly selective individual determination of manganese and calcium and/or magnesium in all materials rich in manganese.

Extraktion der Metallionen Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) mit geschmolzenem Oxin und Bestimmung der extrahierten Metalle mit Hilfe von Röntgenfluoreszenz: B. Magyar and F. I. Lobanov, *Talanta*, 1973, **20**, 55. (Laboratorium für Anorganische Chemie, Eidg. Techn. Hochschule, Zürich, Schweiz).

Summary—The accuracy of the determination by X-ray fluorescence spectrometry of a number of metals in pressed tablets of oxine has been investigated. A procedure is described which has been used for the determination of trace metals in fresh water and in sugar, in which molten oxine is used as the extractant.

Электронное поглощение и флуоресценция атофана, атофановой кислоты и их метиловых эфиров; двупротонная фототаутомерия однопротонированного рода: B. Zalis, A. C. Capomacchia, D. Jackman and S. G. Schulman, *Talanta* 1973, **20**, 33

Резюме — Изучена зависимость спектров поглощения и флуресценции атофановой кислоты (хинолин-4-карбоновой кислоты), атофана (2-фенилхинолин-4-карбоновой кислоты) и их метиловых эфиров от pH и кислотности Гамметта. Амфионы являются преобладающим незаряженным родом основного состояния, полученным из свободных кислот. Прототропические равновесия слишком медленны чтобы конкурировать флуоресценции в деактивации возбужденного состояния при концентрациях водородного иона приказанных шкалой pH. Между тем, смещения флуоресценции, сопровождающие протонацию указывают что карбоксильная группа является более основной чем атом азота в кольце в возбужденном состоянии. В области кислотности Гамметта однозаряженные катионы всех изученных соединений подвергаются фототаутомерии в нижайшем возбужденном состоянии синглета. Скорость этого процесса зависит от кислотности. В сильноконцентрированных растворах серной кислоты образуются двухзаряженные катионы в возбужденном состоянии но не в основном состоянии. Интенсивные эмиссии этих соединений в умеренно концентрированных растворах серной кислоты могли бы быть использованы в количественном анализе при тщательном регулировании кислотности раствора.

Определение означенных с ^{35}S политионатор после разделения методом электрофореза при высоком напряжении: E. Blasius and H. Wagner, *Talanta* 1973, **20**, 43

Резюме — Измерена активность означенных с ^{35}S политионатов на электроферограммах элюированием с последующим осаждением в форме $Ba^{35}SO_4$ и использованием счетчика Гейгера, и непосредственно — на материале использованном в качестве носителя, с использованием жидкофазного сцинтилляционного счетчика. Приведены и сравнены результаты полученные этими двумя методами. Выход счета составляет только 0,25% для первого метода, но 55% для второго, но он терпит от небольшого влияния природы присутствующего иона на определение.

Экстрагирование с аминами с длинной цепью — √1. Выделение марганца в форме комплекса $Mn(CNS)_6^{4-}$ и его определение в известковых веществах комплексонометрическим методом: Rudolf Přibil and Jiři Adam, *Talanta* 1973, **20**, 49

Резюме — Марганец экстрагируют количественно раствором хлорида триоктилметиламмония (ТОМА) в бензоле из раствора содержащего не менее чем 0,25*M* тиоцианата калия при pH 2,5–7. После переноса в разбавленный раствор аммиака, содержащий триэтаноламин (ТЭА) и хлористоводородный гидроксиламин, марганец определяют титрованием с раствором ЭДТА. Даже не следы кальция и магния экстрагируются в этом процессе. Железо экстрагируется вместе с марганцем, а маскируется с ТЭА при переносе. Алюминий также не мешает определению. В водной фазе, после экстрагирования марганца, можно определять кальций и магний обыкновенным титрованием с ЭДТА. Описанный метод позволяет высокоселективное индивидуальное определение марганца или кальция и/или магния во веществах содержащих большие количества марганца.

Экстракция ионов металлов C (III), e(III), Co(II), (II), C (II) и (II) расплавленным оксином и определение экстрагированных металлов методом рентгенфлуоресцентной спектроскопии: B. Magyar and F. I. Lobanov, *Talanta* 1973, **20**, 55

Резюме — Изучена точность определения методом рентгенфлуоресцентной спектроскопии ряда металлов в форме прессованных таблетках оксина. Описана методика использованная для определения следов металлов в свежей воде и в сахаре, используя расплавленный оксин в качестве экстрагирующего агента.

Iron(II)–chloramine-T reaction: V. R. S. RAO and G. ARAVAMUDAN, *Talanta*, 1973, **20**, 65. (Department of Chemistry, Indian Institute of Technology, Madras-36, India).

Summary—When a large excess of the oxidant is used in the iron(II)–chloramine-T reaction at pH 2·56–5·6 the amount of oxidant consumed is well above the stoichiometric amount required to oxidize iron(II) to iron(III). This has been attributed to the formation and subsequent behaviour of free radicals during the reaction. The formation of free radicals has been experimentally demonstrated. They apparently dimerize to give products of the type R–NCl–NCl–R ($R = CH_3C_6H_4SO_2$), which are further oxidized by chloramine-T. The dimerized species liberate iodine very slowly from acidified potassium iodide. This explanation satisfactorily accounts for the observed extent and rate of destruction of excess of chloramine-T in presence of small amounts of Fe(II) or bromide at pH 2·65–4·70. The storage of chloramine-T in metal containers might cause extensive destruction of the oxidant by a similar free radical mechanism and should be avoided.

Infrared macro and semimicro determination of nitrogen in raw nitrocellulose and nitrocellulose contained in propellants: GEORGE NORWITZ and DAVID E. CHASAN, *Talanta*, 1973, **20**, 73. (Frankford Arsenal, Philadelphia, Pa 19137, U.S.A.).

Summary—The infrared procedure for the determination of nitrogen in raw nitrocellulose has been improved. In the original method 0·31–0·32 g of sample was dissolved in 45 ml of tetrahydrofuran, the solution was weighed, and the infrared peak at 6·0 μm was measured. The calibration curve was prepared by plotting absorbance against mg of nitrogen per g of solution. The method has the disadvantage that the height of the peak is affected by the sample weight. In the improved method the error due to the sample weight is eliminated by using 0·3000 g of sample and diluting to 50 ml in a volumetric flask. The calibration curve is prepared by plotting absorbance against % nitrogen. The method was extended to the semimicro scale by using a 30·00-mg sample and diluting to 5 ml in a volumetric flask. The method has been applied on the macro and semimicro scales to the direct determination of nitrogen in nitrocellulose after a methylene chloride extraction. The amounts of graphite and inorganic salts found in nitrocellulose-base propellants do not interfere, but a correction must be made to refer the results to 0·3000 g of nitrocellulose for the macro method or 30·0 mg of nitrocellulose for the semimicro method. The same calibration curve is used for all procedures.

Hydrogen peroxide formation upon oxidation of oxalic acid in presence and absence of oxygen and of manganese(II)—(III). Iron(III) and copper(II) as retarders: I. M. KOLTHOFF, E. J. MEECHAN and MASARY KIMURA, *Talanta*, 1973, **20**, 81. (School of Chemistry, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.).

Summary—The formation of considerable amounts of hydrogen peroxide upon the slow addition of various oxidizing agents to oxalic acid in dilute sulphuric acid in the presence of oxygen and Mn(II) is greatly retarded in the presence of Fe(III) or Cu(II). With hydrogen peroxide as oxidizing agent and a trace of Fe(II) there is considerable decomposition of peroxide, under a nitrogen atmosphere, after a few hours at 25° in light (from a tungsten lamp), and less decomposition in the dark. This decomposition is decreased by Mn(II) and also when the original mixture contains Fe(III). With oxygen as the oxidizing agent Fe(II) is about 100 times as effective an inhibitor of peroxide formation as Fe(III). With all oxidizing agents used, Cu(II) is some 6–10 times more effective as a retarder than Fe(III). The inhibition is accounted for by the reaction $Fe(III)\ [or\ Cu(II)] + CO_2^- \rightarrow Fe(II)\ [or\ Cu(I)] + CO_2$.

Реакция железа(II) с хлорамином Т: V. R. S. Rao and G. Aravamudan, *Talanta* 1973, **20**, 65

Резюме — При использовании большего избытка окислителя в реакции железа(II) с хлорамином Т при pH 2,56–5,6 количество расходованного окислителя значительно больше стехиометрического количества потребляемого для окисления железа(II) в железо(III). Это приписано образованию и последующему поведению свободных радикалов в растворе в течение реакции. Образование свободных радикалов показано экспериментальным путем. Они повидимому димеризируют с образованием продуктов типа $R-NCl-NCl-R(R=CH_3C_6H_4SO_2)$, которые далее окисляются хлорамином Т. Димеризированные радикалы выделяют иод очень медленно из закисленного иодида калия. Это протолкует удовлетворительно обнаруженную степень и скорость разрушения избытка хлорамина Т в присутствии небольших количеств железа(II) или бромида при pH 2,65–4,0. Хранение хлорамина Т в металлических сосудах может вызывать значительное разрушение окислителя путем похожего механизма свободных радикалов и потому надо избегать.

Марко и семимикрометод инфракрасной спектроскопии для определения азота в сырой нитроцеллюлозе и нитроцеллюлозе содержанной в реактивных топливах: George Norwitz and David E. Chasan, 1973, *Talanta* **20**, 73

Резюме — Улучшена методика инфракрасной спектроскопии для определения азота в сырой нитроцеллюлозе. В первоначальной методике 0,31–0,32 г пробы растворяли в 45 мл тетрагидрофурана, раствор взвешивали и измеряли инфракрасный пик при 6,0 мкм. Калибровочную кривую получали нанесением поглошения в зависимости от мг азота содержанных в 1 г раствора. Невыгода метода в том что высота пика зависит от веса пробы. В улучшенном методе исключена ошибка вызвана различным весои пробы, использованием 0,3000 г пробы и разбавлением до 50 мл в мерной колбе. Калибровочная кривая получается нанесением поглощения в зависимости от % азота. Методом можно пользоваться на семимикрошкале, использованием 30,00 мг пробы разбавленной до 5 мл в мерной колбе. Метод применен на макро и семимикрошкале в непосредственном определении азота в нитроцеллюлозе после извлечения метиленхлоридом. Количества графита и неорганических солей обнаруживаемые в реактивных топливах на основе нитроцеллюлозы не мешают определению, но надо сделать коррекцию для сведения результатов к 0,3000 г нитроцеллюлозы в случае макрометода или 30,00 мг нитроцеллюлозы в случае семимикрометода. Тойже калибровочной кривой пользуются во всех случаях.

Образование перекиси водорода при окислении щавелевой кислоты в присутствии и отсутствии кислорода и марганца(II)-III. Использование железа(III) и меди(II) в качестве ингибиторов: I. M. Kolthoff, E. J. Meehan and Masari Kimura, *Talanta* 1973, **20**, 81

Резюме — Образование значительных количеств перекиси водорода при медленном добавлении разных окислителей раствору щавелевой кислоты в разбавленной серной кислоте в присутствии кислорода и марганца(II) в значительной мере замедлено в присутствии Fe(III) или Cu(II). В присутствии перекиси водорода в качестве окислителя и следов Fe(II), имеет место значительное разложение перекиси в атмосфере азота, после несколько часов при 25° в свете вольфрамовой лампы; разложение более медленно в темноте. Разложение уменьшается в присутствии Mn(II) а также в присутствии Fe(III) в начальной смеси. В присутствии кислорода в качестве окислителя действие Fe(II) как ингибитора образования перекиси 100 крат больше чем Fe(III). В случае всех использованных окислителей Cu(II) является 6–10 крат более эффективным в качестве ингибитора чем Fe(III). Ингибиторное действие приказано реакцией $Fe(III)\ [или\ Cu(II)] + CO_2^- \rightarrow Fe(II)\ [или\ C\ (I)] + CO_2$.

Logarithmic diagrams and Gran-curves as an aid in potentiometric titrations in complexometry: AXEL JOHANSSON, *Talanta* 1973, **20**, 89. (Royal Institute of Technology, Stockholm, Sweden).

Summary—A detailed exposition is given of the use of logarithmic diagrams and Gran plots to determinate accurately the equivalence point in potentiometric complexometric titrations.

Preparation and infrared spectra of palladium derivatives of some organophosphorous insecticides: T. F. BIDLEMAN and R. W. FREI, *Talanta*, 1973, **20**, 103. (Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada).

Summary—The preparation of palladium complexes of phosphorodithioate (Guthion, Ethyl Guthion, Imidan and Cidial) and phosphorothioate (Fenthion) insecticides is described. The Pd : pesticide ratios in the derivatives are *ca.* 1 : 1 for the phosphorodithioates and 2 : 1 in the case of Fenthion. The infrared spectra of the derivatives are compared with those of the parent insecticide. Palladium complexation of phosphorodithioates results in a lowering of the P=S frequencies by 60–75 cm^{-1} and also produces changes in the P–O–C region. Milligram quantities of Thimet, Trithion, and Cidial on thin-layer chromatograms were reacted *in situ* with sodium tetrachloropalladate(II). The infrared spectra of the compounds recovered from the plate depend greatly on the Pd : pesticide ratio on the spot, and the analytical significance of these results is discussed.

A new method for the isolation of methylmercury from biological tissues and its determination at the parts-per-milliard level by gas chromatography: V. ZELENKO and L. KOSTA, *Talanta*, 1973, **20**, 115. (Medical Faculty, University of Ljubljana, Yugoslavia and Faculty of Natural Sciences and Technology and Institute "Jožef Stefan," University of Ljubljana, Yugoslavia).

Summary—A new method has been developed for the isolation of methylmercury from biological tissue. It is based on the volatilization of methylmercury cyanide formed in the reaction of methylmercury in the tissue with hydrocyanic acid released in the interaction of potassium hexacyanoferrate(II) with sulphuric acid at elevated temperature. The methylmercury cyanide released is captured on cysteine paper in a microdiffusion cell. The isolated methylmercury is set free with hydrochloric acid, extracted into benzene and determined by gas chromatography. A special closed micro-extractor is used for the final extraction into benzene for samples containing the lowest levels of methylmercury. The method can be used for a wide range of samples and concentrations (including background levels). The simplicity of the method makes it suitable for routine application.

Identification de submicroquantités d'ions iodure: N. GANTCHEV, D. ATHANASSOVA and V. BOGDANOVA, *Talanta*, 1973, **20**, 125. (Chaire de Chimie Analitique, Université "Paissi Hilindarsky," Rue V. Markov, 7, Plovdiv, Bulgaria).

Summary—A spot-test, based on the formation of yellow-brown nitron tri-iodide, permits detection of 0·01 ng of iodide (limit of dilution 1 in 64×10^6).

Использование логарифмических диаграмм и кривых Грана в качестве вспомогательных средств при потенциометрическом титровании в комплексонометрии: Axel Johansson, *Talanta* 1973, **20**, 89

Резюме — Детально описано использование логарифмических диаграмм и кривых Грана для точного определения конца титрования при потенциометрических комплексонометрических титрованиях.

Приготовление и инфракрасные спектры соединений палладия с некоторыми фосфорорганическими инсектицидами: T. F. Bidleman and R. W. Frei, *Talanta* 1973, **20**, 103

Резюме — Описано приготовление комплексов палладия с инсектицидами на основе фосфородитиоата (Гутион, Этилгутион, Имидан и Цидиал) и на основе фосфоротиоата (Фентион). Отношение Pd: инсектицид равно приблизительно 1:1 в случае фосфородитиоатов, а 2:1 в случае Фентиона. Инфракрасные спектры производных сравнены с спектрами основных инсектицидов. Образование комплексов палладия с фосфородитиоатами вызывает снижение частот P=S на 60–75 см$^{-1}$, а также вызывает изменения в области P—O—C колебаний. Миллиграммовые количества Тимета, Тритиона и Цидиала на тонкослойных хроматограммах реагированы *in situ* тетрахлорпалладатом натрия. Инфракрасные спектра соединеный снятих с пластинки зависят в значительной мере от отношения Pd: инсектицид; обсуждена значительность этих результатов с аналитической точки зрения.

Новый метод выделения метилртути из биологических тканей и ее определение на уровне частей на миллиард методом газовой хроматографии: V. Zelenko and L. Kosta, *Talanta* 1973, **20**, 115.

Резюме — Разработан новый метод выделения метилртути из биологических тканей. Метод основан на улетучивании цианида метилртути образующегося в реакции метилртути в ткани с цианистоводородной кислотой, выделяющейся при взаимодействии гексациано-железо II-кислого калия с серной кислотой при повышенной температуре. Выделенный цианид метилртути улавливают на пропытанной цистеином бумаге в микродиффузионной ячейке. Метилртуть, освобожденную обработкой с соляной кислотой, экстрагируют бензолом и определяют методом газовой хроматографии. Специальный закрепленный микроэкстрактор использован для последней экстракции бензолом в случае образцов содержащих весьма низкие концентрации метилртути. Метод может быть применен в широком диапазоне образцов и концентраций (включая фоновые уровни). Несложность метода позволяет его применение в серийном анализе.

Определение субмикроколичеств ионов иода: N. Gantchev, D. Athanassova and V. Bogdanova, *Talanta* 1973, **20**, 125

Резюме — Капельная проба основанная на образовании желтобурого трииодида нитрона позводяет обнаружить 0,01 нг иодида (пределное разбавление 1 в 64.10^6).

Atomabsorbtionsspektralphotometrische besstimmung von Zinc in Galliumarsenid und Galliumaluminiumarsenid: K. Dittrich und W. Zeppan, *Talanta*, 1973, **20**, 126. (Sektion Chemie, Karl-Marx-Universität, DDR 701 Leipzig, Liebigstraße 18, Germany).

Summary—The determination by atomic-absorption spectroscopy of zinc in gallium arsenide and gallium aluminium arsenide is described. In 5–20 mg of sample, 0·1–3 μg of zinc can be determined. The coefficient of variation is 4·5%. The influence of the matrix is described and discussed.

Spectrophotometric determination of osmium with 2R-acid in the presence of other platinum metals: B. V. Agarwala and A. K. Ghose, *Talanta*, 1973, **20**, 129. (Chemical Laboratories, University of Allahabad, Allahabad, India).

Summary—Osmium(VIII) produces two coloured species with λ_{max} 680 nm (green) and 530 nm (red) with excess of 2-amino-8-naphthol-3,6-disulphonic acid in aqueous solution. The green complex is stable between pH 2·5 and 8·0 and the red complex between pH 11·0 and 12·0. The effects of temperature and time, reagent concentration, optimum conditions for the spectrophotometric determination of trace amounts of osmium, and other variables, have been studied at pH 11·5. At this pH, other platinum metals do not interfere. The sensitivity of the colour reaction is 0·2 $\mu g/cm^2$ and the system conforms to Beer's law over a concentration range of 1·5–10 μg of osmium.

Rapid chelometric determination of lead in lubricating oils *via* mercaptoacetate extraction: Samaresh Banerjee and R. K. Dutta, *Talanta*, 1973, **20**, 131. (Research and Control Laboratory, Durgapur Steel Plant, Durgapur-3, West Bengal, India).

Summary—A rapid complexometric method for the estimation of lead in lubricating oil has been developed. The lead naphthenate present in the oil is extracted with a mixture of dilute thioglycollic acid and nitric acid. The aqueous extract containing lead mercaptoacetate is titrated with EDTA at pH 5 with Xylenol Orange as indicator. The lead content can be determined within 15–20 min.

Potentiometric determination of stepwise stability constants of vanadium, molybdenum and tungsten chelates formed with asparagine and glutamine: R. C. Tewari and M. N. Srivastava, *Talanta*, 1973, **20**, 133. (Chemical Laboratories, University of Allahabad, Allahabad, India).

Summary—The metal chelates of V(IV), Mo(VI) and W(VI) formed with asparagine and glutamine have been studied potentiometrically. Stepwise stability constants of 0·1*M* sodium perchlorate at 25°C are reported as follows:
Asparagine chelates—log K_1K_2 14·50 and log K_3 4·04 for V, log K_1 8·06, log K_2 7·29 and log K_3 3·45 for Mo, and log K_1 5·84, log K_2 5·11 and log K_3 3·30 for W.
Glutamine chelates—log K_1K_2 14·45, and log K_3 4·07 for V, log K_1 7·90, log K_2 6·93 and log K_3 3·35 for Mo, and log K_1 5·76, log K_2 5·09 and log K_3 3·20 for W.

The acid stability constants of Alizarin Fluorine Blue: Folke Ingman, *Talanta*, 1973, **20**, 135. (Dept. of Inorganic and Analytical Chemistry, Åbo Akadeki, Åbo, Finland and Dept. of Analytical Chemistry, Royal Institute of Technology, Stockholm, Sweden).

Summary—Two recent attempts to determine the dissociation constants of 3-aminomethylalizarin-*N,N*-diacetic acid are discussed and the results compared with values that can be predicted from earlier work on iminodiacetic acid derivatives and from the absorption spectra of the reagent at different pH values. Results of a potentiometric and spectrophotometric study to determine the stability constants of the various protonated species of the reagent in aqueous solution at ionic strengths 0·1 and 0·5 (potassium chloride) are: log $K^{H}_{HL} = 12{\cdot}1$, log $K^{H}_{H_2L} = 9{\cdot}81$, log $K^{H}_{H_3L} = 5{\cdot}47$, log $K^{H}_{H_4L} = 2{\cdot}54$, and log $K^{H_2L}_{H_5L_2} = 2{\cdot}2$ at ionic strength 0·5.

Определение цинка в арсениде галлия и арсениде галлия-алюминия методом атомно-абсорбционной спектроскопии: K. Dittrich and W. Zeppan, *Talanta* 1973, **20**, 126

Резюме — Описано определение цинка в арсениде галлия и арсениде галлия-алюминия методом атомно-абсорбционной спектроскопии. Метод позволяет определять 0,1–3 мкг цинка в 5–20 мг пробы. Коэффициент вариации равен 4,5%. Описано и рассмотрено влияние матрици пробы на определение.

Спектрофотометрическое определение осмия с использованием 2A кислоты в присутствии других платиновых металлов: B. V. Agarwala and A. K. Ghose, *Talanta* 1973, **20**, 129

Резюме — Осмий дает два окрашенных комплекса, с избытком 2-амино-8-нафтол-3,6-дисульфоновой кислотой в водном растворе, λ_{max} которых 680 нм (зеленый комплекс) и 530 нм (красный комплекс). Зеленый комплекс устойчивый при pH 2,5–8,0, а красный — при pH 11,0–12,0. Изучено при pH 11,5 влияние температуры и времены, концентрации реагента, оптимальных условый для спектрофотометрического определения осмия, и других факторов. При этом pH другие платиновые металлы не мешают определению. Чувствительность цветной реакции равна 0,2 мкг %см^2, а система повинуется закону Бера в области концентраций 1,5–10 мкг осмия.

Быстрый метод хелатометрического определения свинца в смазочных маслах путем экстракции меркаптоацетатом: Samaresh Banerjee and R. K. Dutta, *Talanta* 1973, **20**, 131

Резюме — Разработан быстрый комплексонометрический метод определения свинца в смазочных маслах. Присутствующий в масле нафтенат свинца экстрагируют смесью разбавленной тиогликолевой кислоты и азотной кислоты. Содержащий меркаптоацетат свинца водный экстракт титруют с ЭДТА при pH 5 с использованием ксиленолоранжевого в качестве индикатора. Продолжительность определения свинца составляет 15–20 мин.

Потенциометрическое определение постепенных констант °стойчивости хелатов ванадия, молибдена и Вольфрама с аспарагином и глутамином: R. C. Tewari and M. N. Srivastawa, *Talanta* 1973, **20**, 133

Резюме — Изучены потенциометрическим методом хелаты V(IV), Mo(VI) и W(VI) с аспарагином и глутамином. Определены следующие постепенные константы устойчивости в 0,1M растворе перхлората натрия при 25°:

Хелаты аспарагина — lg K_1K_2 14,50 и lg K_3 4,04 для V; lg K_2 7,29 и lg K_3 3,45 для Mo; lg K_1 5,84 lg K_2 5,11 и lg K_3 3,30 для W.

Хелаты глутамина — lg K_1K_2 14,25 и lg K_3 4,07 для V; lg K_2 6,93 и lg K_3 3,35 для Mo; lg K_1 5,76, lg K_2 5,09 и lg K_3 3,20 для W.

Кислотные константы устойчивости ализаринового флуоринового голубого: Folke Ingman, *Talanta* 1973, **20**, 135

Резюме — Обсуждена два проведенных в настоящее время подхода к определению констант диссоциации 3-аминометилализарин- —, — -диуксусной кислоты и результаты этих исследований сравнены с величинами предсказанными на основе исследованных заранее производных иминодиуксусной кислоты и на основе спектров светопоглощения реагента при разных значениях pH. Получены следующие величины с использованием потенциометрического и спектрофотометрического методов в определении констант устойчивости различных протонированных родов реагента в водном растворе при ионной силе 0,1 и 0,5 (хлорид калия): $\lg K^{H}_{HL} = 12,1$; $\lg K^{H}_{H_2L} = 9,81$; $\lg K^{H}_{H_3L} = 5,47$; $\lg K^{H}_{H_4L} = 2,54$; $\lg K^{H_2L}_{H_5L_2} = 2,2$ при ионной силе 0,5.

NOTICE

EUROPEAN SYMPOSIUM OF THE INTERNATIONAL ASSOCIATION OF FORENSIC TOXICOLOGISTS

This Symposium will be held at the State University of Ghent, Belgium, Faculty of Pharmaceutical Sciences, Department of Toxicology on 31 August and 1 September 1973 This meeting was decided on at the last International Meeting of Forensic Sciences in Edinburgh. The language of the Symposium, as at the previous meetings, will be English

Additional information can be obtained from the following address: Department of Toxicology, State University of Ghent, Hospitaalstraat 13, 9000 Ghent, Belgium.

Talanta, Vol. 20, p. v-vi. Pergamon Press, 1973. Printed in Great Britain

PAPERS RECEIVED

Limits of the molar ratio method: B. W. BUDESINSKY (25 *June* 1973)

Fractional precipitation of rare earth iodates by use of complexation and of hydrolysis of dimethyl sulphate: F. H. FIRSCHING, MICHAEL T. BERGER, PHILIP G. TAYLOR and DENNIS W. THURSTON. (11 *June* 1973)

Improved linear titration plots for weak acid titrations: D. MIDGLEY and C. MCCALLUM. (3 *July* 1973)

The extraction of Prussian Blue into chloroform in the presence of ajatin: A. GALÍK and MRS. J. VOPRAVILOVA. (3 *July* 1973)

Acid-base titration curves for acids with very small ratios of successive dissociation constants: BRUCE H. CAMPBELL and LOUIS MEITES. (4 *July* 1973)

Determination of iodine by atomic-absorption spectrometry, using the platinum-loop technique: J. M. MANFIELD, T. S. WEST and R. M. DAGNALL. (10 *July* 1973)

Study of ion-association complexes used in spectrophotometric determination of iron: ADAM HULANICKI and JOLANTA NIENIEWSKA. (10 *July* 1973)

Stepwise a.c. amperometric titration of cadmium and zinc with EGTA: J. ASPLUND. (10 *July* 1973)

Determination of equivalence volume in potentiometric acid-base titrations, using one titration point—I: ARI IVASKA. (10 *July* 1973)

Determination of equivalence volume in potentiometric acid-base titrations, using one titration point—II: ARI IVASKA. (10 *July* 1973)

Determination of equivalence volume in potentiometric acid-base titrations, using one titration point—III: ARI IVASKA. (10 *July* 1973)

Spectrographic analysis of high-purity nickel oxide for twenty-one trace impurities, using a new buffer: N. P. KARANJIKAR and M. D. SAKSENA. (11 *July* 1973)

Simultaneous ion-beam collection for precise measurement of nuclidic ion-current ratios in spark-source mass spectrometry: ROBERT J. CONZEMIUS and H. J. SVEC. (11 *July* 1973)

Determination of yttrium in rocks by neutron activation and a simple group separation: E. STEINNES. (11 *July* 1973)

Error in potentiometric titration: P. SIDHESWARAN. (11 *July* 1973)

Oxidimetric determination of thiourea, thiosulphate and sulphite with thallic perchlorate in acid medium: P. D. SHARMA and Y. K. GUPTA. (11 *July* 1973)

Trace analysis by microwave excitation of sealed samples—III: P. F. E. VAN MONTFORT and J. AGTERDENBOS. (11 *July* 1973)

Microdetermination of ruthenium, palladium, osmium and platinum by ring-colorimetry in conjunction with solvent extraction: N. K. KAUSHIK. (11 *July* 1973)

Nile Blue and Brilliant Cresyl Blue as redox indicators in iron(II) titrations: K. SRIRAMAM. (17 *July* 1973)

Determination of iodide with chloramine-T: D. VENKAPPAYYA and G. ARAVUMUDAN. (19 *July* 1973)

Studies on chelate formation of glutamine with some rare earth metals: B. S. SEKHON and S. L. CHOPRA. (19 *July* 1973)

Stability constants of vanadyl complexes with some amino-acids: B. S. SEKHON and S. L. CHOPRA. (19 *July* 1973)

Successive determination of chloride, fluoride and sodium on a single sample of orthophosphate by using ion-selective electrodes: E. J. DUFF and J. L. STUART. (19 *July* 1973)

Instrumental advantages obtained with controlled short drop-time a.c. polarography: A. M. BOND. (20 *July* 1973)

Proton magnetic resonance studies of 8-hydroxyquinoline derivatives: A. CORSINI, W. J. LOUCH and M. THOMPSON. (20 *July* 1973)

Inversion voltammetry of antimony with triphenylmethane dyes: KH. Z. BRAININA and A. B. TCHERNYSHOVA. (20 *July* 1973)

Direct determination of oxygen in organic materials—II. Determination of the carbon monoxide: R. BELCHER, G. INGRAM and J. R. MAJER. (20 *July* 1973)

Potentiometric determination of stepwise stability constants and thermodynamic parameters of some yttrium-(III) chelates: S. P. PANDE and K. N. MUNSHI. (25 *July* 1973)

Thermometric titration of acids in pyridine: RAUL VIDAL and L. M. MUKHERJEE. (25 *July* 1973)

Analysis by phase titration of ternary mixtures containing mutually miscible components: S. K. SURI. (25 *July* 1973)

Spectrophotometric determination of cobalt with 1-(2-pyridylazo)-2-naphthol and surfactants: HIROTO WATANABE. (20 *July* 1973)

Proton affinity constants of *N*-salicylideneglycine: MISS R. PANI and B. BEHERA. (25 *July* 1973)

Indirect complexometric determination of beryllium: A. DE SOUSA. (7 *August* 1973)

The determination of traces of Mo in soils and geological materials by AAS, using solvent extraction of the molybdenum thiocyanate complex: C. H. KIM, C. M. OWENS and L. E. SMYTHE. (7 *August*, 1973)

The determination of some 1,4-benzodiozepines and their metabolites in body fluids: JOHN M. CLIFFORD and W. FRANKLIN SMYTH. (7 *August* 1973)

Simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroazoles and criteria for their identification—II. Nitropyrazoles-chromatographic separation and polarographic determination: D. DUMANOVIĆ, R. MAKSIMOVIĆ, D. JEREMIĆ and J. ĆIRIĆ. (7 *August* 1973)

Spectrophotometric study of the reactions of arsenazo III with alkaline earth metals: V. MICHAYLOVA and N. KOULEVA. (25 *July* 1973)

Preparation and storage of aqueous solutions of sodium 1,2,3,4-thiatriazol-5-thiolate, $NaCS_2N_3$: EDUARDO A. NEVES and DOUGLAS W. FRANCO. (15 *August* 1973)

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NOTICE

ANALYTICAL CHEMISTRY DIVISION, IUPAC

Following the elections at the XXVI Conference of IUPAC at Washington D.C., U.S.A., in 1971, the composition of the Division Committee, responsible for the administration of the Division, is as follows:

President: Prof. W. Kemula (Poland)
Vice-President: Prof. N. Tanaka (Japan)
Secretary: Mr. R. W. Fennell, Materials Department,
Royal Aircraft Establishment,
Farnborough, Hants, U.K.
Members: Prof. W. Fischer (Germany)
Prof. H. Freiser (U.S.A)
Prof. I. M. Kolthoff (U.S.A)
Prof. O. Samuelson (Sweden)
Prof. B. Tremillon (France)
Prof. T. S. West (U.K.)
Prof. Yu. A. Zolotov (U.S.S.R.)

The main work of the Division is performed by its seven Commissions whose projects are listed below. Brief notes are added where the title of the project is not self-explanatory.

In addition, three *ad hoc* Committees are studying:

(*a*) the production of a compendium of analytical nomenclature
(*b*) key-coding of abstracts of papers to indicate the presence of numerical and other data
(*c*) information storage and retrieval in analytical chemistry.

Commission V.1 Analytical Reactions and Reagents

Chairman: Prof. R. Belcher (U.K.)
Secretary: Prof. F. Pellerin, Laboratoire de Chimie organique,
Faculté de Pharmacie,
Université de Paris,
4 avenue de l'Observatoire,
F-75 Paris 6^e, France.

Projects: 1.1 Analytical methods for the control of food additives.
The Commission, in cooperation with the Food Section, Applied Chemistry Division, recommends suitable standard methods of analysis of food additives in fulfilment of the contract between IUPAC and CEE.
1.2 Methods for the determination of phenols.
1.3 The identification and determination of polyphenols.
1.4 The identification and determination of amines.
1.5 Study of redox indicators.
1.6 Standard substances.
Sodium carbonate and sulphamic acid have been recommended as standards for acid-base titrimetry; attention is now being given to standard materials for complexometric titrations.

Commission V.2 Microchemical Techniques and Trace Analysis

Chairman: Dr. O. G. Koch (Germany)
Secretary: Dr. M. Pinta, Office de la Recherche scientifique et technique Outre-Mer,
70–74 route d'Aulnay,
F-93 Bondy, France.

Projects: 2.1 Study on the accuracy and precision of the determination of fluorine in organic compounds.
2.2 The expression of errors in the organic analysis. An examination of the justification for the retention of the classical ±0.3% absolute as a basis for a satisfactory analysis.

2.3 Study on the accuracy and precision of the determination of nitrogen (according to Dumas) in organic compounds.
2.4 Study on the accuracy and precision of the determination of carbon and hydrogen in organic compounds containing heteroelements.
2.5 Study on the accuracy and precision of the determination of metals in organic compounds.
2.6 Study on mass absorption coefficients used in electron beam microanalysis.
2.7 The determination of carbon, hydrogen and nitrogen in organometallic compounds.
2.8 Preconcentration of elements for trace analysis. Difficulties in the destruction of organic matter. and methods of overcoming these, are being studied.
2.9 Availability of standards for trace analysis: Up-to-date data will be compiled about standard substances for trace analysis throughout the world.
2.10 Evaluation of methods of calibration in trace analysis. A study is being made of the most accurate method of calibration for the particular element and matrix.
2.11 Trace analysis of high purity acids. An examination of convenient methods for trace analysis of high purity acids will be made by means of interlaboratory tests.

Commission V.3 Analytical Nomenclature

Chairman: Prof. H. M. N. H. Irving (U.K.)
Secretary: Prof. T. S. West, Department of Chemistry,
Imperial College,
London SW7 2AY, U.K.

Projects: 3.1 Scale of working. Recommendations are being formulated for the exact definition of hitherto ill-defined terms such as micro-, submicro- and trace-analysis.
3.2 Recommendations for the use of the concepts of molarity and normality.
3.3 Trivial names and synonyms of analytical reagents.
3.4 Nomenclature of chromatography.
3.5 Nomenclature of thermal analysis.
3.6 Nomenclature of mass spectrometry.
3.7 Nomenclature of contamination phenomena.
3.8 Nomenclature for a selectivity index. A means whereby the selectivity of a reagent may be simply but accurately indicated is being devised.
3.9 Presentation of analytical papers for publication. The essential information required in the description of newly devised method of analysis is being defined.
3.10 Nomenclature of liquid-liquid extraction.
3.11 Criteria for sensitivity, detection limits, precision and accuracy.
3.12 Nomenclature for ion-selective electrodes.
3.13 Nomenclature of data processing.
3.14 Nomenclature for kinetic methods of analysis.

Commission V.4 Spectrochemical and Other Optical Procedures for Analysis

Chairman: Prof. V. A. Fassel (U.S.A)
Secretary: Mr. B. F. Scribner, Division of Analytical Chemistry,
National Bureau of Standards,
Washington DC 20234, U.S.A.

Projects: 4.1 Terms and symbols related to analytical functions, sensitivity, limit of detection, accuracy and precision.
4.2 Nomenclature of analytical flame spectroscopy and associated procedures.
4.3 Nomenclature of analytical X-ray spectroscopy and associated procedures.
4.4 Systematic classification and description of spectrochemical radiation sources.

These projects will be reported under the general heading "Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis"; Part I "General Atomic Emission Spectroscopy" has been approved for publication in Pure and Applied Chemistry.

Commission V.5 Electroanalytical Chemistry

Chairman: Prof. R. G. Bates (U.S.A.)
Secretary: Prof. J. F. Coetzee, Department of Chemistry,
University of Pittsburgh,
Pittsburgh,
Pennsylvania 15213, U.S.A.

Projects: 5.1 Purification of selected organic solvents. Reports on ethylenediamine, acetonitrile, *N*-methylacetamide, dimethylsulphoxide, pyridine and propylene carbonate have been published; acetic acid, *N*-methylformamide, *N*-methylproprionamide and *N,N*-dimethylformamide are now being considered.
5.2 Purification of electrolytes. Methods for the purification of materials most useful as "supporting electrolytes", *e.g.*, potassium chloride, tetramethylammonium chloride, in electroanalytical measurements.
5.3 Half-wave potentials in *N,N*-dimethylformamide and sulfolane as solvents.
5.4 Nomenclature of electroanalytical methods.
5.5 Pretreatment of solid electrodes.
5.6 p*K* values in *N,N*-dimethylformamide as solvent.
5.7 Conditional diffusion coefficients.
5.8 Recommended symbol for the medium (or solvent) activity coefficient.
5.9 Standardization of ion-selective electrodes and scales of ion activity.
5.10 Application and potentialities of electroanalytical methods in environmental analysis.
5.11 Standard reference materials for calibration of electro-analytical techniques.
5.12 Standard potentials in fused salts.
5.13 Electric double layers at electrode–solution interfaces.

Commission V.6 Equilibrium Data

Chairman: Prof. D. N. Hume (U.S.A.)
Secretary: Dr. F. J. C. Rossotti, Department of Inorganic Chemistry,
University of Oxford,
South Parks Road,
Oxford OX1 3QR, U.K.

Projects: 6.1 Tables of stability constants.
6.2 Distribution equilibria. Phosphorus-containing and oxygenated extractants, alkyl ammonium salts and chelating extractants are being considered.
6.3 Critical surveys of solution equilibrium constants. EDTA, cyanide, gold and halide complexes are under consideration.
6.4 Standard ionic media.
6.5 Information retrieval.
6.6 Symbols and terms for mixed-ligand equilibrium constants.
6.7 Tables of ion exchange equilibrium constants.
6.8 Solubility data.
6.9 Non-aqueous equilibrium data.

Projects 6.8 and 6.9 are feasibility studies of the need for coordination by IUPAC of the compilation of data under the respective headings.

Commission V.7 Analytical Radiochemistry and Nuclear Materials

Chairman: Dr. M. B. A. Crespi (Argentina)
Secretary: Prof. R. E. Wainerdi, Activation Analysis Research Laboratory,
Texas A and M University,
College Station,
Texas 77843, U.S.A.

Projects: 7.1 Application of high-energy photon activation to analysis.
7.2 Light elements (H to F) analysis by radioanalytical methods.

7.3 Intercomparison of analytical methods.

7.4 Reference materials for trace analysis. The Commission has selected samples of (*a*) orchard leaves and (*b*) doped glasses, prepared by the NBS, U.S.A., as reference materials for (*a*) biological and (*b*) inorganic and geochemical trace determination, and is promoting detailed work with them.

7.5 "State of the art" of nuclear materials analysis. At present, uranium oxides, graphite and fissile elements are under study.

7.6 Information sources for analytical radiochemistry and nuclear materials.

7.7 Nomenclature.

7.8 Purity of reagents. The purity of commercial radioactive preparations and the constancy of isotopic composition of some analytical reagents has been queried and the Commission is keeping the subject under review.

7.9 Revision and updating of conventions for flux monitoring.

7.10 Nuclear methods for the determination of key elements in pollution problems. Radioanalytical methods for the determination of lead, mercury and cadmium are being critically reviewed.

SUMMARIES FOR CARD INDEXES

Electronic absorption and fluorescence of 9-anthraldehyde and its conjugate cation: John F. Young and Stephen G. Schulman, *Talanta*, 1973, **20**, 399. (College of Pharmacy, University of Florida, Gainesville, Florida 32601, U.S.A.).

Summary—The appearance or lack of vibrational structure in the ^1L_a and ^1L_b absorption bands of the neutral species and cation derived from 9-anthraldehyde is explained in terms of adherence to or violation of the Franck-Condon principle. The lack of vibrational structure is attributed to the motions of the aldehyde group during the course of electronic transition, a process which destroys vibration quantization in the Franck-Condon excited state. The appearance of well-defined vibrational structure in the ^1L_a band of the cation establishes that intramolecular charge-transfer alone, without accompanying vibrational or solvent relaxation which is contemporaneous with electronic transition, is not responsible for the lack of structure in most intramolecular charge-transfer transitions. The previously reported fluorescence of 9-anthraldehyde in hydroxylic solvents is found to be in error and is likely to originate from an impurity produced by photo-reduction. The actual fluorescence of 9-anthraldehyde is at much lower frequency than previously reported.

The adsorption of silver on potassium cyanocobalt(II)ferrate(II): M. Wald, W. Soyka and B. Kaysser, *Talanta*, 1973, **20**, 405. (Zentralinstitut für Analytische Chemie der Kernforschungsanlage Jülich, 517 Jülich, Bundesrepublik Deutschland).

Summary—A procedure is described for recovering silver from industrial sewage (mining and photo-industry, *etc*) with the aid of the ion-exchanger potassium cyanocobalt(II)ferrate(II) (KCFC). Silver is easily removed by simple mixing with KCFC, even from solutions containing less than 1 g of silver per ton of solution. The process is performed at room temperature at pH $\leqq 7$. There is no interference from a 600-fold amount of Ca, Cu(II), Zn, Cd, Pb, and Fe(II). Pure silver may be obtained by dissolution of the ion-exchanger in potassium cyanide solution, subsequent precipitation as sulphide, and roasting, or by melting it out of the ion-exchanger after heat treatment in a high-frequency furnace. With 1 kg of KCFC, 1·25 kg of silver may be extracted from solution. The process is simple and economic.

Microtitrimetric determination of uranium in tributylphosphate (30%)–n-dodecane–nitric acid medium in the presence of excess of ion, magnesium and aluminium,: V. Mareška and V. Šraier, *Talanta*, 1973, **20**, 411 (Nuclear Research Institute ČSKAE, Řež near Prague, Czechoslovakia).

Summary—A method is described for microdetermination of uranium in aqueous phases containing nitric acid, iron, magnesium, aluminium and traces of TBP, and in organic phases containing TBP, n-dodecane and nitric acid. Treatment of the organic phase strips the uranium, reduces it to U(IV), and destroys any nitrite present.

Indirect atomic-absorption determination of boron by solvent extraction as tris(1,10-phenanthroline)cadmium tetrafluoroborate: Y. Hayashi, S. Matsushita, T. Kumamaru and Y. Yamamoto, *Talanta*, 1973, **20**, 414. (Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima, Japan).

Summary—An indirect atomic-absorption method for boron has been developed. Boric acid is converted into tetrafluoroborate and extracted into nitrobenzene with Tris(1,10-phenanthroline)cadmium(II). The cadmium in the extract is determined by its atomic-absorption at 228·8 nm. A five-fold molar excess of the cadmium chelate is necessary for the extraction from pH 4·3–6·0 medium. The sensitivity for boron is thus made about the same as that of cadmium, 0·005 ppm. Metal ions that react with fluoride or phenanthroline interfere. A procedure is described for determination of boron in steel.

Злектронное поглощение и флуоресценция 9-антральдегида и его сопряженного катиона: John F. Young and Stephen G. Schulman, *Talanta* 1973, **20**, 399.

Резюме — Присутствие или отсутствие вибрационной структуры в полосах поглощения ${}^1L_a$ и ${}^1L_b$ нейтрального рода и катиона произведенного из 9-антральдегида протолковано на основе почитания или нарушения принципа Франка-Кондона. Отсутствие вибрационной структуры приписывают движению альдегидной группы в течение перескока электронов — процессу, разрушающему квантизацию вибрации в возбужденном состоянии Франка-Кондона. Появление хорошо определенной вибрационной структуры в полосе ${}^1L_a$ катиона показывает что отсутствие структуры в большинстве интрамолекулярных переходов на основе переноса заряда не надо приписать только интрамолекулярному переносу заряда, без сопровождающей вибрационной или растворителевой релаксации, которая появляется одновременно с переходом электронов. Приведенная ранее флуоресценция 9-антральдегида в гидроксильных растворителях оказалась ошибочной; она вероятно вызвана примесью, произведенной фотовосстановлением. Действительная флуоресценция 9-антральдегида появляется при частоте существенно ниже чем опубликованной раньше.

Адсорбция серебра на цианокобальто(II)феррате(II) калия: M. Wald, W. Soyka and B. Kaysser, *Talanta* 1973, **20**, 405.

Резюме — Описан метод рекуперации серебра из сточных вод промышленности (рудной и фотографической) с помощью ионообменника цианокобальто(II)феррата(II) калия (ЦКФК). Серебро рекуперируют простим смешиванием с ЦКФК, даже из растворов содержащих меньше чем 1 г серебра в тоне раствора. Процесс проводят при комнатной температуре и pH <7. 600-кратный избыток Ca, Cu(II), Zn, Cd, Pb, и Fe(II) не мешает выделению. Чистое серебро можно получить растворением ионообменника в растворе цианида калия, осаждением в форме сульфида и кальцинированием, или плавлением из ионообменника после обработки в высокочастотной печи. Один кг ЦКФК позволяет извлечь 1,25 кг серебра из раствора. Процесс является несложным и экономным.

Микротитрометрическое определение °рана в растворах трибутилфосфат(30%)-н-додекан-азотная кислота в присутствии избытка железа, магния и алюминия: V. Mareška and V. Šraier, *Talanta* 1973, **20**, 411

Резюме — Описан метод микроопределения урана в водных растворах содержащих азотную кислоту, железо, магний, алюминий и следы ТБФ, и в органических средах содержащих ТБФ, н-додекан и азотную кислоту. Обработка органической фазы устраняет уран, восстанавливает его в U(IV) и разлагает нитрит если присутствует в растворе.

Косвенное определение бора методом атомно-абсорбционной спектрометрии на основе экстрагирования растворителем в форме тетрафторбората трис(1,10-фенантролин)кадмия: Y. Hayashi, S. Matsushita, T. Kumamaru and Y. Yamamoto, *Talanta* 1973, **20**, 414.

Резюме — Разработан косвенный метод атомно-абсорбционной спектрометрии для определения бора. Борную кислоту превращают в тетрафторборат и экстрагируют раствором трис(1,10-фенантролин/кадмия(II) в нитробензоле. Кадмий в экстракте определяют на основе его атомного поглощения при 228,8 нм. Надо использовать пятикратный избыток хелата кадмия для экстрагирования из среди при pH 4,3–6,0. Этим образом чувствительность для бора равна чувствительности для кадмия — 0,005 ч. на миллион. Реагирующие с фторидом или фенантролином ионы металлов мешают определению. Описана методика определения бора в стали.

Separation and quantitative determination of the cerium group lanthanides by gas–liquid chromatography: CHARLES A. BURGETT and JAMES S. FRITZ, *Talanta*, 1973, **20**, 363. (Ames Laboratory, USAEC, Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.).

Summary—A gas chromatographic method is reported for the separation and subsequent quantitative determination of the cerium group lanthanides. The lanthanides (RE) are synergistically extracted from aqueous solution with the polyfluorinated β-diketone 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD), as ligand, and di-n-butylsulphoxide, DBSO, as neutral donor. The composition of the extracted species is reported to be $RE(FHD)_3 \cdot 2DBSO$. Thermogravimetric analysis of the complexes is reported. Analytical curves were prepared and found to be usable over the range of 0·1–10 μg of metal. Individual lanthanides were determined with 99·0% recovery with a relative mean deviation of ±2·0%. Mixtures of lanthanides were analysed with 101·2% recovery with a relative mean deviation of ±2·2%.

Coulometric titration of acids in isopropanol—II. Electrode reactions with lithium chloride and tetraethylammonium bromide as supporting electrolytes: B. G. COOKSEY, B. METTERS, J. M. OTTAWAY and D. W. WHYMARK, *Talanta*, 1973, **20**, 371 (Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow, C.1, Scotland).

Summary—Cathodic reactions in methanol and isopropanol have been investigated in the presence of both lithium chloride and tetraethylammonium bromide as supporting electrolytes. A side-reaction in lithium chloride medium leads to the formation of insoluble lithium hydroxide but base is generated stoichiometrically in tetrathylammonium bromide by reduction of solvent, oxygen and traces of water. Tetraethylammonium bromide is recommended as supporting electrolyte for the coulometric titration of acids in isopropanol.

Some observations on the redox behaviour of *N*-phenylanthranilic acid indicator in iron(II) titrations: K. SRIRAMAM, *Talanta*, 1973, **20**, 383. (Department of Chemistry, Andhra University Postgraduate Centre, Guntur-5 (A.P.), India.)

Summary—The optimum conditions for the successful use of *N*-phenylanthranilic acid as indicator in titrations of iron(II) with dichromate, cerium(IV) sulphate and vanadate have been established. The influence of iron(III) on the indicator action, and the nature of a green compound formed from the indicator in iron(II) titrations, have been investigated spectrophotometrically.

Determination of nanogram amounts of sulphide by release of radioactive iodide: V. KRIVÁŇ, S. PAHLKE and G. TÖLG, *Talanta*, 1973, **20**, 391. (Max-Planck-Institut für Metallforschung, Laboratorium für Reinststoffe, Schwäbisch Gmünd, German Federal Republic).

Summary—Two variants of a technique for determination of ng-amounts of sulphide ions in liquid samples are presented. They are based on the replacement of radioactively labelled iodide from silver iodide by sulphide. In the first variant, suitable for small sample volumes, the labelled silver iodide is fixed on a filter paper disc which is then shaken with the solution to be analysed until equilibrium is attained. In the second variant, suitable for sample volumes up to 300 ml. the sample solution is passed through a filter paper disc carrying labelled silver iodide or through a labelled silver iodide precipitate. The amount of sulphide is determined from the activity of the released radioiodide by comparison with standards which have been processed radioiodide by comparison with standards which have been processed in the same way. The method is applicable to sulphide amounts greater than 5 ng and concentrations greater than 0·2 ppM. The interference by many common accompanying anions and cations has been investigated.

Разделение и количественное определение цериевой группы лантанидов методом газо-жидкостной хроматографии: Charles A. Burgett and James S. Fritz, *Talanta* 1973, **20**, 363

Резюме — Приведен метод газо-жидкостной хроматографии для разделения и последующего количественного определения цериевой группы лантанидов. Лантаниды (RE) экстрагируются синергетически из водного раствора с помощью полифторированного дикетона 1,1,1,2,2,6,6,7,7,7-декафтор-3,5-гептандиона Н(ФГД) в качестве диганда и ди-н-бутилсульфоксида ДБСО в качестве нейтрального донора. Состав экстрагированного соединения — RE(ФГД)$_3$. 2ДБСО. Приведены результаты термогравиметрического анализа комплексов. Построены аналитические кривые, которые оказались используемыми в диапазоне 0,1.10 мкг металла. Индивидуальные лантаниды определены с выходом 99,0%, а с относительной стандартной ошибкой ±2,0%. Смеси лантанидов анализированы с выходом 101,2%, а с относительной стандартной ошибкой ±2,2%.

Кулонометрическое титрование кислот в изопропаноле — II. Злектродные реакции в присутствии хлорида лития и бромида тетраэтиламмония в качестве фонового электродита: B. G. Cooksey, B. Metters, J. M. Ottaway and D. W. Whymark, *Talanta* 1973, **20**, 371

Резюме — Изучены катодные реакции в метаноле и изопропаноле в присутствии хлорида лития и бромида тетраэтиламмония в качестве фонового электролита. Побочная реакция в растворе хлорида лития водит к образованию нерастворимой гидроокиси лития, но стехиометрическое количество основы образуется в бромиде тетраэтиламмония, восстановлением растворителя, кислорода и следов воды. Бромид тетраэтиламмония предложен в качестве фонового электролита для кулонометрического титрования кислот в изопропаноле.

Некоторые наблюдения в связи с окислительно-восстановительным характером индикатора *N*-фенилантраниловой кислоты при титровании железа(II): K. Sriramam, *Talanta* 1973, **20**, 383.

Резюме — Определены оптимальные условия использования *N*-фенилантраниловой кислоты в качестве индикатора для титрования железа(II) дихроматом, сульфатом церия(IV) и ванадатом. Исследованы спектрофотометрическим методом влияние железа(III) на действие индикатора и природа зеленого соединения образующегося из индикатора при титровании железа(II).

Определение нанограммовых количеств сульфида на основе выпускания радиоактивного иодида: V. Krivan, S. Pahlke and G. Tölg, *Talanta* 1973, **20**, 391.

Резюме — Предложены два варианта метода определения нанограммовых количеств сульфидионов в жидких пробах. Они основаны на замещению радиоактивного иодида из иодида серебра сульфидом. В первом варианте, подходящем для небольших объемов пробы, меченый иодид серебра фиксируют на диске фильтровальной бумаги, который затем встряхивают с анализируемым раствором до получения равновесного состояния. Во втором варианте, подходящем для объемов пробы вплоть 300 мл, раствор пробы пропускают через диск фильтровальной бумаги с меченым иодидом серебра или через осадок меченого иодида серебра. Количество сульфида определяют на основе активности освобожденного радиоиодида сравнением с эталонами, обработанными тем же путем. Метод применим для количеств сульфидов больше чем 5 нг и концентраций больше чем 0,2 ч. на миллиард. Исследовано влияние ряда обыкновенных сопровождающих анионов и катионов.

Sulphonated azo-dyes as extractive metallochromic reagents: Colin Woodward and Henry Freiser, *Talanta*, 1973, **20**, 417. (Department of Chemistry, University of Arizona, Tucson, Arizona 87521, U.S.A.).

Summary—A survey has been made of analytically useful extractable ion-pair complexes that are formed by the use of a series of metallochromic indicator–metal complexes in conjunction with quarternary ammonium ions. The reagents were *o,o'*-dihydroxyazo dyes and azo-oxines.

N-(2-acetyl-1,3-indandione-1-hydrazone)trialkylammonium iodides as a new group of reagents for the carbonyl group: M. K. Bachlaus and K. L. Menaria, *Talanta*, 1973, **20**, 420. (Defence Laboratory, Jodhpur, Rajasthan, India, and Department of Chemistry, University of Jodhpur, Jodhpur, India).

Summary—Monohydrazones of *N*-(2-acetyl-1,3-indandione)trialkylammonium iodides have been synthesized and used as reagents for the carbonyl group. Aldehydes, ketones, keto-acids and cyclic ketones react with these compounds, producing a yellow colour. Carbonyl compounds can be identified by the absorption of their derivatives with these reagents.

Sulpholane as colour-enhancing and stabilizing agent for silicomolybdic acid: H. Flaschka and J. J. Tive IV, *Talanta*, 1973, **20**, 423. (School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, U.S.A.).

Summary—Addition of between 20 and 40% v/v sulpholane gives a colour enhancement of silicomolybdic acid better than that achieved with acetone. The β-silicomolybdic acid is stabilized, and solutions yielding a pH-meter reading of 0·1–1·8 give the best results. The photometric measurement is made at about 400 nm. Another advantage of sulpholane is its much lower volatility.

o-Amino heterocyclic azo-dyes as analytical reagents—II. Spectrophotometric determination of cobalt with 3-[(5-chloro-2-pyridyl)azo]-2,6-diaminopyridine: Shozo Shibata, Masamichi Furukawa and Kazuo Goto, *Talanta*, 1973, **20**, 426. (Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya, Japan).

Summary—Cobalt(II) and 3-[(5-chloro-2-pyridyl)azo]-2,6-diaminopyridine (5-Cl-PADAPy) in slightly acid, neutral or alkaline media form a blue complex which is very stable even in the presence of mineral acids. The complex has two absorption maxima, at 575 and 620 nm, in 1·2*M* hydrochloric acid. The system conforms to Beer's law; the optimal range for a 1-cm cell is 0·2–1.2 ppm cobalt. Milligram amounts of common anions and cations do not interfere. The molar absorptivity is 3·69 × 10^4 l.mole^{-1}.cm^{-1} at 620 nm.

Metal complexation with 2-hydroxy-6-methylpyridine-3-carboxylic acid: Veena Kushwaha, R. P. Singh and Mohan Katyal, *Talanta*, 1973, **20**, 431. (Department of Chemistry, University of Delhi, Delhi-7, India and St. Stephen's College, Delhi-7, India).

Summary—Metal complexation with 2-hydroxy-6-methylpyridine-3-carboxylic acid has been studied. The ligand finds use in detection and determination of iron(III). The order of stability constants of the bivalent transition metal complexes is Cu > Zn > Fe > Ni > Co > Mn.

Сульфонированные азокрасители в качестве экстрактивных металлохромных реагентов: Colin Woodward and Henry Freiser, *Talanta* 1973, **20**, 417

Резюме — Приведен обзор используемых в анализе экстрагируемых комплексов на основе парных ионов, образующихся с использованием ряда металлохромных комплексов индикаторметалл в присутствии ионов четвертичного аммония. Реагенты представляли собой *о,о*'-диоксиазокрасители и азооксины.

Иодиды *N*-(2-ацетил-1,3-индандион-1-гидразон)триалкиламмония в качестве новой группы реагентов для карбонильной группы: K. Bachlaus and K. L. Menaria, *Talanta* 1973, **20**, 420.

Резюме — Синтезированы моногидразоны иодидов *N*-(2-ацетил-1,3-индандион/триалкиламмония и использованы в качестве реагентов для карбонильной группы. Альдегиды, кетоны, кетокислоты и циклические кетоны реагируют с этими соединениями с проявлением желтого цвета. Карбонильные соединения могут быть идентифицированы на основе поглощения их производных с этими соединениями.

Сульфолан в качестве усиливающего и стабилизирующего цвет реагента для силикомолибденовой кислоты: H. Flaschka and J. J. Tive IV, *Talanta* 1973, **20**, 423.

Резюме — Добавление раствору 20–40% по объему сульфолана усиливает цвет силикомолибденовой кислоты лучше чем ацетон. Реагент стабилизирует β-силикомолибденовую кислоту, а самые лучшие результаты получены в растворах показывающих pH 0,1–1,8. Светопоглощение измеряют при 400 нм. Еще одним премуществом сульфолана является его низкая летучесть.

***о*-Амино гетероциклические азокрасители в качестве аналитических реагентов — II. Спектрофотометрическое определение кобальта 3-[(5-хлор-2-пиридил)азо]-2,6-диаминопиридином:** Shozo Shibata, Masamichi Furukawa and Kazuo Goto, *Talanta* 1973, **20**, 426.

Резюме — Кобальт(II) образует с 3-[(5-хлор-2-пиридил)азо]-2,6-диаминопиридином (5-Cl-ПАДАП) в слабокислых, нейтральных или шелочных растворах синий комплекс, который является весьма устойчивым даже в присутствии минеральных кислот. Комплекс показывает два максимума светопоглощения, при 575 и 620 нм, в 1,2*M* соляной кислоте. Система почитает закон Бера. Оптимальная област концентраций с использованием кюветки 1 см — 0,2–1,2 ч. на миллион кобальта. Миллиграммовые количества обыкновенных анионов и катионов не мешают определению. Молярное светопоглощение составляет $3{,}69 \times 10^4$ л.моль$^{-1}$.см$^{-1}$ при 620 нм.

Образование комплексов металлов с 2-окси-6-метилпиридин-3-карбоновой кислотой: Veena Kushwaha, R. P. Singh and Mohan Katyal, *Talanta* 1973, **20**, 431.

Резюме — Изучено образование комплексов металлов с 2-окси-6-метилпиридин-3-карбоновой кислотой. Лигандом можно пользоваться в обнаружении и определении железа(III). Константы устойчивости комплексов двувалентных переходных металлов уменьшаются в порядке Cu > Zn > Fe > Ni > Co > Mn.

SUMMARIES FOR CARD INDEXES

Locating the more acidic hydroxyl group on dihydroxy compounds. *o,o'*-dihydroxyazo-dye metal-ion indicators: FREDERICK LINDSTROM and ANN EDWARDS WOMBLE, *Talanta*, 1973, **20**, 589 (Department of Chemistry and Geology, Clemson University, South Carolina 29631, U.S.A.).

Summary—In *o,o'*-dihydroxyazo-dye metal-ion indicators, one hydroxyl group is 10^4 times more acidic than the other. The location of the more acidic group has been a mystery. By methylation of the acidic group, reduction of the monomethylated compound, isolation and characterisation of the split methoxyamine and hydroxyamine, the location of the acidic group has been established. Indicators examined include Calmagite, Eriochrome Black T, Eriochrome Blue Black R and 4-(2-pyridylazo)resorcinol (PAR).

Application of various electrodes in potentiometric titration of calcium: ADAM HULANICKI and MAREK TROJANOWICZ, *Talanta*, 1973, **20**, 599. (Institute of Fundamental Problems in Chemistry, University of Warsaw, Poland).

Summary—In complexometric titrations various indicator electrodes may be employed for monitoring the course of titration and for detection of the end-point. Several of them, including the silver, mercury, bivalent cation membrane, calcium membrane and manganese dioxide electrodes were investigated and compared in their usefulness. As titrant, EDTA was mostly used, but results with similar chelating titrants were also obtained. The practical utility of the electrodes in titrations depends on their selectivity, magnitude of the end-point break and precision in determination of the end-point. For the electrodes studied, in some instances there is good correlation between the theoretical and experimental titration curves, but it is not always possible to predict the electrode response in the low activity range. In other cases poor correlation does not mean that reasonably good analytical results may not be obtained.

Comparative study of titanium(IV)-based exchangers in aqueous and mixed solvent systems: MOHSIN QURESHI, NIGHAT ZEHRA, SYED ASHFAQ NABI and VIRENDRA KUMAR, *Talanta*, 1973, **20**, 609 (Department of Chemistry, Aligarh Muslim University, Aligarh, U.P. India)

Summary—The antimonate, arsenate, tungstate, molybdate and selenite of titanium have been synthesized. Their composition and chemical and thermal stability have been determined. Effects of pH and temperature on ion exchange capacity have been studied. Titanium antimonate was found to be the most thermally stable. The utility of these ion-exchangers for analytical separations was examined by determining the distribution coefficients for 26 metal ions in some aqueous, non-aqueous and mixed solvent systems. Quantitative separations of Hg–Cd, Pb–Cu and Pb–Zn have been achieved on titanium tungstate columns, and La–Ba mixtures have been separated on a titanium arsenate column.

Oxidative coulometric trace determination of sulphur in hydrocarbons: ANDERS CEDERGREN, *Talanta*, 1973, **20**, 621. (Department of Analytical Chemistry, University of Umeå, S-901 87 Umeå, Sweden.)

Summary—A new combustion system for the oxidative coulometric determination of sulphur in liquid hydrocarbons is described. The conditions were selected so that the recovery as SO_2 was close to 100%. The relative standard deviation was <1% for sulphur in the range 2–1000 mg/l., with thiophene in cyclohexane as a test substance. Thermodynamic data on the equilibrium between SO_2, O_2 and SO_3 were used to select the operating conditions. To increase the recovery of SO_2 the combustion gas mixture was diluted with an inert gas to lower the partial pressure of oxygen. A temperature of 1000° in the equilibrium zone resulted in a recovery of 99%. The SO_2 was titrated with coulometrically generated iodine, the concentration of which was controlled by a Pt-redox electrode. The response of this electrode has been examined. A rather high concentration of I^- was used to suppress iodine losses during the analysis. The time of analysis was 2–5 min, and sample sizes were 3–7 μl. An LKB 16300 Coulometric Analyzer governed the titration procedure.

Определение местоположения более кислой гидроксильной группы в диоксисоединениях: *o,o'*-диоксиазокрасители в качестве индикаторов для ионов металлов: FREDERICK LINDSTRÖM and ANN EDWARDS WOMBLF, *Talanta* 1973, **20**, 589.

Резюме — В *o,o'*-диоксиазокрасителях использованных в качестве индикаторов для ионов металлов кислотность одной гидроксильной группы 10^4 выше чем кислотность другой группы. Местоположение более кислой группы было неизвестно. Оно определено метиляцией кислотной группы, восстановлением монометилированного соединения, изолированием и характеризированием отделенных метоксиамина и оксиамина. Изученные индикаторы включали Калмагит, эриохром черный T, эриохром сине-черный R и 4-/2-пиридилазо/резорцинол (ПАР).

Использование различных электродов для потенциометрического титрования кальция: ADAM HULANICKI and MAREK TROJANOWICZ, *Talanta* 1973, **20**, 599

Резюме — При комплексонометрических титрованиях можно пользоваться разными индикаторными электродами для прослеживания хода титрования и для обнаружения конца титрования. Некоторые из них, в том числе серебряный, ртутный электроды, электроды с двувалентной катионной мембраной и кальциевой мембраной и электрод двуокиси марганца были исследованы и их полезность сравнена. В большинстве случаев использовали ЭДТА в качестве титрованного раствора но испытаны также подобные хелатообразующие титранты. Практическая полезность электродов зависит от их селективности, величины скачка потенциала при конце титрования и воспроизводимости определения конца титрования. Для исследованных электродов в некоторых случаях получена хорошая корреляция между теоретическими и экспериментальными титрационными кривыми, но не удалось во всех случаях предсказать ответ электрода в области низких активностях. В других случаях недовольная корреляция не исключает применимость электрода в анализе.

Сравнительное изучение ионообменников на основе титана(IV) в водных средах и средах смешанных растворителей: MOHSIN QURESHI, NIGHAT ZEHRA, SYED ASHFAQ NABI and VIRENDRA KUMAR, *Talanta* 1973, **20**, 609.

Резюме — Приготовлены антимонат, арсенат, вольфрамат, молибдат и селенит титана. Определены их состав и химическая и термическая устойчивость. Изучено влияние pH и температуры на их ионообменную ёмкость. Антимонат титана оказался наиболее термически устойчивым производным. Изучена применимость этих ионообменников в анализе путем определения коэффициентов распределения 26 ионов металлов в некоторых водных, неводных и смешанных систем растворителей. Получены количественные разделения Hg–Cd, Pb–Cu и Pb–Zn на колонках вольфрамата титана, а смеси La–Ba разделены на колонке арсената титана.

Кулонометрическое определение следов серы в углеводородах путем окисления: ANDERS CEDERGREN, *Talanta* 1973, **20**, 621.

Резюме — Описана новая система сжигания для окислительного кулонометрического определения серы в жидких углеводородах. Отобраны условия дающие выход SO_2 около 100%. Относительная стандартная ошибка составляет <1% для серы в пределах 2–1000 мг/л, с использованием тиофена в циклогексане в качестве испытуемого вещества. Условия определения отобраны на основе термодинамических данных для равновесия SO_2, O_2 и SO_3. Для повышения выхода SO_2 смесь сжигаемых газов разбавлена инертным газом для снижения парциального давления кислорода. Температура 1000° в зоне равновесия дала выход 99%. SO_2 титровали иодом генерированным кулонометрическим путем, концентрацию которого регулировали с помощью платинового окислительно-восстановительного электрода. Изучен ответ этого электрода. Использована довольно высокая концентрация I^- чтобы подавились потери иода в течение анализа. Продолжительность анализа 2–5 мин., а объем проб — 3 до 7 мкл. Титрование проведено на кулонометрическом приборе ЛКБ 16300.

Suppression of interference in the AAS determination of chromium by use of ammonium bifluoride: A. Purushottam, P. P. Naidu and S. S. Lal, *Talanta*, 1973, **20**, 631. (Central Laboratories, Airborne Mineral Surveys and Exploration, Geological Survey of India, Faridabad, India).

Summary—Addition of 1% of ammonium bifluoride successfully suppresses interference by diverse ions in the atomic-absorption determination of chromium(VI). If the sample solutions also contain chromium(III) addition of 1% of ammonium bifluoride and 0·2% of sodium sulphate is recommended for the suppression.

***o*-(2-Hydroxy-5-Dodecylphenylazo)Benzoesäure und -Arsonsäure als Chelatbildner flüssiger Ionenaustauscher:** E. Blasius und H. J. Finkenauer, *Talanta*, 1973, **20**, 639. (Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 66 Saarbrücken 15, West Germany).

Summary—The syntheses of two new chelating agents, *o*-(2-hydroxy-5-dodecylphenylazo)benzoic acid and the corresponding arsonic acid, are described. Solutions of these in benzene or in chloroform have been used as liquid ion-exchangers for the separation of Be and Al, and of Zr and Hf. Both have proved useful for the separation of traces of Fe(III) from solutions of salts.

Determination of impurities in high-purity gold, with a gas-stabilized low-temperature arc: B. Zmbova and M. Marinković, *Talanta*, 1973, **20**, 647. (Boris Kidrič Institute, Vinča, 11001 Beograd, Yugoslavia).

Summary—A gas-stabilized arc with aerosol supply has been used for emission spectrometric determination of Al, B, Be, Co, Cr, Fe, Ga, In, Mg, Mn, Ni, Pd, Rh and Zn, as impurities in high-purity gold. Two analytical procedures were compared: (*a*) direct aspiration of dissolved samples containing 2% of gold and 0·25*M* KCl as buffer, and (*b*) separation of impurities by ether extraction of gold from 1*N* HCl followed by impurity determination with a stabilized arc. Limits of detection, precision and recovery of the extraction procedure are given.

Application of the zone-melting technique to metal chelate systems—VI. A new apparatus for zone-melting chromatography: Shigeru Maeda, Hiroshi Kobayashi and Keihei Ueno®, *Talanta*, 1973, **20**, 653. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.)

Summary—An improved apparatus has been constructed for zone-melting chromatography. An essential feature of the apparatus is that the length of the molten zone can be kept constant during the zone-melting operation, by employing heating and cooling compartments which are separated from each other by double partition plates. Each compartment is heated or cooled with jets of hot or cold air. The apparatus is suitable for organic materials melting in the range between 40° and 180°. The distribution of metal ion along the column after zone melting of copper acetylacetonate in 2-methoxynaphthalene was a smooth curve. The plot of the position of maximum concentration, x_{max}, against the number of zone passes, n, gave a relationship in accordance with theoretical prediction.

A polarographic study of the pre-sodium type catalytic hydrogen wave exhibited by selenocystine: V. Voicu and A. Căluşaru, *Talanta*, 1973, **20**, 659. (Institute of Atomic Physics, Bucharest, Romania).

Summary—Selenocysteine, formed by reduction of selenocystine at the DME at about −0·6 V in an ammoniacal buffer, produces a pre-sodium catalytic hydrogen wave. The effects on this wave of variation of several physico-chemical parameters such as selenocystine concentration, mercury column height, buffer capacity and concentration, and ionic strength, have been studied. The results obtained all support the conclusion that the wave is of pre-sodium type. The partially protonated species of selenocysteine seem to be catalytically active. An analytical determination of selenocystine in the presence of selenocysteine, based on this study, is proposed.

Подавление помех в определении хрома методом атомно-абсорбционной спектрометрии с использованием бифторида аммония: A. Purushottam, P. P. Naidu and S. S. Lal, *Talanta* 1973, **20**, 631.

Резюме — Добавление 1% бифторида аммония успешно устраняет мешающее действие некоторых ионов при определении хрома(VI) методом атомно-абсорбционной спектрометри. В случае присутствия в пробе хрома(III) предложено добавление раствору 1% бифторида аммония и 0,2% сульфата натрия.

о-(2-Окси-5-додецилфенилазо)бензойная и-арсоновая кислоты в качестве хелатообразующих жидких ионообменников: E. Blasius and H. J. Finkenauer, *Talanta* 1973, **20**, 639.

Резюме — Описан синтез двух новых хелатообразующих агентов — *о*-(2-окси-5-додецилфенилазо)бензойной кислоты и соответствующей арсоновой кислоты. Растворы этих кислот в бензоле или хлороформе использованы в качестве жидких ионообменников для разделения Be и Al и Zr и Hf. Оба ионообменника оказались полезными для выделения следов Fe(III) из растворов солей.

Определение примесей в высокочистотном золоте с использованием стабилизированной газом низкотемпературной дуги: B. Zmbova and M. Marinković, *Talanta* 1973, **20**, 647.

Резюме — Стабилизированная газом дуга с аеросоловым питанием использована для определения Al, B, Be, Co, Cr, Fe, Ga, In, Mg, Mn, Ni, Pd, Rh и Zn в форме примесей в высокочистотном золоте методом эмиссионной спектрографии. Сравнены два аналитических метода: а) непосредственная аспирация растворенных образцов содержащих 2% золота и 0,25 *M* KCl в качестве буффера, и б) отделение примесей экстрагированием золота эфиром из 1 *N* HCl с последующим определением примесей с использованием стабилизированной дуги. Приведены чувствительность, воспроизводимость и выход экстракционного метода.

Применение метода зонального плавления на системы хелатов металлов — VI. Новый прибор для хроматографии на основе зонального плавления: Shigeru Maeda, Hiroshi Kobayashi and Keihei Ueno[R], *Talanta*, 1973, **20**, 653.

Резюме — Сконструирован улучшенный прибор для хроматографии на основе зонального плавления. Сущность прибора в том что он позволяет поддерживать длину расплавленной зоны постоянной в течение операции зонального плавления, пользуясь камерами для нагревания и охлаждения, разделенными двойними перегородками. Каждая камера нагревается или охлаждается струёй горячего или холодного воздуха. Прибор подходящий для органических веществ плавящихся в области 40–180°. Распределение ионов металлов вдоль колонки после зонального плавления ацетилацетоната меди в 2-метоксинафталине представлено гладкой кривой. Зависимость местоположения максимальной концентрации $x_{\text{макс}}$ от числа зональных проходов *n* была в согласности с теоретическими предсказаниями.

Полярографическое изучение каталитической водородной волны переднатриевого типа проявленной селеноцистином: V. Voicu and Calusaru, *Talanta* 1973, **20**, 659.

Резюме — Селеноцистеин, образующийся при восстановлении селеноцистина на капельном ртутном электроде при −0,6 в, в растворе аммиачного буффера, дает переднатриеву каталитическую водородную волну. Изучено влияние на эту волну ряда физикохимических параметров, в том числе концентрации селеноцистина, высоты ртутного столба, ёмкости и концентрации буффера и ионной силы. Все полученные результаты подтверждают переднатриевый характер волны. Кажется что частично протонированный род селеноцистеина обладает каталитической активностью. Предложен аналитический метод определения селеноцистина в присутствии селеноцистеина, основанный на этой работе.

Microdetermination of deuterium in organic compounds: DANIEL FRAISSE, DENISE GIRARD and ROGER LEVY, *Talanta*, 1973, **20**, 667. (Service Central de Microanalyse, du Centre National de la Recherche Scientifique, 2, rue Henry Dunant—94320 Thisis—France).

Summary—A simple method is described for the microdetermination of deuterium in organic compounds. It involves a flash combustion of the weighed sample in a hot empty chamber at 950–1050° and swept by oxygen at 60 ml/min. Together with this combustion in the gaseous phase, an oxidation of the primary combustion gases on cupric oxide at 850° is necessary. Oxidation products containing halogens and sulphur are retained on silvered alumina at 750–800°. Combustion water containing deuterium oxide and hydroxide is frozen out from the combustion gases in a special trap with two five-way stop-cocks which make possible the simultaneous flow of oxygen and hydrogen; the latter is used as a carrier-gas in the apparatus from the trap downwards. The frozen water is then vaporized by heating in a hydrogen flow of 30 ml/min and reduced on magnesium at 600°. Deuterium is obtained as deuterium hydride in hydrogen; it is measured versus pure hydrogen, with a thermal conductivity detector. A determination within a series can be completed in 15 min. The precision of the results is that obtained in classical organic microanalysis.

Use of vitreous carbon as a working electrode in coulometric titration of potassium hydrogen phthalate: V. J. JENNINGS, A. DODSON and G. TEDDS, *Talanta*, 1973, **20**, 681. (Department of Chemistry and Metallurgy, Lanchester Polytechnic, Coventry, U.K.).

Summary—The use of a vitreous carbon electrode as a cathode in the amperostatic coulometric titration of aqueous potassium hydrogen phthalate solution is described. It is shown that 10 mg of the phthalate can be titrated with a precision better that 0·5%. Current–voltage curves for platinum and vitreous carbon cathodes show that there is an overpotential on the latter relative to the former.

Spectrophotometric investigation of the reaction of Cu(II) and Cu(I) with 1-isonitroso-(1,2,3,4)-tetrahydrophenazine: CARLA BERTOGLIO RIOLO, TERESA FULLE SOLDI and GIOVANNI SPINI, *Talanta*, 1973, **20**, 684. (Istituto di Chimica Generale, dell Università di Pavia, 27100 Pavia, Viele Teramelli 12, Italy).

Summary—The reactions of Cu(II) and Cu(I) with 1-isonitroso-(1,2,3,4)-tetrahydrophenazine (HITF) have been studied spectrophotometrically. Both ions form complexes with metal/ligand ratio 1 : 2. The complex of Cu(I) and ITF can be used for copper determination in the range 2–$50 \times 10^{-6}M$, and has been separated as the perchlorate in crystalline form. The spectrophotometric characteristics and the equilibrium constants for the ligand and for the complexes are reported.

Spectrophotometric microdetermination of hydroxytriazenes: D. N. PUROHIT and KUSUM C. GOSWAMI, *Talanta*, 1973, **20**, 689. (Department of Chemistry. School of Basic Sciences and Humanities, University of Udaipur, Udaipur, India).

Summary—A method is reported for the determination of hydroxytriazenes, based on development GOSWAMI. *Talanta*. 1973, **20**, 689. (Deportment of Chemistry, School of Basic Sciences and and can be used for the determination of any hydroxytriazenes.

Atomabsorptionspektralphotometrische (A.A.S.) bestimmung von chrom in elektrodenkoks: K. DITTRICH and G. LIESCH, *Talanta*. 1973, **20**, 691. (Sektion Chemie der Karl-Marx-Universität Leipzig, 701. Leipzig. Leibigstr. 18, D.D.R.)

Summary—A method is described for the determination of chromium in electrode-grade coke in the range 0·1–2 ppm (or 1–20 μg/ml in solution). The limit of detection is 0·4 μg/ml, the standard deviation is 0·008 absorbance units and the sensitivity is 0·02 absorbance units per μg. The influence of sulphuric acid and potassium hydrogen sulphate concentrations is discussed.

Микроопределение дейтерия в органических веществах: Daniel Fraisse, Denise Girard and Roger Levy, *Talanta* 1973, **20**, 667.

Резюме — Описан несложный метод микроопределения дейтерия в органических веществах. Он основан на мгновенном сжигании взвешенного образца в пустой камере при 950–1050° и вымывании кислородом скоростью 60 мл/мин. Вместе с этим сжиганием в газовой фазе необходимо окисление первичных продуктов сжигания на окиси меди при 850°. Содержащие галоиды и серу продукти сжигания удерживают на посеребренной окиси алюминия при 750–800°. Образованную в сжигании воду содержащую окись и гидроокись дейтерия вымораживают из газов сжигания в специальной ловушке с двума пятиходовыми кранами которые позволяют одновременный поток кислорода и водорода; последный служит в качестве газа-носителя после ловушки. Вымораженную воду затем испаривают нагреванием в потоке водорода 30 мл/мин и восстанавливают на магнии при 600°. Дейтерий определяют в форме гидрида дейтерия в водороде и измеряют детектором на основе теплопроводности в сравнении с чистым водородом. Продолжительность одного серийного определения — 15 мин. Воспроизводимость результатов сравнима с воспроизводностью классического органического микроанализа.

Использование стекловидного углерода в качестве рабочего электрода при кулонометрическом титровании вторичного кислого фталата калия: V. J. Jennings, A. Dodson and G. Tedds, *Talanta* 1973, **20**, 681.

Резюме — Предложено использование стекловидного углеродного электрода в качестве катода при амперостатическом кулонометрическом титровании водного раствора вторичного кислого фталата калия. Показано что метод позволяет определять 10 мг фталата с воспроизводимостью лучше чем 0,5%. Кривые тока-напряжения для платинового и стекловидного углеродного электродов показывают присутствие перенапряжения на последнем электроде относительно к прежнему.

Спектрофотометрическое исследование реакции Cu(II) и Cu(I) с 1-нитрозо-(1,2,3,4)-тетрагидрофеназином: Carla Bertoglio Riolo, Teresa Fulle Soldi and Giovanni Spini, *Talanta* 1973, **20**, 684.

Резюме — Изучены спектрофотометрическим методом реакции Cu(II) и Cu(I) с 1-изонитрозо-(1,2,3,4)-тетрагидрофеназином (НИТФ). Оба иона образуют комплексы с отношением металл-лиганд 1:2. Комплекс Cu(I) с ИТФ можно использовать для определения меди в области $2–50 \cdot 10^{-6}\ M$; он выделен в кристаллической форме в форме перхлората. Приведены спектрофотометрические характеристики и константы равновесия для лиганда и комплексов.

Определение окситриазенов спектрофотометрическим микрометодом: D. N. Purohit and Kusum C. Goswami, *Talanta* 1973, **20**, 689.

Резюме — Приведен метод определения окситриазенов, основывающийся на проявлении розового цвета реакцией окситриазенов с α-нафтиламином. Метод является общеприменимым и им можно пользоваться для определения каких-либо окситриазенов.

Определение хрома в электродном угле методом атомно-абсорбционной спектрофотометрии: K. Dittrich and G. Liesch, *Talanta* 1973, **20**, 691.

Резюме — Описан метод определения хрома в электродном угле в области 0,1–2 ч. на миллион (или 1–20 мкг/мл в растворе). Чувствительность метода 0,4 мкг/мл, стандартная ошибка составляет 0,008 единиц поглощения а предел обнаружения — 0,02 единиц поглощения/мкг. Рассмотрено влияние концентраций серной кислоты и вторичного кислого сульфата калия.

Determination of iron(II) with bipyridylglyoxal dithiosemicarbazone: J. L. BAHAMONDE, D. PÉREZ BENDITO and F. PINO, *Talanta*, 1973, **20**, 694. (Department of Analytical Chemistry, Faculty of Sciences, University of Seville, Seville, Spain.)

Summary—Bipyridylglyoxal dithiosemicarbazone reacts with iron(II) or (III). The Fe(III) complex is yellow (λ_{max} 400 nm). Fe(II) forms a red-violet 1 : 2 complex at pH 2·5 (λ_{max} 550 nm) and a green-blue 1 : 1 complex at pH 5–10 (λ_{max} 590–610 nm). Both ferrous complexes can be oxidized to the ferric complex; this reaction is reversible. The quantitative application of the ferrous complex has been studied.

Dichloramine-T as a new oxidimetric titrant in non-aqueous and partially aqueous media—II: C. G. RAMACHANDRAN NAIR and V. RAJASEKHARAN NAIR, *Talanta*, 1973, **20**, 696. (Department of Chemistry, University of Kerala, Trivandrum-1, India).

Summary—Potentiometric titration procedures are described for the determination of hydroquinone, hydrazine, Sn(II), Sb(III), Tl(I), oxine, cinnamic acid and ferrocyanide, with dichloramine-T dissolved in glacial acetic acid.

Thin-layer chromatographic method for separation and determination of papaverine and its oxidation products: G. M. HABASHY and NAGY A. FARID, *Talanta*, 1973, **20**, 699. (The American University, Cairo).

Summary—A method is presented for the separation of papaverine, papaverinol and papaveraldine by TLC on silica gel with chloroform saturated with ammonia as the solvent system. The spots are extracted with absolute methanol and each compound determined spectrophotometrically in 1*M* hydrochloric acid. Papaveraldine is also determined polarographically in Britton–Robinson buffer, pH 4·1, after its separation and elution. The method is rapid and sensitive and permits the determination of papaverine, after its extraction from drugs, without interference by papaverinol and papaveraldine.

Native fluorescence of analgesics derived from *N*-phenylanthranilic acid: ANIL C. MEHTA and STEPHEN G. SCHULMAN, *Talanta*, 1973, **20**, 702. (College of Pharmacy, University of Florida, Gainesville, Florida 32601, U.S.A.).

Summary—The native fluorescence of mefenamic, flufenamic and meclofenamic acids is more useful for determination of these drugs than is the fluorescence of the derivative substituted acridones and benzoxazines obtained from these drugs by treatment with sulphuric acid or formaldehyde respectively.

Определение железа(II) бипиридилглиоксалдитиосемикарбазоном: J. L. Bahamonde, D. Perez Bendito and F. Pino, *Talanta* 1973, **20**, 694.

Резюме — Бипиридилглиоксалдитиосемикарбазон реагирует с железом(II) или(III). Комплекс с Fe(III) показывает желтый цвет (λ_{max} 400 нм). Fe(II) образует краснофиолетовый комплекс 1:2 при pH 2,5 (λ_{max} 550 нм) и зеленосиний комплекс 1:1 при pH 5–10 (λ_{max} 590–610 нм). Оба комплекса железа(II) окисляются в комплекс железа(III); эта реакция обратима. Изучено применение комплекса железа(II) в количественном анализе.

Дихлорамин Т в качестве нового оксидиметрического титрованного раствора для неводных и частично водных средах — II: C. G. Ramachandran Nair and V. Rajasekharan Nair, *Talanta* 1973, **20**, 696.

Резюме — Приведены методики потенциометрического титрования для определения гидрохинона, гидразина, Sn(II), Sb(II), Tl(I), оксина, коричной кислоты и ферроцианида с использованием дихлорамина Т в растворе ледяной уксусной кислоты.

Метод тонкослойной хроматографии для разделения и определения папаверина и продуктов его окисления: G. M. Habashy and Nagy A. Farid, *Talanta* 1973, **20**, 699.

Резюме — Предложен метод тонкослойной хроматографии на силикагеле для разделения папаверина, папаверинола и папаверальдина с насыщенным аммиаком хлороформом в качестве подвыжной фазы. Пятна экстрагируют абсолютным метиловым спиртом и каждое соединение определяют спектрофотометрическим методом в 1 *M* соляной кислоте. Папаверальдин также определяют полярографическим методом в буффере Бриттона-Робинсона при pH 4,1, после разделения и елюирования. Метод является быстрым и чувствительным и позволяет определять папаверин после его экстрагирования из наркотиков, без влияния папаверинола и папаверальдина.

Природная флуоресценция анальгетиков на основе *N*-фенилантраниловой кислоты: Anil C. Mehta and Stephen G. Schulman, *Talanta* 1973, **20**, 702.

Резюме — Природная флуоресценция мефенаминовой, флуфенаминовой и медофенаминовой кислот оказалась более полезной для определения этих веществ чем флуоресценция замещенных акридонов и бензоксазинов, получаемых из этих веществ обработкой с серной кислотой или формальдегидом.

SUMMARIES FOR CARD INDEXES

Development and publication of new methods in kinetic analysis: Harry B. Mark, Jr., *Talanta*, 1973, **20**, 257. (Department of Chemistry, University of Cincinnati, Cincinatti, Ohio 45221, U.S.A.).

Summary—A review is made of the various factors, such as the mathematical basis, measurement instrumentation, reaction mechanism, synergistic effects, *etc*, affecting the accuracy and precision of kinetic-based analytical methods. Recommendations are made concerning the research involved in developing new methods and/or applications and concerning the manner of presentation of the results for publication.

Chromatographic behaviour of 47 metal ions on titanium(IV) arsenate papers: Mohsin Qureshi, Jagdish P. Rawat and Veena Sharma, *Talanta*, 1973, **20**, 267 (Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P., India).

Summary—Titanium arsenate papers with As/Ti ratios 0·2–2·2 have been prepared and 47 metal ions chromatographed on these papers in 10^{-5}–4*M* nitric acid. The effect of pH and of the Ti/As ratio on the R_f values have been studied. A new quantity R_t ($R_t = R_f$ on untreated papers minus R_f on treated papers) has been defined. The effect of the concentration of the loading reagents on the Ti/As ratio of the ion-exchanger precipitated on the papers has been determined. Contrary to Alberti, it is shown that Lederer's equation is obeyed by titanium arsenate papers in the sodium form if the activity of Na^+ ions is considered instead of their concentration. It has also been demonstrated that the selectivity sequence for cations on titanium arsenate papers is not the same as that on titanium arsenate columns.

A phosphorimetric investigation of the external heavy-atom effect in aqueous solution and its correlation with phosphorescence intensity and quantum efficiency: J. J. Aaron, J. J. Mousa and J. D. Winefordner, *Talanta*, 1973, **20**, 279 (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.).

Summary—Excitation and emission phosphorescence spectra, lifetimes, and relative quantum efficiencies of benzene and ten monosubstituted benzenes were determined at 77 K in methanol/water 10/90 v/v and in sodium iodide/methanol/water solutions. Substituents—CHO, —$COCH_3$, —COC_2H_5, —OH, —OCH_3, —CH_3, —C_2H_5, —CH_2OH and —$N(CH_3)_2$ were investigated. Aqueous sodium iodide solutions were found to be a suitable heavy-atom solvent for phosphorimetry. Heavy-atom enhancement factors ranged from 1·2 to 8·3 according to the molecular structure and a marked decrease of the lifetime was observed for nine compounds in aqueous sodium iodide solution. A linear log–log correlation was obtained between the relative corrected phosphorescence intensity and the heavy-atom enhancement factor of the monosubstituted benzenes. A similar correlation was found between the quantum efficiencies and the heavy-atom enhancement factors. The analytical usefulness of these correlations is evident for the prediction of the magnitude of the heavy-atom effect.

2,2′-Dimercaprodiethylsulphide: A potential analytical reagent: A. Corsini and E. Nieboer, *Talanta*, 1973, **20**, 291. (McMaster University, Hamilton, Ontario, Canada).

Summary—The compound 2,2′-dimercaptodiethylsulphide has been investigated with regard to the stability of its solutions to air oxidation, its acid strength, its reactivity towards metal ions, the nature of its Ni(II) and Pd(II) complexes in solution, and its applicability to the determination of small amounts of Ni(II) and Pd(II). Studies on the Ni(II) complex extend the work reported previously by others and are not in complete accord with it. The results presented show that 2,2′-dimercaptodiethylsuiphide is a promising analytical reagent.

Разработка и опубликование новых методом кинетического анализа: Harry B. Mark, Jr., *Talanta* 1973, **20**, 257

Резюме — Приведен обзор разных факторов, как на пример математической основы, измерительный приборов, механизма реакции, синэргетических эффектов, и т. д., влияющих на точность и воспроизводимость методов кинетического анализа. Предложены смери изучения для разработки новых методов и/или их применеиня и форма опубликования полученных результатов.

Хроматографические характеристики 47 ионов металлов на бумаге пропытанной арсенатом титана(IV): Mohsin Qureshi, Jagdish P. Rawat and Veena Sharma, *Talanta* 1973, **20**, 267

Резюме — Приготовлены бумаги арсената титана имеющие отношение As/Ti 0,2–2,2 и использованы для хроматографии 47 ионов металлов в 10^{-5}–4 *M* растворах азотной кислоты. Изучено влияние pH и отношения Ti/As на величину значений R_f. Выведен новый параметр R_l (R_i = разница между величинами значения R_f на необработанной бумаге и на бумаге пропытанной реагентом). Определено влияние концентрации реагентов на отношение Ti/As ионообменника осажденного на бумаге. В противоречности с Алберти показано что бумаги арсената титана в форме натрия повинуются уравнению Ледерера, если учитивается активность ионов NaZ, а не их концентрация. Также показано что порядок селективности катионов на бумагах арсената титана не отвечает порядке на колонках арсената титана.

Фосфориметрическое исследование эффекта тяжелого атома в водном растворе и его корреляция с интенсивностью фосфоресценции и квантовым выходом: J. J. Aaron, J. J. Mousa and J. D. Winefordner, *Talanta* 1973, **20**, 279

Резюме — Определены фосфоресцентные спектры возбуждения и эмиссии, периоды и относительные квантовые выходы бензола и 10 однозамещенных бензолов при 77K в водном растворе метанола (10:90 по объему) и в растворах иодид натрия-метанол-вода. Исследованы заместители —CHO, —COCH$_3$, —COC$_2$H$_5$, —OH, —OCH$_3$, —CH$_3$, —C$_2$H$_5$, —CH$_2$OH, и —N(CH$_3$)$_2$. Водные растворы иодида натрия оказались подходящим растворителем с тяжелими атомами для фосфориметрии. Получены факторы усиления тяжелими атомами 1,2 до 8,3 в зависимости от молекулярной структуры и обнаружено выраженное сокращение периода в случае девять соединений в водном растворе иодида натрия. Получена линейная зависимость на логарифмической шкале относительной корригированной интенсивности фосфоресценции от фактора усиления тяжелими атомами для однозамещенных бензолов. Обнаружено что похожая зависимость существует между квантовым выходом и фактором усиления тяжелими атомами. Очевидна используемость этих корреляций в анализе для предсказания величины эффекта тажелих атомов.

2,2'-Димеркаптодиэтилсульфид — перспективный аналитический реагент: A. Corsini and E. Nieboer, *Talanta* 1973, **20**, 291

Резюме — 2,2'-Димеркаптодиэтилсульфид изучен с целью определить стабильность его растворов против окисления в воздухе, его кислотность, реактивность с ионами металлов, природу его комплексов с Ni(II) и Pd(II) в растворе, и его применимость в определении небольших количеств Ni(II) и Pd(II). Изучение комплекса Ni(II) протягивает опубликованные ранее работы других исследователей, а полученные результаты не всегда соглашаются с их результатами. На основе приведенных данных 2,2'-димеркаптодиэтилсульфид оказывается перспективным аналитическим реагентом.

Stripping voltammetry with collection at a rotating ring–disk electrode: DENNIS C. JOHNSON and ROBERT E. ALLEN, *Talanta*, 1973, **20**, 305. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.).

Summary—A new electroanalytical technique is described, called "stripping voltammetry with collection." The technique involves the use of a rotating ring–disk electrode and is an improvement over traditional voltammetric stripping at a single electrode in that it is characterized by a lower limit of detection and that the period of deposition before stripping can be shorter. The use of the technique is illustrated by the determination of $10^{-10}M$ Ag^+ in $0{\cdot}1M$ H_2SO_4 by use of a ring–disk electrode having a disk electrode constructed of glassy carbon and a ring electrode constructed of platinum.

Mass spectrometric study of the deterioration of polystyrene-based ion-exchangers: G. M. ARMITAGE and S. J. LYLE, *Talanta*, 1973, **20**, 315 (Chemical Laboratory, University of Kent, Canterbury, Kent, U.K.).

Summary—A mass spectrometric study of the aging effects in polystyrene-based ion-exchangers has been made. Fragments in the *m/e* range 10–70 were examined and attributed to OH^+, H_2O^+, CO^+, CO_2^+, supplemented by SO^+ and SO_2^+ from sulphonic-acid cation-exchangers. Ion-current intensities were found to be dependent on the state of the resin.

Emission spectrometric detection of metal chelates separated by gas chromatography: HIROSHI KAWAGUCHI, TAKESHI SAKAMOTO and ATSUSHI MIZUIKE, *Talanta*, 1973, **20**, 321 (Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan).

Summary—An emission spectrometric detector is used in the determination of metal acetylacetonates. Spectra are excited in the plasma of a 2450 MHz electrodeless discharge. Measuring the intensities of the atomic emission lines of aluminium, beryllium and chromium after gas chromatography provides a highly sensitive and selective method for the determination of the acetylacetonates of these metals. Detection limits are 100 ng for aluminium, 0·01 ng for beryllium and 1 ng for chromium. An analytical procedure is proposed for beryllium down to 10 ppm in aluminium.

Some aspects of the Winkler determination of oxygen in water: MICHAEL W. MULLEN and MARK M. JONES, *Talanta*, 1973, **20**, 327. (Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203, U.S.A.).

Summary—The reactions in the Winkler determination of oxygen have been examined with a rotating platinum electrode and a recording polarograph. In this manner the extent of the reaction has been determined over the pH range 7–10; at a pH of 7 only about 5% of the dissolved oxygen reacts; at a pH of 9 or above the reaction is essentially quantitative. The reaction of dissolved oxygen with manganese(II) is quite rapid. The sluggish response of the polarograph recorder prevented an accurate determination of the rate, but the reaction half-times were about 2 sec or less over the pH range used.

A novel method for the estimation of arsenic(V) in organic compounds: SARJIT SINGH SANDHU, SARVINDER SINGH PAHIL and KRISHAN DEV SHARMA, *Talanta*, 1973, **20**, 329. (Chemistry Department, Punjabi University, Patiala, India).

Summary—A novel method for the determination of arsenic(V) in organic compounds has been developed by reducing combined arsenic(V) to arsenic(III) in aqueous acetic acid medium with zinc dust. In some cases, addition of ethyl alcohol is necessary to dissolve the compound and to keep the arsenic(III) compound in solution. The arsenic(III) is titrated with iodine and the end-point is detected visually with starch as indicator or potentiometrically.

Стриппинг вольтамперометрия с накоплением на вращающемся кольцево-дисковом электроде: Dennis C. Johnson and Robert E. Allen, *Talanta* 1973 **20**, 305

Резюме — Описан новый электроаналитический метод — «стриппинг вольтамперометрия с накоплением». Метод использует вращающийся кольцево-дисковый электрод и представляет собой улучшение обыкновенного метода стриппинг вольтамперометрии с одним электродом, потому что метод обладает большой чувствительностью и потому что период накопления перед стриппингом короче. В качестве иллюстративного примера приведено определение $10^{-10}M$ Ag^+ в $0,1M$ H_2SO_4, с использованием кольцево-дискового электрода, состаящегося из дискового электрода из стекловидного углерода и платинового кольцевого электрода.

Изучение ухудшения ионообменников на основе полистирола методом масс-спектрометрии: G. M. Armitage and S. J. Lyle, *Talanta* 1973, **20**, 315.

Резюме — Изучены эффекты старения ионообменников на основе полистирола методом масс-спектрометрии. Изучены фрагменты в области m/e 10–70 и приписаны OH^+, H_2O^+, CO^+ и $CO_2{}^+$ так же как и O^+ и $O_2{}^+$ в случае катионообменников на основе сульфоновых кислот. Обнаружено что интенсивности ионного тока зависимы от сотояния смолы.

Обнаружение разделенных газо-хроматографическим путем хелатов металлов методом эмиссионной спектрометрии: Hiroshi Kawaguchi, Takeshi Sakamoto and Atsushi Mizuike, *Talanta* 1973, **20**, 321.

Резюме — Использован эмиссионно-спектрометрический детектор для определения ацетилацетонатов металлов. Спектры возбуждены в плазме безэлектродного разряда при 2450 мгц. Измерение интенсивностей линий атомной эмиссии алюминия, бериллия и хрома после разделения методом газовой хроматографии представляет собой высокочувствительный и избирательный метод определения ацетилацетонатов этих металлов. Чувствительность метода равна 100 нг для алюминия, 0,01 нг для бериллия и 1 нг для хрома. Предложена методика определения бериллия вплоть до 10 ч. на миллион в алюминии.

Некоторые взгляды на метод Винклера для определения кислорода в воде: Michael W. Mullen and Mark M. Jones, *Talanta* 1973, **20**, 327

Резюме — Реакции на которым основан метод Винклера для определения кислорода изучены с использованием вращающегося платинового электрода и самопишущего полярографа. Этим образом реакция исследована в области pH 7–10; при pH 7 реагирует только 5% растворенного кислорода, при pH 9 — реакция практически количественная. Реакция растворенного кислорода с марганцем(II) довольно быстрая. Медленный ответ самопишушчего прибора полярографа предупредил аккуратное определение скорости реакции, но полупериоды реакций были равны не больше чем 2 сек. в исследованной области pH.

Новый метод определения мышьяка(V) в органических соединениях: Sarjit Singh Sandhu, Sarvinder Singh Pahil and Krishan Dev Sharma, *Talanta* 1973, **20**, 329

Резюме — Разработан новый метод определения мышьяка(V) в органических соединениях, основанный на восстановлении связанного мышьяка(V) в мышьяк(III) с цинковой пылью в водном растворе уксусной кислоты. В некоторых случаях раствору надо добавить этилового спирта для растворения вещества и для сохранения соединения мышьяка(III) в растворе. Мышьяк(III) определен титрованием с иодом, применяя визуальное или потенциометрическое обнаружение конца титрования (индикатор крахмал).

Indirect polarographic determination of tripolyphosphate ions in the presence of other polyphosphates, with octyltin chloride: S. Shaw and A. Townshend, *Talanta*, 1973, **20**, 332. (Chemistry Department, Birmingham University, P.O. Box 363, Birmingham 15, U.K.).

Summary—Tripolyphosphate ions form a soluble complex with mono-octylin cations, thus reducing the polarographic wave height of the octyltin. This provides a method for the determination of 2×10^{-4}–$4 \times 10^{-3}M$ tripolyphosphate in the presence of $2 \times 10^{-3}M$ ortho-, pyro-, trimeta-, and $10^{-3}M$ tetrametaphosphate, together, or in any combination. The method is also insensitive to less than $2 \times 10^{-3}M$ magnesium or calcium and less than $10^{-2}M$ sulphate.

Formation of ferricyanides—I. Silver(I), copper(II), and cadmium(II): Athos Bellomo, Agatino Casale and Domenico De Marco, *Talanta*, 1973, **20**, 335. (Institute of Analytical Chemistry, University of Messina, 98100 Messina, Italy).

Summary—With potassium ferricyanide copper(II) forms $KCu_{10}[Fe(CN)_6]_7$ quantitatively in 0·5*M* potassium nitrate medium. Cadmium forms $Cd_3[Fe(CN)_6]_2$ if the ferricyanide is added to the cadmium solution in absence of extra potassium, and $KCd_{10}[Fe(CN)_6]_7$ if potassium is added first, or if the cadmium solution is added to the ferricyanide Silver forms $Ag_3Fe(CN)_6$ only.

The use of furfural thiosemicarbazone for the gravimetric determination of palladium: J. M. Cano Pavon and F. Pino, *Talanta*, 1973, **20**, 339. (Department of Analytical Chemistry, University of Seville, Seville, Spain).

Summary—The use of furfural thiosemicarbazone as a gravimetric reagent for palladium is described. The optimum analytical conditions for precipitation of the palladium complex and the effect of possible interferences have been investigated.

Extractive spectrophotometry of the molybdenum(III) 1,10-phenanthroline thiocyanate and 2,2′-bipyridyl thiocyanate complexes: Amal Kanti Bhadra and Siddheswar Banerjee, *Talanta*, 1973, **20**, 342. (Central Chemical Laboratories, Geological Survey of India, Calcutta-13, India).

Summary—New extraction spectrophotometric methods for the determination of small amounts of molybdenum have been developed, using thiocyanate and 1,10-phenanthroline or 2-2′-bipyridyl as reagents in the presence of chlorostannous acid. Extracts of the ternary complexes of tervalent molybdenum in 1,2-dichloroethane obey Beer's law in the range 1–10 μg/ml at 525 nm. A 10-fold excess of iron and vanadium and 100-fold excess of tungsten, phosphorus and silicate do not interfere.

Determination of gold in germanium by neutron-activation analysis: R. Gijbels, *Talanta*, 1973, **20**, 346. (Institute for Nuclear Sciences, State University of Ghent, Belgium).

Summary—Gold was determined in gold-doped germanium by neutron-activation analysis. The irradiated samples were dissolved in *aqua regia* in the presence of gold carrier. The matrix activity was eliminated by distillation, and gold precipitated in the residue with hydroquinone. The gold fraction was essentially radiochemically pure. For a neutron dose of 5×10^{15} n/cm^2, a sensitivity of 1 ppM Au can be obtained, with a 2·4-g sample. The samples investigated contained from 24 to 36 ppM Au.

Estimation of allyl alcohol by chloramine-T: D. S. Mahadevappa and H. M. K. Naidu, *Talanta*, 1973, **20**, 349. (Department of Post-graduate Studies and Research in Chemistry, Manasagangothri, Mysore-6, India).

Summary—A simple but rapid and accurate method for the estimation of allyl alcohol in aqueous solution has been developed, based on its oxidation with chloramine-T at room temperature, in 0·5–1·0*M* hydrochloric acid medium. The reaction involves a two-electron change. The effect of such variables such as pH of the medium, presence of foreign ions and perchloric or sulphuric acid, on the rate of oxidation, is discussed.

Косвенное полярографическое определение триполифосфатионов в присутствии других полифосфатов с использованием хлорида октилолова: S. Shaw and A. Townshend, *Talanta* 1973, **20**, 332

Резюме — Триполифосфатионы образуют растворимые комплексы с катионом моно-октилолова, снижая этим образом полярографическую волну октилолова. На этом факте основан метод определения 2,10^{-4} до 4,10^{-3} *M* триполифосфата в присутствии 2,10^{-3} *M* орто-, пиро-, три-, мета-, и 10^{-3} *M* тетраметафосфата, вместе или в любой комбинации. Магний и кальций в концентрациях не больше чем 2,10^{-3} *M* и сульфат в концентрациях не больше чем 10^{-2} *M* также не мешают определению.

Образование ферроцианидов: I. Серебро(I), медь(II) и кадмий(II): Athos Bellomo, Agatino Casale and Domenico de Marco, *Talanta* 1973, **20**, 335

Резюме — Феррицианид калия с медью(II) образует количественно $KCu_{10}[Fe(CN)_6]_7$ в 0,5 *M* растворе нитрата калия. Кадмий образует $Cd_3[Fe(CN)_6]_2$ если феррицианид добавляют раствору кадмия в отсутствии избытка калия, или $KCd_{10}[Fe(CN)_6]_7$ если сперва добавляют калий или если раствор кадмия добавляют раствору феррицианида. Серебро образует только $Ag_3Fe(CN)_6$.

Использование тиосемикарбазона фурфурала для весового определения палладия: J. M. Cano Pavon and F. Pino, *Talanta* 1973, **20**, 339

Резюме — Описано использование тиосемикарбазона фурфурала в качестве гравиметрического реагента для палладия. Изучены оптимальные условия для осаждения комплекса палладия и мешающее влияние других веществ.

Зкстрактивная спектрофотометрия комплексов молибден(III)-1,10-фенантролин-тиоцианат и молибден(III)-2,2'-дипиридил-тиоцианат: Amal Kanti Bhadra and Siddheswar Banerjee, *Talanta* 1973, **20**, 342

Резюме — Разработаны новые экстракционно-спектрофотометрические методы определения небольших количеств молибдена, с использованием тиоцианата и 1,10-фенантролина или 2,2'-дипиридила в качестве реагентов в присутствии олово(II)-хлористоводородной кислоты. Экстракты тройних комплексов трехвалентного молибдена в 1,2-дихлорэтане повинуются закону Бера в пределах 1 . 10 мкг/мл при 525 нм. 10-кратный избыток железа и ванадия и 100-кратный избыток вольфрама, фосфора и силиката не мешают определению.

Определение золота в германии методом нейтроно-активационного анализа: R. Gijbels, *Talanta* 1973, **20**, 346

Резюме — Золото в германии определяли методом нейтроноактивационного анализа. Облученные образци растворяли в царской водке в присутствии носителя для золота. Активность матрицы устранена дистилляцией, а золото осаждали в остатке гидрохиноном. Фракция золота была в сущности радиохимически чиста. В случае 2,4 г пробы получена чувствительность 1 ч. на миллион Au с использованием дозы нейтронов 5 × 10^{15} н/см^2. Исследованные образци содержали 24–36 ч. на миллион Au.

Определение аллилового спирта с помощью хлорамина-Т: D. S. Mahadevappa and H. M. K. Naidu, *Talanta* 1973, **20**, 349

Резюме — Разработан несложный, но быстрый и точный метод определения аллилового спирта в водном растворе, основан на окислении хлорамином-Т при комнатной температуре, в растворе 0,5 – 1,0*M* соляной кислоты. Реакция основана на обмене двух электронов. Обсуждено влияние разных факторов, как на пример pH среды, присутствии других ионов и хлорной или серной кислот, на скорость окисления.

Precipitation of calcium oxalate from homogeneous solution by cation release: R. GRZESKOWIAK and T. A. TURNER, *Talanta*, 1972, **20**, 351. (Department of Chemistry, Thames Polytechnic, London, S.E.18.)

Summary—Calcium oxalate can be precipitated from homogeneous solution by oxidation of the calcium/EDTA complex, in the presence of oxalate ion, with hydrogen peroxide in boiling solution, at pH 6–8. The method gives large crystals and enables calcium to be determined in the presence of lead, which remains complexed.

Formation of ferrocyanides-III. Fe(III), La(III) and Ce(III): ATHOS BELLOMO, DOMENICO DE MARCO and AGATINO CASALE, *Talanta*, 1973, **20**, 355. (Institute of Analytical Chemistry, University of Messina, 98100 Messina, Italy).

Summary—Potassium ferrocyanide forms $Fe_4[Fe(CN)_6]_3$ with Fe(III), $KLaFe(CN)_6$ with La(III) and $KCeFe(CN)_6$ with Ce(III). The thermodynamic data for the two lanthanide compounds have been determined.

Distribution coefficients of Rb^+ on zirconium phosphate in mixed aqueous–organic media: D. L. MASSART, *Talanta*, 1973, **20**, 358. (Laboratorium voor Analytische Scheikunde, Farmaceutisch Instituut, Vreij Universiteit Brussels, Paardenstraat 67, B-1640 Sint-Genesius-Rode).

Summary—The distribution coefficients have been determined for Rb^+ distributed between zirconium phosphate and 0.85*M* hydrochloric acid in aqueous solutions of methanol, n-propanol, isopropyl alchcol, t-butyl alcohol, dimethylsulphoxide, dimethylformamide, tetrahydrofuran, acetone, dioxan, "Methylcellosolve", "Propylcellosolve", acetic acid and sulpholane, in 0–88% concentration.

Potentiometric determination of stepwise stability constants of zirconium, thorium and uranium chelates of asparagine and glutamine: R. C. TEWARI and M. N. SRIVASTAVA, *Talanta*, 1973, **20**, 360. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—The metal chelates of Zr(IV), Th(IV) and U(VI) with asparagine and glutamine have been studied potentiometrically. Stepwise stability constants in 0·1*M* sodium perchlorate at 25° are as follows. *Asparaginate chelates*—log K_1 8·80, log K_2 6·25 for Zr, log K_1 6·79, log K_2 6·16 for U, log K_1 8·28, log K_2 7·77 and log K_3 7·72 for Th. *Glutaminate chelates*—log K_1 8·75, log K_2 6·10 for Zr, log K_1 6·63, log K_2 6·22 for U, and log K_1 8·30, log K_2 7·61 and log K_3 7·55 for Th.

Осаждение оксалата кальция из гомогенного раствора путем выпуска катиона: R. Grzeskowiak and T. A. Turner, *Talanta* 1973, **20**, 351

Резюме — Осаждение оксалата кальция из гомогенного раствора можно провести окислением комплекса кальция с ЭДТА, в присутствии оксалатиона, перекисью водорода в кипящем растворе при pH 6–8. Этим методом получаются крупные кристаллы, а кальций можно определять в присутствии свинца, который остается в форме комплекса.

Образование ферроцианидов — III. Fe(III), La(III) и Ce(III): Athos Bellomo, Domenico de Marco and Agatino Casale, *Talanta* 1973, **20**, 355

Резюме — Ферроцианид калия образует $Fe_4[Fe(CN)_6]_3$ с Fe(III), $KLaFe(CN)_6$ с La(III) и $KCeFe(CN)_6$ с Ce(III). Определены термодинамические данные для двух соединений лантанидов.

Коэффициенти распределения Rb^+ на фосфате циркония в смешанных водно-органических средах: D. L. Massart, *Talanta* 1973, **20**, 358

Резюме — Определены коэффициенты распределения Rb^+ между фосфатом циркония и 0,85*M* соляной кислоты в водных растворах метилового, этилового, н-пропилового, изопропилового и трет-бутилового спиртов, диметилсульфоксида, диметилформамида, тетрагидрофурана, ацетона, диоксана, «метилцеллосольв», «пропилцеллосольв», уксусной кислоты и сульфолана, в концентрациях 0 - 88%.

Потенциометрическое определение шаговых констант устойчивости хелатов аспарагина и глутамина с цирконием, торием и ураном: R. C. Tewari and M. N. Srivastava, *Talanta* 1973, **20**, 360

Резюме — Изучены потенциометрическим методом хелаты аспарагина и глутамина с Zr(IV), Th(IV) и U(VI). Определены следующие шаговые константы устойчивости в 0,1*M* растворе перхлората натрия при 25°: *Хелаты аспарагина:* lg K_1 8,80, lg K_2 6,25 для Zr, lg K_1 6,79, lg K_2 6,16 для U, lg K_1 8,28, lg K_2 7,77 и lg K_3 7,72 для Th. *Хелаты глутамина:* lg K_1 8,75, lg K_2 6,10 для Zr, lg K_1 6,63, lg K_2 6,22 для U, и lg K_1 8,30, lg K_2 7,61 и lg K_3 7,55 для Th.

SUMMARIES FOR CARD INDEXES

An ion-selective electrode system for continuously monitoring cyanide ion, based on a computerized Gran plot technique: B. FLEET and A. Y. W. HO, *Talanta*, 1973, **20**, 793. (Chemistry Department, Imperial College, London SW7 2AY, U.K.).

Summary—A procedure for the continuous monitoring of cyanide ion with an ion-selective electrode is described, based on the use of the Gran plot standard-addition technique. The mean concentration of the sample reservoir is measured continuously during a time span of 6 min. The use of a computer programme facilitates calculation of the results. Because the combined weights of several data points are used to calculate the unknown concentration, random errors tend to be eliminated and in addition there is no need for reference calibration curves.

Determination of Hg(II) in acidic media by stripping voltammetry with collection: ROBERT E. ALLEN and DENNIS C. JOHNSON, *Talanta*, 1973, **20**, 799. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Stripping voltammetry with collection at a rotating ring-disk electrode having a platinum ring and a glassy-carbon disk was used for the determination of Hg(II) in 1·0*M* H_2SO_4 medium in the range 0·10–4·00 ppM. Satisfactory results were obtained only after a thin film of Au (two monolayer equivalents) was electroplated on the disk electrode. The average relative deviation of the results for determination at the 0·10-ppM level was 7·5%. The limit of detection for the technique is approximately 0·01 ppM.

Systems theory in analysis—I. Definitions and interpretations of the basic terms of systems theory: G. GOTTSCHALK and I. L. MARR, *Talanta*, 1973, **20**, 811. (Osram-Studiengesellschaft, 8 München 90, Hellabrunner Straße 1, Germany).

Summary—The twelve basic terms of systems theory—system, element, relation, function, structure, organization, feedback, Black Box, model, input–output analysis, trial-and-error method, simulation—are given general definitions and are also interpreted in terms of chemical analysis. The distinction between a generally acceptable brief and precise definition and an interpretation peculiar to one particular specialized field avoids, in the case of universally used terms, a biased view and conception. Simple systems are deliberately chosen and the terms used are clarified by means of diagrams. A systems-oriented approach is outlined, with feedback-coupled stages (defining the problem, setting the limits, designing the model, simulation) which has proved useful in practical systems analysis and in systems design. The working group will report, in subsequent publications, on specific analytical systems which are of considerable importance in automation. Those with special interests in these fields are warmly invited to communicate their critical opinions, suggestions, and examples of interpretations based on these definitions.

Effects of auxiliary complex-forming agents on the rate of metallochromic indicator colour change: GENKICHI NAKAGAWA and HIROKO WADA, *Talanta*, 1973, **20**, 829. (Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya, Japan).

Summary—The rate of colour change reactions of metallochromic indicators such as XO, PAN, PAC and TAC at the equivalence point were measured in the chelatometric titration of copper, nickel, zinc or cobalt. Hexamine buffer has strong disturbing effects on the rate of colour change of the copper or nickel XO chelate. The effects of various auxiliary complex-forming agents were also examined. Bathophenanthroline, 2,2′-bipyridyl, 8-hydroxyquinoline, TPTZ, ethylenediamine, iminodiacetic acid, acetylacetone, 1,10-phenanthroline and glycine improve the colour change of the XO and PAN chelates of copper. Some titration methods for copper or nickel with XO or PAN as indicator are proposed.

Система на основе ионоизбирательного электрода для непрерывного измерения цианидиона, с использованием электроновычислительной машины и метода Грана: B. Fleet and A. Y. W. Ho, *Talanta* 1973, **20**, 793.

Резюме — Описан метод непрерывного измерения цианидиона с помощью ионоизбирательного электрода, основывающийся на методе стандартных добавлений с использованием диаграммы Грана. Среднюю концентрацию резервуара пробы измеряют непрерывно в течение 6 мин. Использование электроновычислительной машины облегчает вычисление результатов. Неизвестную концентрацию вычисляют на основе комбинированного веса ряда измерительных точек; этим образом избежаются случайные ошибки и кроме того необходимость эталонных калибровочных кривых.

Определение Hg(II) в кислых средах методом стриппинг вольтамперометрии с накоплением: Robert E. Allen and Dennis C. Johnson, *Talanta* 1973, **20**, 799.

Резюме — Метод стриппинг вольтамперометрии с накоплением на вращающемся кольцево-дисковом электроде, состоящемся из платинового кольца и диска из стекловидного углерода, использован для определения Hg(II) в растворе 1,0 *M* H_2SO_4 в пределах 0,10–4,00 ч. на миллион. Получены удовлетворительные результаты только после электроосаждения тонкой пленки Au (эквивалентной двумя мономолекулярным слоям) на дисковом электроде. Средная стандартная ошибка результатов полученных на уровне 0,10 ч. на миллион составляет 7,5 %. Чувствительность метода приблизительно 0,01 ч. на миллион.

Применение системной теои рив анализе — ;. Дефиниции и обьяснения основных терминов системной теории: G. Gottschalk and I. L. Marr, *Talanta* 1973, **20**, 811.

Резюме — Приведены общие дефиниции двенадцать основных терминов системной теории — система, элемент, реляция, функция, структура, организация, обратная связь, черная коробка, модель, анализ входа-выхода, метод попытки и ошибки, симуляция; эти термины также протолкованы в терминах химического анализа. Различение между общепринятой короткой и прецизионной дефиницией и обьяснением особенным для данной специальной области избегает, в случае общеприменимых терминов, односторонные взгляды и концепции. Намеренно избраны несложные системы, а использованные термины объяснены с помощью диаграмм. Описан подход на основе систем, с стадиями связанными обратной связью (дефиниция проблемы, определение пределов, проектирование модели, симуляция), который оказался полезным в практическом анализе систем и в проектировании систем. Авторы сообщат в следующих публикациях специфические аналитические системы, значительные для автоматизации. Заинтересованные в этой области читатели сердечно приглашаются сообщать их критические взгляды, советы и примеры интерпретаций, основывающиеся на этих дефинициях.

Влияние добавочных комплексообразующих агентов на скорость перемены цвета металлохромного индикатора: Genkichi Nakagawa and Hiroko Wada, *Talanta* 1973, **20**, 829.

Резюме — Измерена скорость изменения цвета металлохромных индикаторов — в том числе КсО, ПАН, ПАК и ТАК — в точке эквивалентности при хелатометрическом титровании меди, никеля, цинка или кобальта. Гексаминовый буфер сильно нарушает скорость изменения цвета хелата меди или никеля с КсО. Также изучено влияние разных добавочных комплексообразующих агентов. Батофенантролин, 2,2'-бипиридил, 8-оксихинолин, ТПТЗ, этилендиамин, иминодиуксусная кислота, ацетилацетон, 1,10-фенантролин и глицин улучшают изменение цвета хелатов меди с КсО и ПАН. Предложены методы титрования меди или никеля с использованием КсО или ПАН в качестве индикатора.

Analysis of precision of activation-analysis methods: K. HEYDORN and KRISTA NØRGÅRD, *Talanta*, 1973, **20**, 835. (Isotope Division, Danish Atomic Energy Commission Research Establishment Risø, Roskilde, Denmark).

Summary—The precision of an activation-analysis method prescribes the estimation of the precision of a single analytical result. The adequacy of these estimates to account for the observed variation between duplicate results from the analysis of different samples and materials, is tested by the statistic T, which is shown to be approximated by a χ^2 distribution. Application of this test to the results of determinations of manganese in human serum by a method of established precision, led to the detection of airborne pollution of the serum during the sampling process. The subsequent improvement in sampling conditions was shown to give not only increased precision, but also improved accuracy of the results.

Precise determination of oxygen and silicon in rocks by 14-MeV neutron-activation analysis: K. HUYSMANS, R. GIJBELS and J. HOSTE, *Talanta*, **20**, 843 (Institute for Nuclear Sciences, Ghent University, Ghent, Belgium.)

Summary—Oxygen and silicon have been determined in the six new U.S. Geological Survey standard rocks and two standard refractory materials by 14-MeV neutron-activation analysis, followed by both single and multichannel analyser counting of the induced ^{16}N (4·5–8 MeV gamma radiation) and ^{28}Al activities (1·78 MeV photopeak). Owing to the long analysing time per pulse, dead-time corrections are necessary in multichannel analyser counting. Four methods were investigated in this work: counting time in the live-time mode without additional correction, short counting corrected by an external live-time scaler, the method of Bartošek, and the method of Schonfeld. Each measurement was controlled by a simultaneous measurement with a single-channel analyser. Silica ignited at 1000° was used as a reference. Correction was made for the interfering elements, F. P, Al, Fe and Mg, using literature data. Attention was paid to neutron, gamma and beta attenuation. For oxygen the mean coefficient of variation for a single determination with a single-channel analyser was 1·7%, for silicon 1·1%. The mean results for single-channel counting were compared with literature values.

Quantitative phosphorescence study of interactions of cytosine and cytidine and its nucleotides in frozen aqueous solution. Evidence for anomalous heavy-atom effect: J. J. AARON, W. J. SPANN and J. D. WINEFORDNER, *Talanta*, 1973, **20**, 855. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—Phosphorescence *vs.* pH titration curves of cytosine, cytidine, cytidine-5′-monophosphate (CMP), -diphosphate (CDP) and -triphosphate (CTP) were obtained in methanol/water 10/90 v/v and in various sodium halide aqueous frozen solutions at 77°K. As shown by the shape of the titration curves, molecular aggregates or "puddles" of cytosine and cytidine were shown to occur only in relatively concentrated frozen solution ($10^{-3}M$), these aggregates being dissociated in dilute frozen solutions ($\leq 10^{-4}M$) or in $\sim 1M$ sodium chloride. No molecular aggregation could be found even in concentrated solutions of CMP, CDP, and CTP. Lower concentrations of sodium bromide or iodide ($10^{-1}M$) were demonstrated to give "reversed" sigmoidal phosphorescence titration curves in the case of cytidine, due to an *anomalously large heavy-atom enhancement factor* in acidic solution, ranging between 30 and 50.

Анализ воспроизводимости методов нейтроноактивационного анализа: K. Heydorn and Krista Nørgård, *Talanta* 1973, 20, 835.

Безюме — Воспроизводимость метода активационного анализа предписывает определение воспроизводимости только одного результата анализа. Адекватность этих оценок обнаруженной вариации между параллельными результатами определена путем статистической величины *T*, приближеной функцией распределения X^2. Применение этой оценки на результаты определения марганца в сыворотке человека методом, воспроизводимость которого была определена ранее, привела к открытию загрязнения сыворотки воздухом в течение взятия проб. Последующее улучшение условий взятия проб улучшало воспроизводимость, а также точность результатов.

Прецизионное определение кислорода и кремния в горных породах методом 14-мэв нейтроноактивационного анализа: K. Huysmans, R. Gijbels and J. Hoste, *Talanta* 1973, 20, 893.

Безюме — Кислород и кремний определены в шести новых эталонных горных пород U.S. Geological Survey и в двух эталонных огнеупорных материалах методом 14-мэв нейтроноактивационного анализа, с последующим считанием индуцированных активностей ^{16}N(4,5–8 мэв гамма-излучение) и ^{28}Al(1,78 мэв фотопик), с помощью одно- и многоканального анализатора. В результате продолжительного анализа для каждого импульса, надо применять коррекции для мертвого времени при использовании многоканального анализатора. В предлежащей работе исследовано четыре методов: время считания в способе живого времени без дополнительной коррекции, короткое считание корригировано с помощью внешнего скалера живого времени, метод Бартошека и метод Шонфельда. Каждое измерение контроллировано одновременным измерением с помощью одноканального анализатора. Нагреванная до 1000° двуокись кремния использована в качестве эталона. Коррекции для мешающих элементов F, P, Al, Fe и Mg сделаны на основе литературных данных. Внимание обращено ослаблению нейтронного, гамма и бета излучения. Средный коэффициент вариации для одного определения с использованием одноканального анализатора равен 1,7% для кислорода, а — 1,1% для кремния. Средные результаты, полученные одноканальным считанием сравнены с литературными данными.

Количественное изучение фосфоресценции при взаимодействии цитозина и цитидина и их нуклеотидов в замороженном водном растворе: J. J. Aaron, W. J. Spann and J. D. Winefordner, *Talanta* 1973, 20, 855.

Безюме — Получены кривые зависимости фосфоресценции от титрации pH для цитозина, цитидина, цитидин-5'-монофосфатат (ЦМФ), -дифосфата (ЦДФ) и -трифосфата (ЦТФ) в растворе метанол-вода 10:90 по объему и в разных замороженных растворах галоидов натрия при 77°K. Форма титрационных кривых показывает что молекулярные агрегаты или «лужицы» цитозина и цитидина появляются только в сравнительно концентрированных замороженных растворах (10^{-3} *M*); эти агрегаты диссоциируются в разбавленных замороженных растворах ($=10^{-4}$ *M*) или в ~ 1 *M* растворе хлорида натрия. Молекулярные агрегации не обнаружены даже в концентрированных растворах ЦМФ, ЦДФ и ЦТФ. Показано что низкие конзентрации бромида или иодида натрия (10^{-1} *M*) дают «обратные» сигмоидальные фосфоресцентные титрационные кривые в случае цитидина в результате *больше чем нормального фактора усиления тяжелыми атомаюи* в кислом растворе, величины 30 до 50.

Aromatic sulphonate ion-selective electrode membrane with Crystal Violet as ion-exchange site: NOBUHIKO ISHIBASHI, HITOSHI KOHARA and KAZUO HORINOUCHI, *Talanta*, 1973, **20**, 867. (Department of Applied Analytical Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan).

Summary—Four triphenylmethane derivatives (cations) and a high molecular-weight quaternary ammonium ion were used as the ion-exchange site in the liquid membranes of electrodes responsive to aromatic sulphonate ions, such as benzenesulphonate and α-naphthalenesulphonate. The nitrobenzene or 1,2-dichloroethane membrane containing the Crystal Violet–aromatic sulphonate pair had good sensitivity, showing an approximately Nernstian response down to $10^{-4}M$ sulphonate. The potential of the Crystal Violet membrane was independent of pH variation from 2·5 to 12. Chloride and sulphate ions in the aqueous sample solution did not affect the electrode potential. 1,3,6-Naphthalenetrisulphonate exerted essentially no influence on the potential of α-naphthalenesulphonate electrode. The interference of the nitrate ion was relatively large. The conductivity and association of the solute species in the membrane were estimated.

Thermometric titration in investigation of the formation of polyanions of molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI)—comparison of thermometric and potentiometric titration curves: NOBUTOSHI KIBA and TSUGIO TAKEUCHI, *Talanta*, 1973, **20**, 875. (Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan).

Summary—A new twin-cell thermometric titrator has been devised and used for thermometric titration of solutions of sodium molybdate, sodium tungstate, sodium orthovanadate, ammonium metavanadate, and potassium chromate with perchloric acid. The thermometric titration curves were compared with corresponding pH-titration curves for elucidation of the reactions occurring in the titrations. Thermometric titrimetric methods have been developed for the determination of tungsten, vanadium and chromium.

Separation of molybdenum from interfering elements by extraction as phosphomolybdenum blue: V. YATIRAJAM and JASWANT RAM, *Talanta*, 1973, **20**, 885. (Chemistry Department, University of Kurukshetra, Kurukshetra, India).

Summary—A simple method is described for the separation of molybdenum from titanium, zirconium, chromium, manganese, iron, cobalt, nickel, uranium and aluminium in a wide variety of samples in <30 min. Phosphomolybdenum blue is produced by boiling for 2 min a molybdate solution containing phosphate to give Mo/P = 20–37 (w/w) with hydrazine sulphate in $0{\cdot}1N$ sulphuric acid. The volume and acidity are adjusted to give a molybdenum concentration of 0·6–5 mg/ml in $0{\cdot}4$–$0{\cdot}5N$ sulphuric acid. The phosphomolybdenum blue is 99·5% extracted with methyl isobutyl ketone in a single extraction. The residual molybdenum and hydrazine in the aqueous phase are oxidized with a few drops of liquid bromine and the molybdenum is quantitatively extracted with the same solvent from $1N$ sulphuric acid as its reddish brown thiosulphato complex. The molybdenum is stripped by ammonia-hydrogen peroxide solution. The back-extract is heated to boiling and filtered to remove the insoluble hydroxides of traces of accompanying elements. The thiosulphate in the filtrate is destroyed by boiling for 4–5 min with excess of hydrogen peroxide in slightly ammoniacal medium. The molybdenum is determined finally by cerimetry or other standard methods.

Determination of calcium oxide in calcined phosphate ores: R. S. YOUNG, *Talanta*, 1973, **20**, 891. (1178 Beach Drive, Victoria, B.C., Canada).

Summary—It has been shown that an existing procedure to differentiate calcium oxide from the carbonate and silicate of calcium can be used in the presence of the phosphate, fluoride and sulphate of calcium, and of the carbonate and oxide of magnesium. It is based on the reaction in aqueous solution of calcium oxide with sucrose to form calcium saccharate, and subsequent titration with oxalic acid solution. The method has application for a direct chemical determination of calcium oxide in phosphate rock where calcination of accompanying carbonate is necessary in beneficiation processes.

Мембрана ароматического сульфоната для ионоселективного электрода использующая кристальный фиолетовый в качестве местоположения ионного обмена: Nobuhiko Ishibashi, Hitoshi Kohara and Kazuo Horinouchi, *Talanta* 1973, **20**, 867.

Безюме — Четыре производных трифенилметана (катионы) и высокомолекулярный ион четвертичного аммония использованы в качестве местоположения ионного обмена в жидких мембранах электродов реагирующих на ароматические сульфонатионы, в том числе бензолсульфонат и α-нафталинсульфонат. Мембраны из нитробензола или 1,2-дихлорэтана, содержащие пару кристальный фиолетовый-ароматический сульфонат обладали хорошой чувствительностью и показали приблизительно нернстовский ответ вплоть до 10^{-4} *M* сульфоната. Потенциал мембраны из кристального фиолетового оказался независимым от pH в области 2,5 до 12. Хлорид- и сульфатионы в водном растворе пробы не влияли на потенциал электрода. 1,3,6-Нафталинтрисульфонат также не влиял естественно на потенциал электрода α-нафталинсульфоната. Нитратион показал довольно сильное мешающее действие. Определены проводимость и ассоциация растворенного вещества в мембране.

Исследование образования полианионов молибдена(*VI*), вольфрама(*VI*), ванадия(*V*) и хрома(*VI*) методом термометрического титрования — сравнение термометрических и потенциометрических титрационных кривых: Nobutoshi Kiba and Tsugio Takeuchi, *Talanta* 1973, **20**, 875.

Безюме — Сконструирован новый термометрический титратор использующий двойную ячейку и применен в термометрическом титровании растворов молибдата натрия, вольфрамата натрия, ортованадата натрия, метаванадата аммония и хромата калия хлорной кислотой. Термометрические титрационные кривые сравнены с соответствующими потенциометрическими кривыми для разъяснения реакций имеющих место в титрациях. Разработаны методы термометрического титрования для определения вольфрама, ванадия и хрома.

Отделение молибдена от мешающих элементов путем экстракции в форме фосфомолибденового синего: V. Yatirajam and Jaswant Ram, *Talanta* 1973, **20**, 885.

Резюме — Описан несложный метод отделения молибдена от титана, циркония, хрома, марганца, железа, кобальта, никеля, урана и алюминия в разных веществах в меньше чем 30 мин. Фосфомолибденовый синий образуют кипячением раствора молибдата, содержащего фосфат в отношении Mo/P = 20–37 (по весу) в течение 2 мин. с сернокислым гидразином в 0,1*N* растворе серной кислоты. Объем раствора и кислотность регулируют для получения концентрации молибдена 0,6–5 мг/л в 0,4–0,5*N* серной кислоте. Одним экстрагированием метилизобутилкетоном экстрагируется 99,5% фосфомолибденового синего. Остаточный молибден и гидразин в водной фазе окисляют с немногими каплями жидкого брома, а молибден экстрагируют количественно тем же растворителем из 1*N* серной кислоты в форме его красноватокоричневого тиосульфатокомплекса. Молибден извлекают аммиачным раствором перекиси водорода. Поворотный экстракт нагревают до кипения и фильтрируют для устранения нерастворимых гидроокисей следов сопровождающих элементов. Тиосульфат в растворе разрушают кипячением в течение 4–5 мин. с избытком перекиси водорода в слабоаммиачной среде. Молибден конечно определяют цериметрическим или другими стандартными методами.

Определение окиси кальция в кальцинированных фосфатных рудах: R. S. Young, *Talanta* 1973, **20**, 891.

Резюме — Показана возможность использования имеющейся методики для различения окиси кальция от карбоната и силиката кальция в присутствии фосфата, фторида и сульфата кальция и карбоната и окиси магния. Метод основан на реакции в водном растворе окиси кальция с сахарозой для образования сахарата кальция, с последующим титрованием с раствором шавелевой кислоты. Методом можно пользоваться для непосредственного химического определения окиси кальция в фосфатных горных породах где надо провести кальцинацию сопровождающего карбоната в процессах улучшения качества руды.

Application of the fission-track technique to the determination of uranium in natural waters: TSUYOSHI TAKEBAYASHI, HIDEKI MATSUDA and SHUNJI UMEMOTO, *Talanta*, 1973, **20**, 892. (Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, Japan.)

Summary—A procedure for the determination of the uranium content of natural waters is presented. To 100 ml of natural waters, 200 ml of conc. hydrochloric acid are added and this solution is passed through a 6-ml column of Dowex 1-X8. The uranium is eluted with 60 ml of 0·1*M* hydrochloric acid, and the eluate is evaporated to dryness. The residue is subjected to the fission-track technique described previously. The uranium content of the river waters in Fukuoka City was determined.

Determination of copper in ammonium fluoride solutions by extraction and atomic-absorption spectrophotometry: M. BRISKA and W. HOFFMEISTER, *Talanta*, 1973, **20**, 895. (IBM Laboratories, Component Development, Dept., 3192, D-7030 Boeblingen, Schoenaicher Strasse 220, West Germany).

Summary—Extraction with sodium diethyldithiocarbamate, followed by mineralization and atomic-absorption spectroscopy is used to determine down to $10^{-7}\%$ Cu in 40% ammonium fluoride solution used in the manufacture of semiconductors.

Emissionsspektrographische Bestimmung von Germanium und Zinn in Galliumarsenid: K. DITTRICH and H. RÖSSLER, *Talanta*, 1973, **20**, 897. (Sektion Chemie der Karl-Marx-Universität Leipzig, 701 Leipzig, Liebigstr. 18, DDR).

Summary—An emission spectrographic determination of germanium and tin in gallium arsenide is described. For a sample of 5 mg the limit of detection is 3·1 ppm germanium and 7·7 ppm tin. The relative standard deviations are 11% for germanium and 16% for tin. The evaporation of the elements during the excitation is discussed.

Determination of hydrogen peroxide by thallium(III) in the presence of iron(II): P. D. SHARMA and Y. K. GUPTA, *Talanta*, 1973, **20**, 903. (Department of Chemistry, University of Rajasthan, Jaipur. India).

Summary—A method for estimating hydrogen peroxide by oxidation with excess of thallium(III) in the presence of iron(II) and iodometric determination of excess of thallium(III) is described. Nitrate, sulphate, manganese(II) and copper(II) have no effect. Chloride interferes.

Determination of lithium stearate in sebacate-based lubricants by atomic absorption: GEORGE NORWITZ and HERMAN GORDON, *Talanta*, 1973, **20**, 905. (Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.)

Summary—An accurate method is proposed for the determination of lithium stearate in sebacate-based lubricants. The sample is treated with dilute hydrochloric acid and an extraction is performed with ethyl ether to remove di-isopropyl phosphite which would otherwise interfere by causing the subsequent precipitation of lithium phosphate or lithium metaphosphate. The aqueous extract is then evaporated to fuming with perchloric acid and the lithium is determined by atomic absorption.

Hydrazine sulphate as reagent for titrimetric determination of vanadium(V) and chromium(VI): P. V. KRISHNA RAO and G. GOPALA ROA, *Talanta*, 1973, **20**, 907. (Department of Chemistry, Andhra University, Waltair 530003, India).

Summary—Conditions have been developed for the direct titration of vanadium(V) and chromium(VI) with hydrazine sulphate, barium diphenylaminesulphonate being used as indicator and osmium tetroxide as catalyst.

Применение метода следа фиссии в определении урана в природных водах: T. Takebayashi, H. Matsuda and S. Umemoto, *Talanta* 1973, 20, 892.

Резюме — Предложена методика определения урана в природных водах. К 100 мл природной воды добавляют 200 мл концентрированной соляной кислоты и раствор пропускают через колонку 6 мл смолы Дауекс I-X8. Уран элюируют с 60 мл 0,1 *M* соляной кислоты и элюат выпаривают до сухого. Остаток исследуют описанным раньше методом следа фиссии. Определено содержание урана в речных водах города Фукуока.

Определение меди в растворах фторида аммония методом экстракции и атомно-абсорбционной спектрофотометрии: M. Briska and W. Hoffmeister, *Talanta* 1973, 20, 895.

Резюме — Экстракция с диэтилдитиокарбаминатом натрия с последующей минерализацией и определением методом атомно-абсорбционной спектрофотометрии использована для определения меди вплоть до $10^{-7}\%$ в растворе фторида аммония, примененном в производстве полупроводников.

Определение германия и олова в арсениде галлия спектрографическим методом: K. Dittrich and H. Rössler, *Talanta* 1973, 20, 897.

Резюме — Описан метод емиссионной спектрографии для определения германия и олова в арсениде галлия. В случае пробы 5 мг чувствительность метода составляет 3,1 ч. на миллион германия и 7,7 ч. на миллион олова. Относительные стандартные ошибки равны 11% для германия, а — 16% для олова. Рассмотрено выпарывание элементов в течение возбуждения.

Определение перекиси водорода таллием(III) в присутствии железа(II): P. D. Sharma and Y. K. Gupta, *Talanta* 1973, 20, 903.

Резюме — Описан метод определения перекиси водорода основывающийся на окислении с избытком таллия(III) в присутствии железа(II) и иодометрическом определении избытка таллия(III). Нитрат, сульфат, марганец(II) и медь(II) не влияют на определение. Хлоридион мешает определению.

Определение стеарата лития в основанных на себацате смазочных маслах методом атомно-абсорбционной спектрофотометрии: George Norwitz and Herman Gordon, *Talanta* 1973, 20, 905.

Резюме — Предложен точный метод определения стеарата лития в основанных на себацате смазочных маслах. Пробу обрабатывают разбавленной соляной кислотой и экстрагируют этиловым эфиром для устранения диизопропилфосфита который мешает определению, вызывая осаждение фосфата или метафосфата лития. Водный экстракт выпарывают с хлорной кислотой до появления паров и определяют литий методом атомно-абсорбционной спектрофотометрии.

Сернокислый гидразин в качестве реагента для определения ванадия(V) и хрома(VI) титриметрическим методом: P. V. Krishna Rao and G. Gopala Rao, *Talanta* 1973, 20, 907.

Резюме — Разработаны условия для непосредственного титрования ванадия(V) и хрома(VI) сернокислым гидразином, с использованием дифениламинсульфоната бария в качестве индикатора, а четырехокиси осмия — в качестве катализатора.

Desorption of small quantities of chloraurate ions retained on anion-exchangers, in the separation of gold from base metals: L. L. KOCHEVA and R. GECHEVA, *Talanta*, 1973, **20**, 910. (Department of Chemistry, University of Sofia, Bulgaria).

Summary—Favourable conditions have been found for the elution of chloraurate ions, separated from base metals by sorption on Dowex 1. The elution is done at 50° with a hydrochloric acid solution of thiourea. A reversible column is proposed for the purpose, the use of which decreases the eluate volume. The conditions established have been applied in the separation of microgram amounts of gold from nickel, copper and iron as well as for determining gold in anodic copper.

A twinned mercury-filled glass electrode system for acid–base titrations in a number of non-aqueous solvents: M. BRÉANT and J. GEORGES, *Talanta*, 1973, **20**, 914. (Laboratoire de Chimie Analytique et Industrielle, 20 Ave. A. Einstein, 69 621 Villeurbanne, France).

Summary—A pair of mercury-filled glass electrodes is proposed for acid–base titrations in non-aqueous solvents or their mixtures with each other or with water.

Non-aqueous cerimetric determination of thioureas: BALBIR CHAND VERMA and SWATANTAR KUMAR, *Talanta*, 1973, **20**, 916. (Department of Chemistry, Punjabi University, Patiala, India).

Summary—Ammonium hexanitratocerate (in acetonitrile) solution has been used as an oxidimetric reagent for the visual and potentiometric determination of thiourea and its alkyl derivatives in acetonitrile medium. The thioureas are oxidized to their corresponding disulphides. The method is simple, accurate, reliable and widely applicable.

Analytical properties of 3-hydroxy-picolinaldehyde azine: A. GARCIA DE TORRES, M. VALCARCEL and F. PINO, *Talanta*, 1973, **20**, 919. (Department of Analytical Chemistry, Faculty of Sciences, University of Sevilla, Spain).

Summary—The synthesis and analytical properties of 3-hydroxypicolinaldehyde azine (3-OH-PAA), salicylaldehyde azine and picolinaldehyde azine are described. 3-OH-PAA is isolated for the first time. The solubility, spectral characteristics *pK* values and reactions with 36 cations were examined.

Chelating properties of α-oximinocarboxamides—II. *Syn*-α-oximinophenylacetamide: copper(II) complexes: HAMED M. EL FATATRY, ALFRED W. VON SMOLINSKI, CECILIO E. GRACIAS and DOMINICK A. COVIELLO, *Talanta*, 1973, **20**, 923. (Department of Chemistry, College of Pharmacy, University of Illinois at the Medical Center, Chicago, Illinois 60612).

Summary—*Syn*-α-oximinophenylacetamide forms two complexes with Cu(II), a CuL complex at $pH < 8{\cdot}4$ and CuL_2 at $pH > 8{\cdot}4$. $\log K_1 = 7{\cdot}82 \pm 0{\cdot}07$; $\log \beta_2 = 14{\cdot}32 \pm 0{\cdot}06$.

Десорбция небольших количеств хлораурат-ионов, задержанных на ионообменниках, при отделении золота от неблагородных металлов: L. L. Kocheva and R. Gecheva, *Talanta* 1973, **20**, 910.

Резюме — Разработаны подходящие условия для элюирования хлораурат-ионов, отделенных от неблагородных металлов сорбцией на смоле Дауекс I. Элюирование проводят при 50° солянокислым раствором тиомочевины. Для этой целью предложена реверсибильная колонка, которая уменьшает потребуемый объем элюата. Установленные условия применены в отделении микрограммовых количеств золота от никеля, меди и железа, также как и в определении золота в анодной меди.

Двойная, заполненная ртутью система стеклянных электродов для кислотно-щелочных титрований в разных неводных растворителях: M. Bréant and J. Georges, *Talanta* 1973, **20**, 914.

Безюме — Предложена пара заполненных ртутью стеклянных электродов для кислотно-щелочных титрований в неводных растворителях или их смесях и смесях с водой.

Неводное цериметрическое определение тиомочевин: Balbir Chand Verma and Swatantar Kumar, *Talanta* 1973, **20**, 916.

Безюме — Раствор гексанитратоцерата в ацетонитриле использован в качестве оксидиметрического реагента для визуального и потенциометрического определения тиомочевины и ее алкилпроизводных растворенных в ацетонитриле. Тиомочевины окисляются в соответствующие дисульфиды. Метод является несложным, аккуратным, надёжным и широко применимым.

Аналитические характеристики 3-оксипиколинальдегидазина: A. Garcia de Torres, M. Valcarcel and F. Pino, *Talanta* 1973, **20**, 919.

Безюме — Описаны синтез и аналитические характеристики 3-оксипиколинальдегидазина (3-OH-ПАА), салицилальдегидазина и пиколинальдегидазина. Удалось выделить 3-OH-ПАА в первый раз. Изучены растворимость, спектральные характеристики, величины pH и реакции с 36 катионами.

Хелатообразующие характеристики α-оксиминокарбоксамидов — II. Комплексы *син*-α-оксиминофенилацетамида с медью(II): Hamed M. El Fatatry, Alfred W. von Smolinski, Cecilio E. Gracias and Dominick A. Coviello, *Talanta* 1973, **20**, 923.

Резюме — *син*-α-Оксиминофенилацетамид образует два комплекса с Cu(II): комплекс CuL при pH $< 8{,}4$ и комплекс CuL_2 при pH $> 8{,}4$.

PUBLICATIONS RECEIVED

Progress in Nuclear Energy Series IX, Analytical Chemistry Vol. II: H A ELION and D. C STEWART (eds.) Pergamon, Oxford, 1972. Pp vi + 269 £13.50.

This volume is concerned with new techniques of emittance and reflectance spectroscopy The individual articles are on surface chemistry by reflection spectroscopy (Hansen), neutron spectroscopy (Trevino), far infrared for minerals and inorganics (Karr), infrared emission and reflectance for condensed phases (Aronson), laser Raman (Tobin). Fourier transform spectroscopy (Low) and photon counting (Malmstadt) It is a cerebral brew in which the basics are clearly put on a quantitative footing The choice of topics and authors is excellent, and the production up to the high standard of the series with one important exception. it would seem that the typescripts were submitted in 1969, consequently some major developments have been missed. Despite this the editors have maintained the high standards which make this one of the best and most original series of analytical tests

Identification and Analysis of Plastics, 2nd Ed.: J. HASLAM, H A. WILLIS and D C M SQUIRRELL Iliffe, London, 1972 Pp. 748 £18 00

Since the publication of the first edition of this book in 1965 there have been several important advances in polymer analysis These advances, which exploit techniques such as nuclear magnetic resonance, thin-layer chromatography, pyrolysis–gas chromatography and X-ray fluorescence, are included in this recast and expanded edition Instrumental methods, including basic principles, are dealt with in the introductory chapter The second chapter is concerned with elemental analysis, burning and other tests, and the interpretation of infrared spectra Each of the next eight chapters describes in detail the analyses of individual polymers or polymer types, such as vinyl resins, polyesters, nylons, rubbers, thermosetting resins *etc* The analysis of fillers, plasticizers and other additives is dealt with in the final chapter The useful appendix comprises a comprehensive selection of infrared spectra. Each chapter is concluded with a list of key references which go up to 1971

AUTHOR INDEX

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SUMMARIES FOR CARD INDEXES

Application of indirect methods in analysis by atomic-absorption spectrometry: G. F. KIRKBRIGHT and H. N. JOHNSON, *Talanta*, 1973, **20**, 433.
(Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—The use of indirect methods for the determination by atomic-absorption spectrometry of those elements not normally amenable to sensitive determination by this technique is reviewed. The available indirect methods are classified into five general types of procedure; specific reported procedures for the determination of metals, non-metals and some organic compounds are discussed.

Arsenazo III as metallochromic indicator for complexometric determination of calcium in slightly alkaline medium: V. MICHAYLOVA and N. KOULEVA, *Talanta*, 1973, **20**, 453. (Department of Chemistry, University of Sofia, Sofia 26, Bulgaria).

Summary—Arsenazo III is proposed as metallochromic indicator for calcium in slightly alkaline medium. The visual titration with EDTA was performed at pH 8 and 40 μg–12 mg of calcium were determined. The interference of some ions was considered and it was found that phosphate does not interfere appreciably. Spectrophotometric detection of the end-point was used for titration of calcium in the presence of magnesium at pH 9. For the estimation of the titration error, the conditional stability constants of the calcium-arsenazo III complex were found.

Ultramicro atomic-absorption spectroscopy with a tungsten-filament atom-reservoir: J. E. CANTLE and T. S. WEST, *Talanta*, 1973, **20**, 459. (Chemistry Department, Imperial College of Science and Technology, London, S.W 7, 2AY, U.K.).

Summary—The detection and measurement of traces of zinc, lead, copper and silver by atomic-absorption spectroscopy with a tungsten-filament atom-reservoir (TFAR), hollow-cathode lamps and limited-field viewing is described. The performance of this atom cell is compared with that of the carbon-filament atom-reservoir for determination of lead. Greater sensitivity and fewer matrix effects are observed with the TFAR system. The lifetime of the tungsten filament is almost indefinite.

Rapid destruction of plant material with concentrated nitric acid vapour (vapour phase oxidation): A. D. THOMAS and L E. SMYTHE, *Talanta*, 1973, **20**, 469. (Department of Analytical Chemistry, University of New South Wales, Sydney, Australia).

Summary—Concentrated nitric acid vapour is used in a simple rapid method for the destruction of organic matter in plant tissue before analysis for trace elements. About 90% of the organic matter is destroyed by the nitric acid vapour within 5–6 min and destruction is then completed by the addition of perchloric acid. The method gives zero or low blank values and has comparable precision and accuracy to conventional acid digestion methods.

Automatic control of the ion-illumination angle in a spark-source mass spectrometer: R. J. CONZEMIUS and H. J. SVEC, *Talanta*, 1973, **20**, 477. (Ames Laboratory, USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Automatic adjustment of only the spark-gap width in a spark-source mass spectrometer does not ensure that optimum conditions of electrode geometry are maintained with respect to the ion-optics system. A device has been developed which simultaneously maintains a constant gap width and also a more constant z-axis ion-illumination angle. This is the first development to utilize ion-optics parameters to adjust the sparking electrodes automatically. The system maintains the electrodes in an optimum configuration such that higher and more constant instrument sensitivity is maintained automatically. In addition, a significant improvement in the precision of instrumental response is demonstrated. It appears that relative isotopic abundances can be determined directly by the spark-source method which are comparable to those obtained in some cases by surface ionization or by electron bombardment. Results are given that support this contention.

Применение косвенных методов анализа с использованием атомно-абсорбционной спектрофотометрии: G. F. Kirkbright and H. N. Johnson, *Talanta* 1973, **20**, 433.

Резюме — Приведен обзор косвенных методов определения элементов методом атомно-абсорбционной спектрометрии которые нормально не удаются определять этим чувствительным методом. Имеющиеся косвенные методы классифицированы в пять общих типов процедур; обсуждены индивидуальные методы определения металлов, неметаллов и некоторых органических соединений.

Арсеназо III в качестве металлохромного индикатора для комплексонометрического определения кальция в слабощелочной среде: V. Michaylova and N. Kouleva, *Talanta* 1973, **20**, 453.

Резюме — Арсеназо III предложен в качестве металлохромного индикатора для кальция в слабощелочной среде. Визуальное титрование с ЭДТА проведено при pH 8, для определения 40 мкг–12 мг кальция. Изучено влияние некоторых ионов; установлено что фосфат не мешает определению в значительной мере. Спектрофотометрическое обнаружение конца титрования использовано для титрования кальция в присутствии магния при pH 9. Для обсуждения ошибки титрования определены кондициональные константы устойчивости комплекса кальция с арсеназо III.

Ультрамикрометод атомно-абсорбционной спектроскопии с использованием вольфрамовой нити в качестве резервуара атомов: J. E. Cantle and T. S. West, *Talanta* 1973, **20**, 459.

Резюме — Описано обнаружение и определение следов цинка, свинца, меди и серебра методом атомно-абсорбционной спектроскопии с использованием вольфрамовой нити в качестве резервуара атомов (ВНКРА), ламп с полым катодом и осматривания в ограниченном поле. Характеристики этой атомной ячейки сравнены с характеристиками углеродной нити в качестве резервуара атомов для определения свинца. Чувствительность больше а матричные эффекты выражены меньше в случае системы ВНКРА. Продолжительность службы вольфрамовой нити почти неограниченная.

Быстрое разрушение растительных веществ парами концентрированной азотной кислоты (окисление в парной фазе): A. D. Thomas and L. E. Smythe, *Talanta* 1973, **20**, 469.

Резюме — Пары концентрированной азотной кислоты использованы в несложном и быстром методе для разрушения органического вещества в растительной ткани перед определением следовых элементов. Около 90% органического вещества разрушено парами азотной кислоты через 5–6 мин.; полное разрушение получается добавлением хлорной кислоты. Слепой опыт метода равен нулью или весьма низкий, а точность и воспроизводимость сравнимы с обыкновенными методами дигерирования кислотами.

Автоматический контроль угла иллюминации ионов в масс-спектрометре с искровым источником: R. J. Conzemius and H. J. Svec, *Talanta* 1973, **20**, 477.

Резюме — Автоматическое регулирование только искрового промежутка в масс-спектрометре с искровым источником не обеспечивает поддерживание оптимальных условий геометрии электрода в отношении на ионооптическую систему. Сконструирован прибор позволяющий одновременно поддерживать постоянную ширину промежутка а также более постоянный угол иллюминации ионов с осью z. Это представляет собой первую попытку использования ионооптических параметров для автоматического регулирования искровых электродов. Система поддерживает электроды в оптимальной конфигурации что позволяет поддерживать автоматически более постоянную чувствительность прибора. Кроме того получается значительное улучшение воспроизводимости ответа прибора. Указана возможность непосредственного определения относительных концентраций изотопов искровым методом, которые сравнимы с концентрациями, полученными в некоторых случаях поверхностной ионизацией или бомбардированием электронами. Приведены результаты поткрепляющие эти выводы.

Acid–base equilibria in ethylene glycol—I. Definition of pH and determination of p*K*-values of acid-base indicators: P. ZIKOLOV and O. BUDEVSKY, *Talanta*, 1973, **20**, 487 (Faculty of Pharmacy, Academy of Medicine, Ekz. Josif No. 15, Sofia, Bulgaria).

Summary—A pH-scale in ethylene glycol is defined, based on potentiometric measurements for a cell without liquid junction:

$$\begin{array}{c} \text{Glass} \\ \text{electrode} \end{array} \Big\| \; 0{\cdot}1M\,(\text{HCl} + \text{KCl}), \begin{array}{c} \text{ethylene} \\ \text{glycol} \end{array} \Big| \; \text{AgCl, Ag}$$

and a potentiometric-spectrophotometric method for the determination of p*K*-values of acid–base indicators in ethylene glycol on the basis of this pH scale is proposed, in which the pH scale is established and the p*K*-value determined in a single titration at constant ionic strength. The following p*K*-values of indicators are reported: Cresol Red—3·00, Thymol Blue—3·39, Bromophenol Blue—6·49, Bromocresol Green—7·38, Bromocresol Purple—9·00 and Cresol Red (2nd change)—11·07 A linear relationship was found between the p*K*-values of four sulphonphthalein indicators in ethylene glycol and in water according to the equation $(\text{p}K_{\text{HI}}^{\text{c}})_{\text{EG}} = 2{\cdot}3 + 1{\cdot}1\,(\text{p}K_{\text{HI}}^{\text{c}})_{\text{W}}$ An attempt is made to explain this dependence, based on the idea of solute–solvent interaction of species of the same charge type.

Trace analysis by microwave excitation of sealed samples—I. Preliminary investigations: A. VAN SANDWIJK, P. F. E. VAN MONTFORT and J. AGTERDENBOS, *Talanta*, 1973, **20**, 495. (Analytisch Chemisch Laboratorium, Rijksuniversiteit Utrecht, Croesestraat 77A, Utrecht, Netherlands)

Summary—An important limitation to the sensitivity of analytical methods using atomic spectroscopy is the short residence-time of the atoms in the light-path. The possibility has been studied of sealing the samples in a quartz tube where they are forced to emit light by microwave excitation. The detection of amounts below one ng in a volume of 0·5 ml seems possible.

The signal *vs.* concentration relationships in fluorimetry: R. VAN SLAGEREN, G. DEN BOEF, and W. E. VAN DER LINDEN, *Talanta*, 1973, **20**, 501 (Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 125, Amsterdam, The Netherlands).

Summary—Formulae for the fluorescence signal are derived which take into account some factors hitherto neglected. From these formulae conditions are deduced, for which a linear relationship exists between the concentration of the fluorescent components and the intensity of the fluorescence. In some cases of practical interest the fulfilment of these conditions cause too low a sensitivity. For such cases a method of optimization is outlined, by means of which the conditions are found which lead to the least deviation from linearity at the required sensitivity.

New spot-test for cyanide ion and cyanogen gas: S. K. TOBIA, Y. A. GAWARGIOUS and M. F. EL-SHAHAT, *Talanta*, 1973, **20**, 513. (Chemistry Department, Faculty of Science, A'in Shams University, and Microanalytical Chemistry Unit, National Research Centre, Dokki, Cairo, U.A R.).

Summary—A new, rapid and simple spot test has been developed for detection of both cyanide ion and cyanogen gas. The cyanogen gas must first be converted into cyanide ion by reaction with sodium hydroxide On addition of a Cu(II) solution the cyanocuprate(I) complex formed reduces the molybdate solution to molybdenum blue.

Spectrophotometric determination of the stability constants of HgCl_3^- and HgCl_4^{2-} in aqueous ethanol: R ANANTARAMAN, A. BALASUBRAMANIAN and K. SARAMMA, *Talanta*, 1973, **20**, 515. (Department of Chemistry, University of Kerala, Trivandrum-1, India).

Summary—The stability constants of HgCl_3^- and HgCl_4^{2-} in 60% aqueous ethanol (v/v) were determined by spectroscopy at 25° and constant ionic strength and acidity: β_1 was 3 ± 1 and β_2 9 ± 3

Кислотно-щелочные равновесия в этиленгликоле — I. Дефиниция pH и определение величины pK индикаторов для определения концентрации водородных ионов: P. Zikolov and O. Budevsky, *Talanta* 1973, **20**, 487.

Резюме — Дефинирована шкала pH в этиленгликоле, основанная на потенциометрических измерениях в ячейке без жидкостного моста:

$$\text{стекляный электрод} \parallel 0{,}1M(\mathrm{HCl} + \mathrm{KCl}), \text{ этиленгликол} \mid \mathrm{AgCl};\ \mathrm{Ag}$$

и предложен потенциометрическо-спектрофотометрический метод определения величин pK кислотно-щелочных индикаторов в этиленгликоле, основывающийся на этой шкале pH. Метод позволяет установить шкалу pH и определять величины pK только одной титрацией при константной ионной силе. Приведены следующие величины pK индикаторов: крезоловый красный 3,00; тимоловый голубой 3,39; бромофеноловый синий 6,49; бромокрезоловый зеленый 7,38; бромокрезоловый пурпурный 9,00 и крезоловый красный (вторая перемена цвета) — 11,07. Обнаружено линейное отношение между величинами pK четыре сульфонфталеиновых индикаторов в этиленгликоле и воде, приказано уравнением $(\mathrm{p}K_{\mathrm{HI}}{}^{\mathrm{c}})_{\mathrm{EG}} = 2{,}3 + 1{,}1(\mathrm{p}K_{\mathrm{HI}}{}^{\mathrm{c}})_{\mathrm{W}}$. Сделана попытка протолковать это отношение на основе взаимодействия между растворенным веществом и растворителем в случае классов того же типа заряда.

Анализ следов путем возбуждения микроволнами закрытых образцев — I. Предварительные исследования: A. van Sandwijk, P. F. E. van Montfort and J. Agterdenbos, *Talanta* 1973, **20**, 495.

Резюме — Короткое время пребывания атомов в пучке света является важным ограничением чувствительности методов анализа на основе атомной спектроскопии. Изучена возможность закрытия образцев в кварцевых трубках и их возбуждения микроволнами для эмиссии света. Оказывается возможным обнаружение меньше чем 1 нг элемента в объеме 0,5 мл.

Отношение между сигналом и концентрацией в флуориметрии: R. vanSlageren, G. den Boef and W. E. van der Linden, *Talanta* 1973, **20**, 501.

Резюме — Выведены уравнения для сигнала флуоресценции, принимающие во внимание некоторые пренебрегнутые до сих пор факторы. Из этих уравнений выведены условия при которых существует линейное отношение между концентрацией флуоресцирующих компонентов и интенсивности флуоресценции. В некоторых случаях выполнение этих условий вызывает чрезвичайно низкую чувствительность. Для этих случаях предложен метод оптимизации для обнаружения условий при которых отклонение от линейности в минимуме при требуемой чувствительности.

Новая капельная проба для цианидиона и газообразного цианогена: S. K. Tobia, Y. A. Gawargious and M. F. El-Shahat, *Talanta* 1973, **20**, 513.

Резюме — Разработана новая быстрая и несложная капельная проба для обнаружения цианидиона и газообразного цианогена. Цианоген превращают в цианидион поглощением в растворе гидроокиси натрия. Добавлением к раствору Cu(II) образуется комплекс цианокупрата(I), который восстанавливает раствор молибдата до молибденового синего.

Спектрофотометрическое определение констант устойчивости $\mathrm{HgCl_3}^-$ и $\mathrm{HgCl_4}^{2-}$ в водном спирте: R. Anantaraman, A. Balasubramanian and K. Satamma, *Talanta* 1973, **20**, 515.

Резюме — Определены константы устойчивости $\mathrm{HgCl_3}^-$ и $\mathrm{HgCl_4}^{2-}$ в 60%-тном водном растворе этанола (по объему) с применением спектрофотометрического метода при 25° и постоянной ионной силы и кислотности; получены величины 3 ±1 для β_1 и 9 ±3 для β_2.

SUMMARIES FOR CARD INDEXES

Automated wet chemical analysers and their applications: J. T. VAN GEMERT, *Talanta*, 1973, **20**, 1045 (Research Laboratory, Kodak (Australasia) Pty., Ltd., P.O. Box 90, Coburg, Vic. 3058, Australia.)

Summary—A review is presented of automated analysis, including instrumentation and applications.

Precipitation of magnesium ammonium phosphate from homogeneous solution by means of hydrolysis of *p*-nitrophenylphosphate with an alkaline phosphatase: SEIICHIRO HIKIME, HITOSHI YOSHIDA, MITSUHIKO TAGA and SHIGERU TAGUCHI, *Talanta*, 1973, **20**, 1077. (Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.)

Summary—In the precipitation of magnesium ammonium phosphate from homogeneous solution, phosphate ions were generated by means of hydrolysis of *p*-nitrophenylphosphate with an alkaline phosphatase. Conditions for the gravimetric determination of magnesium ion as magnesium ammonium phosphate hexahydrate were investigated.

Tetracyanoethylene π-complex chemistry: Indirect spectrophotometric determination of Diels-Alder-active 1,3-dienes: DALE A. WILLIAMS and GEORGE H. SCHENK, *Talanta*, 1973, **20**, 1085. (Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.)

Summary—An indirect spectrophotometric method, based on the rapid Diels-Alder reaction between cisoid 1,3-dienes and tetracyanoethylene (TCNE) and the destruction of an aromatic-TCNE π-complex, was developed to determine eleven 1,3-dienes in the $0{\cdot}05$–$1{\cdot}00 \times 10^{-3}M$ range. These dienes were cyclopentadiene; 1,3-cyclohexadiene; *trans*-1,3-pentadiene; 2,4-dimethyl-1,3-pentadiene; *trans*-2-methyl-1,3-pentadiene; 2-methyl-1,3-butadiene; 9-methylanthracene; 9,10-dimethylanthracene; 1,6-diphenyl-1,3,5-hexatriene; 2,3-dimethyl-1,3-butadiene; and 1,4-diphenyl-1,3-butadiene. Three 1,3-dienes were determined in the $0{\cdot}05$–$1 \times 10^{-4}M$ range: cyclopentadiene, *trans*-2-methyl-1,3-pentadiene, and anthracene. The limit of detection for cyclopentadiene in carbon tetrachloride solutions is 0·11 μg/ml. Fourteen 1,3-dienes were found to form stable π-complexes and could not be determined by the proposed method. For these 1,3-dienes, the spectra of some of the π-complexes are reported; in addition, relative equilibrium constants for the π-complexes of 2,5-dimethyl-2,4-hexadiene, *cis*-1,3-pentadiene, 4-methyl-1,3-pentadiene, and 1,3-cyclo-octadiene were estimated. An explanation of the transient colour in the 1,3-diene–TCNE Diels-Alder reaction is suggested.

Coulometric microdetermination of peroxides—I. Hydrogen peroxide: ULLA FIEDLER, *Talanta*, 1973, **20**, 1097. (Department of Analytical Chemistry, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden.)

Summary—An electroanalytical method, based on controlled-potential coulometry in the iodine-iodide system, has been developed for determination of small amounts of hydrogen peroxide. The sample is added to an electrolyte containing an acid solution of iodide and the iodine, which is produced rapidly, is reduced at a rotating platinum electrode. The number of coulombs consumed in the cell reaction is determined by electronic integration. Samples containing 1 μg–1 mg of hydrogen peroxide were analysed with an accuracy of ±0·2%. The analysis time ranged from 3 to 7 min.

Автоматические анализаторы на основе классических методов анализа и их применение: J. T. van Gemert, *Talanta* 1973, 20, 1045.

Резюме — Приведен обзор автоматического анализа, включая приборы и их применение.

Осаждение смешанного фосфата магнезия и аммония из гомогенного раствора путем гидролиза п-нитрофенолгипофосфита фосфатазой в щелочном растворе: Seiichiro Hikime, Hitoshi Yoshida, Mitsuo Taga and Shigeru Taguchi, *Talanta*, 1973, 20, 1077.

Резюме — Осаждением смешанной фосфорнокислой соли магния и аммония в гомогенном растворе, генерировались ионы фосфата путем гидролиза *p*-нитрофенилфосфата с щелочным фосфатазом. Исследовались условия для гравиметрического определения иона магнезия как гексигидрита смешанной фосфорнокислой соли магния и аммония.

Химия π-комплексов с тетрацианоэтиленом: Косвенное спектрофотометрическое определение Дилс-Альдер-активных 1,3-диенов: Dale A. Williams and George H. Schenk, *Talanta*, 1973, 20, 1083.

Резюме — Разработан косвенный спектрофотометрический метод основывающийся на быстрой реакции Дилс-Альдер *цис*-1,3-диенов с тетрацианоэтиленом (ТЦНЭ) и разрушении ароматического π-комплекса с ТЦНЭ, для определения II 1,3-диенов в области концентраций 0,05–1,00 × 10^{-3} *M*. Испытаны следующие диены: циклопентадиен; 1,3-циклогексадиен; *транс*-1,3-пентадиен; 2,4-диметил-1,3-пентадиен; *транс*-2-метил-1,3-пентадиен; 2-метил-1,3-бутадиен; 9-метил-антрацен; 9,10-диметилантрацен; 1,6-дифенил-1,3,5-гексатриен; 2,3-диметил-1,3-бутадиен; и 1,4-дифенил-1,3-бутадиен. Три 1,3-диена определены в области 0,05–1 × 10^{-4} *M*: циклопентадиен, *транс*-2-метил-1,3-пентадиен и антрацен. Чувствительность метода для циклопентадиена в растворе тетрахлорметана составляет 0,11 мкг/мл. Обнаружено что 14 1,3-диенов образуют устойчивые π-комплексы и потому их не удалось определить этим методом. Для этих 1,3-диенов приведены спектры некоторых π-комплексов; к тому же определены относительные константы равновесия π-комплексов 2,5-диметил-2,4-гексадиена, *цис*-1,3-пентадиена, 4-метил-1,3-пентадиена и 1,3-циклооктадиена. Предложено объяснение переходной окраски обнаруженной в реакции Дилс-Альдер 1,3-диенов с ТЦНЭ.

Кулонометрическое микроопределение перекисей — I. Перекись водорода: Ulla Fiedler, *Talanta*, 1973, 20, 1097.

Резюме — Разработан электроаналитический метод для определения небольших количеств перекиси водорода, пользующийся кулонометрией при контроллированном напряжении в системе иод-иодид. Пробу добавляют электролиту, содержащему кислый раствор иодида, а быстро образующийся иод восстанавливается на вращающемся платиновом электроде. Число кулонов, расходованных реакцией в ячейке, определено электронным интегрированием. Пробы содержащие 1 мкг–1 мл перекиси водорода анализированы точностью ±0,2%. Продолжительность анализа 3–7 мин.

Selectrode—The universal ion-selective electrode—Complex formation studies with the Cu(II) Selectrode: E. H. Hansen and J. Ruzicka, *Talanta*, 1973, **20**, 1105. (Chemistry Department A, The Technical University of Denmark, Building 207, 2800 Lyngby, Denmark.)

Summary—The Cu(II) Selectrode, calibrated in a series of Cu(II) buffers at various pH levels, has been used for the determination of the stability constants of the Cu(II) complexes of glycine and EGTA at an ionic strength of 0·1. Methods for the calculation of the stability constants of chelate complexes from pH and pM values are presented. The values obtained compare very favourably with those recorded in the literature. For the Cu(II)–EGTA system, for which only a few stability constants have been determined, the following constants were found: $\log K_{\mathrm{CuL}}^{\mathrm{Cu,L}} = 16{\cdot}80$; $\log K_{\mathrm{CuHL}}^{\mathrm{H,CuL}} = 5{\cdot}30$; $\log K_{\mathrm{CuH2L}}^{\mathrm{2H,CuL}} = 7{\cdot}64$; $\log K_{\mathrm{CuH2L}}^{\mathrm{H,CuHL}} = 2{\cdot}34$; $\log K_{\mathrm{CuHL}}^{\mathrm{Cu,HL}} = 12{\cdot}56$; and $\log K_{\mathrm{CuH2L}}^{\mathrm{Cu,H2L}} = 5{\cdot}97$. Examples of the application of the Cu(II) Selectrode in replacement reactions are illustrated.

TRIEN and TETREN as titrants in potentiometry with a silver indicator electrode: Adam Hulanicki, Marek Trojanowicz and Joanna Domanska, *Talanta*, 1973, **20**, 1117. (Institute of Fundamental Problems in Chemistry, University of Warsaw, Warsaw, Poland.)

Summary—The possibility of application of triethylenetetramine (TRIEN) and tetraethylenepentamine (TETREN) in metal titrations with the silver electrode as indicator was investigated. Copper, cadmium and zinc were determined in the presence of calcium, magnesium, aluminium and iron(III) in the concentration range from 0.02 to 2m*M*. The errors did not exceed 1 %. On a similar basis copper and iron may be successfully determined in their mixtures under carefully controlled conditions. Copper is titrated with TRIEN, and both metals with EDTA at pH 7·5–8·0 in sulphosalicylate medium. The results obtained were in good agreement with those predicted theoretically.

Selective separation of uranium from other elements by cation-exchange chromotography in hydrobromic acid– and hydrochloric acid–acetone mixtures. F. W. E. Strelow and C. H. S. W. Weinert, *Talanta*, 1973, **20**, 1127. (National Chemical Research Laboratory, P.O. Box 395, Pretoria, Republic of South Africa.)

Summary—U(VI) can be separated from Ga, Fe(III), Bi, Pb, Cd, Zn, Cu(II) and Au(III) by quantitative elution with 0·50*M* HBr in 86 % acetone or with 0·35*M* HBr in 90 % acetone from a column of AG50W-X4 cation-exchange resin of 200–400 mesh particle size. U(VI) and many other ions are retained. U(VI) can then be eluted selectively with 0·50*M* HCl in 83 % acetone or with 0·35*M* HCl in 85 % acetone. Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th and La are quantitatively retained by the column. At the higher acid concentration (0·50*M*) the separation between U(VI) and Li is not satisfactory but is excellent at the lower acid concentration; the U(VI) peak is sharper at the higher acid concentration. Separations are sharp and quantitative, as is demonstrated by results for some synthetic mixtures. Distribution coefficients and elution curves are presented.

Селектрод — Универсальный ионоселективный електрод: — Изучение комплексообразования с использованием электрода С (II): E. H. Hansen and J. Ruzicka, *Talanta*, 1973, **20**, 1105.

Резюме — Селектрод Cu(II), калиброванный в ряде буферных растворов Cu(II) при разных pH, использован для определения констант устойчивости комплексов Cu(II) с глицином и ЕГТА при ионной силе 0,1. Предложены методы расчета констант устойчивости хелатных комплексов на основе величины pH и pM. Полученные величины хорошо соглашаются с значениями опубликованными в литературе. Следующие константы получены для системы Cu(II)-ЭГТА, для которой были определены только немногие константы устойчивости:

$$\lg K^{\mathrm{Cu,\,L}}_{\mathrm{CuL}} = 16{,}80; \quad \lg K^{\mathrm{H,\,CuL}}_{\mathrm{CuHL}} = 5{,}30; \quad \lg K^{\mathrm{2H,\,CuL}}_{\mathrm{CuH2L}} = 7{,}64;$$

$$\lg K^{\mathrm{H,\,CuHL}}_{\mathrm{CuH2L}} = 2{,}34; \quad \lg K^{\mathrm{Cu,\,HL}}_{\mathrm{CuHL}} = 12{,}56; \quad \text{и} \quad \lg K^{\mathrm{Cu,\,H2L}}_{\mathrm{CuH2L}} = 5{,}97.$$

Приведены примеры для иллюстрации применения Селектрода С (II) в реакциях замещения.

Использование триена и тетрена в качестве титрованных растворов в потенциометрии с серебряным индикаторным электродом: Adam Hulanicki, Marek Trojanowicz and Joanna Domanska, *Talanta* 1973, **20**, 1117.

Резюме — Исследована применимость триэтилентетрамина (ТРИЭНа) и тетраэтиленпентамина (ТЕТРЭНа) для титрования металлов с использованием серебрянного электрода в качестве индикатора. Определили медь, кадмий и цинк в присутствии кальция, магния, алюминия и железа(III) в области концентраций 0,02 до 2 ммоля. Ошибки не превышали 1%. На похожем принципе удается определять медь и железо в смесе при тщательно контроллированных условиях. Медь титруют с ТРИЭНом, а оба металла — с ЭДТА при pH 7,5–8,0 в растворе сульфосалицилата. Полученные результаты хорошо соглашаются с результатами предсказанными теорией.

Селективное отделение урана от других элементов методом катионообменной хроматографии с использованием смесей бромистоводородной и соляной кислот с ацетоном: F. W. E. Strelow and C. H. S. W. Weinert, *Talanta* 1973, **20**, 1127.

Резюме — U(VI) отделяется от Ga, Fe(III), Bi, Pb, Cd, Zn, Cu(II) и Au(III) количественным элюированием с 0,50 *M* HBr в 86%-тном ацетоне или с 0,35 *M* HBr в 90%-тном ацетоне из колонки катионообменной смолы AG50W-X4 с размером зерен 200–400 меш. U(VI) и ряд других ионов задержаны на колонке. U(VI) элюируют селективно с 0,50 *M* HCl в 83%-тном ацетоне или с 0,35 *M* HCl в 85%-тном ацетоне. Co(II), Mn(II), Mg, Ca, Ti(IV), Al, Zr, Th и La задержаны количественно на колонке. Отделение U(VI) от Li неудовлетворительно при использовании высшей концентрации кислоты (0,50 *M*) но отлично при использовании нижней концентрации; пик U(VI) более острый при высшей концентрации кислоты. Разделения являются резкими и количественными, о чем свидетельствуют результаты, полученные на синтетических смесях. Приведены коэффициенты распределения и элюционные кривые.

Polarographic procedures without removal of oxygen, and other approaches to making the determinations more rapidly: A. M. BOND, *Talanta*, 1973, **20**, 1139. (Department of Inorganic Chemistry, University of Melbourne, Parkville, 3052, Victoria, Australia.)

Summary—One disadvantage of conventional d.c. polarography as an analytical method has always been its relative slowness. The possibility of simplifying and speeding up analyses by avoiding the necessity for removal of oxygen is demonstrated under suitable conditions with current-sampled d.c. pulse and a.c. polarography. In particular it is shown that high-frequency phase-selective a.c. polarography gives considerable discrimination against the oxygen electrode process in some aqueous media. Under these conditions, the high-frequency a.c. technique can be combined with the method of short drop-time, fast scan-rate rapid a.c. polarography to provide a most attractive method of routine analysis. Polarographic analysis in non-aqueous media without removal of oxygen is also discussed.

Determination of vanadium and molybdenum by atomic-absorption spectrophotometry: J. KORKISCH and H. GROSS, *Talanta*, 1973, **20**, 1153. (Analytical Institute, Division: Analysis of Nuclear Raw Materials, University of Vienna, Währingerstrasse 38, A-1090 Vienna, Austria.)

Summary—A method is described for the determination by atomic-absorption spectrophotometry of vanadium and molybdenum, up to the milligram level, in samples of yellow cake, uranium-bearing minerals and geochemical standards. After attack with acids these two elements are separated from each other and from matrix elements by means of anion-exchange in $6M$ hydrochloric acid on the strongly basic anion-exchange resin Dowex 1, X8 (chloride form). Vanadium is unadsorbed and passes into the effluent while molybdenum is adsorbed on the resin. For the elution of molybdenum a mixed aqueous-organic solvent system consisting of methanol and $6M$ hydrochloric acid (9 : 1 v/v) is used. After evaporation of the $6M$ hydrochloric acid effluent and of the mixed aqueous–organic eluate vanadium and molybdenum are determined by atomic-absorption spectrophotometry. The method was tested by analysing numerous sampls with contents ranging from a few ppm to milligram amounts of vanadium and molybdenum. For comparison, the concentrations of these two elements were determined in a large number of samples by spectrophotometric and titrimetric procedures. In all cases very good agreement of results was obtained.

Automated determination of fluoride ion in the parts per milliard range; I. SEKERKA and J. F. LECHNER, *Talanta*, 1973, **20**, 1167. (Department of the Environment, Canada Centre of Inland Waters, Burlington, Ontario, Canada.)

Summary—Fluoride down to 2 ppM has been determined by automated direct potentiometry using a fluoride ion-selective electrode. The method reduces the dilution and contamination effects of TISAB and takes the electrode response-time into consideration. The relative standard deviation for water samples is 1·5–1·8% and the recovery varies from 96 to 107%.

Полярографические методы без удаления кислорода и другие подходы для ускорения определения: A. M. Bond, *Talanta* 1973, **20**, 1139.

Резюме — Медленность определения является одним из убытков применения метода обыкновенной полярографии при постоянном токе в анализе. Показана возможность ускорения и упрощения анализа, избежанием удаления кислорода при подходящих условиях применением импульсной полярографии при постоянном токе и полярографии при переменном токе. Показано, в частности, что высокочастотная фазоселективная полярография при переменном токе позволяет в значительной мере дискриминировать кислородный электродный процесс в некоторых водных средах. При этих условиях можно комбинировать высокочастотную полярографию при переменном токе с коротким периодом капания ртути и быстрой разверткой и получить очень привлекательный метод для серийного анализа. Также обсуждено применение полярографического метода в неводных средах без удаления кислорода.

Определение ванадия и молибдена методом атомно абсорбционной спектрофотометрии: J. Korkisch and H. Gross, *Talanta* 1973, **20**, 1153.

Резюме — Описан метод атомно-абсорбционной спектрофотометрии для определения вплоть миллиграммовых количеств ванадия и молибдена в концентратах, урансодержащих минералах и геохимических эталонах. После обработки с кислотами эта два элемента отделяют один от другого и от матричных элементов путем ионного обмена в 6 *M* соляной кислоте с использованием сильноосновной анионообменной смолы Дауекс 1,X8 в форме хлорида. Ванадий не адсорбируется и проходит в элюат, в то время как молибден адсорбируется на смоле. Элюирование молибдена получается с использованием смешанной водно-растворительной системы, состоящейся из метанола и 6 *M* соляной кислоты (9 : 1 по объему). После выпаривания элюатов состоящихся из 6 *M* соляной кислоты и смеси соляной кислоты с метанолом, ванадий и молибден определяют методом атомно-абсорбционной спектрофотометрии. Метод испытан на ряде образцев содержащих несколько частей на миллион вплоть миллиграммовых количеств ванадия и молибдена. Для сравнения, концентрации этих элементов определены в большом числе образцов спектрофотометрическими и титриметрическими методами. Во всех случаях получено хорошое соглашение результатов.

Автоматическое определение фторидиона в области концентраций частей на миллиард: I. Sekerka and J. F. Lechner, *Talanta*, 1973, **20**, 1167.

Резюме — Автоматической непосредственной потенциометрией при помощи ион-избирательного электрода определялись ионы флуоридного соединения в диапазоне 2 частей на миллион. Этот метод уменьшает эффекты разбавления и загрязнения TISABa и учитывает постоянную времени электрода. Относительное стандартное отклонение образцов воды — 1,5–1,8%, а восстановление варьирует от 96 до 107%.

Distinguishing polyfunctional from monofunctional acids and bases by acid-base titrimetry, multiparametric curve-fitting, and deviation-pattern recognition: LOUIS MEITES and DANA M. BARRY, *Talanta*, 1973, **20**, 1173. (Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676.)

Summary—A new technique for distinguishing diacidic from monoacidic weak bases (or dibasic from monobasic weak acids) is based on fitting the data obtained in a potentiometric acid–base titration to theoretical equations for the titration of a monoacidic base (or monobasic acid). If the substance titrated is not monofunctional the best fit to these equations will involve systematic deviations that, when plotted against the volume of reagent, yield a "deviation pattern" with a shape characteristic of polyfunctional behaviour. Ancillary criteria based on the values of the parameters obtained from the fit are also described. There is a range of uncertainty associated with each of these criteria in which the ratios of successive dissociation constants are so close to the statistical values that it is impossible in the face of the errors of measurement to decide whether the substance is monofunctional or polyfunctional. If the data from one titration prove to lie within that range, the decision may be based on the results of a second titration performed at a different ionic strength. Further fitting to the equations describing more complex behaviour provides a basis for distinguishing non-statistical difunctional substances from trifunctional ones, trifunctional ones from tetrafunctional ones, and so on.

Amperometrically indicated "pseudotitrations"—I Complexometric determination of chromium (III): D. I. BUSTIN and J. MOCÁK, *Talanta*, 1973, **20**, 1185. (Department of Analytical Chemistry, Slovak Technical University, Bratislava, Czechoslovakia.)

Summary—In the pseudotitration no reaction takes place between titrand and titrant in the bulk of the solution. An amperometric indicating system, which generates a small amount of redox catalyst in the vicinity of the electrode, does enable an end-point to be found. Bulk concentrations and diffusion constants are the controlling parameters. This method allows to utilize slow, thermodynamically favourable reactions for titrating purposes. The principle is demonstrated by the direct titration of chromium(III) with EDTA at room temperature.

Amperometrically indicated "pseudotitrations—II. Determination of chromium(III) in the presence of other reacting metal ions: D. I. BUSTIN and J. MOCÁK, *Talanta*, 1973, **20**, 1191. (Department of Analytical Chemistry, Slovak Technical University, Bratislava, Czechoslovakia.)

Summary—Chromium(III) may be determined complexometrically in a pseudotitration, in which reaction does not take place in the bulk of the solution. Redox catalyzed titration reaction proceeds only in the vicinity of the indicating electrode. The titration curves for solutions containing additional metal ions which react with EDTA are discussed and classified according to their reduction potentials, equilibrium constants and reaction rates. In certain combinations two or more metals may be determined simultaneously from one titration curve. Examples given are Cr/Hg, Cr/Cd, and Cr/Zn.

Различение многофункциональных кислот и оснований однофункциональных на основе ацидиметрии и алкалиметрии, многопараметрического приспособления кривых и распознавания шаблона отклонений: Louis Meites and Dana M. Barry, *Talanta* 1973, **20**, 1173.

Резюме — Новый метод различения двукислотных от однокислотных слабых оснований (или двуосновных от одноосновных кислот) основан на приспособлении данных полученных потенциометрическим кислотно-щелочным титрованием к теоретическим уравнениям для титрования однокислотного основания (или одноосновной кислоты). Если титруемое вещество не является однофункциональным, наилучшее приспособление к этим уравнениям будет показать систематические отклонения, которые, приказанные в зависимости от объема реагента, дают «шаблон отклонений», форма которого характеристическая для многофункционального поведения. Также описаны подчиненные критерии, основанные на величиных параметров полученных приспособлением. Область неизвестности связана с каждим из этих критериев, в которой отношения последующих констант диссоциации так близки к статистическим величинам что в рамках экспериментальной ошибки выбор, если данное вещество является однофункциональным или многофункциональным, сделать не возможно. Если данные одного титрования находятся в этой области выбор можно сделать на основе второго титрования проведенного при различной ионной силе. Приспособление к уравнениям описывающим более комплексное поведение позволяет различать нестатистические двуфункциональные вещества от трехфункциональных, трехфункциональные от четырехфункциональных, и т. п.

«Псевдотитрования» с амперометрической индикацией — I. Комплексонометрическое определение хрома(III): D. I. Bustin and J. Mocák, *Talanta* 1973, **20**, 1185.

Резюме — В псевдотитрации титруемое вещество не реагирует с титрованным раствором в объеме раствора, но амперометрическая индикаторная система, образующая небольшое количество окислительно-восстановительного катализатора близко электрода, позволяет обнаружить конец титрования. Разные ионы находящиеся в растворе диффундируют к электроде где реакция катализирована в небольшом масштабе. Объемные концентрации и константы диффузии представляют собой параметры контроллирующие этот процесс. Принцип иллюстрирован на примере непосредственного титрования хрома(III) с ЭДТА при комнатной температуре.

«Псевдотитрования» с амперометрической индикацией — II. Определение хрома(III) в присутствии других реагирующих ионов металлов: D. I. Bustin and J. Mocák, *Talanta* 1973, **20**, 1191.

Резюме — Хром(III) определяют комплексонометрическим путем псевдотитрацией в которой нет реакции в объеме раствора, но реакция проходит только в небольшом масштабе под действием катализатора на поверхности индикаторного электрода. Рассмотрены титрационные кривы для растворов содержащих другие ионы металлов реагирующие с ЭДТА, и классифицированы на основе разных потенциалов восстановления, констант равновесия и скоростей реакции. Некоторые комбинации позволяют определять одновремено два или больше металлов из одной титрационной кривой. В качестве примера приведены системы Cr/Hg, Cr/Ca и Cr/Zn.

Anion-exchange separation and spectrophotometric determination of thorium in geological samples: J. Korkisch and D. Dimitriadis, *Talanta*, 1973, **20**, 1199. (Analytical Institute, Division: Analysis of Nuclear Raw Materials, University of Vienna, Wahringerstraße 38, A-1090 Vienna, Austria.)

Summary—To determine thorium in geological samples it is first separated from all matrix elements by means of anion-exchange. After elution the thorium is determined spectrophotometrically by using thoronol or arsenazo III. The suitability of the method for the determination of both trace and larger amounts of thorium was tested by analysing numerous geochemical standard samples with thorium contents in the range of 1–1000 ppm. In all cases very good agreement was obtained.

Spectrophotometric determination of molybdenum by extraction of a green molybdenum(V) species: V. Yatirajam and Jaswant Ram, *Talanta*, 1973, **20**, 1207. (Chemistry Department, University of Kurukshetra, Kurukshetra, India.)

Summary—A simple method is described for the rapid spectrophotometric determination of molybdenum in samples containing 1–60% Mo, with satisfactory accuracy. Molybdenum is reduced with excess of hydrazine sulphate in boiling $5{\cdot}5M$ hydrochloric acid and extracted with isoamyl acetate from $7M$ hydrochloric acid. The green colour is measured at 720 nm against a reagent blank. Beer's law is obeyed over the range 0·08–5·4 mg of molybdenum per ml. Interference from iron and copper is removed by adding stannous chloride and thiourea respectively in slight excess. Titanium, vanadium, niobium, chromium, tungsten, nickel, uranium, and antimony do not interfere even in large amounts. Only cobalt interferes seriously.

Анионообменное выделение тория и его спектрофотометрическое определение в геологических образцах: J. Korkisch and D. Dimitriadis, *Talanta* 1973, 20, 1199.

Резюме — Для определения тория в геологических образцах, элемент во-первых отделяют от всех матричных элементов с использованием ионного обмена. После элюирования торий определяют спектрофотометрическим путем с использованием торонола или арсеназо III. Применимость метода для определения следовых и больших количеств тория испытана на ряде геохимических эталонов, содержащих 1–1000 ч. на миллион тория. Результаты испытания хорошо соглашались во всех случаях.

Спектрофотометрическое определение молибдена экстрагированием зеленого комплекса молибдена(С): V. Yatirajam and Jaswant Ram, *Talanta*, 1973, 20, 1207.

Резюме — Описан несложный метод быстрого спектрофотометрического определения молибдена в пробах содержащих 1–60% Мо, с удовлетворительной точностью. Молибден восстанавливают с избытком сернокислого гидразина в кипящей 5,5 *M* соляной кислоте и экстрагируют изоамилацетатом из 7 *M* соляной кислоты. Зеленую окраску измеряют при 720 нм в сравнении с слепой пробой для реагентов. Закон Бера почитается в области 0,08–5,4 мг/мл молибдена. Мешающее действие железа и меди устраняют добавлением небольшого избытка хлорида олова(II) и тиомочевины, соответственно. Титан, ванадий, ниобий, хром, вольфрам, никель, уран и сурьма не мешают даже если присутствуют в больших количествах. Только кобальт показывает серьезное влияние.

Thiotropolone as a chromogenic reagent for the simultaneous determination of cobalt(II) and nickel(II): J. N. SRIVASTAVA and R. P. SINGH, *Talanta*, 1973, **20**, 1210. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—Thiotropolone forms chloroform-soluble reddish-brown and violet complexes with cobalt(II) and nickel(II), in the pH range 7·0–8·5 and 6·0–9·0 respectively. Based on this, a sensitive and rapid method for the spectrophotometric determination of traces of cobalt and nickel in metals and alloys has been developed. The two metals can be determined accurately in the range 0·6–2·6 ppm of cobalt and 0·75–4·57 ppm of nickel, simultaneously.

Gravimetric determination of cadmium with *N*-phenylbenzohydroxamic acid: Y. K. AGRAWAL, *Talanta*, 1973, **20**, 1213. (Department of Chemistry, Indian Institute of Technology, Powai, Bombay-76, India.)

Summary—A quantitative gravimetric determination of cadmium in presence of Ag^+, Be^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Mo^{6+} and U^{6+} was made by selective precipitation with *N*-phenylbenzohydroxamic acid from a solution containing 6–15 mg of cadmium acetate at pH 5·8–6·5. The precipitate was weighed directly after drying at 110–120°. The cadmium complex is curdy white, granular and melts at 225°. The analytical results indicate the complex to be $(C_{13}H_{10}NO_2)_2Cd$.

Spectroscopic determination of sulphate in the presence of excess of nitrate and nitrite: B. J. MEEHAN and S. A. TARIQ, *Talanta*, 1973, **20**, 1215. (Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria, Australia.)

Summary—The KBr pellet technique has been used for the determination of alkali metal sulphate in the presence of large excesses of nitrate and nitrite by measuring the absorption of the sulphate at 619 cm^{-1}. The sulphate can be determined in a 400-fold molar excess of nitrate and a 60-fold molar excess of nitrite with a relative standard deviation of about 5%.

Gravimetric determination of uranium (VI) with pyridine-2,6-dicarboxylic acid: G. MARANGONI, S. DEGETTO and U. CROATTO, *Talanta*, 1973, **20**, 1217. (Laboratorio di Chimica e Tecnologia dei Radioelementi, C.N.R., Via Vigonovese, 52, Padova, Italy.)

Summary—Uranium(VI) can be quantitatively precipitated from aqueous solution in the pH range 2.1–6.9 with pyridine-2,6-dicarboxylic acid in the presence of tetraphenylarsonium chloride. This provides a new rapid gravimetric method for of uranyl ion as an organic chelate complex of high molecular weight. Sodium, aluminium, copper and nickel, as well as nitrate, chloride, sulphate and acetate ions, do not interfere, but iron(III) and thorium(IV) do.

Тиотрополон в качестве хромогенного реагента для одновременного определения кобальта (II) и никеля(II): J. N. Srivastava and R. P. Singh, *Talanta* 1973, **20**, 1210.

Резюме — Тиотрополон образует растворимые в хлороформе красновато-коричневые и фиолетовые комплексы в области pH 7,0–8,5 и 6,0–9,0, соответственно. На этой основе разработан чувствительный и быстрый метод спектрофотометрического определения следов кобальта и никеля в металлах и сплавах. Точное одновременное определение этих металлов можно провести в области концентраций 0,6–2,6 ч. на миллион кобальта и 0,75–4,57 ч. на миллион никеля.

Весовой метод определения кадмия с использованием *N*-фенилбензогидроксамовой кислоты: Y. K. Agrawal, *Talanta* 1973, **20**, 1213.

Резюме — Количественное весовое определение кадмия проведено в присутствии Ag^{+}, Be^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Pd^{2+}, Ga^{3+}, Al^{3+}, Bi^{3+}, Sb^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, V^{5+}, Mo^{6+} и U^{6+}, путем селективного осаждения с *N*-фенилбензогидроксамовой кислотой из раствора содержащего 6–15 мг ацетата кадмия при pH 5,8–6,5. Осадок взвешивали непосредственно после осушки при 110–120°. Комплекс кадмия является молочнобелым и зернистым и плавится при 225°. На основе аналитических данных состав комплекса $(C_{13}H_{10}NO_2)_2Cd$.

Спектроскопический метод определения сульфата в присутствии избытка нитрата и нитрита: B. J. Meehan and S. A. Tariq, *Talanta* 1973, **20**, 1215.

Резюме — Метод пользующийся таблеткой KBr применен в определении сульфата щелочных металлов в присутствии большого избытка нитрата и нитрита, путем измерения светопоглощения сульфата при 619 $см^{-1}$. Метод позволяет определять сульфат при 400-кратном молярном избытке нитрата и 60-кратном молярном избытке нитрита с относительной стандартной ошибкой равной приблизительно 5%.

Весовое определение урана(VI) с использованием пиридин-2,6-дикарбоновой кислоты: G. Marangoni, S. Degetto and U. Croatto, *Talanta* 1973, **20**, 1217.

Резюме — Уран(VI) осаждается количественно из водного раствора в области pH 2,1–6,9 пиридин-2,6-дикарбоновой кислотой в присутствии хлорида тетрафениларсония. Это представляет собой новый быстрый метод весового анализа уранилиона в форме органического хелата с высоким молекулярным весом. Натрий, алюминий, медь и никель, нитрат, хлорид, сульфат и ацетат не влияют на определение, но железо(III) и торий(IV) мешают определению.

Quantitative measurement of mixtures of hallucinogens by fluorometry and phosphorimetry: D. M. Fabrick and J. D. Winefordner, *Talanta*, 1973, **20**, 1220. (Department of Chemistry, University of Florida, Gainesville, Florida, 32601, U.S.A.)

Summary—Room-temperature fluorometric and low-temperature phosphorimetric analytical curves of hallucinogens in methanol/water solution have been prepared to demonstrate the absence of interference in common binary mixtures of hallucinogenic drugs. Limits of detection and linear dynamic ranges have been determined for drugs in mixtures. Mixtures containing LSD and another hallucinogen such as STP (DOM), psilocybin, mescaline and phencyclidine have been studied. Detection limits are low, and analytical curves are linear over wide concentration ranges.

Formation and thermodynamic properties of complexes of Ag(I) with thiourea as Ligand: A. Bellomo, D. De Marco and A. De Robertis, *Talanta* 1973, **20**, 1225. (Institute of Analytical Chemistry, University of Messina, Messina, Italy.)

Summary—A potentiometric study has been made of the $Ag(I)–CSN_2H_4–H_2O$ system. Mathematical analysis of the formation functions reveals the existence of the complexes $AgCSN_2H_4^+$, $Ag(CSN_2H_4)_2^+$. $Ag(CSN_2H_4)_3^+$ and $Ag(CSN_2H_4)_4^+$ for which the stability constants have been calculated at different ionic strengths and temperatures. No evidence was found for the formation of polynuclear complexes.

Количественное определение смесей галлюциногенов методами флуорометрии и фосфориметрии: D. M. Fabrick and J. D. Winefordner, *Talanta*, 1973, **20**, 1220.

Резюме — Комнатно-температурные флуорометрические и низкотемпературные фосфориметрические аналитические кривые галлюциноза в растворе метанол-вода построили для демонстрации отсутствия интерференции в простых бинарных смесях галлюцинозных наркотиков. Определялись пределы детекции и линейные динамические диапазоны для наркотиков в смесях. Изучались смеси, содержащие LSD и другой галлюциноз такой как STP (DOM), псилоцибин, месцалин и фенциклидин. Уровни детекции низкие и аналитические кривые являются линейными по широкому диапазону концентраций.

Образование и термодинамические свойства комплексов Ag(I) с тиомочевиной в качестве лиганда: A. Bellomo, D. de Marco and A. de Robertis, *Talanta* 1973, **20**, 1225.

Резюме — Изучена потенциометрическим методом система $Ag(I)$–CSN_2H_4–H_2O. Математический анализ функций образования показывает существование комплексов $AgCSN_2H_4^+$, $Ag(CSN_2H_4)_2^+$, $Ag(CSN_2H_4)_3^+$ и $Ag(CSN_2H_4)_4^+$, константы устойчивости которых рассчитаны при разных ионных силах и температурах. Образование многоядерных комплексов не обнаружено.