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Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, Frenc or German; all papers have abstracts in these three languages and also in Russian. Special importanc is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original pape short communications and reviews are refereed in the normal manner. Preliminary communications a refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemi is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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TITRATION CURVES IN COMPLEXOMETRIC TITRATIONS WITH THE REDOX SYSTEM Fe(III)/Fe(II)

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Summary—Potentiometric titrations of metal ions with EDTA have been carried out with a platinum or graphite electrode and the Fe(III)/Fe(II) redox system. In the absence of oxygen and for pH <2 the titration curves may be described by an equation similar to that given previously for titrations with silver and mercury electrodes. Titration curves for bismuth and indium, which are more strongly complexed than iron, are asymmetrical and useful for analytical purposes. When the titrated ions are complexed less strongly than iron(III) ions the kinetics of metal complexation have a pronounced effect. The titration curves of thorium and copper, which react more rapidly than iron, are analytically useful. The curves recorded rapidly after titrant additions have a better end-point break than those which correspond to thermodynamic equilibrium. When a metal, *e.g.*, nickel, is weakly bound by EDTA, and reacts more slowly than iron, a very small end-point break or none at all is observed.

VARIOUS electrometric methods for end-point detection have been used in complexometric titrations. Some improve the precision or allow in some instances a better insight into the mechanism and equilibria of titration. Several authors have used potentiometric end-point detection by means of an inert electrode and a redox system influenced by complexation. Pribil[1] has titrated iron(III) with EDTA and back-titrated other ions with iron(III) chloride. Štráfelda[2] has presented results for the EDTA titration of iron(III), copper(II) and cobalt(II), which show that very small amounts of the other ion of the redox couple can be monitored by the electrode. Štráfelda and Matoušek[3] have attempted to use the CuY^{2-}/CuY^{3-} system as well as the FeY^{-}/FeY^{2-} system for the titration of several ions (Y^{4} = the EDTA anion). An interesting contribution may be found in the paper of Nomura, Dono and Nakagawa[4] who have thoroughly investigated the application of the FeY^{-}/FeY^{2-} system.

This paper reports the results of an investigation of the complexometric titration of several metal ions in the presence of the redox system Fe(III)/Fe(II) and inert electrodes of platinum or graphite. Special attention is paid to the course of titration as a function of the stability constants of complexes and the rate of complexation.

EXPERIMENTAL

Reagents

EDTA, 0·05*M solution*. Standardized by standard methods.

Bismuth, indium, thorium, copper and nickel nitrates, 0·1*M solutions*. Prepared from reagent-grade salts and standardized by complexometric titration with metallochromic indicators.

Iron(III) *ammonium sulphate*, 0·1*M solution*. Prepared from reagent-grade $FeNH_4(SO_4)_2 \cdot 12H_2O$ and standardized manganometrically.

Iron(II) *ammonium sulphate*, 0·1*M solution*. Prepared from reagent-grade $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and standardized manganometrically. This solution was prepared in deaerated conditions and kept under purified nitrogen.

All solutions were diluted before measurement, if necessary. Doubly distilled water was used throughout.

Buffer solutions, 1*M*. Prepared from trichloroacetic and chloroacetic acids.

Apparatus

Potential and pH measurements. These were performed with a Radiometer PHM 22p. The indicator electrodes used were a bright platinum electrode, of approx. 100 mm² area and a graphite electrode, according to Pungor, of approx. 20 mm² area. The reference electrode was a saturated calomel electrode, connected with a potassium nitrate bridge. A glass electrode was used for pH measurements.

Titrations in the absence of oxygen. These were carried out with a special burette, in an air-tight cell deaerated before measurements and kept under nitrogen.

Procedure

To the solution containing 0·05 mmole of the ion to be determined a mixture of iron(III)–iron(II) solution containing 0·001 mmole of each was added. The pH of this solution was adjusted with the proper buffer and the solution was diluted to 100 ml before titration with 0·01*M* EDTA from a 10-ml burette. If necessary the titrand and the titrant were deaerated with purified nitrogen before measurements.

RESULTS AND DISCUSSION

Titration of iron(III)

In a solution at pH <2, iron(III) is complexed by EDTA, whereas iron(II) is not, as is indicated by the conditional stability constants: for Fe(III)–EDTA at pH 1·3 $K' = 10^{8.5}$, at pH 2·0 $K' = 10^{10.4}$, for Fe(II)–EDTA at pH 2·0 $K' = 1{\cdot}6$. Therefore unless the ligand concentration is high the analytical concentration of iron(II) equals its equilibrium concentration.

When the concentration of iron(II) in the redox couple is very small no sharp end-point is observed. The increase of iron(II) concentration up to $3 \times 10^{-5}M$, in the case of titration of $3 \times 10^{-3}M$ iron(III), is sufficient for a sharp end-point. Further increase shifts the titration curve to lower potential values.

The potential obtained experimentally before the end-point agrees well with the calculated value, but after the end-point in the presence of oxygen, the electrode potentials are shifted to more positive values than would be expected from the stabilities of the complexes (Fig. 1). However exclusion of oxygen leads to observation of the theoretical values even in this region. This suggests that after the end-point, in the presence of ligand excess, the Fe(II)–EDTA complex formed undergoes oxidation to Fe(III)–EDTA complex. The rate of this process increases with pH, and above pH 2 the titration curve has a peculiar shape with a sharp minimum,[4] because of a rapid decrease in iron(II) concentration.

The rate of iron(III) complexation at pH 1·3 is slow, but significantly increases as the pH approaches 2·0. This may confirm the mechanism of complexation which was previously proposed for amperometric titrations,[5] and which is based on rapid complexation of iron(II) and rapid oxidation of the complex by iron(III):

$$\text{Fe(III)} + \text{Fe(II) EDTA} \rightleftharpoons \text{Fe(III) EDTA} + \text{Fe(II)}$$

At pH >2·0 the competing reaction of oxidation by oxygen makes location of the end-point impossible and causes distortion of the curve. The above-indicated reaction of complexation *via* a redox reaction proceeds also in the absence of oxygen and under these conditions steady potential values are reached rapidly.

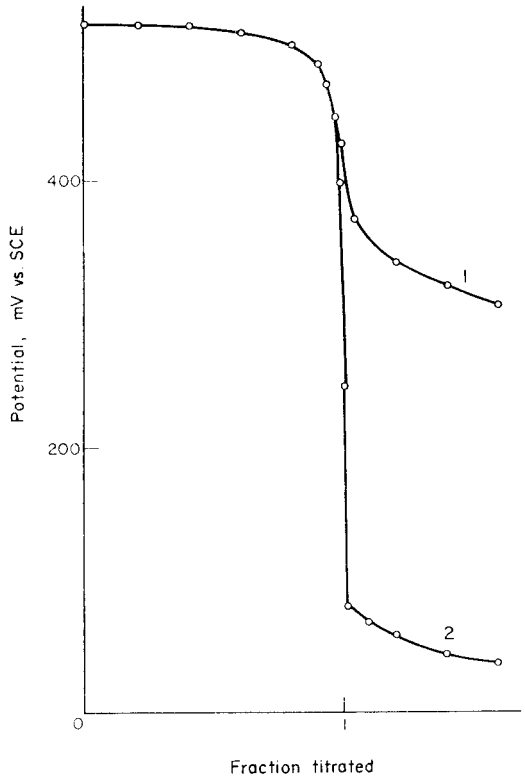

FIG. 1.—Titration of iron(III) ($3 \times 10^{-3}M$) in the presence of $1 \times 10^{-4}M$ Fe(II), at pH 1·9 with (curve 1) and without (curve 2) oxygen present.

Titration of various metals with Fe(III)/Fe(II) *indicator system*

The redox couple Fe(III)/Fe(II) may be used as an indicator system in titration of a metal, M, with EDTA. When titration is performed in the absence of oxygen, at pH <2, the total concentration of Fe(II) may be assumed constant. Under these conditions the inert indicator electrode (platinum or graphite) works as a pFe(III) electrode, and

$$E = E^\circ + \frac{RT}{F} \ln [\text{Fe(III)}]$$

where $E^\circ = E^\circ_{\text{Fe(III)/Fe(II)}} - RT/F \ln [\text{Fe(II)}]$. When there is competition between the two metals, Fe(III) and M, to form EDTA complexes, on the basis of the equilibrium

$$\text{Fe(III) EDTA} + \text{M} \rightleftharpoons \text{MEDTA} + \text{Fe(III)}$$

the concentration of Fe(III) may be described in a way analogous to that used for the silver or mercury electrodes.[6] Then

$$E = E^\circ + \frac{RT}{F} \ln \frac{C_{\text{Fe(III)}} \cdot K_{\text{MY}}'}{\alpha_{\text{Fe(III)}} \left(K_{\text{Fe(III)Y}}' \frac{[\text{MY}']}{[\text{M}']} + K_{\text{MY}}' \right)}$$

where $C_{Fe(III)}$ represents the analytical concentration of iron(III), $\alpha_{Fe(III)}$ its side-reaction coefficient, and $K_{Fe(III)Y}'$ and K_{MY}' the conditional constants of the respective complexes. Before the equivalence point the ratio [MY']/[M'] may be represented by $f/(1-f)$ where f is the fraction titrated. On the basis of this expression two theoretically possible titration curves have been calculated. For the first $K_{MY}'/K_{Fe(III)Y}' = 10^3$, for the second $K_{Fe(III)Y}'/K_{MY}' = 10^3$ were used, and all other conditions were the same ($C_{Fe(III)} = C_{Fe(II)} = 10^{-5}M$, $C_M = 5 \times 10^{-4}M$, pH = 2·0) (Fig. 2). The curve *a* is asymmetric, the curve *b* is symmetric, which is exactly the same as when silver (or mercury) electrodes were used.[6]

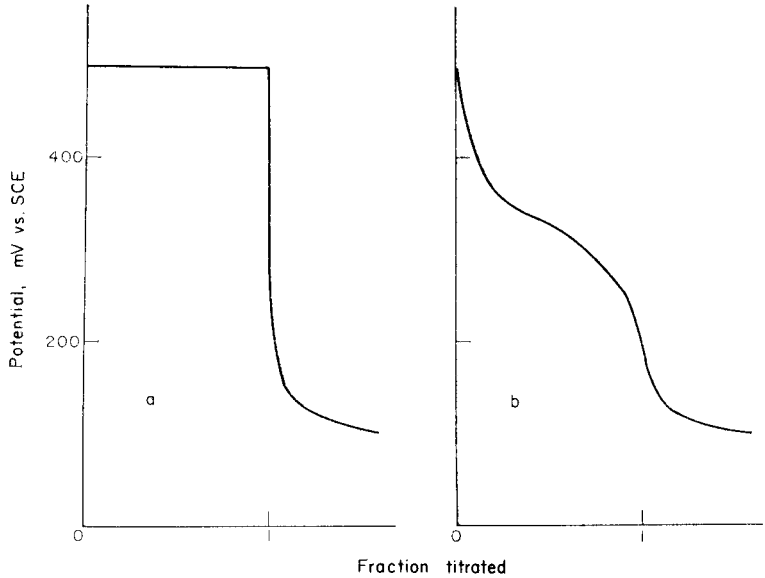

FIG. 2.—Theoretical titration curves for systems where the metal titrated forms a more (curve *a*) or a less (curve *b*) stable complex than Fe(III).
For both titrations $C_{Fe(III)} = C_{Fe(II)} = 10^{-5}M$, pH = 2, $C_M = 5 \times 10^{-4}M$.

The calculated curves of Fig. 2 are valid only when a true thermodynamic equilibrium is attained. When the more stable of the two metal complexes is formed more rapidly than the other, the experimental curves do not differ significantly from the calculated ones. To verify these ideas several metals were titrated under comparable conditions, *i.e.*, at pH 2·0. Their conditional stability constants are Bi–EDTA $10^{13\cdot7}$; In–EDTA $10^{11\cdot3}$; Fe(III)–EDTA $10^{10\cdot4}$; Th–EDTA $10^{9\cdot4}$; Cu(II)–EDTA $10^{5\cdot1}$ and Ni–EDTA $10^{4\cdot9}$. Figure 3 shows the titration curves for two metals more strongly bound than iron(III), *i.e.*, bismuth and indium. The relatively great lability of their complexes is responsible for quite rapid establishment of the potential values. The shape of the curves is similar to that predicted, and the calculated and experimentally determined potential values are in good agreement (Table I).

When a similar titration is carried out in the presence of oxygen the shape of the curve is similar, but the end-point break is much smaller, and the potential readings cannot be predicted on the basis of such a simple discussion.

In titrations of metals which have EDTA complexes with conditional stability constants smaller than that of Fe(III)–EDTA, the shape of the titration curve depends

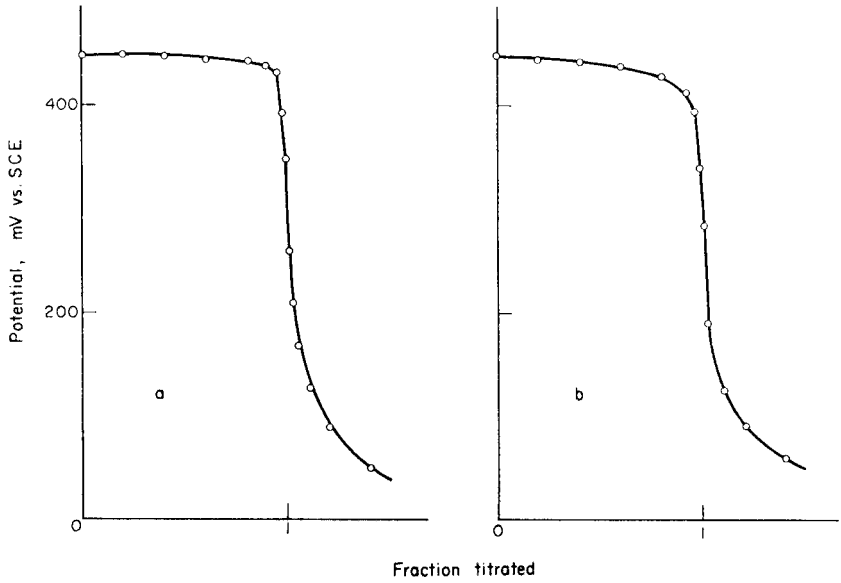

FIG. 3.—Titration curves for titration of (*a*) Bi(III), and (*b*) In(III). $C_M = 5 \times 10^{-4}M$, pH 1·95. $C_{Fe(III)} = C_{Fe(II)} = 10^{-5}M$.

TABLE I.—COMPARISON OF CALCULATED AND DETERMINED POTENTIAL VALUES

Ion	$E_{f=1/2}$, V		$E_{f=1}$, V		$E_{f=2}$, V	
	calc.	detd.	calc.	detd.	calc.	detd.
Bi(III)	0·45	0·45	0·29	0·29	0·01	0·01
In(III)	0·45	0·45	0·29	0·25	0·01	0·01
Th(IV)	0·39	0·39	0·22	0·23	0·01	0·01
Cu(II)	0·15	0·16	0·08	0·09	0·03	0·03
Ni(II)	0·15	0·15	0·08	0·08	0·04	0·03

strongly on the rate of titrant addition and the potential readings. In all these examples, thorium, copper and nickel (Fig. 4), the titration curves correspond to the state of thermodynamic equilibrium and are of the symmetric type and can be predicted on the basis of the equation above. When titrations are performed rapidly, and the initial potential values are taken for plotting the titration curves, two different cases may be distinguished. In the first, which is illustrated by thorium and copper, the initial titration curve is higher than the equilibrium curve. This can be explained on the basis of a lower rate of complexation of the indicator iron(III) ions than of the titrated metal. When no excess of titrant is present the exchange reaction

$$ThY + Fe^{3+} \rightleftharpoons Fe(III)Y^{-} + Th^{4+}$$

proceeds to a negligible degree. Strong complexation of thorium (or copper) also prevents the formation of the intermediate iron(II) complex, which in the absence of other ions makes the complexation of iron(III) more rapid. However, in the vicinity of the end-point such an intermediate redox exchange, as mentioned previously, occurs and the end-point corresponds to the sum of thorium (or copper) and iron(III).

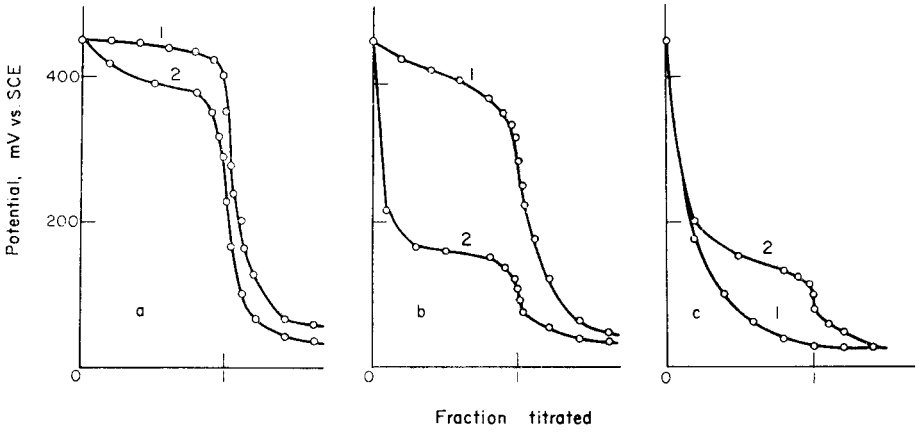

FIG. 4.—Titration curves for titration of (*a*) Th(IV), (*b*) Cu(II), (*c*) Ni(II). $C_M = 5 \times 10^{-4}M$, pH = 2·0, $C_{Fe(III)} = C_{Fe(II)} = 10^{-5}M$. Curves marked "1" correspond to readings just after addition of a titrant, curves marked "2" refer to the equilibrium state.

In the nickel titration, the initial curve is below the equilibrium curve. Such behaviour may be interpreted as the effect of nickel reacting more slowly than iron. The shape of the curve does not permit titration of nickel, under these conditions, to be followed. No end-point occurs for fast titrations; the equilibrium is reached very slowly but also the equilibrium curve has an inadequate end-point break.

These examples show that in titrations with the indicator redox couple Fe(III)/Fe(II), the shape of the titration curve and the absolute values of potentials may be predicted only when no oxidation of the Fe(II)–EDTA complex takes place. This reaction is responsible for many oddly shaped curves given in the papers of other investigators. Such curves, despite their occasional analytical utility, are not easy to use for accurate quantitative interpretation, mainly because of the irreversibility of reactions and the difficulty of maintaining reproducible conditions.

In contrast to titrations with the silver or mercury electrodes, the kinetics of metal complexation play an important role. This is proved by the examples of thorium and copper where fast titration may improve the end-point potential break, and of nickel, for which titration is completely impossible.

Zusammenfassung—Potentiometrische Titrationen von Metallionen mit EDTA wurden mit Hilfe einer Platin- oder Graphitelektrode und des Fe(III)/Fe(II)-Redoxysystems ausgeführt. In Abwesenheit von Sauerstoff und bei pH <2 können die Titrationskurven mit einer Gleichung wiedergegeben werden, die ähnlich aussieht wie die früher für Titrationen mit Silber- und Quecksilber-elektroden angegebenen. Titrationskurven für Wismut und Indium, die stärker komplex gebunden werden als Eisen, sind asymmetrisch und für analytische Zwecke nützlich. Werden die titrierten Ionen schwächer gebunden als Eisen(III), dann hat die Kinetik der Komplexbildung einen ausgeprägten Einfluß. Die Titrationskurven von Thorium und Kupfer, die schneller reagieren als Eisen, sind von analytischem Nutzen. Kurven, die rasch nach Zugabe des Titranten registriert werden, haben einen ausgeprägteren Sprung am Endpunkt als die, die dem thermodynamischen Gleichgewicht entsprechen. Wird ein Metall, z.B. Nickel, von EDTA schwach gebunden und reagiert langsamer als Eisen, dann findet man einen sehr kleinen Sprung am Endpunkt oder gar keinen.

Résumé—On a mené des titrages potentiométriques d'ions métalliques au moyen d'EDTA avec une électrode de platine ou de graphite et le système redox Fe(III)/Fe(II). En l'absence d'oxygène et pour pH <2, les courbes de titrage peuvent être décrites par une équation similaire à celle donnée antérieurement pour les titrages avec des électrodes d'argent et de mercure. Les courbes de titrage pour le bismuth et l'indium, qui sont plus fortement complexés que le fer, sont asymétriques et utiles pour des fins analytiques. Lorsque les ions titrés sont moins fortement complexés que les ions fer(III), la cinétique de complexation du métal a une influence prononcée. Les courbes de titrage du thorium et du cuivre, qui réagissent plus rapidement que le fer, sont analytiquement utiles. Les courbes enregistrées rapidement après les additions d'agent de titrage ont une brisure de fin de dosage meilleure que celles qui correspondent à l'équilibre thermodynamique. Lorsqu'un métal, par exemple le nickel, est faiblement lié à l'EDTA, et réagit plus lentement que le fer, on n'observe qu'une très petite brisure de fin de dosage ou pas de brisure du tout.

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AN INDUCTION FURNACE FOR THE DETERMINATION OF CADMIUM IN SOLUTIONS AND ZINC-BASE METALS BY ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—An induction furnace coupled to a Unicam SP90 atomic-absorption spectrophotometer is described for the determination of traces of volatile elements in solutions and volatile matrices. The apparatus has been used to obtain calibration graphs for 1–20 and 50–750 ng of cadmium in μl-volumes of solution, the 228·8 and 326·2-nm resonance lines respectively being used, and to determine cadmium in 5-mg samples of zinc-base metals within the concentration range 5–400 μg/g by using the less sensitive 326·2-nm line. A furnace temperature of 1350° was used. Data on accuracy and precision are presented. The apparatus could readily be used to determine trace elements in volatile materials at concentrations of 10–1000 ng/g.

AS ATOMIC-ABSORPTION SPECTROSCOPY with flames has become very widely used in recent years, interest in non-flame methods of atomization has also increased. The principal advantages of non-flame methods over flame methods are that they are more sensitive, they can be used for very small volumes of solution and they can be employed to analyse small samples of solid material directly. Most published papers on non-flame methods have dealt with the analysis of materials originally in solution, the chief investigators in this field being L'vov,[1] Massmann,[2] West[3] and Woodriff.[4] Fewer results on the direct analysis of solid samples have been reported, but L'vov,[5] and Nikolaev[6] have analysed mg samples of metals, using an a.c. resistance furnace and the introduction of samples into the furnace on depressions in carbon rods. These methods are very sensitive, 10^{-5}% of impurity element being readily determined. Their precision is usually about 5–8%.

The present authors report the construction of a simple induction furnace to produce vapour from readily volatile elements, and the investigation of an atomic-absorption method using the furnace for the determination of cadmium in standardized zinc-base metals. An induction furnace was employed because many metallurgical firms already possess induction generators for the vacuum fusion of alloys. For comparison, some results are also reported for the analysis of μl samples of cadmium solutions.

EXPERIMENTAL

Apparatus

A diagram of the furnance is shown in Fig. 1. The central core consisted of a cylinder of graphite (Acheson E.G.W. grade) 75 mm long with internal diameter 15 mm and external diameter 38 mm. This cylinder rested in shaped firebrick cylinders, which in turn were situated in a recrystallized alumina tube (Thermal Syndicate Ltd.) which was 300 mm long with external diameter 54 mm and wall thickness of 4 mm. A hole of diameter 10 mm was drilled through the alumina tube and graphite cylinder such that a graphite rod (Le Carbone (G.B.) Ltd., grade 5501) shaped as shown could be raised from below until the tapered portion of the rod came in contact with the alumina cylinder. In this position the top of the rod was level with the bottom inside boundary of the graphite cylinder. An induction coil of six turns was wound around the alumina tube as shown. This coil was connected to a 6-kW Radyne Induction Generator.

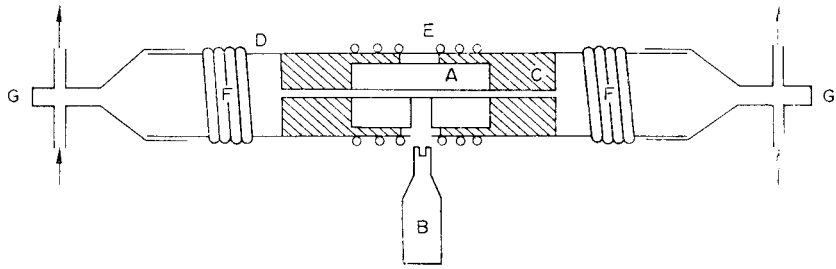

FIG. 1.—Graphite furnace for production of atomic vapour.
A—Graphite core; *B*—graphite electrode; *C*—firebrick packing; *D*—alumina tube; *E*—induction coil; *F*—cooling coils; *G*—Spectrosil windows.

End-pieces of Pyrex glass shaped as illustrated were constructed so that they slid smoothly over the ends of the alumina tube. These were sealed to the tube with Plasticine. Two cooling coils made from copper tubing of external diameter 6 mm were fixed near the ends of the alumina tube. The Pyrex end-pieces had Spectrosil windows (diameter 25 mm) fitted at their outer ends. Each end-piece had an inlet tube and an outlet tube for argon, each fitted with a tap. The inlet tubes were connected through a Y-piece to a flowmeter and a cylinder of argon.

Atomic-absorption measurements were made with the Unicam SP90, using a cadmium electrodeless discharge tube in a ¾-wave cavity powered by a Microtron 200 microwave generator fitted with a voltage stabilizing unit. When the discharge tube was used the lamp holder for hollow-cathode lamps was removed. Since the radiation from the discharge tube was not modulated electronically the SP90 was used in the emission mode, the light being modulated with a vibrating reed before striking the photomultiplier. A slit-width of 0·1 mm was used.

Determination of the absorbance of cadmium vapour in the furnace

Solutions. Flush all air from the furnace by opening the argon inlet tap at one end and the outlet tap at the other and passing argon at 12 l./min for about 5 min. Slowly raise the temperature of the furnace to 1350° by appropriate control of the Radyne Generator. A steady supply of 1·6 kW maintains this temperature. Adjust the controls on the Unicam SP90 so that a full-scale meter reading corresponds to 100% transmission.

Open the remaining two taps and reduce the argon flow-rate to 2 l./min. When the 228·8-nm cadmium line is used, place 10–50 μl of cadmium nitrate solution (cadmium 0·36 mg/l.) in the crater in the graphite rod and raise the rod into the furnace, at the same time shutting off the argon supply (Note 1). After a few seconds the transmission reading starts to fall and after 5–10 sec. reaches a steady value, which is maintained for about 5 sec. Note this transmission reading and from a conversion table read off the absorbance of the cloud of cadmium vapour. Then close the argon outlet tap at one end and the inlet tap at the other and flush out the cadmium vapour at a flow rate of 12 l./min for 2 min. Repeat the procedure as often as required.

Note 1. When the much less sensitive 326·2 nm cadmium line is employed, use 10–50 μl of cadmium nitrate solution (cadmium 7·1 mg/l.) in the crater.

Zinc-base metals. The procedure for metals is the same as for solutions except that 5 mg of metal is used in the crater and the less sensitive 326·2-nm cadmium line is employed. As for solutions the steady transmission reading for the cloud of metal vapour persists for approximately 5 sec.

Conventional determination of cadmium in the zinc-base metals

A 0·25 or 0·5-g sample of metal was dissolved in 5 ml of water plus 5 ml of concentrated hydrochloric acid. The solution was diluted to 25 ml in a graduated flask. The absorbances of these solutions were determined by using the air–acetylene flame of the Unicam SP90 and the 228·8-nm cadmium line. The calibration graphs were prepared from a series of 1% or 2% w/v zinc solutions containing 2–10 μg of cadmium per ml.

Some of the zinc-base metals were supplied by local industry and had been analysed by polarography. The polarographic results and the atomic-absorption spectroscopic results were in good agreement.

RESULTS

Calibration graphs for solutions of cadmium nitrate with the 228·8 and 326·2-nm lines are shown in Figs. 2 and 3 (curve A) respectively. The average absorbance from six aliquots of cadmium solution containing 8·9 ng of cadmium was 0·55 with a

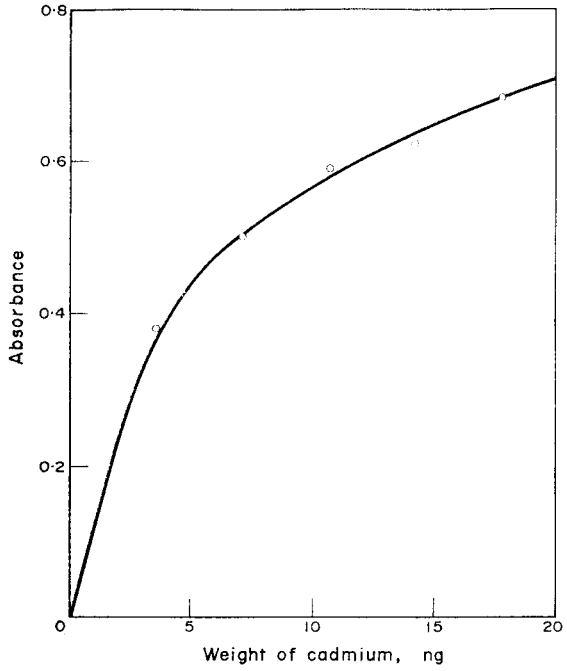

FIG. 2.—Calibration graph for determination of cadmium in solution, using the Cd 228·8-nm resonance line.

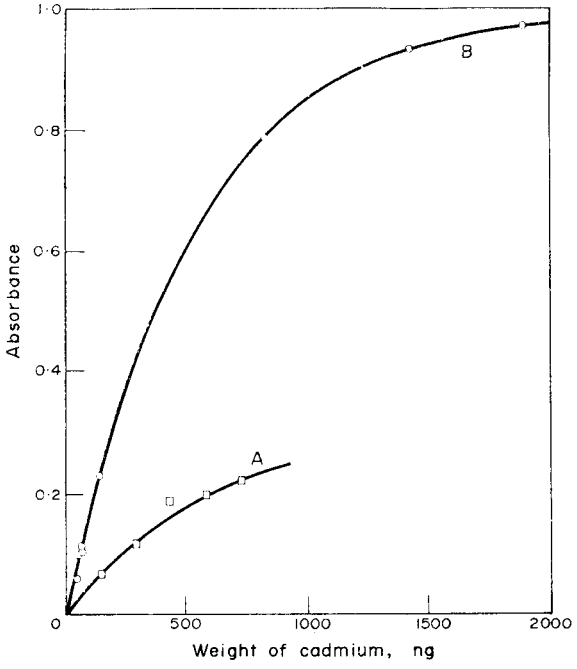

FIG. 3.—Calibration graphs for determination of cadmium in solution (A) and zinc-base metals (B), using the Cd 326·2 nm resonance line.

relative standard deviation of 6·4% (228·8-nm line). The average absorbance from six aliquots of cadmium solution containing 0·36 μg of cadmium was 0·14 with a relative standard deviation of 9·8% (326·2-nm line).

A calibration graph for the determination of cadmium in zinc-base metals is shown in Fig. 3, curve B. This was prepared by using eight of the metal samples that had been analysed by the conventional atomic-absorption spectroscopic method described above. The metals and their cadmium contents are shown in Table I. Alloy 24 was not used in the preparation of this calibration graph.

TABLE I.—THE CADMIUM CONTENTS OF THE ZINC-BASE METALS USED IN THIS STUDY

Metal	Cadmium content, μg/g
"Specpure" zinc (Johnson and Matthey)	8
Zinc powder (Koch-Light)	10
Granulated zinc (British Drug Houses)	12
Zinc shot (AnalaR, Hopkin and Williams)	13
Alloy 24	27
Alloy 17	28
Zinc needles (Prestons)	163
Zinc metal dust (Hopkin and Williams)	284
Zinc metal powder (Hopkin and Williams)	377

Absorbances for eight 5-mg samples of Alloy 24 were obtained during the run used to obtain absorbances for the calibration graph B in Fig. 3. The average absorbance for these samples was 0·22 with a relative standard deviation of 6·9%. The average cadmium content of this alloy, obtained by the furnace technique, was 26 μg/g compared with 27 μg/g by conventional atomic-absorption spectroscopy.

DISCUSSION

The results for the zinc-base metals are considered to be satisfactory. The relative standard deviation of 6·9% is appreciably larger than the standard deviations obtained with conventional atomic-absorption spectroscopy but part of this scatter will result from weighing errors, for the weight of a 5-mg sample could be in error by 0·2 mg, since only a four-place balance was used in this study. Also, when samples of only 5 mg are used, some scatter in the results can be expected from the distribution of cadmium not being completely homogeneous. The precision of 6·9% is also in good agreement with values of 5–8% obtained by L'vov.[1]

The method is quite rapid, for a 5-mg sample of metal can be analysed every 5 min. It must be noted that it is only possible to compare the furnace method with the conventional atomic-absorption spectroscopic method because a much less sensitive cadmium line at 326·2 nm is available. The furnace method using the 228·8-nm line is much too sensitive for the analysis of parts per million of cadmium in materials. However, the method should be especially useful for the determination of concentrations of cadmium at the ng/g level in volatile materials. An assessment of the quality of results for the determination of such concentrations of cadmium in volatile metals could not be made in this study for no standardized samples containing so little cadmium were available. The relative standard deviation of 6·4% obtained for the cadmium nitrate solutions, the 228·8 nm line being used, does indicate, however, that ng/g concentrations of cadmium in solid materials should be capable of determination with similar precision.

The 1% absorption values for the determination of cadmium in solutions and zinc-base metals are 24 pg (228·8 nm), and 9·7 ng (326·2 nm), and 2·3 ng respectively. For zinc-base metals this corresponds to 0·46 μg/g for a 5-mg sample. It will be seen that for solutions the method is 400 times more sensitive with the 228·8 nm line than with the 326·2 nm line. Therefore it can be expected that for zinc-base metals, the 1% absorption value for the 228·8-nm cadmium line will be about 1 ng/g.

It will be observed from Fig. 3 that the calibration graph for the 326·2 nm line has a lower slope for solutions than that for zinc-base metals.

For solutions, interfering effects are to be expected from other ions, particularly anions, since it is likely that many molecular cadmium species will not be completely dissociated at 1350°.

Since a transmission reading steady for approximately 5 sec is obtained after the introduction of a metal sample, it seems unlikely that during this period, there are any solid particles or liquid globules in the light-path, which could scatter light. Therefore interfering effects caused by scattering are considered to be unlikely. As the furnace is operated in a pure argon atmosphere there should be little interference from molecular species in the light-path when zinc samples are analysed for cadmium.

The maximum temperature of operation of the furnace is 1900°. An induction furnace is now being built for the analysis of less volatile alloys at 2500–3000°.

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Zusammenfassung—Ein an ein Unicam SP 90 Atomabsorptions-Spektrophotometer gekoppelter Induktionsofen wird beschrieben; er wird Bestimmung von Spuren flüchtiger Elemente in Lösungen und flüchtigen Matrizen eingesetzt. Das Gerät wurde zur Aufnahme von Eichkurven für 1–20 und 50–750 ng Cadmium in μl-Lösungsvolumina verwendet, wobei die Resonanzlinien bei 228,8 bzw. 326,2 nm benutzt wurden, sowie zur Bestimmung von Cadmium in 5 mg-Proben von Metallen mit Zink als Hauptbestandteil, im Konzentrationsbereich 5–400 μg/g, unter Verwendung der weniger empfindlichen Linie bei 326,2 nm. Der Ofen wurde auf 1350° gehalten. Genauigkeits- und Richtigkeitsdaten werden mitgeteilt. Das Gerät konnte zur Bestimmung von Spuren in flüchtigem Material bei Konzentrationen von 10–1000 ng/g gut verwendet werden.

Résumé—On décrit un four à induction couplé à un spectrophotomètre d'absorption atomique Unicam SP 90 pour le dosage de traces d'éléments volatils en solution et dans des matrices volatiles. L'appareil a été utilisé pour obtenir des courbes d'étalonnage pour 1–20 et 50–750 ng de cadmium dans des μl de solution, les raies de résonance 228,8 et 326,2 nm étant respectivement utilisées, et pour doser le cadmium dans des échantillons de 5 mg de métaux à base de zinc dans le domaine de concentration 5–400 μg/g en utilisant la raie moins sensible 326,2 nm. On a utilisé une température de four de 1350°. On présente des données sur la précision et la fidélité. On peut aisément utiliser l'appareil pour déterminer des éléments à l'état de traces dans des substances volatiles à des concentrations de 10–1000 ng/g.

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COLOUR CHANGES OF CHEMICAL INDICATORS—III

COLOUR SPECIFICATION AND ITS ACCURACY

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Summary—The systematic deviations involved in methods for computation of chromaticity co-ordinates have been studied for the specification of indicator colour changes. The weighted ordinate method ($\Delta\lambda = 10$ nm) has proved to be satisfactory for evaluation both of C.I.E. and complementary co-ordinates. The C.I.E. colour specification should be included among basic data about chemical indicators.

THE CHROMATICITY SYSTEM C.I.E. (1931) has only been used to a limited extent in analytical chemistry in comparison with its wide application in other branches of science and technology (*e.g.*, ref. 1). For example, as advocated already by various authors,[2–5] it would be desirable to specify colour changes of any studied indicator in terms of chromaticity co-ordinates and the relative luminance value. Reilley and co-workers[6] have developed the complementary chromaticity system to specify the colour change of chemical indicators from various aspects. This provides an unambiguous definition of any colour within the colour transition, and necessary information for the calculation of various factors determining the quality of the colour change and the range of visual error. A critical discussion of all these problems has been presented by Kotrlý in an extensive review paper[7] covering the literature up to 1965. It seems, however, that various analytical applications of this basic approach have really remained neglected. In previous contributions to this series we have presented the chromaticity data and other results for some metallochromic[8] and acid-base[9] indicators. However, practically no attention has been paid to the reliability and accuracy of various methods of evaluation of the C.I.E. chromaticity co-ordinates under conditions typical for an indicator colour change.

For a two-colour acid-base indicator, taken as an example, the absorbance of the solution can be written

$$A_\lambda = -\log T_\lambda = dc_I[\varepsilon_{HI}(1 - \alpha) + \varepsilon_I\alpha] \quad (1)$$

where c_I is the total concentration of the indicator, d is the path-length, ε_{HI} and ε_I are the molar absorptivities of both species involved in the dissociation equilibrium $HI \rightleftharpoons I + H^+$, and α is the fraction of indicator in the deprotonated form I, $\alpha = [I]/c_I$.

The specification of any colour is given by two chromaticity co-ordinates, x, y, and a relative luminance value, Y. First, the basic quantities, *i.e.*, the C.I.E.-tristimulus values, X, Y, Z, have to be computed and then used to express the chromaticity co-ordinates:

$$r = R/(X + Y + Z) \quad (2)$$

where r and R may represent any of the three chromaticity co-ordinates or tristimulus values, respectively. The procedure involves evaluation of summations in the visible

region of light:

$$R = k \sum_{\lambda} H_\lambda \bar{r}_\lambda T_\lambda \Delta\lambda \tag{3}$$

where T_λ are the transmittance values between 380 and 780 nm, H_λ is the relative spectral distribution of the light source (C.I.E. standard source C usually being employed), and $\bar{r}_\lambda$ is the respective C.I.E. colour-matching function. The values of the products $H_\lambda \bar{r}_\lambda$ are usually taken from tabulations of recommended data (*e.g.*, refs. 1 and 10).

Each of the three tristimulus values is, therefore, an exponential function of the overall absorbance

$$R = k \sum_{\lambda} H_\lambda \bar{r}_\lambda \, e^{-2{\cdot}303 A_\lambda} \Delta\lambda. \tag{4}$$

As Reilley and his co-workers[6] have shown, the Taylor expansion can be applied to simplify the exponential function if all terms higher than second order can be neglected. In this way, the basic equation for the chromaticity co-ordinates is obtained:

$$\begin{aligned} r &= G_r - J(Q_r - G_r) - J^2(Q_r - G_r + Q_r{}^d) \\ &= G_r - JV_r - J^2 W_r. \end{aligned} \tag{5}$$

The definition of the complementary tristimulus chromaticity system has been a further logical development of this approach. In this case, the tristimulus values, denoted generally as R_c, are calculated on the basis of absorbance values

$$R_c = k \sum_{\lambda} H_\lambda \bar{r}_\lambda A_\lambda \Delta\lambda \tag{6}$$

and the complementary chromaticity co-ordinates are $Q_r = R_c/(X_c + Y_c + Z_c)$. The product $c_I d$ in equation (1), which can be varied according to the experimental conditions, cancels out in the calculation of Q_r. Thus the position of a complementary colour point in the chromaticity diagram is independent both of the indicator concentration and the path-length through the solution being titrated. Reilley *et al.* have suggested, therefore, that the Q_r values of any given indicator form in dilute solution should have the significance of a physical constant. Other symbols in equation (5) possess a certain concrete meaning. The quantity J is the "colour concentration" of the solution,

$$J = Ec_I d = K(X_c + Y_c + Z_c) \tag{7}$$

which is related to the complementary stimuli R_c and represents, on the other hand, an analogue to the Lambert-Beer-Bouguer law. The value of the constant K depends upon the computation approach to the tristimulus values. The source of light employed is characterized by the complementary chromaticity co-ordinates of the so-called "grey point", G_r. The "dichromatistic" deviation, $Q_r{}^d$, is calculated from the squares of absorbance data. Full definitions of all symbols in equations (5) and (7) are given in the original paper.[6]

Complementary data can also be used for calculation of indices of colour quality[6] of the indicator transition, for computation of relative amounts of inert dyestuffs necessary to achieve colour screening[6,11] and for evaluation of equilibrium constants[11,12] involved in the indicator transition equilibrium.

It seems desirable that the data of newly proposed chemical indicators should include chromaticity co-ordinates corresponding to defined coloured forms playing a

part in their colour changes. From this point of view, the accuracy and precision of the chromaticity co-ordinates become of importance. There are two main sources of error. (1) Random or systematic experimental error brought about by numerous and diverse causes, *e.g.*, different purity of commercial preparations of a given chemical indicator, method of preparation of the stock solution, concentration changes in the indicator colour species in the solution to be titrated (differences in c_I, pH or pM, or decomposition processes); furthermore the spectrophotometric measurement is also subject to significant errors. All these sources of error are more or less shown in the transmittance values obtained for a given solution and will be discussed in detail in another contribution to this series. (2) The method employed for the evaluation of the tristimulus values, which is necessarily of an approximative character, also introduces a certain error which may be of a systematic character, as will be set forth in this article.

RESULTS AND DISCUSSION

Only typical examples, which make deliberate use of spectrophotometric data available in the literature, will be given here in order to illustrate the problems involved in evaluation of chromaticity co-ordinates.

Spectrophotometric data

The effect of the path-length of the light through the solution measured is illustrated by the transmittance curves (Fig. 1) of a $1 \times 10^{-5}M$ solution of dithizone in 50% v/v ethanol containing acetate buffer.[13] At pH 4·43 the undissociated form of dithizone (H_2Dz) prevails in the indicator dissociation equilibrium.

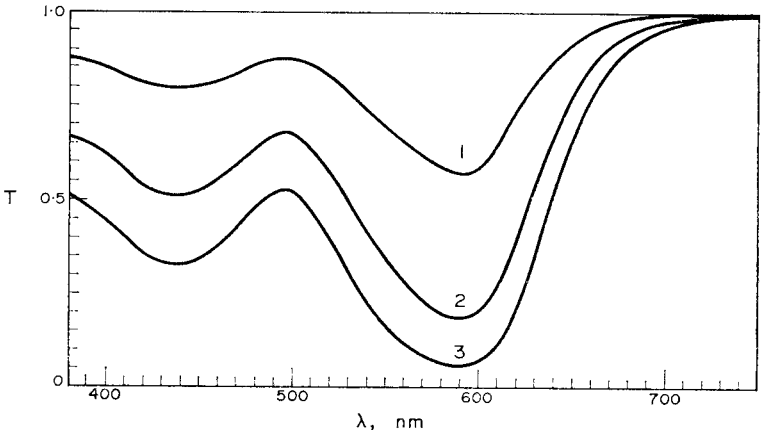

FIG. 1.—Transmittance curves of dithizone solutions (50% v/v ethanolic medium containing acetate buffer, pH 4·43, $c_{H_2Dz} = 1 \times 10^{-5}M$). Path-length (mm): *1*—10; *2*—30; *3*—50.

The absorptivities of the acid and basic forms of Bromothymol Blue and Phenol Red[4] were used to calculate the absorbance and transmittance values of the indicator solutions. In each case, three typical points of the indicator colour change were considered for a 10-mm path-length. The transition of Bromothymol Blue was characterized by $2{\cdot}5 \times 10^{-5}M$ solutions of the indicator at pH values 2·2 ($\alpha = 0{\cdot}00$), 7·00 ($\alpha = 0{\cdot}50$) and 9·8 ($\alpha = 0{\cdot}998$). Three $2{\cdot}9 \times 10^{-5}M$ solutions of Phenol Red

were considered at the following pH values: 3·34 ($\alpha = 0{\cdot}0003$), 7·81 ($\alpha = 0{\cdot}50$) and 10·11 ($\alpha = 0{\cdot}995$).

The absorbance and transmittance values of three standard solutions for spectrophotometric calibrations ($d = 10$ mm)[14] are employed.

(*a*) Solution of 0·0400 g of potassium chromate in 1 litre of 0·05*M* potassium hydroxide.

(*b*) A solution of 14·481 g of ammonium cobalt(II) sulphate hexahydrate containing 10·0 ml of concentrated sulphuric acid (density 1·835) and diluted to 1 litre.

(*c*) A solution of 20·00 g of copper sulphate pentahydrate acidified with 10 ml of concentrated sulphuric acid and diluted to 1 litre.

Computation of C.I.E. chromaticity co-ordinates

All methods which have been suggested for computing the C.I.E. tristimulus values are approximate.

The *weighted ordinate method*, which is essentially based upon equation (3), has been widely used in tristimulus colorimetry. The results given in Table I illustrate the effect of the size of the wavelength interval $\Delta\lambda$ taken in the summations. In the case of a usual type of transmittance spectrum, as exemplified in Fig. 1 by a solution of dithizone, there can be hardly any difference in the chromaticity co-ordinates calculated either for an interval of $\Delta\lambda = 5$ nm or $\Delta\lambda = 10$ nm. Half of the effort necessary to take experimental readings can thus be spared. The chromaticity

TABLE I.—COMPARISON OF CHROMATICITY CO-ORDINATES OF INDICATORS EVALUATED BY VARIOUS METHODS

Indicator	form	x	$\Delta x \times 10^3$	y	$\Delta y \times 10^3$	Y	$\Delta Y \times 10^3$
Dithizone	$d = 10$ mm	0·292[a,b]		0·300[a]		0·715[a]	
		0·292[c]	±0	0·300	±0	0·715	±0
		0·291[d]	−1	0·301	+1	0·718	+3
		0·291[e]	−1	0·300	±0	0·714	−1
	$d = 30$ mm	0·265[a,b]		0·272[a]		0·389[a]	
		0·265[c]	±0	0·273	+0·3	0·390	+1
		0·264[d]	−1	0·272	−0·7	0·389	±0
		0·261[e]	−4	0·272	±0	0·387	−2
	$d = 50$ mm	0·249[a,c]		0·254[a]		0·231[a]	
		0·243[e]	−6	0·252	−2	0·226	−5
Bromothymol Blue	$\alpha = 0{\cdot}00$	0·372[a,c]		0·396[a]		0·906[a]	
		0·372[e]	±0	0·398	+2	0·910	+4
	$\alpha = 0{\cdot}50$	0·274[a,c]		0·317[a]		0·553[a]	
		0·272[e]	−2	0·316	−1	0·550	−3
	$\alpha = 0{\cdot}998$	0·205[a,c]		0·222[a]		0·380[a]	
		0·202[e]	−3	0·217	−5	0·368	−12
Phenol Red	$\alpha = 0{\cdot}00$	0·387[a,c]		0·427[a]		0·922[a]	
		0·387[e]	±0	0·430	+3	0·926	+4
	$\alpha = 0{\cdot}50$	0·383[a,c]		0·277[a]		0·442[a]	
		0·372[e]	−11	0·283	+6	0·447	+5
	$\alpha = 0{\cdot}995$	0·342[a,c]		0·181[a]		0·310[a]	
		0·342[e]	±0	0·176	−5	0·299	−11

[a] Taken as a basis for comparisons. Weighted ordinate method [b] $\Delta\lambda = 5$ nm; [c] $\Delta\lambda = 10$ nm. Selected ordinate method [d] 90 selected ordinates; [e] 30 selected ordinates.
d = path length.

co-ordinates of the solutions of Bromothymol Blue and Phenol Red were also originally evaluated[4] for $\Delta\lambda = 10$ nm. The actual computation can be done easily by calculating machine. We have written a simple program for an electronic computer ODRA 1013 which is of a great help in processing a large volume of experimental data.

The *method of selected ordinates*[15] has also been used to evaluate the tristimulus values of indicators (see *e.g.*, ref. 5). In this method three series of readings are taken—for three sets of wavelengths—from a smooth and clear plot of a transmittance curve. We have found that the reading of 90 transmittance values, each at a non-integral wavelength, is rather time-consuming and somewhat less accurate than the weighted ordinate method for $\Delta\lambda = 10$ nm (see Table I). If only 30 ordinates are taken, the accuracy of the method is substantially decreased, especially in the case of sharp absorption bands. Nearly all the results of this method in Tables I and II are subject to deviations. This is in accordance with the observation by De Kerf[16] who has compared accuracy in tristimulus specification of 31 reflecting surfaces and filters and has found that the 30-selected-ordinate method should be rejected. In addition to a lower level of accuracy, we have also found that there is a certain higher probability of introducing gross personal errors in reading the transmittance values from the graphs. There is no other check possible than a repetition of the whole procedure.

TABLE II.—CHROMATICITY CO-ORDINATES OF SPECTROPHOTOMETRIC STANDARD SOLUTIONS

Standard solution	x	$\Delta x \times 10^3$	y	$\Delta y \times 10^3$	Y	$\Delta Y \times 10^3$
K_2CrO_4	0·3126[a]		0·3217[a]		0·9996[a]	
	0·3160[b]	+3·4	0·3280	+6·3	0·9998	+0·2
$Co(NH_4)_2(SO_4)_2$	0·3307[a]		0·3115[a]		0·8490[a]	
	0·3314[b]	+0·7	0·3112	−0·3	0·8466	−2·4
$CuSO_4$	0·2896[a]		0·3122[a]		0·9235[a]	
	0·2896[b]	±0·0	0·3134	+1·2	0·9294	+5·9

[a] Weighted ordinate method, $\Delta\lambda = 10$ nm, was taken for comparison.
[b] 30-Selected-ordinate method.

A basic specification of any indicator should include, therefore, a colour specification in terms of the chromaticity co-ordinates and the relative luminance which have been obtained, preferably by the weighted ordinate method. Besides a higher level of accuracy attained, another advantage of this method is that it can be easily used to design a program for an electronic computer.

Complementary tristimulus values

Any indicator colour can also be specified by the complementary chromaticity co-ordinates, Q_x, Q_y, and by the colour concentration J. The computation, as outlined by Reilley and co-workers[6] and taken over by other authors, has been essentially based upon the 30-selected-ordinate method. However, the weighted ordinate method can be used with advantage to calculate the complementary tristimulus values from absorbance readings, especially if the tedium of the numerical computation is removed by employing a computer. The procedure for such a program will be published in a subsequent paper of this series. As can be seen from the results

summarized in Table III, the 30-selected-ordinate method yields results showing quite significant discrepancies. The value of complementary tristimulus co-ordinates as a specification is thus lowered. The inaccuracy in the tristimulus values is even summed

TABLE III.—COMPLEMENTARY CHROMATICITY CO-ORDINATES

Coloured species		Q_x	$\Delta Q_x \times 10^3$	Q_y	$\Delta Q_y \times 10^3$	J	$\Delta J \times 10^3$
Dithizone	$d = 30$ mm	0·377[a]		0·375[a]		0·877[a]	
		0·379[b]	+2	0·374	−1	0·882	+5
Bromothymol	$\alpha = 0{\cdot}00$	0·148[a]		0·087[a]		0·402[a]	
Blue		0·150[b]	+2	0·081	−6	0·403	+1
	$\alpha = 0{\cdot}50$	0·375[a]		0·318[a]		0·615[a]	
		0·376[b]	+1	0·319	+1	0·620	+5
	$\alpha = 0{\cdot}998$	0·485[a]		0·429[a]		0·827[a]	
		0·484[b]	−1	0·435	+6	0·843	+16
Phenol	$\alpha = 0{\cdot}00$	0·148[a]		0·059		0·541	
Red		0·151[b]	+3	0·052	−7	0·540	−1
	$\alpha = 0{\cdot}50$	0·247[a]		0·400[a]		0·825[a]	
		0·259[b]	+12	0·393	−7	0·832	+7
	$\alpha = 0{\cdot}995$	0·295[a]		0·565[a]		1·106[a]	
		0·296[b]	+1	0·569	+4	1·102	−4
K_2CrO_4		0·1693[a]		0·0069[a]		0·0198[a]	
		0·1493[b]	−20·0	0·0019	−5·0	0·0389	+19·1
$Co(NH_4)_2(SO_4)_2$		0·1755[a]		0·3512[a]		0·1555[a]	
		0·1716[b]	−3·9	0·3547	+3·5	0·1567	+1·2
$CuSO_4$		0·6178[a]		0·3655[a]		0·0741[a]	
		0·6328[b]	+15·0	0·3507	−14·8	0·0696	−4·5

[a] Weighted ordinate method ($\Delta\lambda = 10$ nm) was used in computation.
[b] 30-Selected-ordinate method.

in the value of the colour concentration J[see equation (7)]. The resulting deviation may be then quite serious (compare *e.g.*, the J values for potassium chromate solution in Table III). As the colour concentration is directly proportional to the product dc_I, the extent of the discrepancy in this variable shows a linear increase.

Computation of C.I.E. chromaticity co-ordinates from the tristimulus complementary data

The approximate equation (5) represents an important link between both systems of colour specification, as the data in the complementary chromaticity system alone are of limited value in giving direct information about the colour actually observed. However the problem of the accuracy attainable in its application has not yet been properly elucidated. The data in Table IV show that the weighted ordinate method ($\Delta\lambda = 10$ nm) helps to minimize the deviations which are inevitable when equation (5) is used. The value of J decides, however, the range of discrepancy in chromaticity co-ordinates in comparison with the values obtained directly from a transmittance curve.

The 30-selected-ordinate method is evidently inferior even in this respect and, as Table IV shows, the C.I.E. chromaticity co-ordinates, which have been obtained *via* equation (5), should be critically considered. The range and the systematic character of the deviations can be seen in Fig. 2. If a certain colour concentration is exceeded

TABLE IV.—COMPARISON OF CHROMATICITY CO-ORDINATES CALCULATED FROM COMPLEMENTARY TRISTIMULUS DATA WITH RESPECT TO THE VALUES IN TABLES I AND II

Coloured species		Weighted ordinate method, $\Delta\lambda = 10$ nm				30-Selected-ordinate method			
		x	$\Delta x \times 10^3$	y	$\Delta y \times 10^3$	x	$\Delta x \times 10^3$	y	$\Delta y \times 10^3$
Dithizone	$d = 10$ mm	0·292	±0	0·300	±0	0·291	−1	0·300	±0
	$d = 30$ mm	0·263	−2	0·271	−1	0·260	−5	0·271	−1
	$d = 50$ mm	0·245	−4	0·247	−7	0·239	−10	0·246	−8
Bromothymol	$\alpha = 0{\cdot}00$	0·375	+3	0·400	+4	0·375	+3	0·402	+6
Blue	$\alpha = 0{\cdot}50$	0·274	±0	0·317	±0	0·272	−2	0·316	−1
	$\alpha = 0{\cdot}998$	0·198	−7	0·208	−14	0·193	−12	0·202	−20
Phenol	$\alpha = 0{\cdot}00$	0·394	+7	0·436	+9	0·394	+7	0·439	+12
Red	$\alpha = 0{\cdot}50$	0·388	+5	0·279	+2	0·375	−8	0·285	+8
	$\alpha = 0{\cdot}995$	0·363	+21	0·204	+23	0·360	+18	0·196	+15
K_2CrO_4		0·3125	−0·1	0·3216	−0·1	0·3160	+3·4	0·3280	+6·3
$Co(NH_4)_2(SO_4)_2$		0·3307	±0	0·3115	±0	0·3315	+0·8	0·3112	−0·3
$CuSO_4$		0·2898	+0·2	0·3121	−0·1	0·2897	+0·1	0·3133	+1·1

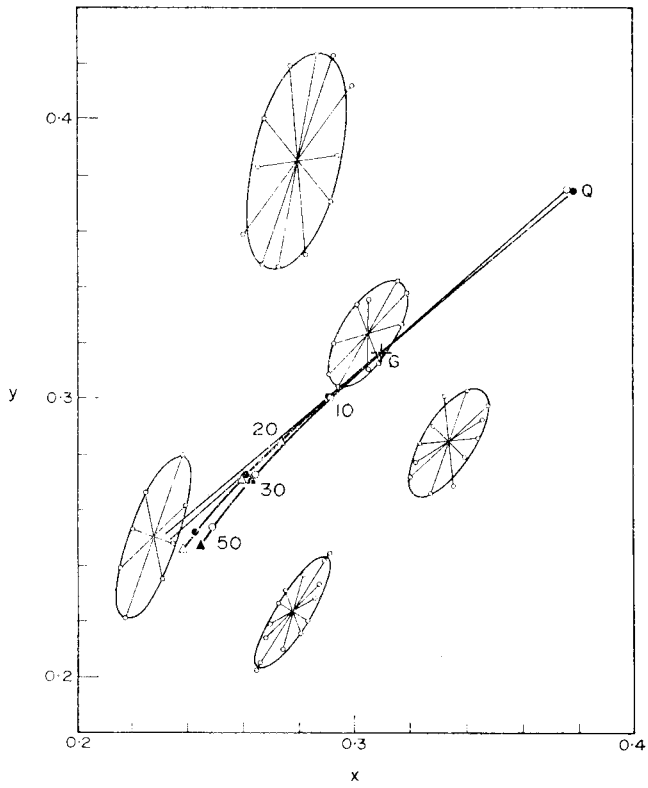

FIG. 2.—Section from the C.I.E. chromaticity diagram with MacAdam's ellipses (magnified ten times) showing the effect of the path-length (indicated in mm for particular families of points) and of various methods of computation: ○ weighted ordinate method, $\Delta\lambda = 10$ nm; ● 30-selected-ordinate method; the calculation based upon equation (5), the tristimulus complementary data being obtained by —▲ weighted ordinate method; —Δ 30-selected-ordinate method.

($J \gtrsim 1$), the resulting discrepancy is quite significant even if the absorption bands are of favourable shape, and may surpass the standard deviation inherent in a visual observation, which is indicated to a certain extent by the size of a particular MacAdam's ellipse.

Zusammenfassung—Die systematischen Abweichungen, die bei der Berechnung von Normfarbwerte vorkommen, wurden bezüglich der Angabe von Indikator-Farbändrungen untersucht. Das Gewichtsordinaten-Verfahren ($\Delta\lambda = 10$ nm) erwies sich als zur Ermittlung von C.I.E.- und Komplementär-Koordinaten zufriedenstellend geeignet. Zusammen mit den grundlegenden Daten über chemische Indikatoren sollte die C.I.E.-Farbspezifikation angegeben werden.

Résumé—Les déviations systématiques liées aux méthodes pour le calcul des coordonnées de chromacité ont été étudiées pour la spécification des changements de coloration d'indicateur. La méthode d'ordonnée pondérée ($\Delta\lambda = 10$ nm) s'est montrée satisfaisante pour l'évaluation des coordonnées tant C.I.E. que complémentaires. La spécification de couleur C.I.E. devrait être incluse parmi les données de base sur les indicateurs chimiques.

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COMPARISON OF A MODIFIED KJELDAHL AND A VACUUM FUSION TECHNIQUE FOR DETERMINATION OF NITROGEN IN TANTALUM ALLOYS

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Summary—Results obtained for the determination of nitrogen in the tantalum alloys T-111 (Ta–8W–2Hf) and T-222 (Ta–10W–2·5Hf–0·1C) by Kjeldahl and vacuum fusion procedures are compared. Results obtained by each technique are shown for the determination of nitrogen in the MAB T-111 sample, two commercial T-111 samples and a commercial sample of T-222 alloy. In the 5–25 ppm range, the relative standard deviation was 3–9% by the Kjeldahl procedure and 4–8% by vacuum fusion. This is a measure of the homogeneity of the material as well as of the reproducibility of the results. The agreement of the results obtained by these two techniques increases confidence in the vacuum fusion results for nitrogen in tantalum.

THE REFRACTORY ALLOYS T-111 and T-222 are promising candidates for structural use in a space power reactor. Uranium nitride fuel is sealed in a T-111 capsule with a tungsten barrier to minimize loss of nitrogen at high temperature.

Thus, it is important to be able to monitor changes in nitrogen content and to be able to determine nitrogen in these metals and alloys in the ppm range. The usual concentration of nitrogen in molybdenum and tungsten is well below 5 ppm, while in niobium and tantalum it may be 10–50 ppm or higher. Low contents of nitrogen in metals have been determined either by vacuum fusion techniques or by variations of the Kjeldahl procedure.

On the refractory metals there has been only a limited amount of work done showing a comparison of results obtained for nitrogen in the same material by the Kjeldahl and vacuum fusion methods. Where comparisons have been made, results by vacuum fusion are generally low[1,2] compared with results by the Kjeldahl method. The vacuum fusion method, however, appears to be more sensitive (the blank is 0·5–1·0 μg of nitrogen) and thus better suited to the determination of nitrogen at the lowest levels in those metals which release all their nitrogen when heated in a platinum bath.

The purpose of this paper is to evaluate the vacuum fusion method, as compared to a modified Kjeldahl method, for the determination of nitrogen in tantalum alloys. Vacuum fusion has many advantages but because quantitative release of nitrogen from different metals is not always obtained under a given set of conditions, it is necessary to use the chemical Kjeldahl method for reference. However, the latter method has been limited by a higher blank and a lower sensitivity. Recent developments have improved the Kjeldahl method in both respects, so it should now be possible to evaluate nitrogen determinations at low levels in the refractory metals niobium, tantalum, molybdenum, and tungsten.

The chemical dissolution procedure used was developed by Kallmann *et al.*[3] The distillation procedure was adapted from one described by Ciaranello.[4] The

indophenol reaction[5–11] was used for measurement of ammonia; the spectrophotometric procedure used was that previously described by Mann.[10] The method used to monitor ammonia in the laboratory atmosphere was similar to that of Leithe and Petschl.[12]

EXPERIMENTAL

Vacuum Fusion Procedure

Apparatus and materials

The apparatus used is described in the "1969 Book of ASTM Standards, Part 32". All temperature measurements were made with an optical pyrometer.

Platinum for the bath and flux was prepared by cutting 12-gauge wire into uniform 1-g pieces. Tin was added to the bath as 6 × 6 mm pellets, weighing about 1·3 g each.

Sample preparation

Samples were cut from T-111 and T-222 rods with a water-cooled abrasive wheel. Burrs were cleaned from the edges of each section with a file. The samples to be analysed were cut from these sections on a hand-operated flat shear.

Samples were etched for 10 min in hydrofluoric acid (1 + 1) heated on a steam-bath. The samples were washed, dried and rinsed in ethyl ether before being weighed (0·5–1·0 g).

Preparation of a fusion bath

After the crucible had been outgassed at 2400° for about 2 hr, it was allowed to cool to below 1600°. The platinum for the bath was then added to the crucible. The tin was added next, a few seconds being allowed for each piece to react before the next was dropped. The power to the induction furnace was then reset to give a temperature of 2000 ± 50° in the crucible. Finally a 0·3–0·5-g piece of T-111 was added to condition the bath, and the bath was outgassed for about 1 hr.

Analysis of samples

Each sample was added to the crucible along with a 1-g piece of platinum wire. No attempt was made to maintain intimate contact of sample and platinum at the moment of addition to the bath. The extraction time for samples and blanks was 20 min. Outgassing progress was monitored with a liquid-nitrogen-trapped ionization gauge attached to the furnace.

Initial composition of the bath was 80Pt:20Sn, exclusive of conditioner. The final composition ranged from 8·7 to 10 parts of bath plus flux to one part of sample. No additional tin was added to the crucible once the bath had been prepared for each day. A typical furnace loading consisted of two 30-g portions of platinum wire and two 7·8-g portions of tin for the bath. Twelve samples and one platinum wire for each sample plus two or three for blanks completed the load.

In a single day, one blank plus six samples with their fluxes were analysed. At the end of the day, the second portion of platinum and tin bath was added to the crucible and outgassed for about 30 min. From two to four replicate analyses were made for each sample rod on at least three days. The blank nitrogen, from the bath and platinum wire, ranged from 3·9 to 15·7% of the total nitrogen measured.

Kjeldahl Procedure

Apparatus

The Kjeldahl apparatus used is shown in Fig. 1. It incorporates a 300-ml round-bottom flask with an outer 29/42 standard taper joint, sealed by an ethylene-propylene *O*-ring on the inner joint. A polyethylene diffuser tip with holes made by a number 53 drill is fashioned from a surgical needle guard.

The spectrophotometer was a Beckman Model "B", with 10-mm cells.

Narrow-mouth Teflon FEP bottles, 250 ml, with tapered, solid Teflon stoppers, 60 mm long and 20 mm in diameter, weight approximately 25 g, and polyethylene automatic measuring dispensers were used.

Reagents

Sodium phenate solution. Add 12 g of phenol to 100 ml of cold water, then add 7·6 g of $Na_3PO_4 \cdot 12H_2O$ and 5·8 g of sodium hydroxide. Stir and add small portions of water until dissolved, finally diluting to 200 ml. Prepare as needed and do not chill as the solution is nearly saturated at room temperature.

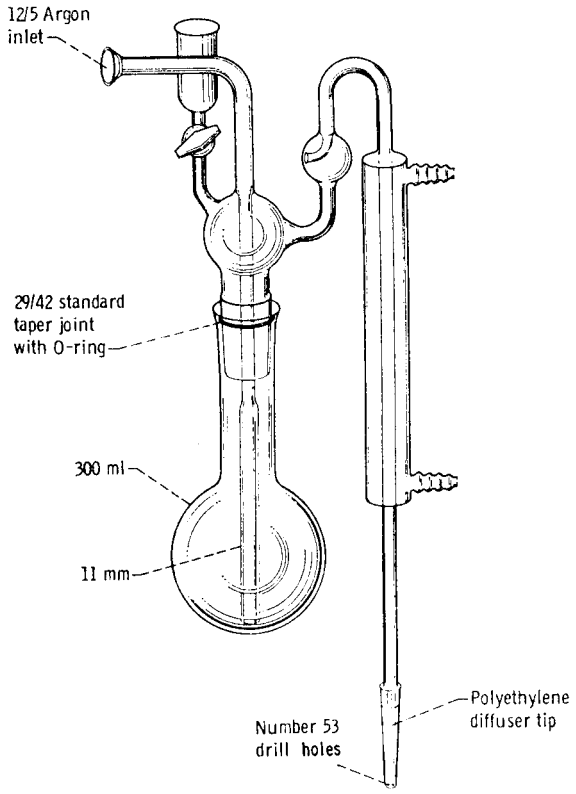

FIG. 1.—Kjeldahl distillation apparatus.

Sodium nitroprusside solution. Dissolve 25 mg of $Na_2Fe(CN)_5NO \cdot 2H_2O$ in water and dilute to 200 ml. Store the solution in the refrigerator and use within 1 hr.

Sodium hypochlorite solution. Dilute 8·0 ml of commercial bleach (5·25% solution of sodium hypochlorite) to 200 ml with water and store in the refrigerator. Freshly opened bleach is usually about 0·75*M* in "available chlorine" as determined by iodometric titration.[3]

Standard nitrogen solution. Dissolve 3·819 g of ammonium chloride (dried at 110°) in water to make 1 litre of stock solution containing 1000 μg of nitrogen per ml. This stock solution is diluted to obtain a standard solution containing 1 μg of nitrogen per ml.

Sodium hydroxide solution, 50%. Weigh 500 g of sodium hydroxide flakes into a Teflon-lined stainless-steel beaker. Add 600 ml of distilled water, cover with a ribbed watch glass, and boil for 15–20 min. Cool rapidly in ice water and store in a polyethylene bottle.

Boric acid solution, 2·5%. Dissolve 25 g of boric acid crystals in water and dilute to 1 litre.

"*Ammonia-free*" *water.* All water used is distilled and then passed through two mixed-resin demineralizer columns, unless indicated otherwise.

Argon gas. Minimum purity 99·998%.

Analysis of samples

Cut a 1–2-g piece of tantalum-base alloy sample, preferably from a rod. Chemically etch the sample by heating it for a few minutes in a Teflon beaker with a few ml of hydrofluoric and phosphoric acids and a little potassium chromate. Rinse well with water, then with a little acetone, and dry. Weigh a 1–2-g piece of the metal sample into a 260-ml Teflon FEP bottle. Add 5·0 g of potassium chromate, 50 ml of 48% hydrofluoric acid and 5·0 ml of 85% phosphoric acid to the bottle and loosely insert a solid tapered Teflon stopper. Carry two blanks and two standards through the procedure along with the samples. The blanks contain only the reagents. The standards are treated the same as the blanks except that they are spiked with 5–20 μg of nitrogen (added to the flask as a solution of ammonium chloride) just before the distillation.

Boil the samples vigorously on a hot-plate for 1–2 hr or until dissolved. Remove the stoppers and evaporate most of the excess of hydrofluoric acid, using infrared lamps for additional heating, until salts just begin to precipitate. Move the bottles to a low-heat hot-plate, and replace the stoppers if the samples are not to be distilled at once.

Remove the stopper from the bottle containing the first sample to be distilled and chill under a stream of cold water. Transfer the slurry of salts to the distillation flask, rinsing the bottle with portions of water to give about 100 ml total volume. Before distilling the first sample, purge the distillation apparatus by boiling two 10-ml portions of 50% sodium hydroxide solution in 150 ml of water for periods of 20 min while bubbling argon at 1 l./min through the solution. After each purge, discard the sodium hydroxide solution and rinse the flask several times, first with tap water, then dilute hydrochloric acid and finally with doubly demineralized water before reassembly. The same rinsing procedure is used between each blank, standard and metal sample.

Connect the flask to the distillation assembly and seal by means of the *O*-ring joint. Allow the condenser to dip into a receiver containing 5 ml of 2·5% boric acid solution and 10 ml of water. Connect the inert gas line to the gas inlet tube and adjust the flow to 1 l./min. As a precaution, the argon is previously bubbled through a gas-washing bottle containing 2·5% boric acid solution to remove any impurities which might otherwise be trapped in the distillate and possibly interfere in the colour development.

Slowly add 40 ml of 50% sodium hydroxide solution through the dropping funnel and rinse with 10 ml of water. The solution will change in colour when excess of alkali is present.

Begin heating the distillation flask. Start the timer, set for 20 mins, when the spray trap becomes hot to the touch. About 1 min before stopping the distillation, lower the receiver so that the condenser tip is above the level of the distillate. Stop the distillation after 20 mins, disconnect the flask, discard the salts, rinse the flask and add the next sample. Transfer the collected distillate, which should total about 50 ml, to a 100-ml volumetric flask, rinsing with a few ml of water. Keep the volume to 60–65 ml.

Store the flasks (containing the distillates) in a refrigerator until the reagents for the development of the indophenol colour are to be added.

Indophenol colour development and measurement

To the chilled distillates in 100-ml volumetric flasks, add, in turn, swirling between each addition, 10 ml each of sodium phenate, sodium nitroprusside, and sodium hypochlorite reagent solutions. These reagents are conveniently added by means of polyethylene automatic measuring dispensers. Place the flasks in a water-bath at about 40° and keep at 30–40° for 30 mins. Remove the flasks from the bath and dilute the solutions nearly to the mark with water. Then place the flasks for a few minutes in a water-bath at 20° before finally diluting the solutions exactly to the mark.

Mix the solutions well and measure the blue indophenol colour in 10-mm cells at 630 nm against a reagent blank. Beer's law is obeyed and the colour is quite stable for 24 hr. Find the amount of ammonia nitrogen in the sample from a calibration curve prepared by carrying 5–30 μg of nitrogen (added as standard ammonium chloride solution) through the colour development procedure and plotting absorbance against amount of nitrogen added. If the absorbance is too large to be read directly, dilute equal aliquots of the sample solution, a reference standard and the reagent blank with 1 volume of sodium phenate solution and 9 volumes of water. Alternatively, measure the high absorbance against a 30-μg nitrogen standard after zeroing the spectrophotometer with the standard solution.

DISCUSSION

Vacuum fusion method

The vacuum fusion method has been used for many years to determine gases in metals. The greatest emphasis has been on the determination of oxygen. Values for nitrogen are normally obtained along with those for oxygen. Nitrogen values are considered less accurate than those for oxygen in metals such as niobium, tantalum, molybdenum, and tungsten.[13] The lack of confidence has been fostered by the inability of vacuum fusion to yield nitrogen values that agree with those from the chemical Kjeldahl method. There has been a general belief that low nitrogen values indicate incomplete extraction. The Kjeldahl method usually gives higher values for nitrogen than does the vacuum fusion method. For this reason, the Kjeldahl method has been the preferred method for determining nitrogen in refractory metals.

Goward, however, in his review of the status of vacuum fusion analysis for nitrogen in metals, stated his belief that the platinum bath vacuum fusion technique would eventually prove successful for the refractory metals.[1] In an article on the determination of nitrogen by a carrier gas and fusion method, Dallmann and Fassel cited a few vacuum fusion results for nitrogen in refractory metals but no comparison of precision was shown between Kjeldahl and vacuum fusion results.[14]

Kjeldahl procedure

At the present time, the method most often used for the determination of nitrogen is a modified Kjeldahl procedure. It is applicable to all metals and is usually regarded as more reliable and precise than vacuum fusion.[15] In a recent report, Kallmann and co-workers stated that nitrogenous impurities in reagents could be reduced to ammonia during sample dissolution.[3] This reduction does not occur in the blank because of the absence of oxidizable sample metal. Kallmann proposed a method in which a high concentration of stable oxidant was maintained during sample dissolution. When Kallmann's method was used to determine nitrogen in the niobium alloy FS-85, good agreement was shown with results obtained by the platinum bath vacuum fusion method.[16] At low concentration levels, *i.e.*, 0–100 ppm, a spectrophotometric measurement is now used instead of the titrimetric finish used for higher amounts, in which ammonium borate is titrated to boric acid with 0·007*N* standard acid (1 ml $\simeq$ 0·1 mg N), the colour change of the mixed indicator "Methyl Purple" being used to find the equivalence point. Formerly, Nessler's reagent[17] was used, first visually and later colorimetrically, to measure the ammonia nitrogen in the Kjeldahl distillate. Recently, the advantages of the indophenol spectrophotometric method have won it wide popularity.

There are several sources of ammonia nitrogen that cause high blanks in the Kjeldahl determination. These include chemical reagents, laboratory air, and the preparation of the sample surface. Sulphuric acid and hydrogen peroxide are known to contain traces of ammonium ions. Other reagents contain traces of nitrate ions, which do not affect the blank but may be reduced by metal to ammonium ions and thus cause high nitrogen results for the sample. Potassium dichromate is a stable oxidant. It does not coat the sample with insoluble products and does not oxidize ammonium ions to free nitrogen. Since dichromate is present in large excess, there is little chance for reduction of nitrate by the sample.[3]

There is also ammonia present in the laboratory air. For this reason, it is frequently recommended that nitrogen determinations be made in a location isolated from the main chemical laboratory. In our chemical laboratory, the air usually contains 5–6 μg of ammonia nitrogen per m^3 of air when samples are being analysed for nitrogen and no ammonia is being used in the immediate area. This is believed to be a major source of nitrogen contamination. In our procedure, ammonia is absorbed in dilute boric acid[18] instead of dilute sulphuric acid, but otherwise the procedure for measuring ammonia in air is similar to that of Leithe and Petschl.[12]

The preliminary surface treatment of the sample is another possible source of contamination. Before analysis, samples are commonly filed and/or chemically etched. Very small or irregular samples are more easily etched than filed. The best sample form is the one with the least exposed surface. In the work reported here, all samples were etched with acid before both Kjeldahl and vacuum fusion analysis.

The chemical dissolution of metal samples by Kallmann's procedure greatly reduces exposure to atmospheric contamination. Samples are usually dissolved in less than 2 hr. If loosely stoppered bottles are used, samples are dissolved without addition of more acid and exposure to laboratory air is further minimized.

Chemical reagents may often be purified to remove traces of impurities. The "ammonia-free" water[11,19] used here is distilled and then passed through two mixed-bed demineralizer columns, the last pass just before use. The 50% sodium hyroxide solution is boiled in a Teflon-lined stainless steel beaker for 15–20 min, then quickly cooled and stored in a plastic bottle. Phosphoric acid may be freed from ammonia by heating five parts with one part of perchloric acid until fuming ceases. Potassium chromate may be purified by evaporating a litre of 70% w/v solution in the presence of 3 g of potassium hydroxide, followed by gradual heating to 500° in a muffle furnace.[20] Purification of our reagents had only a slight effect on the blank. The size and variation of the blank in the Kjeldahl method has previously made unreliable the determination of less than 25 ppm of nitrogen. In our laboratory, the blank usually amounts to 8–10 μg of nitrogen, of which a major part is attributed to atmospheric contamination.

The first modification of the standard method (see Fig. 1) is to use a 300-ml distillation flask in order to accommodate the large amount of salts formed by the addition of excess of alkali to hydrofluoric–phosphoric–chromic acid solutions of refractory metals. The round-bottom distillation flask has an outer 29/42 standard taper joint and is sealed with an ethylene-propylene *O*-ring on the inner joint. This prevents "freezing" of the joint and permits easy disassembly for cleaning after contact with alkali. The diameter of the bottom 0·12 m of the gas inlet tube was increased from 8 to 11 mm in order to prevent clogging by salts during the distillation.

The next modification is the use of an inert carrier gas and direct heating of the distillation flask (instead of the usual flow of steam) for distillation of ammonia. This change makes the manipulations easier and faster. With this system, it is unnecessary to heat a large volume of water to generate steam, and the inert gas flow is easily regulated so that there is no chance of a sudden pressure decrease with resultant loss of sample. Also, it is feasible to run two or more distillation systems simultaneously, using a separate inert gas cylinder for each system to aviod pressure fluctuations.

Recent developments have considerably increased the sensitivity of the colorimetric measurement. The intense blue indophenol colour given by the reaction of ammonia with phenol and hypochlorite was discovered by Berthelot in 1859.[21] The sensitivity of the indophenol procedure can be further increased by the presence of various catalysts. Iron, chromium, and manganese accelerate the reaction, but copper and oxidants such as persulphate inhibit it.[8] The catalysed indophenol reaction is more sensitive than that of ammonia with thymol and hypochlorite[11,22] and it is also about ten times more sensitive than the Nessler reaction[17,19] which has the disadvantages that the reaction product is colloidal and the blank value is large and variable.

Chaney and Marbach[5] were the first to recommend the use of sodium nitroprusside as catalyst. This reagent not only accelerates the reaction but also increases to a maximum the conversion of ammonia into indophenol. The procedure described here is similar to one recommended by Mann.[10] The molar absorptivity at 630 nm

is $2{\cdot}24 \times 10^3$ l.mole^{-1}.mm^{-1}, the same as that reported by Bach *et al.*,[6] using a slightly different indophenol procedure. Several Japanese investigators[22,23] have further increased the sensitivity of the indophenol procedure by using solvent extraction.

The principal advantage of high sensitivity is that relatively small samples of solid material are sufficient for determination of low nitrogen content. Such small samples may now be dissolved rapidly with a minimum of atmospheric contamination, permitting determination of less than 25 ppm of nitrogen with a higher degree of precision than was formerly possible.

Results

The results reported in Table I indicate that equivalent results for the determination of nitrogen in the tantalum alloys T-111 and T-222 are obtained by vacuum fusion and Kjeldahl techniques. The precision of the vacuum fusion results is not significantly different from the precision of the Kjeldahl results in spite of the much larger blank of the latter method.

TABLE 1.—COMPARISON OF RESULTS FOR THE DETERMINATION OF NITROGEN IN T-111 AND T-222 BY KJELDAHL AND VACUUM FUSION METHODS

	Nitrogen, *ppm*							
	#1*		#2†		#3§		#4‡	
	Kjeldahl	Vacuum fusion	Kjeldahl	Vacuum fusion	Kjeldahl	Vacuum fusion	Kjeldahl	Vacuum fusion
	8·7	10·0	7·7	7·6	9·4	9·4	20·9	21·3
	7·9	9·0	6·9	7·9	9·7	10·2	24·2	21·9
	7·7	9·6	7·4	6·9	9·4	9·0	23·9	22·2
	8·4	9 9	7·3	7·0	9·3	9·6	20·6	22·2
	8·1	9·5	7·0	6·4	9·6	9·9	22·6	21·0
	8·1	9·8	6·8	7·2	8·7	10·5	24·9	21·6
	8·7	9·9	7·5	7·1	9·4	10·0	28·7	22·6
		10·3		6·6	9·2	9·8	23·1	22·5
		10·1		7·4	9·1	8·7	25·0	24·8
		9·2		8·3	9·0	9·4	24·7	24·8
					9·8		21·9	
					9·2		22·5	
					9·3		22·2	
							25·3	
Average, *ppm*	8·2	9·7	7·2	7·2	9·3	9·6	23·6	22·5
Std. devn, *ppm*	0·4	0·4	0·4	0·6	0·3	0·5	2·1	1·3
Rel. std. devn, %	4·9	4·1	5·6	8·3	3·2	5·2	8·9	5·8
Blank, *μg*	10·8	0·7–0·9	7·5	0·7–0·9	8·4	0·7–0·9	8·4	0·7–0·8

* $\frac{1}{4}''$ diameter T-111 rod from Materials Advisory Board.
† $\frac{3}{4}''$ diameter T-222 rod, commercial source.
§ $\frac{1}{2}''$ diameter T-111 rod, commercial source.
‡ $\frac{3}{4}''$ diameter T-111 rod, commercial source.

In the case of the Kjeldahl results, samples numbers 1 and 2 were analysed on one day, sample number 3 was analysed on two days and sample number 4 was analysed on three days. Each Kjeldahl blank reported is the average of two or more values. For the vacuum fusion results, samples numbers 1 and 2 were analysed on three days and samples numbers 3 and 4 were analysed on four days. A single vacuum fusion blank was run each day.

MAB* T-111 (sample #1) was included among the samples analysed because it is supposed to be a uniform reference material. It has been available by request from the National Bureau of Standards since 1965 and has been analysed by many laboratories interested in the determination of traces of carbon, nitrogen, oxygen and hydrogen in refractory metal alloys.[24]

Chase[25] reported in 1965 results obtained for nitrogen in two series of collaborative analyses of the MAB T-111 alloy by 12 participating laboratories using the Kjeldahl procedure, and these may be compared with our results.

	Series #1	Series #2
Average N, *ppm*	31	20
Standard deviation, *ppm*	41	9
Rel. stand. deviation, %	132	45
Range, *ppm*	2–162	11–38

The blank values ranged from 0 to 30 μg. The co-operating laboratories experienced great difficulty with this determination because a method for dissolving solid pieces of material in a reasonable period of time was not then available. It was stipulated that 1-g solid undivided samples should be used, prepared by filing and then rinsing in a residue-free solvent. All analyses were performed three times, once each on three days, by a Nessler photometric procedure. The samples were dissolved in 20 ml of hydrofluoric acid (1 + 1) and up to 15 ml of 30% hydrogen peroxide. The peroxide was added 5 ml at a time at 45–60-min intervals. Dissolution was carried out in polyethylene or platinum beakers (covered with a sheet of Teflon) by heating on a water-bath at about 50° for 2½–4 hr. Ammonium chloride was used for calibration. As usual, intra-laboratory agreement was much better than agreement between different laboratories. Chase stated that great care had been taken to ensure that the material used was reasonably homogeneous, so the differences must have been due to variations in procedure and techniques.

Only one contributor reported nitrogen results obtained by vacuum fusion. These were 9·2, 9·2 and 10 ppm of nitrogen. The conditions used were: 0·2-g sample, 1900° platinum bath and 20-min extraction.

We can only speculate that the reason for the discrepancy between our results of 8–10 ppm and Kallmann's Kjeldahl results of about 28 ppm nitrogen[3] in MAB T-111 is non-homogeneity. A similar dissolution method was used in both cases.

Control of the dissolution and blank determination appear to be the critical steps of the Kjeldahl procedure. Once a sample is in solution, the isolation and measurement of nitrogen can be done very easily and accurately.

CONCLUSIONS

The analytical and precision results reported here serve to validate the applicability of the vacuum fusion technique for the determination of nitrogen in the tantalum alloys T-111 and T-222. The fact that the vacuum fusion nitrogen values were obtained simultaneously with the determination of oxygen and have an accuracy and precision equivalent to Kjeldahl values is of great importance. Vacuum fusion conditions can be accurately reproduced, the blank is very low and constant, both

* Materials Advisory Board.

sample and time are conserved, the oxygen and nitrogen values are related to each other, and no calibration or standards are necessary.

Kjeldahl results depend on the laboratory atmosphere and thus may be higher or lower in different locations and at different times in the same location. The modified Kjeldahl apparatus and procedure described here have several advantages over usual Kjeldahl practice for the determination of nitrogen in refractory metals. The apparatus is easy to clean. The inert flushing gas is more easily controlled than steam distillation, avoids the need to heat a large volume of water, and does not contribute to the blank. The high sensitivity obtainable by using the nitroprusside-catalysed indophenol reaction for the spectrophotometric measurement of ammonia nitrogen permits the use of relatively small (1–2 g) samples and the precise determination of 10 ppm nitrogen in tantalum alloys.

Since Kallmann's dissolution procedure is applicable to niobium, molybdenum, and tungsten as well as to tantalum, it should now be possible to re-examine the determination of nitrogen in many of the refractory alloys of these metals by comparison of vacuum fusion and Kjeldahl results.

Zusammenfassung—Die Ergebnisse von Stickstoffbestimmungen in den Tantallegierungen T-111 (Ta-8W-2Hf) und T-222 (Ta-10W-2,5Hf-0,1C) nach Kjeldahl und nach dem Vakuumschmelzverfahren werden verglichen. Nach beiden Verfahren erhaltene Ergebnisse der Stickstoffbestimmung werden für eine MAB-Probe T-111 sowie zwei T-111-Proben und eine T-222-Probe aus dem Handel angegeben. Im Bereich 5–25 ppm betrug die relative Standardabweichung beim Kjeldahlverfahren 3–9% und bei der Vakuumschmelze 4–8%. Das stellt ein Maß dar sowohl für die Homogenität des Materials als auch für die Reproduzierbarkeit der Ergebnisse. Die Übereinstimmung der nach diesen beiden Verfahren erhaltenen Ergebnisse stärkt das Vertrauen auf Vakuumschmelzwerte von Stickstoff in Tantal.

Résumé—On a comparé les résultats obtenus pour le dosage de l'azote dans les alliages de tantale T-111 (Ta-8W-2Hf) et T-222 (Ta-10W-2,5Hf-0,1C) par les techniques de Kjeldahl et de fusion sous vide. On présente les résultats obtenus par chaque technique pour le dosage de l'azote dans l'échantillon MAB T-111, deux echantillons commerciaux T-111 et un échantillon commercial de l'alliage T-222. Dans le domaine 5–25 p.p.m., l'écart type relatif est de 3–9% par la technique de Kjeldahl et 4–8% par la fusion sous vide. Ceci est une mesure de l'homogénéité de la matière aussi bien que de la reproductibilité des résultats. L'accord des résultats obtenus par ces deux techniques accroît la confiance dans les résultats de la fusion sous vide pour l'azote dans le tantale.

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POLAROGRAPHISCHE BESTIMMUNG VON BERYLLIUM MIT *o*-(2-HYDROXY-5-METHYL-PHENYLAZO)-BENZOESÄURE

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Zusammenfassung—*o*-(2-Hydroxy-5-methyl-phenylazo)benzoesäure ist zur polarographischen Berylliumbestimmung in Wasser–Methanol-Gemischen gut geeignet; 10^{-9} Mol/ml werden gleichstrompolarographisch erfaßt. Aluminium stört bis zu einem fünffachen Überschuß nicht. Größere Aluminium mengen können durch den Chelataustauscher auf der Basis von *o*-(2-Hydroxyphenylazo)benzoesäure abgetrennt werden.

DIE VORLIEGENDE Arbeit stellt eine Fortsetzung unlängst veröffentlichter Untersuchungen[1] dar.

Eine direkte polarographische Reduktion des Berylliums in wäßrigen Lösungen ist zur quantitativen Bestimmung praktisch nicht geeignet.[2] Mit Lithiumchlorid als Leitelektrolyt können höchstens 10^{-4} Mol angezeigt werden.[3] Bestimmungsverfahren in wasserfreien Lösungsmitteln[4,5] entsprechen wenig der analytischen Praxis.

Eine indirekte polarographische Bestimmung in Wasser–Methanol-Gemischen wird durch Komplexbildung mit *o*-Hydroxy-*o'*-carboxy substituierten Phenylazonaphthalinen z.B. Mordant Red 74 möglich.[6] Die bevorzugte Chelatbildung mit Beryllium(II) läßt seine Bestimmung bis zu einem fünffachen Aluminium-Überschuß zu. Nachteilig macht sich bemerkbar, daß die Differenz der Halbstufenpotentiale maximal 0,12 V beträgt und gleichstrompolarographisch die Bestimmungsgrenze bei 10^{-7} Mol Beryllium pro ml liegt. Die Eichkurveist nur in kleinen Konzentrationsbereichen linear und die Standardlösung des Komplexbildners begrenzt haltbar.

Dagegen bildet *o*-(2-Hydroxy-5-methyl-phenylazo)benzoesäure (HMPB) mit Beryllium(II) einen Chelatkomplex, dessen Halbstufenpotential in Acetatpufferlösungen (pH 5,0) gegenüber der freien Azoverbindung um 0,18 V zu negativeren Potentialen verschoben ist. Enthält das Lösungsmittel mehr als 40% Methanol, werden kompensierte Gleichstrompolarogramme bis zu einer Bestimmungsgrenze von 10^{-9} Mol Beryllium pro ml aufgelöst. Die Elektrodenreaktionen sind diffusionskontrolliert. Eichgeraden bleiben in Konzentrationsbereichen, die eine Zehnerpotenz nicht überschreiten, linear. Aluminium stört die Bestimmung bis zu einem fünffachen Überschuß nicht wesentlich. Das Reagenz kann durch einfache Kupplungs-Reaktion hergestellt werden.[7,8] Die methanolische Standardlösung ist haltbar.

EXPERIMENTELLER TEIL

Verwendet wird der selbstschreibende Gleichstrompolarograph PO3 der Fa. Radiometer. Als Elektrodensystem ist eine Quecksilbertropfelektrode mit einer gesättigten Kalomelgegenelektrode angeschlossen.

Elektrolysestromkonstante	$a = 4{,}04 \cdot 10^{-2}$ μA/mm
Verstärkung	$m_1 \cdot m_2 = 200$ bis 5
Effektive Höhe des Quecksilberniveaus	480 mm
Mittlere Durchflußgeschwindigkeit	$\overline{m} = 4{,}26$ mg/sec.

Chemikalien

o-(2-Hydroxy-5-methyl-phenylazo)benzoesäure.[7,8] Zur Herstellung der Standardlösung werden 4 g HMPB in 1 l. Methanol *p.a.* gelöst.

Berylliumsulfat, "reinst" (Merck). Aus dem mit 0,05% Aluminium verunreinigten Präparat werden 10^{-2}, 10^{-3} und 10^{-4} molare Eichlösungen hergestellt.

Aluminiumnitrat, "reinst" (Merck). Die Stammlösung ist $10^{-3}M$.

Acetatpuffer aus 0,3*M* CH_3COONa, 0,7*M* CH_3COOH. Das System puffert in Wasser bei pH 5,0. Der in Wasser–Methanol-Gemischen mit einer Glaselektrode bestimmte pH-Wert steigt auf 5,5, wenn 100 ml endgültig zusammengesetzte Testlösung 50 ml Methylalkohol enthalten.

Kaliumchloridlösung, 1*M*, als Leitelektrolyt.

Zusammensetzung der Grundlösung

Zur Bestimmung der optimalen Zusammensetzung der Grundlösung wird der Einfluß der Lösungsmittelbestandteile auf die Diffusions-Grenzstromhöhen der freien und im Beryllium(II)-Komplex gebundenen HMPB untersucht.

Ausgangslösung: Kaliumchlorid (0,1*M*, 100 ml) mit 0,008% HMPB und 36 μg Beryllium.

In Übereinstimmung mit Ergebnissen an dem Chelataustauscher auf der Basis von *o*-(2-Hydroxyphenylazo)benzoesäure und Extraktionsversuchen, zeigt eine voltammetrische Titration, daß der Beryllium-Komplex zwischen pH 4,0 und 6,0 ausreichend hydrolysebeständig ist, um ihn zur polarographischen Bestimmung zu verwenden. Die Differenz der Halbstufenpotentiale erreicht in diesem Bereich ein Maximum. Den Einfluß der Pufferkonzentration auf die Stufenhöhe zeigt Abb. 1.

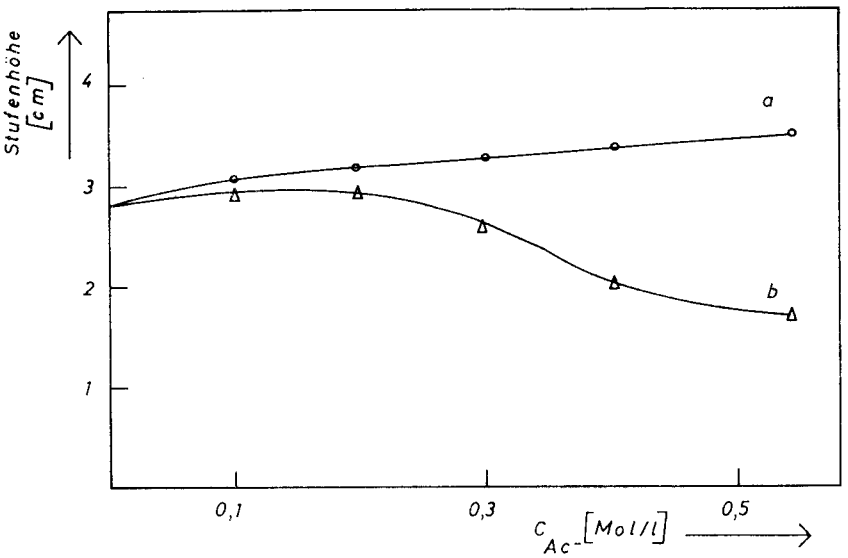

ABB. 1. Abhängigkeit der Stufenhöhe von der Konzentration des Puffers (CH_3COONa + CH_3COOH)
a: HMPB, b: Be(II)-Komplex der HMPB (Grundlösung: H_2O, 0,1 M KCl, pH = 5,0).

Für weitere Messungen wird ein pH-Wert von 5,0 mit 10 ml Pufferlösung (0,3*M* Natriumacetat, 0,7*M* Essigsaüre) pro 100 ml Probelösung stabilisiert. Eine gute Auflösung der polarographischen Stufen wird durch Methanolzusätze erreicht (Abb. 2). Dies kann mit einer Verminderung der Protonenaktivität[9] erklärt werden. Zusätzlich erhöht sich das Ausmaß der Komplexbildung.[10] In Lösungen mit 40 bis 60 Vol.-% Methanol verändern sich die Stufenhöhen nicht merklich. Daher sollte die Grundlösung *ca.* 50 Vol.-% Methanol enthalten.

Den Einfluß der Kaliumchloridkonzentration zeigt Abb. 3. Die Verwendung 0,1*M* Kalium chlorid ist am günstigsten.

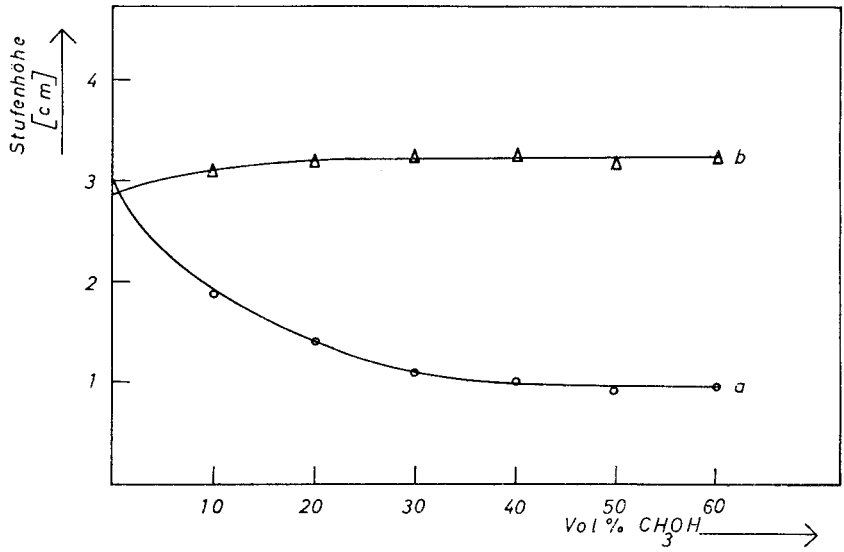

ABB. 2. Abhängigkeit der Stufenhöhe von der Methanolkonzentration a: HMPB, b: Be(II)-Komplex der HMPB (Grundlösung: H_2O, 0,1 M Acetat-Puffer, pH = 5,0).

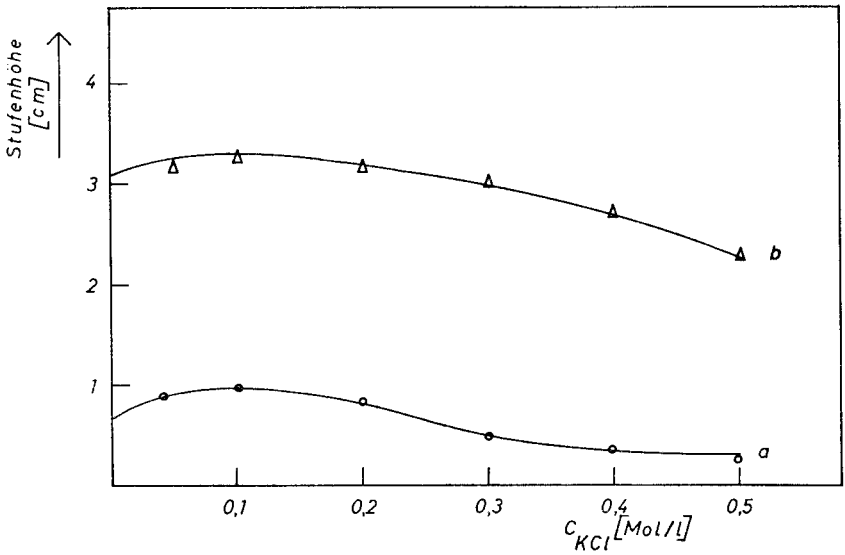

ABB. 3. Abhängigkeit der Stufenhöhe von der Kaliumchloridkonzentration a: HMPB, b: Be(II)-Komplex der HMPB (Grundlösung: H_2O, 0,1 M Acetat-Puffer, 50 Vol-% Methanol, pH = 5,5).

Die Auswertung dieser Ergebnisse gibt die folgende Arbeitsvorschrift. Mit ihr werden die in Abb. 4 dargestellten Polarogramme erhalten.

Arbeitsvorschrift

Für Berylliumbestimmungen werden Probelösungen in 100 ml Meßkolben wie folgt zusammengesetzt:

Grundlösung:

10 ml 1*M* Kaliumchlorid
10 ml 1*M* Acetat-puffer
40 ml Methanol
10 ml 0,012 bis 0,4%-ige Lösung von HMPB in Methanol je nach Konzentrationsbereich.

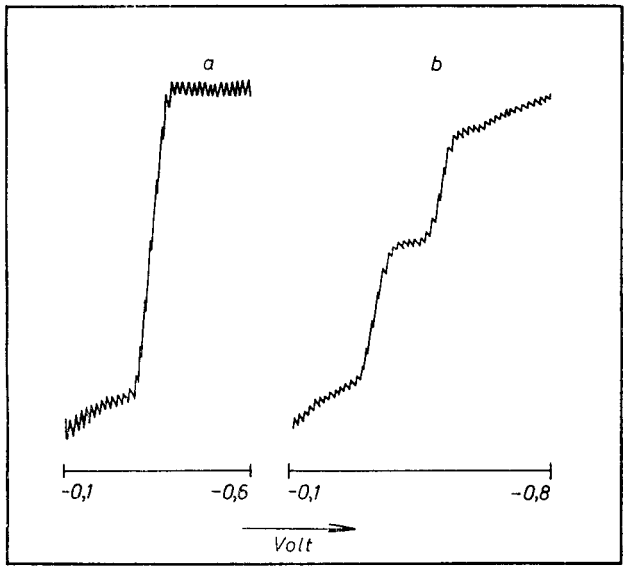

ABB. 4. Gleichstrompolarogramme a: 0,32 μMol HMPB/ml, b: 0,32 μMol HMPB/ml und 0,04 μMol Be(II)/ml.

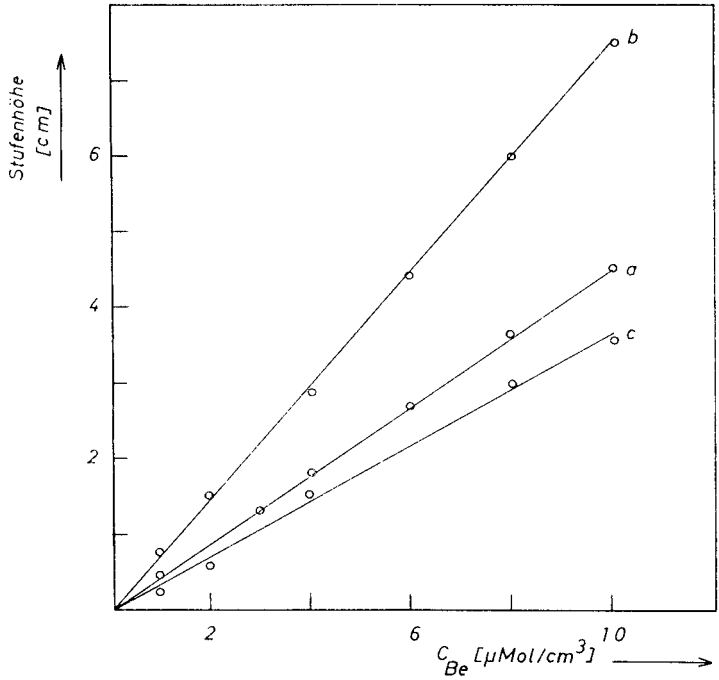

ABB. 5. Eichgeraden zur Be(II)-Bestimmung a: Halbmikrobereich 1,0 bis 0,1 μMol Be(II)/ml, b: Mikrobereich I 0,1 bis 0,01 μMol Be(II)/ml, c: Mikrobereich II 0,01 bis 0,001 μMol Be(II)/ml.

Zur vollständigen Komplexbildung werden alle Proben 5 min in Meßkolben bei 60° auf dem Wasserbad erwärmt, nach dem Abkühlen mit Wasser auf 100 ml aufgefüllt und 15 min mit gereinigtem Stickstoff gespült.

Es wird unter der Stickstoffatmosphäre zwischen −0,10 und −0,80 V bei 20° polarographiert. Die Stufenhöhe der durch das Halbstufenpotential $E_{1/2} = -0{,}52$ V charakterisierten polarographischen Welle ist der Berylliumkonzentration proportional.

Die nach dieser Arbeitsvorschrift aufgenommenen Eichgeraden sind in Abb. 5 enthalten.

DISKUSSION

Die Korrelationsrechnung[11] bei konstanter Verstärkung für den Halbmikro- und Mikrobereich (I) zeigt, daß das Linear-Gesetz von Ilkovič erfüllt ist. Die Standardabweichungen betragen 0,014 μMol/ml bzw. 0,002 μMol/ml. Die Bestimmungsgrenze liegt bei 0,001 μMol/ml.

In Abb. 6 ist eine Eichkurve in Gegenwart von Al(III) dargestellt. Ab $c_{Be}:c_{Al} \leqslant 1:5$ ist die Eichgrade nicht mehr linear.

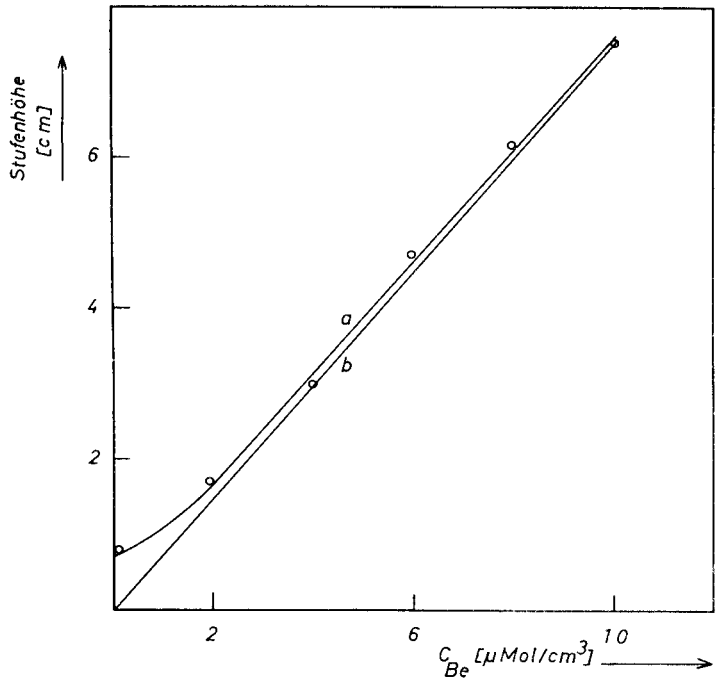

ABB. 6. Eichkurve zur Be(II)-Bestimmung in Gegenwart von Al(III) a: 0,1 bis 0,01 μMol Be(II)/ml, 0,1 μMol Al(III)/ml, b: 0 1 bis 0 01 μMol Be(II)/ml.

Störungen

(*a*) Übergangsmetallkationen

(*b*) Al(III) für $c_{Be}:c_{Al} \leqslant 1:5$. Beseitigung: Ionenaustauschchromatographie mit einem Chelataustauscher auf der Basis von *o*-(2-Hydroxy-phenylazo)benzoesäure oder Extraktion des Berylliumkomplexes mit Chloroform.

(*c*) Anionen, die mit Beryllium(II) stabilere Komplexe bilden als HMPB.

Für die Bereitstellung von Mitteln danken wir dem Bundesministerium für Bildung und Wissenschaft.

Summary—Beryllium can be determined polarographically in aqueous methanol solutions as its complex with *o*-(2-hydroxy-5-methyl-phenylazo)benzoic acid. As little as 10^{-9} mole/ml can be determined. Aluminium interferes when present in a molar concentration five times that of the beryllium or greater, though larger amounts may be separated by using a chelate-exchanger based on *o*-(hydroxyphenylazo)-benzoic acid.

Résumé—On peut doser polarographiquement le béryllium dans des solutions de méthanol aqueux sous forme de son complexe avec l'acide *o*-(2-hydroxy 5-méthyl phénylazo)benzoïque. On peut déterminer des quantités aussi petites que 10^{-9} mole/ml. L'aluminium gêne lorsqu'il est présent à une concentration molaire égale ou supérieure à cinq fois celle du béryllium, quoique de plus grandes quantités peuvent être séparées en utilisant un échangeur de chélate basé sur l'acide *o*-(hydroxyphénylazo)benzoïque.

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EXTRACTION OF TUNGSTEN WITH 8-HYDROXY-QUINOLINE AND SOME OF ITS DERIVATIVES

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Summary—The extraction of tungsten by chloroform solutions of 8-hydroxyquinoline(I), 2-methyl-8-hydroxyquinoline(II), 5,7-dibromo-8-hydroxyquinoline(III) and 8-mercaptoquinoline(IV), as a function of the concentration of tungsten and reagent and the acidity of the aqueous phase, has been studied. Evidence was obtained for the quantitative extraction of tungsten over a wide range of acidity. The degree of extraction of tungsten at $10^{-5}M$ concentration with I, III and IV gives two maxima when plotted against acidity. The extraction maximum for the more acidic solutions lies in the region where the reagents exist in the protonated form and its position depends on the reagent used. It is suggested that different tungsten complexes are extracted, depending on the acidity of the aqueous phase.

THE EARLIER IDEA of tungsten being incapable of combining with 8-hydroxyquinoline (HOx) and its derivatives[1–2] has been disproved by a number of studies published recently[3–18] although the first evidence for the formation of insoluble WO_2Ox_2 was reported as far back as 1933. Of the reagents under consideration, only two (8-hydroxyquinoline and 8-mercaptoquinoline) have previously been investigated as reagents for tungsten. These results could be interpreted as meaning that the other reagents of this group would also interact with tungsten and it was therefore of interest to look into such a problem.

EXPERIMENTAL

We have investigated the extraction of tungsten(VI) by chloroform solutions of 8-hydroxyquinoline (HOx), 2-methyl-8-hydroxyquinoline (HCH_3Ox), 5,7-dibromo-8-hydroxyquinoline (HBr_2Ox) and 8-mercaptoquinoline (HSx) as a function of the concentration of tungsten and reagent and the acidity of the aqueous phase from pH 10 to 10*N* (hydrochloric acid). The radioactive tungsten isotopes ^{187}W with $t_{1/2} = 23{\cdot}85$ hr and ^{185}W with $t_{1/2} = 73$ days were used as tracers. The reagents and chloroform were purified by recommended methods. For extractions from weakly acidic solutions, chloride (hydrochloric acid and potassium chloride), perchlorate (perchloric acid and sodium perchlorate), biphthalate and acetate buffer solutions were used to obtain and maintain the required values of pH. The experimental procedure has been described previously.[19]

To determine the time required to obtain equilibrium in the distribution of tungsten between the phases, we first studied the kinetics of tungsten extraction as a function of the acidity of the aqueous phase. Some typical results are given in Tables I and II; they are similar to those obtained with molybdenum.[19]

It follows from Tables I and II that distribution equilibrium is attained after mechanical agitation of the phases for less than 2·5 hr, even at minimum concentrations of tungsten and reagent. That period was therefore used in the investigation of extraction. The lower tungsten recovery on prolonged extraction with 8-hydroxyquinoline and thio-oxine (Table I) at an initial pH of 1·6 is explained by a change in the pH of solutions which have been agitated for a long time. The approximately equal values of the tungsten distribution for extraction and stripping (Table II) indicate that the distribution equilibrium is attainable within 2·5 hr.

RESULTS AND DISCUSSION

The results of the investigations are given in Figs. 1–4.

From the figures shown it follows that there is a very large excess of reagent needed. For fixed concentrations of tungsten and reagent the pH range of extraction

TABLE I.—KINETICS OF EXTRACTION OF TUNGSTEN ($10^{-7}M$) BY $10^{-3}M$ CHLOROFORM SOLUTIONS OF 8-HYDROXYQUINOLINE (pH = 1·6), 8-MERCAPTOQUINOLINE (pH = 1·6) AND 5,7-DIBROMO-8-HYDROXYQUINOLINE (pH = 5·3)

Reagent	% Extraction in shaking period (*min*)													
	15	30	45	60	75	90	110	115	120	130	150	180	210	240
8-Hydroxy-quinoline	—	35·1	44·3	50·4	—	67·8	—	67·8	—	—	68·2	52·9	47·4	48·5
8-Mercapto-quinoline	—	35·6	45·8	55·5	—	58·4	—	—	68·2	—	85·5	84·8	59·8	42·2
5,7-Dibromo-8-hydroxyquino-line	33·8	38·0	40·8	44·3	45·3	49·5	50·4	—	—	50·7	50·8	50·6	50·8	—

TABLE II.—KINETICS OF EXTRACTION AND STRIPPING OF TUNGSTEN ($10^{-5}M$) WITH AND FROM $10^{-2}M$ 5,7-DIBROMO-8-HYDROXYQUINOLINE

Shaking period, *hr*	pH = 0.85		pH = 2·5		1*M* HCl	
	% ext.	% stripped	% ext.	% stripped	% ext.	% stripped
2·5	96·8	96·0	97·8	97·0	92·4	92·5
5·5	96·7	96·2	96·5	96·2	91·9	91·7
9·15	96·7	95·7	97·2	97·6	90·2	91·5
12	96·6	96·0	97·4	98·0	92·3	94·6
18	96·1	96·4	96·4	96·5	92·4	92·5

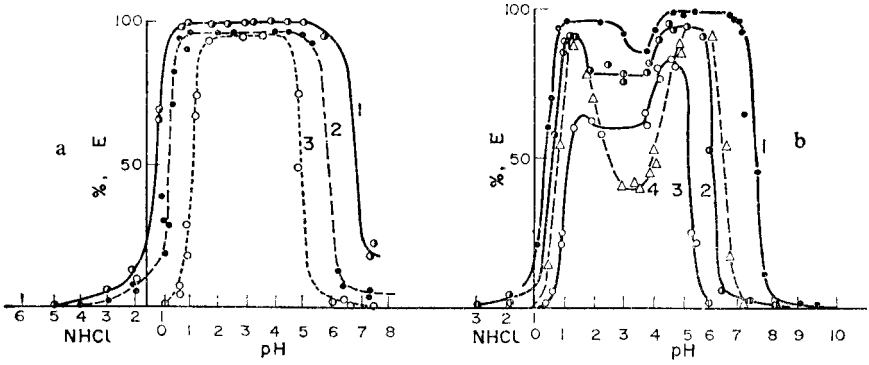

FIG. 1.—Extraction of tungsten by chloroform solutions of HOx.
(*a*) [W]: $10^{-7}M$; [HOx]: *1*—$10^{-1}M$, *2*—$10^{-2}M$, *3*—$10^{-3}M$; (*b*) [W]: $10^{-5}M$; [HOx]: *1*—$10^{-1}M$, *2*—$10^{-2}M$, *3*—$10^{-3}M$; *4*—[W]: $10^{-4}M$; [HOx]: $10^{-2}M$.

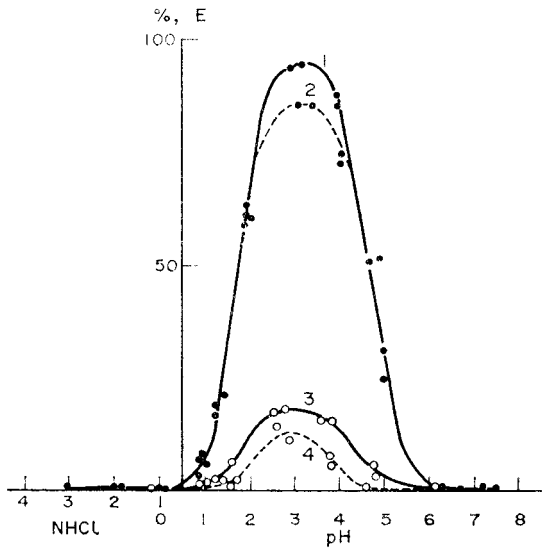

FIG. 2.—Extraction of tungsten by chloroform solutions of HCH_3Ox.
[W]: *1* and *3*—$10^{-7}M$: *2* and *4*—$10^{-5}M$; [HCH_3Ox]: *1*—$10^{-2}M$, *2*—$10^{-2}M$; *3* and *4*—$10^{-3}M$.

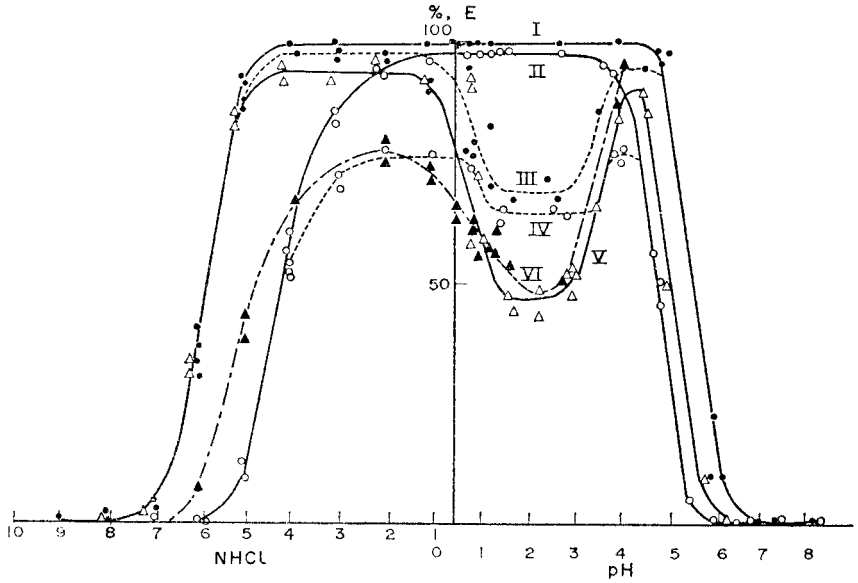

FIG. 3.—Extraction of tungsten by chloroform solutions of HBr_2Ox.
[W]: *I* and *II*—$10^{-7}M$, *III*-*V*—$10^{-5}M$, *VI*—$10^{-4}M$; [HBr_2Ox]: *I*, *III*, *V* and *VI*—$10^{-2}M$; *II* and *IV*—$10^{-3}M$.

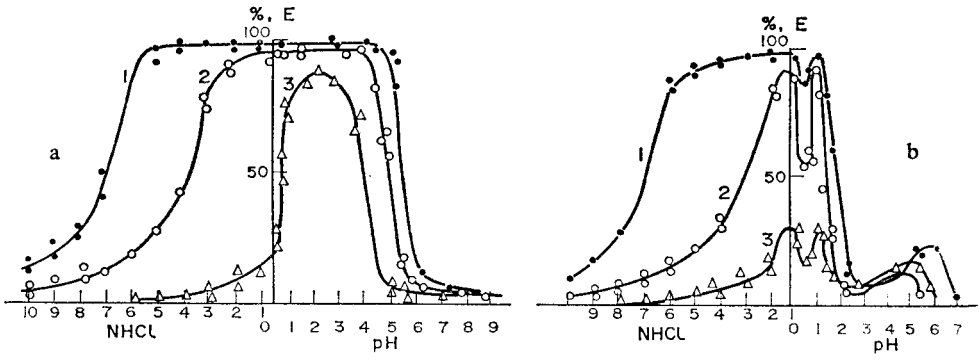

FIG. 4.—Extraction of tungsten by chloroform solutions of HSx.
(*a*) [W]: $10^{-7}M$; [HSx]: *1*—$10^{-1}M$, *2*—$10^{-2}M$, *3*—$10^{-3}M$; (*b*) [W]: $10^{-5}M$; [HSx]: *1*—$10^{-1}M$, *2*—$10^{-2}M$, *3*—$10^{-3}M$.

is narrower, the narrower the pH range for existence of the molecular form of the reagent (Fig. 5). It is evident from Fig. 6 that the solvent used for the reagent does not affect the extraction, but quite clearly the composition of the aqueous phase has a bearing on the degree of extraction (there is better solubility of a tungsten compound in an aqueous phase containing ethanol or acetate, which acts as a complexing anion). The degree of extraction depends to a greater extent on the absolute concentration of the reagent than on its relative concentration (with respect to tungsten). If we ignore the minimum between the double maxima of the extraction curves, the degree of extraction is higher with 0·1*M* HOx for $10^{-5}M$ tungsten (curve 1, Fig. 1*b*) than with 0·001*M* HOx for $10^{-7}M$ tungsten (curve 3, Fig. 1*a*). The same is true for curves IV and VI (Fig. 3) for HBr_2Ox, and for curves 1 (Fig. 4*b*) and 3 (Fig. 4*a*) for HSx.

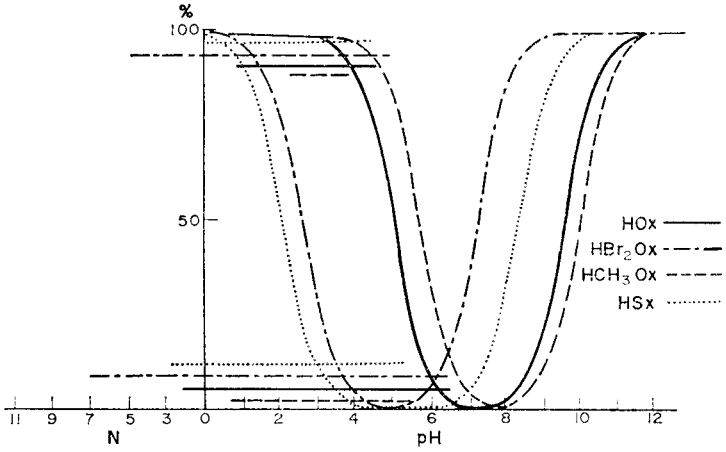

FIG. 5.—Domains of existence of the protonated, molecular and anionic forms of reagents, and pH ranges for tungsten extraction.
Lower horizontal straight lines—pH ranges for 5–95% extraction of tungsten. Upper horizontal straight lines—pH ranges for >98% extraction of tungsten.

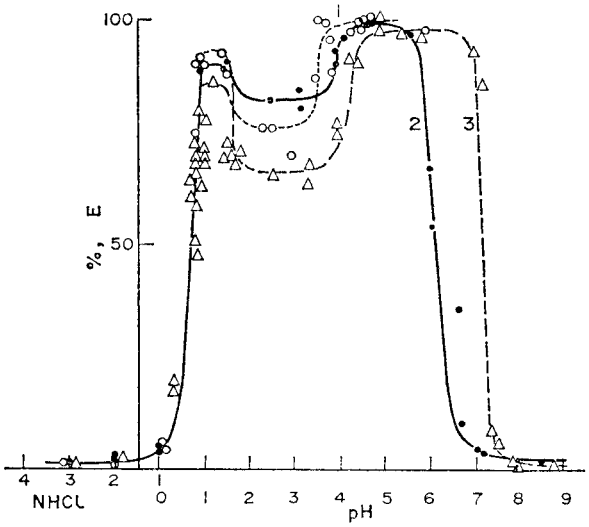

FIG. 6.—Effect of the method of HOx addition on the degree of tungsten extraction. [W]: $10^{-5}M$; [HOx]: $10^{-2}M$. HOx solutions: *1*—in acetic acid, *2*—in chloroform, *3*—in ethanol.

The double maximum in the extraction curves (which was emphasized previously[8]) in the tungsten concentration range 10^{-4}–$10^{-5}M$ is of particular interest. It is attributable either to the presence of other forms of tungsten at higher concentrations in the pH region of the extraction minimum (polymerization in the aqueous phase) or to the extraction of different forms of complex at different acidities of the aqueous phase. A decline in extraction (deepening of the minimum) with increase in tungsten concentration and non-existence of the minimum at an initial tungsten concentration of $10^{-7}M$ would speak in favour of the first supposition but against this is the fact that the position and width of the minimum vary for different reagents (curves 1–4, Fig.

1*b*, and 1–3, Fig. 4). The minimum is shifted to a region which is the more acidic, the greater the reagent protonation constant.

Thus, we may suggest that extraction of different tungsten complexes is involved: in the region of high concentrations of acid where the concentration of the reagent anion is vanishingly small, tungsten complexes with a protonated form of the reagent (H_2Ox^+, $H_2Br_2Ox^+$, H_2Sx^+) are extracted, and in the less acidic region, those with an anionic form of the reagent (chelates) are extracted. The disappearance of the minimum when an initial concentration of tungsten of $10^{-7}M$ is used, is explained by merging of the two separate curves. From Fig. 7, which presents in logarithmic

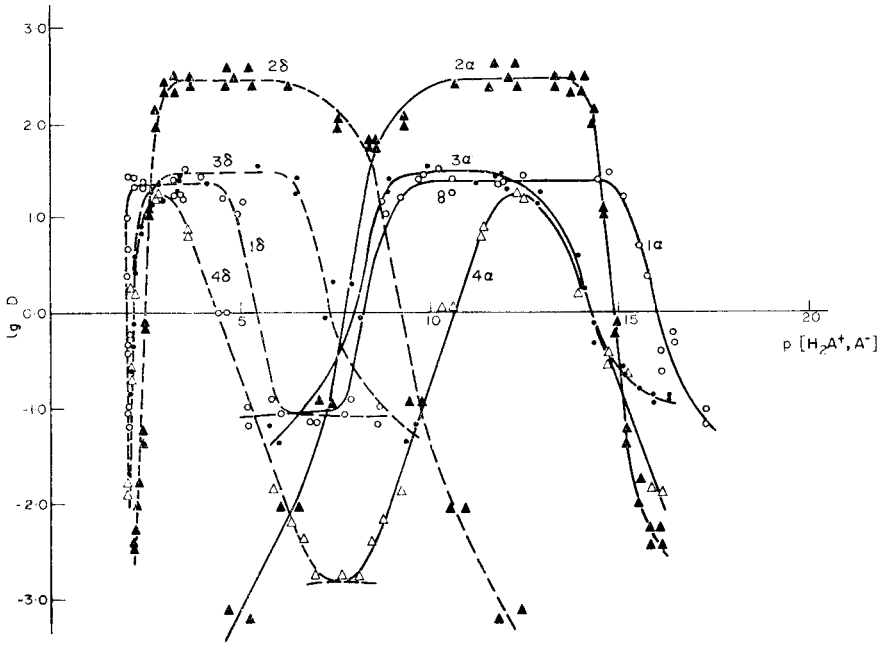

FIG. 7.—Dependence of the distribution factor (log *D*) on concentration.
(α) Reagent in anionic form, p(Ox^-); (δ) Reagent in protonated form, p(H_2Ox^+).
1—HOx, *2*—HBr_2Ox, *3*—HSx, *4*—HCH_3Ox.

co-ordinates the degree of tungsten extraction ($10^{-7}M$ initial concentration) as a function of the concentration of the cationic (pH_2A^+) and anionic (pA^-) forms of the reagents ($10^{-2}M$), it follows that the extraction with any of the reagents studied occurs under conditions where the concentration of the protonated form of the reagent is far in excess of that of the anionic form. Solving the problem of the composition of the complex extractable at high acidity and the problem of the origin of the two extraction maxima requires further studies.

Zusammenfassung—Die Extraktion von Wolfram durch Chloroformlösungen von 8-Hydroxychinolin(**I**), 2-Methyl-8-hydroxychinolin(**II**), 5,7-Dibrom-8-hydroxychinolin(**III**) und 8-Mercaptochinolin(**IV**) wurde in Abhängigkeit von den Konzentrationen von Wolfram und Reagens sowie von der Acidität der wäßrigen Phase untersucht. In einem großen Bereich von Säurekonzentrationen wurde quantitative Extraktion von Wolfram gefunden. Der Extraktions-grad von Wolfram bei der Konzentration 10^{-5}M gibt mit **I**, **III** und **IV** zwei Maxima,

wenn man ihn gegen die Acidität aufträgt. Das Extraktionsmaximum bei den saureren Lösungen liegt in dem Bereich, wo die Reagentien in protonierter Form vorliegen; seine Lage hängt vom verwendeten Reagens ab. Es wird vermutet, daß je nach der Acidität der wäßrigen Phase verschiedene Wolframkomplexe extrahiert werden.

Résumé—On a étudié l'extraction du tungstène par des solutions chloroformiques de 8-hydroxyquinoléine(**I**), 2-méthyl-8-hydroxyquinoléine(**II**), 5,7-dibromo 8-hydroxyquinoléine(**III**) et 8-mercaptoquinoléine(**IV**) en fonction de la concentration en tungstène et en réactif et de l'acidité de la phase aquese. On a obtenu des preuves de l'extraction quantitative du tungstène dans un large domaine d'acidité. Le degré d'extraction du tungstène à la concentration $10^{-5}M$ avec **I**, **III** et **IV** donne deux maximums lorsqu'on le rapporte à l'acidité. Le maximum d'extraction pour les solutions les plus acides se trouve dans la région où les réactifs existent sous la forme protonée et sa position dépend du réactif utilisé. On suggère qu'on extrait différents complexes du tungstène, dépendant de l'acidité de la phase aqueuse.

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DIFFERENTIAL THERMAL ANALYSIS OF TRANSITIONS IN FINELY-DIVIDED SOLIDS SUSPENDED IN LIQUID MEDIA

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Summary—The experimental difficulties associated with differential thermal analysis (DTA) are reviewed. Quantitative work has always required calibration of the equipment, and conventional solid diluents have serious disadvantages. It is shown that calibration is not strictly necessary, given appropriate conditions. Dilute suspensions of polymer crystals in organic liquids provide ideal media for DTA when used as diluent and as reference material. Convection currents are suppressed and the medium can support fine particles of the solid under test, even when the solid has a relatively high specific gravity. The new theory and techniques have been tested experimentally by measuring the heats of fusion of two inorganic salt hydrates. The results are in excellent agreement with literature values. A novel arrangement with a double thermocouple junction is shown to have considerable potentialities as a means of making precise measurements quite simply.

THE MAIN FEATURES of differential thermal analysis (DTA) are well known, and it is recognized as a useful analytical tool provided that the problem of calibration can be overcome.

In general, DTA equipment may be calibrated by using specimens of known heats and temperatures of fusion in conjunction with some standard reference material. Various reference materials have been used, such as powdered alumina, silica or magnesium oxide, also silicone oil and glass beads. The specimen is normally diluted with the reference material so that sample and reference may have similar thermal properties apart from the transition being observed. It is convenient to define the *specimen* as the material under test which undergoes the transition, while the *sample* is constituted by the mixture of specimen and diluent.

DTA has been used by mineralogists and chemists since the turn of the century, but more recently it has found many applications in biology and polymer science. The present work is concerned largely with the development of a satisfactory technique for the quantitative DTA of liquid samples, a problem which presents several interesting and unusual features.

The basic difficulty is that convection in the liquid part of a sample gives rise to an increase in heat transfer, and the unpredictable temperature field makes quantitative DTA particularly awkward to achieve. In their work on reaction kinetics, Borchard and Daniels[1] stirred the contents of the sample and reference cells continuously so that each was of uniform temperature throughout. The removal of any temperature gradient within the cells meant that the heat transfer coefficient of the cell wall became important. Other authors attempted instead to restrain convection by using gelatin or agar jelly.[2,3] Barrall and Rogers[4] claimed that suitable liquid diluents are superior to solid diluents for work on solid phase transitions and dehydrations. Their thermograms for 20% w/w $CuSO_4 \cdot 5H_2O$ in Nujol mineral oil showed improved resolution over those obtained with a solid carborundum diluent. Repetitive runs were possible

with a given sample when the mineral oil was used, because water evolved during dehydration of the salt was mostly recovered on cooling. With carborundum as diluent the water was lost.

In the context of polymer systems, stirred cells have been used to establish solubilities,[5] and Ke[6] suggested that DTA could be used to investigate the effects of solvents and plasticizers on crystalline polymers. A pasty mixture of polyethylene and α-chloronaphthalene[6] gave a satisfactory DTA curve, presumably because convection was negligible and sedimentation of the solid polymer did not occur. Some experiments on the DTA of the dissolution and recrystallization of solution-grown crystals of polyethylene were reported by Blackadder and Schleinitz.[7] For concentrations of suspended polymer crystals in excess of about 0·75 % w/w in *p*-xylene no sedimentation occurred. Apart from being a necessary condition for meaningful experiments, the non-sedimenting properties of the system were, perhaps surprisingly, associated with negligible convection. It appears that a low concentration of suspended lamellar crystals provides an effectively continuous solid matrix of high porosity which restrains convection currents in the supporting liquid. Unfortunately, the disappearance of the crystals on dissolution was accompanied by the appearance of convection and the DTA curve plunged to a new baseline as dissolution occurred. Heats of dissolution could be estimated by calibration with other materials but the method was extremely imprecise. Koenig and Carrano[8,9] later performed similar experiments on single crystals of several polyethylenes suspended in tetrachloroethylene. At low concentrations their crystals floated because the solvent was denser than polyethylene, and the baseline problem described above overshadowed the investigation. Adjusted baselines were drawn for the region following completion of the dissolution process, but the procedure was not illustrated and appears to have been quite empirical.

The present work originates from the previous observation[7] that a low concentration of suspended polyethylene crystals provides an effectively convection-free system. It seemed likely that such a suspension could also support fine particles of some other solid which, by itself, would both sediment and permit convection. Transitions in solid particles supported by a suspension of polymer crystals might then be observed under ideal DTA conditions, provided that the polymer did not dissolve to a signicant extent over the temperature range of interest. The basic need was thus to produce a suitable "backing" suspension to confer on a liquid system those properties necessary for accurate DTA. A 1 % w/w suspension of polyethylene crystals in *p*-xylene dissolves at below 100° and it was felt that this would limit the range of transitions which could be studied. In addition, the use of some other polymer to provide the inert non-dissolving "backing" suspension would actually permit the study of polyethylene dissolution under conditions far superior to those obtainable in the earlier work of Blackadder and Schleinitz.[7]

Suspensions of polyoxymethylene crystals proved to be ideal and this polymer has a negligible solubility in organic liquids at temperatures below about 150°. The polyoxymethylene suspension can be readily transferred from one organic liquid to another since most organic liquids are completely miscible with one another. The rheological properties of these suspensions have been investigated and described elsewhere.[10] It appears that they are Bingham Plastic Fluids and, apart from exhibiting no convection, they are able to hold particles of high specific gravity in suspension.

In a DTA experiment the particles therefore behave as though they were embedded in a solid of describable thermal properties and this is of the greatest importance in relating theory and practice. The thermal properties of the samples used here are, except during transitions, essentially the properties of the liquid which accounts for at least 97% of the mass of the system. The thermal conductivity, specific heat and density of common organic liquids are well-documented functions of temperature, and the possibility arises of measuring heats of fusion and dissolution by DTA without recourse to calibration. This is not possible with wholly solid samples.

THEORY

An understanding of basic DTA theory is an essential prerequisite for the design of suitable apparatus. There have been many attempts to derive the key expressions for DTA and that by Soulé[11] is probably the most general. A condensed version of his treatment is now given as a foundation for what follows.

A homogeneous sample and a geometrically identical reference are assumed to have similar thermal properties (specific heat and thermal conductivity) except during a transition in the sample. The outer surfaces of each are subjected to a constant rate of temperature rise which can be maintained even during the transition if, for example, the sample holder is a fairly massive block with an effectively infinite thermal conductivity.

The heat, dQ, entering an element of volume anywhere in the sample or reference during time dt is equal to the stored heat:

$$\lambda \nabla^2 T \, dt = dQ = \rho c \, dT. \tag{1}$$

This assumes that λ, the thermal conductivity, is independent of temperature, T, over the range involved in any subsequent integration. The density of the material is ρ, and its specific heat is c.

With thermocouple junctions similarly positioned in the sample and in the reference, the equation for each can be integrated between the time t_1 before the onset of the transition and a time t_2 sufficiently far beyond the transition for the temperature distribution in the sample to be once more essentially the same as in the reference.

$$\text{Reference:} \quad \lambda \int_{t_1}^{t_2} \nabla^2 T_R \, dt = \rho \int_{T_1}^{T_2} c \, dT_R. \tag{2}$$

Here T_1, T_2 are the values of T_R, the reference temperature, at times t_1, t_2 respectively. As with λ, it is now assumed that ρ is independent of temperature over the range T_1–T_2. In practice the value of ρ at the peak is an effective mean value.

$$\text{Sample:} \quad \lambda \int_{t_1}^{t_2} \nabla^2 T_S \, dt = \rho \int_{T_1}^{T_2} c' \, dT_S = \rho \left[\int_{T_1}^{T_2} c \, dT_R - L_S \right]. \tag{3}$$

The specific heat of the sample is taken to be the same as that of the reference except during a transition; in that case the *apparent* specific heat of the sample is represented by c'; this includes L_S, the latent heat of the sample. It should be noted that L_S does not strictly apply to a specified temperature as a heat of fusion should, but the resulting uncertainty is likely to be extremely small. T_S in equation (3) is the sample temperature.

Subtracting (3) from (2) gives

$$\lambda \nabla^2 \int_{t_1}^{t_2} (T_R - T_S) \, dt = \lambda \nabla^2 I = \rho L_S. \tag{4}$$

At the boundaries, $T_R = T_S$ at all times, and the integral $I = 0$. Soulé noted that an analogous condition applies to the temperature difference, ϕ, between a point in the sample and a point at the boundary when the thermal properties are uniform and the heating rate is constant. At the boundary $\phi = 0$ and, from (1)

$$\lambda \nabla^2 \phi = \rho c \beta, \tag{5}$$

where β, the rate of heating, equals dT/dt. Combining (4) and (5), we have

$$I/\phi = L_S/c\beta. \tag{6}$$

($\nabla^2 I/\nabla^2 \phi = I/\phi$ in this context because of the uniqueness of the solution.) Now the temperature of the boundary of the sample rises at the same constant rate as the temperature of any point in the reference, and the temperature difference between the boundary and a point in the sample may be plotted against the boundary temperature, or the temperature somewhere else in the reference.

$$\int_{T_1}^{T_2} (T_R - T_S)\, dT_R = \beta I = A, \tag{7}$$

where A is the area of the peak on the DTA curve, and $dT_R = \beta\, dt$. From (6) and (7),

$$L_S = \frac{Ac}{\phi}. \tag{8}$$

In general ϕ is difficult to measure, but if λ is known the problem can be circumvented.

$$\lambda \nabla^2 A = \rho L_S \beta \quad (A = 0 \text{ at the boundary}) \tag{9}$$

and has the solution

$$A = \frac{gR^2 \rho L_S \beta}{\lambda}. \tag{10}$$

Here R is a characteristic dimension of the sample and g is a factor which depends on the shape of the sample and on the position of the thermocouple junction. The value of g is known for simple geometric forms; at the centre of a sphere of radius R it is $\frac{1}{6}$, at a point on the axis of an infinite cylinder of radius R it is $\frac{1}{4}$, and midway between two infinite parallel planes a distance $2R$ apart it is $\frac{1}{2}$. Eriksson,[12] and Sewell and Honeybourne,[13] have studied the problem of the finite cylinder which may considered either as a cylinder of radius R or as a slab of thickness $2R$. Values of g were calculated for various ratios of length to diameter, with centrally located thermocouple junctions, and it appears that for all practical purposes a sample can be regarded as an infinite cylinder when its height is greater than three times its diameter, and as an infinite slab when its diameter is at least six times its height.

Thus equation (10), which relates peak area to latent heat, is potentially a useful equation, and indeed has been universally employed despite the fact that it requires strictly controlled geometrical conditions plus a knowledge of the cell dimensions, the thermal conductivity of the material, and the rate of heating. All calibration procedures tacitly assume equation (10).

The fact remains, however, that equation (8) could be much more convenient to use, because the specific heat of the sample is the only piece of information required in

addition to that provided by the experimental DTA curve. Unfortunately the DTA curve concerned requires the measurement of a boundary (*i.e.*, wall) temperature. This appears to be impossibly difficult, at least for quantitative work on heats of fusion, though transition temperatures have been measured.[14,15] The problem is that for quantitative work a metal heating block is desirable, and the measurement of the wall temperature in such circumstances is fraught with experimental difficulties.

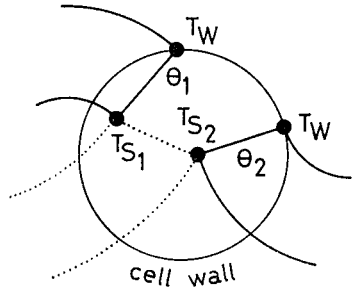

FIG. 1.—The "double junction" thermocouple arrangement.

An extension of basic DTA theory eliminates the problem. In Fig. 1 a hypothetical sample cell contains two differential thermocouples, each with a junction at the cell wall of temperature T_W. The other junctions are at temperatures T_{S_1}, T_{S_2} respectively. From equation (8)

$$L_S = \frac{A_1 c}{\phi_1} = \frac{A_2 c}{\phi_2}, \tag{11}$$

where $\phi_1 = T_W - T_{S_1}$, $\phi_2 = T_W - T_{S_2}$, and A_1, A_2 are the corresponding peak areas. Except during the transition, ϕ_1 and ϕ_2 are virtually constant.
Thus

$$L_S = \int_{T_1}^{T_2} (T_R - T_{S_1})\, dT_R \cdot \frac{c}{T_W - T_{S_1}} = \int_{T_1}^{T_2} (T_R - T_{S_2})\, dT_R \cdot \frac{c}{T_W - T_{S_2}}. \tag{12}$$

Cross-multiplying these relationships and subtracting one from the other gives

$$L_S = \int_{T_1}^{T_2} (T_{S_2} - T_{S_1})\, dT_R \cdot \frac{c}{T_{S_2} - T_{S_1}} = \frac{A' c}{\theta} \tag{13}$$

provided that $T_{S_2} \neq T_{S_1}$. In this expression A' is the nett peak area for the double thermocouple junction arrangement and θ, representing $T_{S_2} - T_{S_1}$, is best described as the baseline displacement. Evidently equation (8) remains valid when the differential temperature is simply that between two junctions of the same thermocouple within the sample (dotted line in Fig. 1) and there is no need to measure the wall temperature.

Figure 2 shows the most convenient experimental arrangement prompted by this new result. The conventional reference is used to provide the absolute temperature as before, along the X axis. Figure 3, obtained in an actual run, shows the characteristic shape of the DTA curve. The nett area A' is essentially the difference between a small

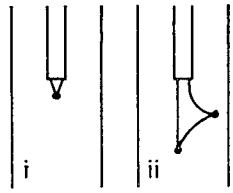

FIG. 2.—(i) Conventional thermocouple junction. (ii) The new "double junction" arrangement.

peak area below the baseline and a much larger peak area above it. The curious shape of the curve is not a disadvantage, since in DTA the peak contour bears no simple relation to the variation of the apparent specific heat during melting. It can be seen in Fig. 3 that a steady value of θ is quickly attained and maintained.

Any errors in A' and θ, jointly caused by mislocation of the baseline, would be additive, and this underlines the importance of avoiding any spurious changes in the position of the baseline. In the heavily diluted, yet convection-free, systems used here the thermal conductivity is very nearly constant during a transition and the baseline is unchanged. It should also be noted that the thermal conductivity is not required in using equation (8), merely the specific heat of the sample, and this is very largely the specific heat of the organic liquid forming about 97% of the total mass. Good data for this are commonly available and corrections are easily made to allow for the presence of the material under test and the "backing" polymer.

The precise position of the two thermocouple junctions (Fig. 2) is unimportant, and there is no need to support them rigidly. Furthermore, no correction need be made for the presence of the supporting ceramic tube, which can be situated so far from the junctions that its effect on the system is negligible. It should be obvious, however, that the peak area will be greatest when one junction is at the centre of the

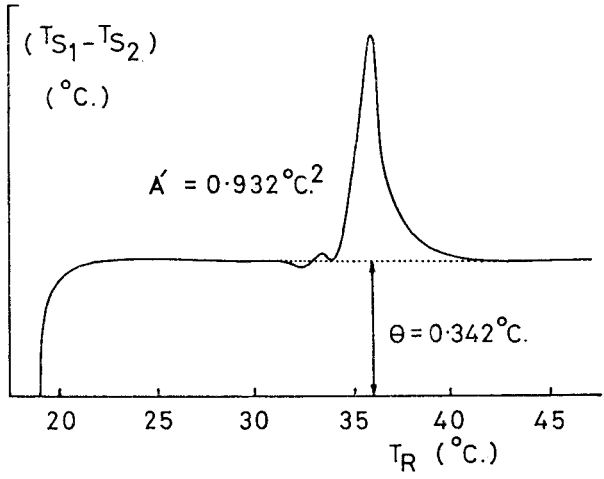

FIG. 3.—Typical thermogram produced by the new "double junction" arrangement. (Fusion of 0·1 g of $Na_2SO_4 \cdot 10H_2O$ in 5 ml of *p*-xylene with "backing" suspension of polymer crystals.)

sample while the other is at the wall. With one at the centre and the other half-way to the wall the peak area would be about a quarter of the maximum value as a consequence of the parabolic temperature profile. (It can be shown, by considering an infinite cylinder, that the transient part of the expression for the temperature distribution dies away to become negligible in a very short time from the start of an experiment, and a parabolic profile is appropriate thereafter.) In practice the second junction was placed about three-quarters of the way from the centre to the wall, thus giving a peak area of just over half of the maximum.

It might be supposed that heat conduction along the wire connecting the two thermocouple junctions would tend to equalize their temperatures and cause errors. To a first approximation the heat conduction along the wire is proportional to the temperature difference between the extremities. The baseline displacement θ, and the nett area A', would thus be reduced in the same proportion, resulting in no nett error. Likewise any heat loss *via* the ceramic stem would be much the same for each junction.

The new double junction arrangement is less good than the conventional arrangement in determining transition temperatures ($\pm 1°$ as against $\pm 0{\cdot}1°$) but is superior for the measurement of heats, for the reasons set out above.

EXPERIMENTAL

A fully automatic DTA apparatus was constructed which, though basically conventional, incorporated a number of novel features. Figure 4 shows the heating block and a thermocouple insert.

At the end of a run the outer cylinder, *b* which was a push fit on each of three identical blocks, a, was slipped off and cooled rapidly with an air blower, after which another block was inserted. With this arrangement the inevitably slow cooling of the heating blocks caused no inconvenience. In order to facilitate cleaning, most DTA equipment features separate sample and reference cells which

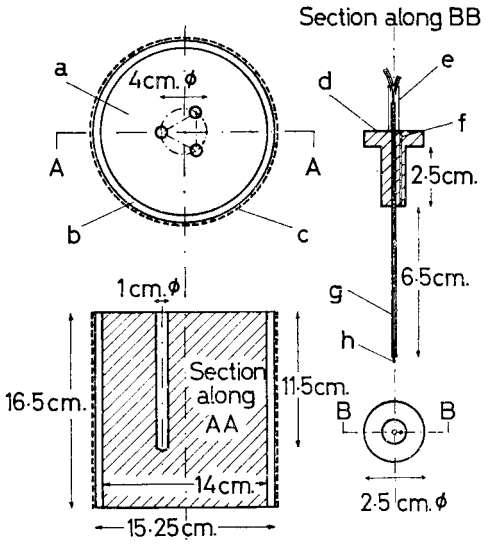

FIG. 4.—Heating block and thermocouple insert.
(*a*) Dural block; (*b*) Dural cylinder; (*c*) heating windings between layers of asbestos paper; (*d*) Dural well cap; (*e*) epoxy resin joint; (*f*) 1-mm diameter vent; (*g*) 2-mm diameter twin-bore silica tube; (*h*) thermocouple junction.

are inserted in the block. Unfortunately this invalidates the assumption that the whole block assembly has effectively infinite thermal conductivity, because there is a resistance to heat transfer at the cell/block interface, and this resistance is liable to vary from run to run. In the present apparatus cells were eliminated by placing the sample and reference materials directly in holes, designed for 5-ml samples, drilled in the blocks. The cap of each hole, *d*, was machined to a push fit and held the thermocouple junction rigidly and centrally. When dismantled, each block could be scrubbed clean quite easily. The interface between the block and the outer cylinder was lubricated with silicone grease, which also ensured even heat-transfer.

The large heat capacities of the blocks ensured that transitions in the samples had no significant effect on the temperature of the blocks. The thermal diffusivity of metal is so much larger than that of organic materials that the walls of the drillings could be regarded as isothermal surfaces. Any variations in heat transfer around the edges of the blocks where they contacted the heating cylinder were damped out well clear of the holes. The inside surfaces of the holes were smooth, vertical and of precise diameter.

The resistance wire constituting the heating coil c, was wound non-inductively round the heating cylinder and secured with epoxy resin to several layers of asbestos paper insulating it from the metal cylinder. A preset variable transformer provided a heat input of up to 1 kW. The rate of heat input and the heat capacity of the block jointly determined the rate of temperature rise. For a constant heat input this was so nearly linear that a control device was not necessary. Small deviations from linearity were caused by the slight increase in the resistance of the heater windings with temperature, by the increase in the heat capacity of the block with temperature and by heat loss to the surroundings. To minimize heat loss, the blocks were placed on thick asbestos sheets and surrounded with a removable layer of fibre glass 75 mm thick.

Iron–constantan thermocouples, which have an almost linear response, were made by welding wires of diameter 0·2 mm. The practice of using the same reference thermocouple junction in both the direct measurement and differential temperature circuits is not to be recommended unless a doubly-balanced circuit is employed, because the large difference in voltage between the two circuits causes interaction and baseline drift.[16] It proved simpler to use two identical reference wells, one of which contained a reference junction connected to an ice junction, while the other contained a junction in opposition to that in the sample. Only one reference well was used when testing the "double junction" arrangement.

Electrical noise can be a very severe problem in DTA, but it was eliminated by careful shielding of all circuits. The heating cylinder was earthed to prevent eddy currents developing and to eliminate the effect of any current leakage from the heater. All electrical connections were made very firmly and heavily lagged with fibre-glass to protect them from transient disturbances in the ambient temperature; the use of a temperature equalizer[13] to eliminate adventitious thermocouple effects was therefore unnecessary.

The temperature difference signal was preamplified twentyfold, and a Bryans XY plotter was set at a sensitivity of 8·0 μV/mm on the X axis (reference temperature) and 8·0 or 20·00 μV/mm on the Y axis (differential temperature). The arm of the XY plotter actuated a microswitch and relay to shut down the equipment at the end of a run. The mains electricity supply was stabilized by means of a large constant-voltage transformer. A pulse generator provided a time-base for the XY plotter so that the heating rate could be checked semi-continuously. A "blip" was produced on the curve at regular intervals, usually every minute.

RESULTS

The apparatus and the theory of operation were tested with powdered inorganic salt hydrates, of analytical reagent quality, as specimens. Literature values of the heats of fusion were available.[17] The high stability of $Na_2S_2O_3 \cdot 5H_2O$ made its use exceptionally satisfactory, but even the deliquescent salt $Na_2SO_4 \cdot 10H_2O$ could be studied if bright crystals were selected. Hygroscopic hydrated salts, such as nitrates, were inconvenient.

Since thermocouple response varies slightly with the composition of the component wires, the thermocouple to be used for direct measurement of temperature was calibrated against a series of NPL thermometers to an accuracy better than $\pm 0{\cdot}1°$. When all three wells of the heating block were filled with organic liquid containing the backing polymer suspension there was no detectable difference between the thermocouple junction temperatures (conventional arrangement), even when the temperature

difference between the centre and wall of each well was as high as 5°. Under typical experimental conditions the temperature difference was only about 1°. The wells and thermocouples were evidently identical in geometry and heating characteristics.

Conventional arrangement of thermocouples

Crystals of an inorganic salt hydrate were powdered with a small pestle and mortar, and a microscope slide was used to weigh out 0·1000-g specimens. The powdered crystals showed no gain or loss of weight during the brief handling time, and were added to a small quantity of organic liquid, "backed" with 1 % w/w polyoxymethylene crystals, in a specially calibrated 10-ml measuring cylinder. The volume was made up to about 5 ml with more of the "backed" organic liquid, added in drops, and the total volume was noted. The mixture was then shaken, vigorously at first but later more slowly to remove any trapped air-bubbles. The sample was poured down the wall of the appropriate well in the heating block. Each reference well contained 5 ml of the "backed" organic liquid. The zero of the plotter was set and after elapse of a few minutes for thermal equilibration, the run was started.

The ratio of the height of the sample to its diameter being greater than three, the sample was assumed to behave as an infinite cylinder, and equation (10) could be rewritten as

$$L_S = \frac{4Ak}{\beta R^2 \rho}, \tag{14}$$

g being replaced by $\frac{1}{4}$. The density, ρ, of the sample refers to the peak temperature, T_f. If, at 20°, the volume and density of the sample are represented by V_{20} and ρ_{20} respectively, then the total mass of the sample is $V_{20}\rho_{20}$. For a mass, m, of specimen contained in this sample it follows that

$$\frac{V_{20}\rho_{20}}{m} L_S = L \tag{15}$$

where L is now the latent heat per unit mass of the actual specimen. (See *Introduction* for definitions of sample and specimen.) From (14) and (15),

$$L = \frac{4AkV_{20}\rho_{20}}{\beta R^2 m \rho}. \tag{16}$$

The ratio of the density of the sample at 20° to its density at the peak temperature was negligibly different from the corresponding ratio for the organic liquid, present in great excess. (The peak temperature was found from the DTA curve by subtracting the height of the peak in °C, from the temperature of the reference at the peak.) For the common organic liquids used in the work the literature[18] provided values of the densities as functions of temperature.

Since the thermal conductivity of any sample was governed mainly by the thermal conductivity of the organic liquid it was necessary to seek reliable literature values for the latter quantity. A review by Jamieson and Tudhope,[19] together with more recent papers[20–22], provided some of the information, but no adequate data were found for the thermal conductivity of *p*-xylene as a function of temperature. For this liquid the value of the thermal conductivity at 20° was found in the literature and an empirical formula was used to obtain the temperature coefficient.[23] A small correction

for the presence of the specimen was applied by using Tareef's equation for the thermal conductivity of solid-liquid suspensions.[24] The effect of the backing polymer was so small as to require no correction term. When hydrates melt they may be considered to dissolve in their own water of crystallization. The concentration of anhydrous salt in these solutions was calculated and the thermal conductivity deduced from the literature.[19] Fortunately the thermal conductivities of the solid hydrates appear to be indistinguishable from those of the corresponding solutions.

A correction was made for the alumina stem of the thermocouple. Its heat capacity was so close to that of the organic liquids that no adjustment was required on this score, but the finite volume of the stem excluded the specimen from that region. To assess the magnitude of the resulting error several runs were carried out with a dummy tube fixed *below* the thermocouple bead, on the grounds that this should double the error. The presence of the dummy tube reduced the apparent heat of fusion by 2·0%, and it was assumed that the original and necessary tube produced the same effect. These values are consistent with expectations. A continuous tube of the appropriate dimensions running down the centre of the sample would reduce the cross-sectional area by about 4%, and peak area is proportional to the cross-sectional area of the sample.

Table I shows the results of the experiments with all corrections applied, and two of the actual DTA curves are reproduced in Fig. 5. The experimental values for the heats of fusion of the two hydrates are in excellent agreement with literature values, except for the case when benzene was used as the organic liquid. This could be due to the slight solubility of water in benzene and its accompanying heat of solution.

Double junction arrangement

For these experiments the samples were made up by a slightly different procedure. A known volume of organic liquid with "backing" polymer was blended with a suitable known mass of specimen.

The zero position on the differential temperature axis was very slightly different from its nominal position because no two thermocouples are exactly alike in response. The true zero was found by equilibrating the whole apparatus in a constant temperature room.

Table II shows the results of tests carried out at a heating rate of about 1·3°/min. A typical DTA curve was shown previously in Fig. 3. As before, the specific heat of the sample was dominated by that of the liquid but corrections for the salt and the polymer were applied nevertheless.

The agreement with literature values of the heats of fusion is again excellent, and it should be noted that both arrangements constitute entirely independent DTA techniques.

CONCLUSIONS

The experimental results bear out the theory proposed here for the DTA of solid-liquid systems, and the apparatus is evidently very suitable for the purpose. The new techniques have a number of advantages over conventional DTA using dry powdered specimens mixed with solid diluent. Quantitative DTA has always been difficult, mainly because of the problem presented by the thermal conductivity of the sample. This conductivity is usually unknown since it depends on the amount of

TABLE I.—RESULTS OBTAINED WITH THE CONVENTIONAL ARRANGEMENT OF THERMOCOUPLES

Specimen	Organic liquid:		T_t, °C	T_t, °C avge	T_t, °C lit[23]	A, K^2	V, cm^3	β, $K\,min^{-1}$	L, Jg^{-1}	L, Jg^{-1} avge	L, Jg^{-1} lit[17]
$Na_2SO_4 \cdot 10H_2O$	*p*-xylene	†	36·0	35·2	32·4	4·11	5·14	1·334	215	214	214
			36·1			4·21	4·96	1·329	213		
			36·0			4·05	5·08	1·319	211		
			34·0			4·04	5·02	1·299	212		
			34·4			4·24	4·93	1·314	216		
			34·5			4·05	5·15	1·309	216		
	p-xylene*		36·2	35·9	32·4	4·16	4·88	1·319	213	212	
			35·6			3·93	4·98	1·289	210		
	cyclohexane		34·8	34·8	32·4	2·22	5·40	1·324	216	211	
			34·8			2·34	5·10	1·349	211		
			34·9			2·17	5·20	1·314	205		
	benzene		34·3	34·0	32·4	1·87	5·23	1·324	212	200	
			33·9			1·71	5·19	1·294	198		
			33·7			1·65	5·22	1·294	191		
$Na_2S_2O_3 \cdot 5H_2O$	*p*-xylene		48·5	49·0	48·0	3·62	4·99	1·214	200	200	200
			49·3			3·57	5·19	1·239	201		
			48·9			3·57	5·00	1·199	200		
			49·3			3·71	4·94	1·239	199		
		†	49·1			3·56	5·10	1·214	201		
	p-xylene*		49·5	49·4	48·0	3·46	5·07	1·204	199	200	
			49·3			3·83	4·99	1·309	200		
			49·5			3·78	5·05	1·309	200		

* For the runs in *p*-xylene so marked the ceramic stem of the thermocouple was extended downwards by a dummy tube of similar dimensions. A multiplying correction of 100/96 was applied to the values of L so obtained, compared with a correction of 100/98 in all other experiments.

† The DTA curves for these runs appear in Fig. 5.

The mass of the specimen was 0·100 g in each experiment, except for those in cyclohexane and benzene where 0·0500 g was used.

The thermal conductivities of the various samples at the appropriate peak temperatures were as follows, the figures in brackets being the thermal conductivities of the pure organic liquids, also at the peak temperatures. The values have been multiplied by 10^5 and the units are J $mm^{-1}K^{-1}s^{-1}$.

$Na_2SO_4 \cdot 10H_2O$ *p*-xylene 134·5 (131), cyclohexane 118·5 (116·5), benzene 142 (140·5)
$Na_2S_2O_3 \cdot 5H_2O$ *p*-xylene 131 (129)
The ratio ρ_{20}/ρ [see equation (16)] had the following values at the peaks
$Na_2SO_4 \cdot 10H_2O$ *p*-xylene 1·015, cyclohexane 1·017, benzene 1·018
$Na_2S_2O_3 \cdot 5H_2O$ *p*-xylene 1·030.
The radius of each well was 4·96 mm, hence $R^2 = 24{\cdot}6$ mm^2.

contact between the particles, which in turn involves the composition of the sample, its packing density, the particle size, and even the size distribution.[25] Very frequently the thermal conductivity of a sample is not the same before and after a transition and this inevitably causes the baseline to be at a different level on either side of the peak. Numerous empirical methods of dealing with the problem have been proposed,[26] and dilution of the finely-divided sample with at least 70% w/w of inert solid certainly minimizes the effect.[27] Even in favourable circumstances, however, the variation of thermal conductivity with temperature demands calibration of the apparatus at the temperature of the transition, a point which is sometimes overlooked. Powdered solids

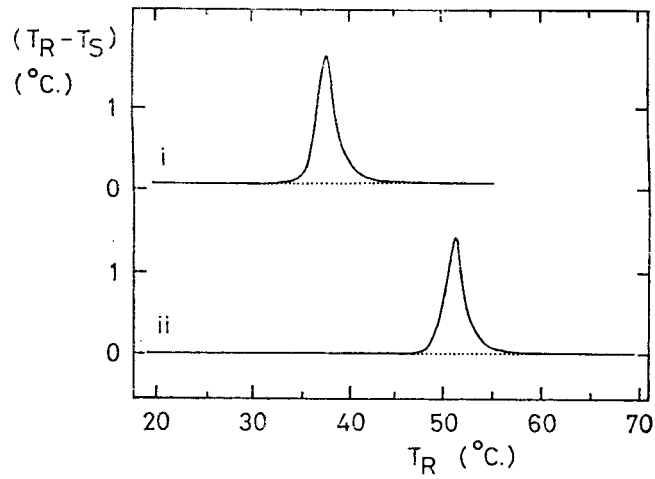

FIG. 5.—Typical thermograms produced by the conventional arrangement of thermocouples. (Fusion of 0·1 g of (i) $Na_2SO_4 \cdot 10H_2O$ and (ii) $Na_2S_2O_3 \cdot 5H_2O$ in 5 ml of *p*-xylene with "backing" suspension of polymer crystals.)

are unsatisfactory materials for other reasons. On heating there may be shrinkage and sintering effects which make the sample draw away from the holder; the resulting air gap decreases the effective thermal conductivity and is a further cause of baseline drift.[28]

The use of systems in which the solid under test is suspended in a large excess of convection-free liquid overcomes all of these problems. The supreme advantage of a predominantly liquid system lies in its predictable thermal properties, which make it possible, within a range limited by the boiling point of the liquid or the solubility of the polymer, to determine heats of transition without recourse to calibration. This is the first time it has been possible to make such a claim. The method is particularly appropriate for determining the heats of fusion of compounds such as hydrates, because the water produced is trapped in the form of fine droplets instead of being

TABLE II.—RESULTS OBTAINED WITH THE NEW DOUBLE JUNCTION ARRANGEMENT OF THERMOCOUPLES

Specimen	Organic liquid		A', K^2	θ, °C	Mass of organic liquid, g	c, $Jg^{-1}K^{-1}$	L, Jg^{-1}	L, lit[17] Jg^{-1}
$Na_2SO_4 \cdot 10H_2O$	*p*-xylene	*	0·932	0·342	4·40	1·74	215	214
			0·866	0·312	4·30		214	
			1·210	0·436	4·32		215	
	heptane		0·742	0·281	3·57	2·24	217	
			1·356	0·503	3·48		216	
	carbon tetrachloride		0·851	0·285	8·10	0·86$_5$	216	
			0·890	0·309	8·59		214	
$Na_2S_2O_3 \cdot 5H_2O$	*p*-xylene		0·953	0·387	4·36	1·78	198	200
			0·885	0·358	4·31		196	
			0·793	0·320	4·38		199	

* The DTA curve for this run appears in Fig. 3.

partially lost as vapour. The application of the new techniques to polymer systems will be described elsewhere and it also appears to be suitable for biological specimens. Steim[3] noted that jellied samples overcame many of the traditional difficulties of DTA but he had difficulty in finding a suitable standard for calibration, the samples being essentially aqueous suspensions. The techniques described in the present paper would have eliminated the calibration stage completely, since the thermal properties of water are particularly well known.

Finally, the remarkable simplicity of the new double junction arrangement must be emphasized. The sample need not be of any particular size or shape provided that the temperature of its bounding surface can be constrained to rise at a constant rate, though it is not even necessary to know this constant rate. The positioning of the thermocouple junctions is unimportant and need not be reproduced from run to run. For teaching or demonstration purposes extremely simple DTA equipment could be built, and the underlying theory verified by experiments appropriate for class work.

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APPENDIX

Curves of Differential Temperature plotted against Sample Temperature

There has been some discussion in the literature as to whether the differential temperature should be plotted against time, reference temperature or sample temperature.[29] The use of sample temperature would be convenient sometimes, because the transition temperature could be read directly from the curve. The temperature of a point within the sample does not rise at a constant rate, however (Fig. 6), and the question arises as to whether the peak area would be affected.

It will now be shown that the peak area is the same whether the differential temperature is plotted against sample or reference temperature. Consider Fig. 7. It is necessary to prove that

$$\int_{T_1}^{T_2}(T_R - T_S)\,dT_R = \int_{T_1}^{T_2}(T_R - T_S)\,dT_S.$$

When $T_R = T_1$, $T_S = T_1$, and when $T_R = T_2$, $T_S = T_2$.

$$\int_{T_1}^{T_2}(T_R - T_S)\,dT_R = \left[\frac{T_R^2}{2}\right]_{T_1}^{T_2} - \int_{T_1}^{T_2} T_S\,dT_R = \left[\frac{T_2^2 - T_1^2}{2}\right] - \int_{T_1}^{T_2} T_S\,dT_R$$

$$= [T_2^2 - T_1^2] - \int_{T_1}^{T_2} T_S\,dT_R - \left[\frac{T_2^2 - T_1^2}{2}\right]$$

$$= [T_R T_S]_{T_1}^{T_2} - \int_{T_1}^{T_2} T_S\,dT_R - \left[\frac{T_S^2}{2}\right]_{T_1}^{T_2}$$

$$= \int_{T_1}^{T_2}(T_R - T_S)\,dT_S \text{ as required.}$$

In view of the identity above, the differential temperature may be plotted against T_R or T_S. For routine testing, T_S would be the most convenient, but it is less suitable for the present work. Two reference wells were used to avoid circuit interaction, but

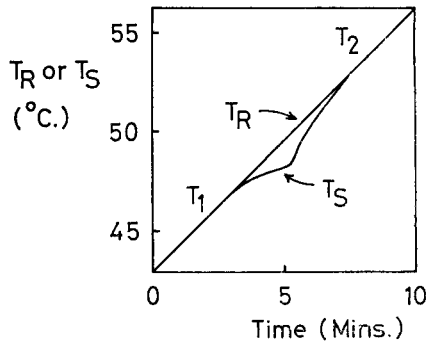

FIG. 6.—Temperatures at the centres of sample and reference cells (T_S and T_R respectively) as functions of time. (Fusion of 0·1 g of $Na_2S_2O_3 \cdot 5H_2O$ in 5 ml of *p*-xylene with "backing" suspension of polymer crystals.)

it would be unwise to attempt to use two sample wells. Although it is easy to make up two identical references it would be difficult to provide two identical samples. If T_S is to be plotted there is a clear case for using the alternative doubly-balanced thermocouple circuit with a common sample thermocouple.

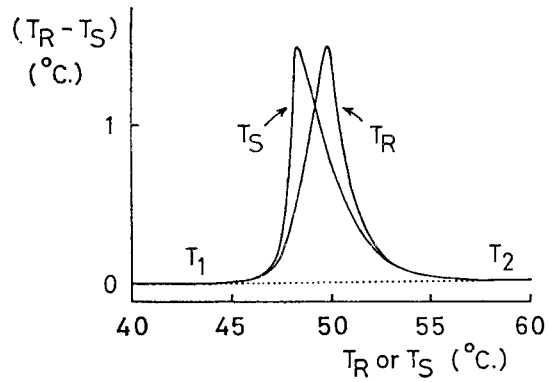

FIG. 7.—Differential temperature plotted against sample and reference temperatures. (Fusion of 0·1 g of $Na_2S_2O_3 \cdot 5H_2O$ suspended in 5 ml of *p*-xylene with "backing" suspension of polymer crystals.)

Zusammenfassung—Es wird eine Übersicht über die experimentellen Schwierigkeiten bei der Differentialthermoanalyse gegeben. Quantitatives Arbeiten erforderte stets eine Eichung des Geräts, und die üblichen festen Verdünnungsmittel haben schwerwiegende Nachteile. Es wird gezeigt, daß unter geeigneten Bedingungen eine Eichung nicht unbedingt notwendig ist. Verdünnte Suspensionen von Polymer-Kristallen in organischen Flüssigkeiten zeigen als Verdünnungsmittel und als Vergleichsmaterial fast ideale Eigenschaften. Konvektionsströme werden unterdrückt und das Medium kann feine Teilchen des untersuchten Festkörpers tragen, auch wenn der Festkörper ein relativ hohes spezifisches Gewicht hat. Die neue Theorie und das neue Verfahren wurden experimentell geprüft durch Messung der Schmelzwärmen zweier anorganischer Salzhydrate. Die Ergebnisse stimmen mit Literaturdaten ausgezeichnet überein. Eine neuartige

Anordnung mit einem Doppel-Thermoelement bietet offenbar große Möglichkeiten, auf ganz einfache Weise Präzisionsmessungen auszuführen.

Résumé—On passe en revue les difficultés expérimentales associées à l'analyse thermique différentielle (ATD). Le travail quantitatif a toujours exigé l'étalonnage de l'appareillage, et les diluants solides habituels ont de sérieux désavantages. On montre que, dans ces conditions appropriées, l'étalonnage n'est pas strictement nécessaire. Des suspensions diluées de cristaux de polymères dans des liquides organiques fournissent des milieux idéaux pour l'ATD lorsqu'on les utilise comme diluant et comme substance de référence. Les courants de convection sont supprimés et le milieu peut supporter de fines particules du solide à l'essai, même si le solide a un poids spécifique relativement élevé. La nouvelle théorie et les techniques ont été essayées expérimentalement en mesurant les chaleurs de fusion de deux hydrates de sels minéraux. Les résultats sont en excellent accord avec les valeurs de la littérature. On montre qu'un nouveau dispositif avec une double jonction de thermocouple a des possibilités considérables comme moyen d'effectuer des mesures précises de manière tout à fait simple.

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AN INDIRECT ATOMIC-ABSORPTION METHOD FOR THE DETERMINATION OF SELENIUM

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Summary—Because of the difficulty in determining selenium directly, an indirect atomic-absorption method has been developed, based on two selective reactions that lead to the formation of the $Pd(DanSe)_2Cl_2$ complex and measurement of the palladium absorption. Reaction conditions, separation techniques, effect of foreign ions, instrumental conditions and sample analysis in the sub-ppm range are described. The method is more sensitive than existing atomic-absorption methods for selenium.

BECAUSE of the nutritional value of selenium at low concentrations and toxic effects at higher concentrations,[1,2] there is a demand for analytical methods for trace determination of this element. The most sensitive method employs 2,3-diaminonaphthalene (Dan) as a fluorometric reagent,[3,4] but is susceptible to interferences. Atomic-absorption spectroscopy should be ideal since it combines the advantages of both sensitivity and selectivity for many elements, but selenium is difficult to determine by this technique, because of the formation of selenium dioxide in the flame and the strong absorption of the resonance wavelength of selenium by the flame at 196 nm.[5,6] It has been reported[6] that over 90% of the emission of the selenium line is absorbed during the normal operation of a conventional air-actylene flame and even in the absence of the flame, the 196-nm selenium line is strongly absorbed by atmospheric oxygen. In spite of efforts to improve the sensitivity and detection limit of the atomic-absorption method, mainly by using a stronger emission source or a flame which is less absorbing in the ultraviolet region, the improvement was very light, even when organic extraction was used. Since selenium is difficult to determine directly, an indirect method might be used advantageously.

Many non-metals and anions such as phosphates, nitrates, halides and sulphates cannot be determined directly by atomic-absorption spectroscopy because their principal resonance lines are found in the far ultraviolet region. They can be determined indirectly by allowing them to react chemically with a metal that absorbs in the useful range of the spectrophotometer,[7] and then determining the amount of metal in the compound produced and separated. Palladium may be determined easily by atomic-absorption spectroscopy, and it will also react selectively with certain selenium compounds, so this indirect approach may be used. The reactions are:

I. $\underset{\text{(Dan)}}{C_{10}H_6(NH_2)_2} + SeO_3^{2-} + 2H_3O^+ \xrightarrow{\text{pH } 1{\cdot}5\text{–}2{\cdot}5} \underset{\text{(DanSe)}}{C_{10}H_6N_2Se} + 5H_2O$

II. $2DanSe + PdCl_2 \xrightarrow{\text{pH} \leqslant 6} Pd(DanSe)_2Cl_2$ (purple)

III. $2DanSe + 2PdCl_2 \xrightarrow{\text{pH} \leqslant 6} Pd_2(DanSe)_2Cl_4$ (green)

IV. $Dan + PdCl_2 \xrightarrow{\text{pH } 0\text{–}12}$ White polymeric complex

where **(I)**–**(III)** are quantitative reactions for which both Dan and DanSe (naphtho-[2,3-*d*]-2-selena-1,3-diazole) have been employed as analytical reagents for selenium and palladium respectively.[8,9]

In the proposed reaction scheme, selenium as selenite (the most common and most stable form of selenium in aqueous solution) is allowed to react with an excess of Dan to form DanSe. Depending on the relative concentrations, DanSe can then react with palladium (II) chloride to form either the purple or the green complex. Which complex is formed depends also on which organic solvent is used to contain the DanSe for the two-phase reaction with palladium. By aspiration of a solution of either complex into the burner of the atomic-absorption spectrophotometer and measurement at 244·8 nm, the palladium content and hence the amount of selenium can be determined. However, excess of Dan in reaction **(I)** must be removed before the reaction with palladium, because Dan also reacts with palladium(II) chloride to form a complex, and this side-reaction, if not prevented, will result in a highly erroneous selenium value, since any additional palladium aspirated into the burner would be measured and calculated as selenium in the sample.

Reported here is an indirect atomic-absorption method for the determination of selenium in the sub-ppm range, which is successful in the presence of an excess of a large number of foreign ions. It is more sensitive than existing atomic-absorption methods for selenium.

EXPERIMENTAL

Apparatus

A Perkin–Elmer model 303 Atomic Absorption Spectrophotometer with a standard Boling air–acetylene burner head and Jarrell Ash palladium hollow-cathode tube (operated at 20 mA) was used for the atomic-absorption measurements. The sample solution was forced into the nebulizer at 2·5 ml/min by means of a 20-ml motor-driven clinical syringe.[10]

Reagents

A standard selenium solution was prepared by dissolving 8·2 g of selenous acid in 1 litre of water, and standardized with 2,3-diaminonaphthalene.[8] Other selenium solutions were prepared by dilution of this stock solution with distilled water.

A selenium-75 solution (as selenous acid) was diluted to a specific activity of about $5{\cdot}8 \times 10^7$ cpm/ml. Other radioactive selenium solutions were prepared by dilution of this stock solution with 5-ppm selenium solution.

A standard palladium(II) solution was prepared by dissolving 1·13 g of reagent grade palladium(II) chloride in 1 litre of 0·1*M* hydrochloric acid and filtering, and then standardized by precipitation with nioxime.[11] A $2{\cdot}1 \times 10^{-4}M$ solution buffered at pH 3 was prepared by mixing 33 ml of this standard solution with 20 ml of buffer (1*M* sodium acetate adjusted to pH 3 with hydrochloric acid) and diluting to 1 litre with water.

2,3-Diaminonaphthalene solution, 0·1% in 1*M* hydrochloric acid.

Dowex cation-exchanger 50W × 8, 100-mesh.

Sodium pyrophosphate solution, 0·1*M*.

Solutions of foreign ions, 0·01*M*.

Procedure

To a 100-ml sample containing from 0 to 1 ppm of selenium add 4 ml of sodium pyrophosphate solution. Adjust to approximately pH 2·5 with hydrochloric acid or sodium hydroxide solution, then pass the sample solution through a 50-ml burette filled to the 38-ml mark with Dowex cation-exchange resin (H^+-form) at a flow-rate of 2 ml/min to remove foreign cations. Collect the effluent in a separatory funnel, and wash any traces of selenium from the column with four 5-ml portions of hydrochloric acid at pH 2·5. Add 2 ml of 2,3-diaminonaphthalene solution, shake the separatory funnel briefly, and then place it in a water-bath at 50° for 25 min. Then add 9 ml of concentrated hydrochloric acid, cool, and extract the DanSe with 10 ml of chloroform by shaking for 2 min. Run

the organic layer into another separatory funnel that contains 60 ml of the buffered palladium solution and shake it vigorously for 15 min. Aspirate the organic layer into the flame by forced feeding and measure the absorption of the palladium at 244·8 nm. Run a reagent blank. The palladium absorption is an indirect measure of the selenium concentration in the sample; a linear calibration curve is obtained for 0·05–1 ppm of selenium. Quantities can be halved if required.

RESULTS

Separation of excess of Dan from DanSe

A minimum of 4–6-fold molar excess of Dan was needed for the complete formation of DanSe. The side-reaction of this excess with palladium(II) chloride cannot be prevented by pH adjustment or the use of masking agents, and the DanSe must be separated by extraction of the acidified mixture with chloroform. As shown in Fig. 1, only DanSe was extracted at pH 0. The distribution coefficient for the extraction of DanSe into chloroform from 1*M* hydrochloric acid was studied with ^{75}Se tracer and found to be 162, showing that 99·5% of the DanSe was extracted.

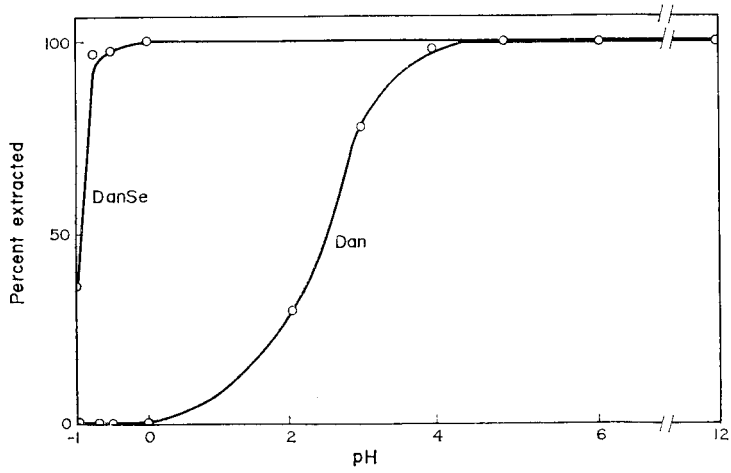

FIG. 1.—Extraction of Dan and DanSe with $CHCl_3$ at different pH values.

Choice of organic solvent

A freshly prepared aqueous solution of pure DanSe was extracted with different organic solvents, and the extracts were shaken vigorously for 20 min with a large excess of aqueous palladium(II) chloride solution adjusted to pH 2–3. Only hexane, pentyl ether and chloroform did not show a side-reaction with palladium(II) chloride. The others either extracted $PdCl_2$ itself or reduced it to metallic palladium. With hexane and pentyl ether, the green $Pd_2(DanSe)_2Cl_4$ complex was formed, but emulsion formation proved a serious problem. Chloroform was therefore used in spite of the fact that only the purple $Pd(DanSe)_2Cl_2$ complex was extracted (thus halving the potential sensitivity); the separation was clean.

Optimum conditions

The effect of pH on the reaction of DanSe in chloroform with palladium(II) chloride in aqueous solution was studied (Fig. 2). At the optimum pH value of 3, the extraction of the purple $Pd(DanSe)_2Cl_2$ complex appeared to reach completion

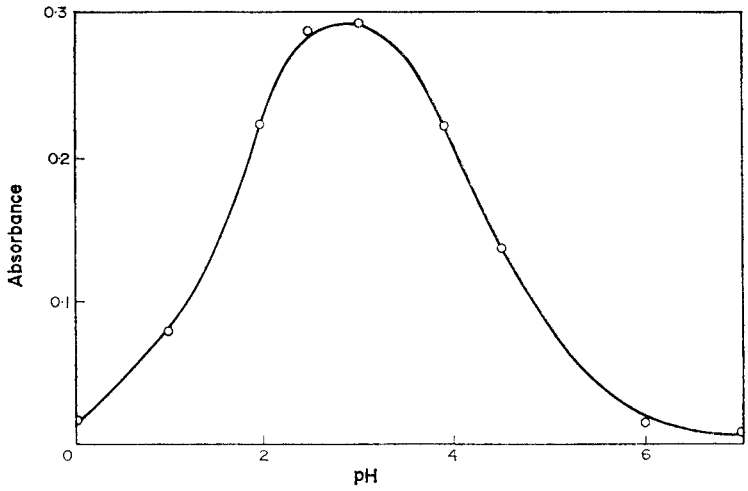

FIG. 2.—Effect of pH on the reaction of DanSe in $CHCl_3$ with aqueous $PdCl_2$.

in 15 min, as shown by spectrophotometry at 392 nm (formation of the purple complex) and 380 nm (rate of consumption of the DanSe); see Fig. 3.

The instrumental conditions for maximum sensitivity were found to be an acetylene flow-rate of 3 l./min and air flow-rate of 23·3 l./min with a burner-height setting of 24 mm below the incident light beam, but settings of 3·0–3·4 l./min for the acetylene, 26–28 l./min for the air and 11–18 mm for the height setting give maximum tolerance (Figs. 4 and 5). Other optimum instrumental settings are a gain of 5, slit-width of 0·3 mm, and scale expansion setting of 5 on the Perkin–Elmer instrument.

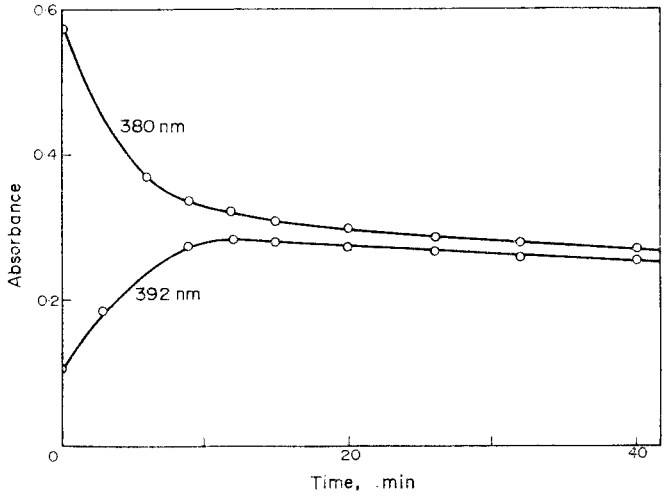

FIG. 3.—Agitation reaction time for DanSe in $CHCl_3$ with aqueous $PdCl_2$ at pH 3 to form $Pd(DanSe)_2Cl_2$.

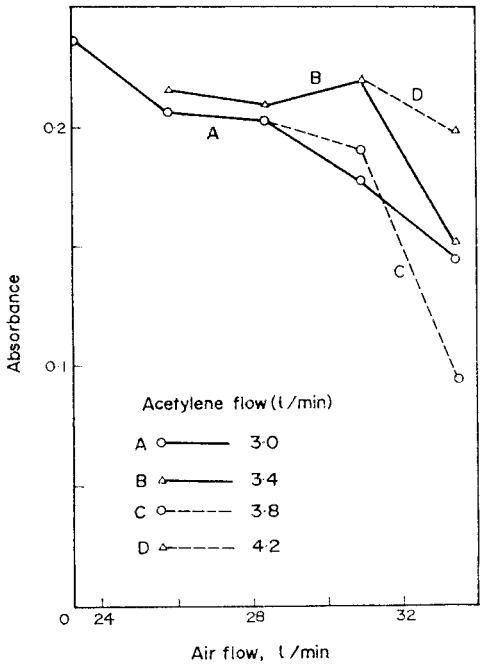

FIG. 4.—Effect of air and acetylene flow on the atomic absorbance of $Pd(DanSe)_2Cl_2$ in $CHCl_3$.

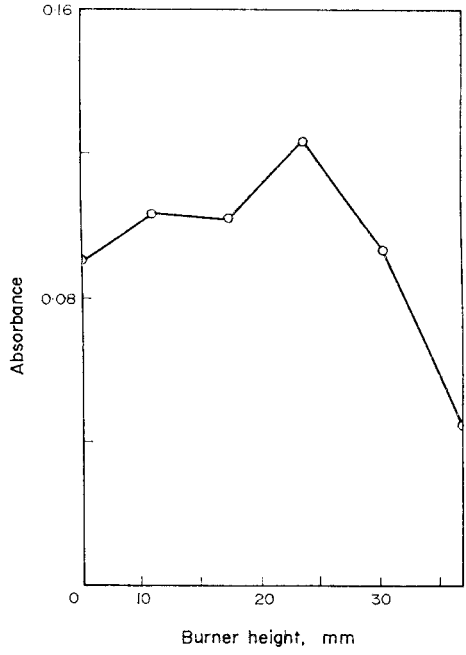

FIG. 5.—Effect of burner height (distance below incident beam) on the atomic absorbance of $Pd(DanSe)_2Cl_2$ in $CHCl_3$

Interference studies and sample analysis

The effect of fifty foreign ions on determination of 0·5 ppm of selenium was investigated with each ion above a 60-fold molar excess level. The primary interference is from Fe(III), Sn(IV) and Ce(IV), but this can be prevented by the use of pyrophosphate as masking agent and the ion-exchange separation (Table I). A ^{75}Se tracer study of retention of selenium in the cation-exchange column showed that 96% of the selenium was recovered. The retention of selenium by the column in the presence of a large excess of Sn(IV) was interesting, and might be used as a method of concentrating selenium. Tin(IV) selenite is itself an inorganic cation-exchanger.[12] However, such retention of selenium in the column can be prevented by addition of sodium pyrophosphate to the sample solution.

TABLE I.—IONS TESTED FOR INTERFERENCE. (⌒) NO INTERFERENCE: (○) INTERFERENCE BUT THIS CAN BE PREVENTED BY ION-EXCHANGE SEPARATION AND PYROPHOSPHATE MASKING AGENT

Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac†														

* Elements 58–71:	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
† Elements 90–103:	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

NO_3^-, $P_2O_7^{-4}$, $C_2O_4^=$, $C_4H_4O_6^=$, HCO_3^-, $SO_4^=$, $C_2H_3O_2^-$, ClO_3^-, Br^-, Cl^- F^-

A series of nine synthetic solutions was prepared, each containing an equal amount of four diverse ions in large excess relative to the amount of selenium. The samples were analysed by the procedure described, and the results are reported in Table II.

DISCUSSION

As shown in Tables I and II, the determination of less than 1 ppm of selenium is practicable with this method. The relative freedom from chemical interferences is the result of (*a*) the use of two reactions that are themselves highly selective for selenium and palladium respectively,[8,9] (*b*) the masking and cation-exchange separation, (*c*) the initial solvent extraction. After cation-exchange, the sample

TABLE II.—ANALYSIS FOR Se(IV) IN THE PRESENCE OF FOREIGN IONS

Foreign ions added				Se found *ppm*
Mn(II)	Ca(II)	Ba(II)	Na(I)	0·505
Zn(II)	UO_2(II)	Cu(II)	Ga(III)	0·540
Fe(III)	Ni(II)	Al(III)	Mo(VI)	0·490
V(V)	Dy(III)	K(I)	Co(II)	0·505
Mg(II)	Co(II)	Hg(II)	Li(I)	0·490
Cd(II)	Rh(III)	Ir(III)	Cr(III)	0·475
$C_4H_4O_6^=$	HCO_3^-	$C_2H_3O_2^-$	$SO_4^=$	0·470
$C_2O_4^=$	ClO_3^-	Br^-	NO_3^-	0·480
Ba(II)	In(III)	Te(IV)	Be(II)	0·510
		relative standard deviation		4·4%

All samples were 0·500 ppm in Se(IV) and contained over 60-fold molar excess of each foreign ion

solution is presumably relatively free from foreign cations. The initial organic extraction not only concentrates the sample and increases the sensitivity, but also separates DanSe from excess of Dan and foreign anions, which will remain in the aqueous layer.

With a standard single-slot burner head the flame was noisy, sooty and easily extinguished between sample aspirations. A nitrous oxide flame showed very low sensitivity. With the recommended Boling three-slot burner head, such difficulties were prevented, and the flame did not require critical adjustment of the fuel and air flow-rates. The conditions chosen agree with recommendation of the use of a lean flame for palladium determination when the Boling burner is used.[13] It is not recommended, however, that a leaner flame be tried, because then the burner head gets too hot and the slots may warp. Even with the present setting, damage to the slots could occur unless a liquid (solvent or water) is aspirated continuously into the flame. With the Boling burner head, the flame is sufficiently stable, but, owing perhaps to air turbulence in the nebulizer system, the sample aspiration rate (by conventional sample feeding) does not remain constant over an extended period, though the range of readings obtained is reproducible for a given sample. To minimize this uncertainty, mechanical forced feeding was used. The higher feed rate improves the sensitivity. The relative standard deviation was 4·4%.

The method is more sensitive than existing atomic-absorption methods for selenium (Table III).

TABLE III.—DETECTION LIMIT AND SENSITIVITY FOR Se DETERMINATION WITH ATOMIC-ABSORPTION SPECTROSCOPY

Method	Detection limit, μg/ml	Sensitivity, μg/ml/1%	Reference
Air–C_2H_2	0·5	1–2	5, 14, 15
Se–APDC*	0·1	—	17
Se–DDTC†	—	0·3	6
Air–C_3H_8	—	1·0	5
Air–H_2	0·05	0·27	16
N_2–H_2	0·1	0·5	18
N_2-separated air–C_2H_2	1·2	0·6	19
Indirect $Pd(DanSe)_2Cl_2$	0·018	0·017	This work

* APDC = 1-pyrrolidinecarbodithioic acid, ammonium salt.
† DDTC = diethyldithiocarbamate.

Acknowledgement—This work was supported in part by a U.K.C. summer graduate student fellowship from the University of Missouri-Kansas City to H. K. Y. L., for which the authors wish to express their thanks.

Zusammenfassung—Wegen der Schwierigkeit, Selen direkt zu bestimmen, wurde eine indirekte Atomabsorptionsmethode entwickelt. Sie beruht zuf zwei selektiven Reaktionen, die zur Bildung des Komplexes $Pd(DanSe)_2Cl_2$ führen; die Palladiumabsorption wird dann gemessen. Reaktionsbedingungen, Abtrennverfahren, Einfluß von Fremdionen, Geräteeinstellungen und Probenanalyse im Bereich unter 1 ppm werden mitgeteilt. Das Verfahren ist empfindlicher als die bekannten Atomabsorptionsverfahren für Selen.

Résumé—A cause de la difficulté à déterminer le sélénium directement, on a élaboré une méthode d'absorption atomique indirecte, basée sur deux réactions sélectives qui mènent à la formation du complexe Pd-$(DanSe)_2$ Cl_2 et à la mesure de l'absorption du palladium. On décrit les conditions de réaction, les techniques de séparation, l'influence d'ions étrangers, les conditions instrumentales et l'analyse d'échantillon dans le domaine sub-p.p.m. La méthode est plus sensible que les méthodes d'absorption atomique existant pour le sélénium.

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PHOTOMETRIC COMPLEX-FORMATION TITRATIONS OF SUBMICROMOLE AMOUNTS OF METALS IN THE PRESENCE OF AN APPROXIMATELY EQUIVALENT AMOUNT OF INDICATOR

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Summary—The photometric titration of the metal indicator complex MI with a ligand L is discussed. A tangent procedure is adopted for the determination of the end-point. From this procedure, in combination with an assumed maximum titration error, titration conditions have been derived. A procedure is introduced which, in conjunction with the derived titration conditions, permits the selection of a suitable titration medium by means of a diagram in which log K, log α and log χ are plotted *vs.* pH. The procedure is applied to determination of lead and zinc in the presence of citric acid, the medium used for their paper-electrophoretic separation. The use of citric acid introduces some limitations; it is shown that the method developed is generally applicable.

COMPLEXOMETRY is widely applicable but not selective. This disadvantage may be overcome by combining the method with a separation technique such as high-voltage paper electrophoresis. The difference in electrophoretic mobility of metal ions is generally not sufficient to obtain a suitable separation. The separation can be improved by the addition of a complexing agent. In the work described here the ions have been separated in citric acid solution imbibed in paper. After the separation the spots are located by an indicator spray (PAN, PAR or oxine). The strips can be cut precisely to yield small pieces of paper each containing one or at most two metals combined with the indicator and an excess of citric acid. The mixture is isolated from the paper simply by washing in a small volume of acidified water (pH < 4). Recoveries between 96 and 100% can be attained.

The main problem in the combined separation–complexometry procedure is not the separation but the development of the titration procedure for the different metals because of the interference of citric acid and the indicator of the spray.

In this paper the necessary theoretical considerations are given for the proper selection of titration conditions. A great number of applications have been made in the author's laboratory on microsamples provided by solid-state physicists.

For a quantitative determination visual end-point detection with metallochromic indicators is impossible because of the low initial metal concentration. The same holds for a logarithmic concentration dependence as in potentiometry. Signals with a linear concentration dependence have several advantages.[1,2] Therefore photometric end-point determination has been applied in this investigation.

The titrations are generally performed in the following way. To the sample solution of the metal M an approximately equivalent amount of indicator I is added. Then the solution is titrated with a ligand L according to

$$MI + L \rightleftharpoons ML + I \qquad (1)$$

The progress of the reaction is followed by measuring the absorbance of MI.

In the first part of this paper the procedure for a suitable determination of the end-point is discussed and titration conditions are derived which have to be satisfied in order to keep the titration error below 1%. In the second part the procedure is presented which permits the selection of suitable titration conditions. The procedure has been applied to lead and zinc as an example.

THEORY

Terminology and symbols used follow present practice in this field of investigation.[3] The only assumption made is that only 1:1 complexes are formed between M and I.

We introduce the notation

C_M = total concentration of metal M present in any form

C_L = total concentration of ligand L present in any form

C_I = total concentration of indicator I present in any form

$f = \frac{C_L}{C_M}$ = titration parameter

$mi = \frac{[MI]}{C_M}$ = fraction of metal bound to the indicator; the absorbance is a linear function of *mi*

$\beta = \frac{C_I}{C_M}$ = relative amount of indicator

It has been shown by Freese[4] that the mathematical treatment of titration curves is greatly simplified by using relative concentrations (such as *mi*) and by using the dimensionless quantities Z instead of the conditional constants.

$$Z_I = C_I \,.\, K_{M'I'(MI)'} \tag{2}$$

$$Z_M = C_M \,.\, K_{M'L'(ML)'} \tag{3}$$

in which the K values are conditional constants defined by

$$K_{M'I'(MI)'} = \frac{[MI']}{[M'] \,.\, [I']} \tag{4}$$

$$K_{M'L'(ML)'} = \frac{[ML']}{[M'] \,.\, [L']} \tag{5}$$

In the conditional constants all side-reactions are taken into account. For convenience the primes will be left out in the following.

The following mass balances hold:

$$C_I = [I] + [MI] \tag{6}$$

$$C_M = [M] + [MI] + [ML] \tag{7}$$

$$C_L = [L] + [ML] = f \,.\, C_M \tag{8}$$

From these equations the titration parameter f is found as a function of *mi*

$$f = 1 - mi - \frac{1}{Z_I} \cdot \frac{mi}{(1 - mi/\beta)} + \frac{1}{mi} \cdot \frac{Z_I}{Z_M} + \frac{mi}{\beta} \cdot \frac{Z_I}{Z_M} - \frac{Z_I}{Z_M} - \frac{1}{Z_M} - \frac{1}{\beta} \frac{Z_I}{Z_M} \tag{9}$$

Similar equations have been derived by Fortuin *et al.*[5] and by some other authors, for $C_M \gg C_I$.

Z_M/Z_I has to be large in order to yield suitable titration curves. Hereafter it will be shown that the condition $\log Z_M/Z_I > 3{\cdot}5$ has to be fulfilled. As the indicator I is added in about the same amount as M the constant β will lie between 0·5 and 1·5. So for such conditions the last four terms in (9) can be neglected. This leads to

$$f = (1 - mi) - \frac{mi}{Z_I(1 - mi/\beta)} + \frac{1}{mi} \cdot \frac{Z_I}{Z_M} \qquad (10)$$
$$= f_1 + f_2 + f_3$$

In Fig. 1 some ideal titration curves are drawn with $Z_I > 10^3$ and $Z_M/Z_I > 10^6$. In Fig. 2 a number of curves is shown for different β-values and $Z_I = 10$. It appears that even when the indicator is added in excess an appreciable curvature may arise for low values of Z_I.

For Mg–Eriochrome Black T–EDTA and Pb–Xylenol Orange–EDTA the experimentally found absorbance *vs.* volume of titrant curves were in perfect agreement with equation (10). This is shown in Fig. 3 for Mg–EDTA. It should be noted that indicators are generally rather impure, so β cannot be calculated from the amounts of substances present in the sample solution.

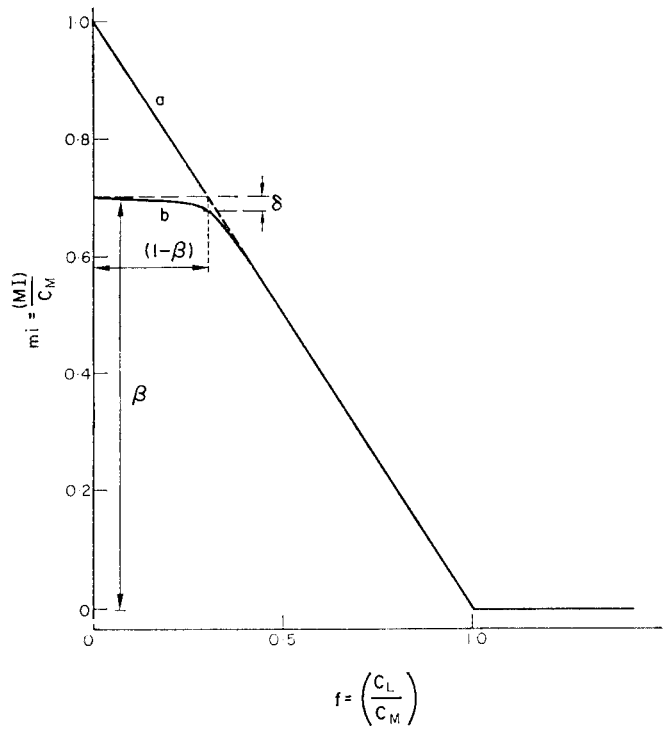

FIG. 1.—Ideal titration curves in the cases $\beta > 1$ (curve *a*) and $\beta < 1$ (curve *b*). Curve *b* is constructed with $Z_I = 1000$, $Z_M = 10^{10}$ and $\beta = 0{\cdot}7$. It may be noted that $\delta/\beta = \sqrt{1/Z_I}$.

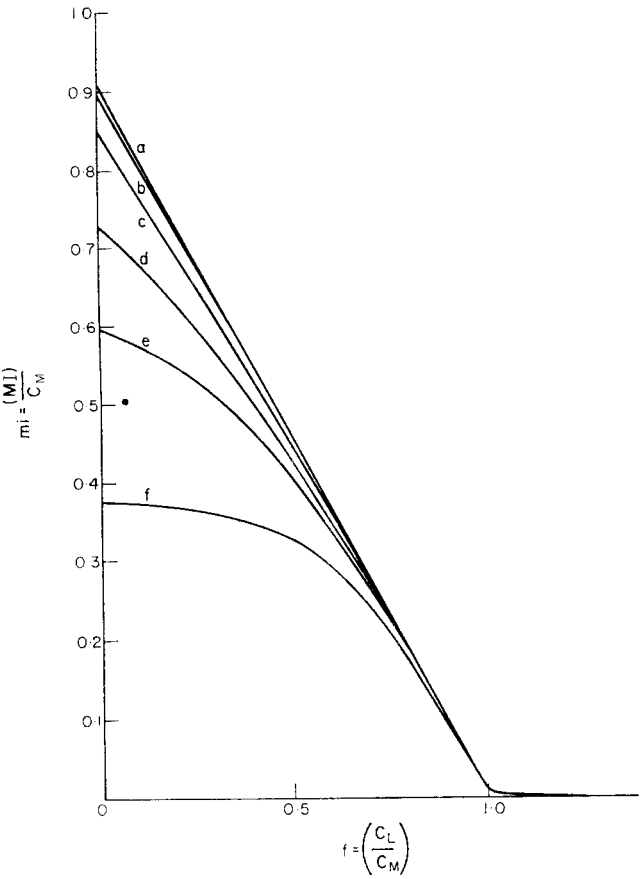

FIG. 2.—Theoretical titration curves representing the influence of the indicator on the curves for different values of $\beta = C_I/C_M$. The curves are constructed with $Z_M = 10^5$, $Z_I = 10$ and $\beta = 100$ (curve *a*), $\beta = 10$ (curve *b*), $\beta = 2$ (curve *c*), $\beta = 1$ (curve *d*), $\beta = 0{\cdot}7$ (curve *e*) and $\beta = 0{\cdot}4$ (curve *f*).

Notes

1. In equation (10) f_3 explains the curvature of the *mi vs. f* curve near the equivalence point, in terms of the dissociation of ML. This curvature is not affected by the occurrence of side-reactions of M because in those cases Z_I and Z_M are changed by the same factor. This also holds for the curvature of absorbance–titrant volume curves.

2. The term f_2 takes into account the dissociation of MI and causes deviation of the upper part of the *mi vs. f* curve from the straight line. The deviation depends on Z_I (and β). This may be used to interpret the changes of absorbance–titrant volume curves owing to the occurrence of side-reactions. Linear branches were obtained in the titration of lead with EDTA (and Xylenol Orange as indicator) buffered with hexamine, while a curved upper portion of the titration curve was observed when citrate ions were present in the corresponding medium. The increase of the curvature is caused by the decrease of Z_I.

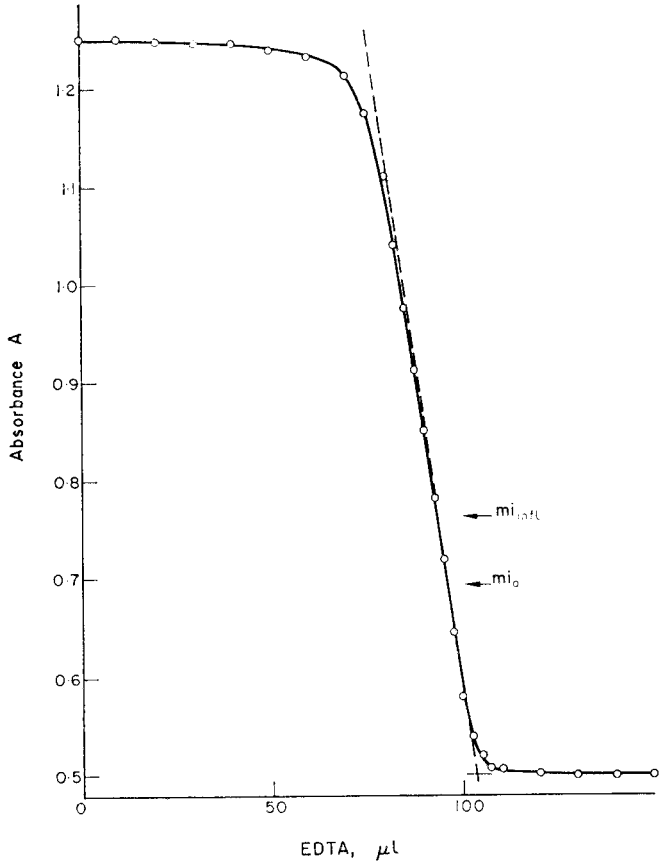

FIG. 3.—Adaptation of the theoretical curve to the measured points in an Mg–EDTA titration with Eriochrome Black T. The titration is performed in 50% alcohol medium. The best fit is for $\beta = 0{\cdot}268$, $Z_I = 70$ and $Z_M = 10^5$. The volume *vs.* f and absorbance *vs.* x relationships are $V = 103f$ and $A = 0{\cdot}50 + 2{\cdot}81\ mi$. The amount of Mg was 12 μg in about 10 ml. The titration is performed with $5 \times 10^{-3}M$ EDTA. The sample solution is buffered at pH 10·5 (ammonia). Alcohol increases $K_{M'L'(ML)'}$ more than $K_{M'L'(MI)'}$ so Z_M/Z_I increases and the end-point determination is improved.[6]

The determination of the end-point and the derivation of the titration curves

As Z_M/Z_I is large, the part of the titration curve after the equivalence point (e.p.) may be considered as straight. If $\log (Z_M/Z_I) > 4{\cdot}3$ the part before the e.p. will also be straight. In these cases the e.p. is obtained as the intersection of two straight lines at each side of the e.p.

The procedure is not satisfactory when $\log (Z_M/Z_I) < 4{\cdot}3$. In this case, which is illustrated in Fig. 4, it will be necessary to draw a tangent. The problem is not how to draw the tangent, but to determine the best place for the tangent point (mi_0; f_0).

Still[7] discusses the systematic deviation Δf_e with the tangent drawn at the inflection point mi_{infl}. Then Δf_e has its minimum value provided that only 1:1 complexes between M and I are formed. When mi_{infl} increases, there is an increase in the contributions to the standard deviations of the equivalence point arising from the fluctuations in the absorbance measurements and the drawing of the tangent.

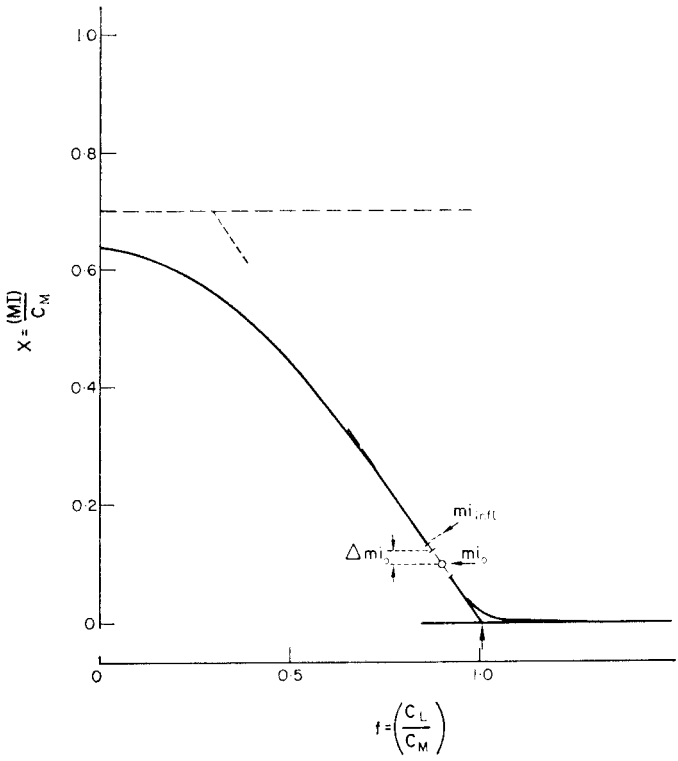

FIG. 4.—Theoretical curve just at the limit of the titration condition [equation (15)]. The curve is constructed with $Z_I = 20$, $\beta = 0{\cdot}7$ and $Z_M/Z_I = 3000$ and illustrates the advantage of the tangent procedure for this case. The downward dashed line is a small part of the ideal curve $f = (1 - mi)$. It intersects the horizontal dashed line $mi = \beta$ in the point $[\beta;\ (1 - \beta)]$, which point is important for an estimation of Z_I by the formula $o/\beta = \sqrt{1/Z_I}$ (see Fig. 1).

We are interested in the best compromise between systematic and statistical deviations. It will be clear that the inflection point will not automatically be the best place to draw the tangent.

With

$$f_e = f(mi_0) - mi_0 \cdot \left(\frac{df}{dx}\right)_{mi_0} \tag{11}$$

it follows from equation (9) that under all practical conditions

$$\Delta f_e = \frac{Z_I}{Z_M} \cdot \frac{2}{mi_0} + \frac{1}{\beta Z_I} \cdot \left(\frac{mi_0}{1 - mi_0/\beta}\right)^2 \tag{12}$$

[the same terms are neglected as in the derivation of equation (10)]. Substitution of $mi_0 = mi_{infl}$ and

$$\frac{1}{mi_{infl}} = \left(\frac{Z_M}{\beta \cdot Z_I^2}\right)^{1/3} + \frac{1}{\beta}. \tag{13}$$

derived by differentiating (9) twice, in equation (12) leads to the minimum value of Δf_e and shows that in this particular case the second term in (13) is half the first.

The second term decreases quadratically with decreasing mi_0, whereas the first term increases in inverse proportion to mi_0, so the second term may be neglected for $mi_0 < mi_{\text{infl}}$. In all cases in which the tangent procedure had to be applied we found $0{\cdot}10 < mi_{\text{infl}} < 0{\cdot}35$. As a reasonable compromise between statistical and systematic errors we adopted a value of $mi_0 = 0{\cdot}10$, which makes that equation (12) can be approximated by

$$\Delta f_e = \left(\frac{Z_I}{Z_M}\right) \cdot \frac{2}{mi_0} = 20\left(\frac{Z_I}{Z_M}\right). \tag{14}$$

From a number of experimental lines it appeared that with $mi_0 = 0{\cdot}10$ the statistical contribution to Δf_e is about 0·4%. In order to maintain the total error below 1% it follows that the systematic deviation has to be smaller than 0·6%. On combining this with equation (14) the following titration condition can be derived:

$$T = \log\left(\frac{Z_M}{Z_I}\right) > 3{\cdot}5. \tag{15}$$

In practice the tangent point may be found by roughly extrapolating the absorbance–volume titrant curve to an L-shape and taking the point at $\frac{1}{10}$ of the height of the descending branch. A refined procedure is to estimate Z_I, β and Z_M/Z_I from the experimental curve. (Z_I may be determined in an analogous way to that indicated below for Z_M/Z_I; see Fig. 1.) This has been done for the titration shown in Fig. 3 where $mi_{\text{infl}} = 0{\cdot}14$ and $mi_0 = 0{\cdot}10$. However, without the aid of a computer this is a laborious procedure.

The tangents are constructed by taking the line through the tangent point parallel to a line through two equidistant points on both sides of the tangent point ($\Delta mi_0/mi_0 < 30\%$, see Fig. 4).

As in practice the absorbance–titrant volume curves are measured, there must be a sufficient formation of MI. This implies that the slope of the *mi vs. f* curve just before the equivalence point, which may be approximated by

$$\frac{dmi}{df} = \frac{Z_I}{Z_I + 1} \tag{16}$$

should not deviate too much from unity. For this reason a minimum value of Z_I is adopted in practice

$$\log Z_I > 1 \tag{17}$$

In the theory section it was assumed that only (1:1) complexes would be considered. Several indicators, however, show stepwise complexation, schematically expressed by

$$M_2I \rightleftharpoons M \rightleftharpoons MI \rightleftharpoons MI_2 \ldots MI_n$$

If mainly an M_2I complex is formed in the solution, large systematic deviations can be expected, because the term f_2 will then give a parabolic contribution to f near the equivalence point. This has been proved to occur in bismuth–EDTA and thorium–EDTA titrations with Xylenol Orange or Pyrocatechol Violet as an indicator. This will be discussed in a separate paper. The formation of M_2I generally should be prevented, by taking a more appropriate indicator.

Kotrlý[8] has considered the stepwise formation of metal–indicator complexes MI_m and the influence of a system of three simultaneously occurring species MI, MI_2 and MI_3 on the shape of the titration curve.

If only MI_m occurs in the solution titration conditions identical to (15) and (17) can be derived in the same way as described before (with $Z_I = C_I^m \cdot K_{MI_m}$).

When mixtures of complexes occur in the solution, an accurate titration can be performed when one complex predominates and when the conditions (15) and (17) are satisfied for this complex.[9] The reason is that just before the equivalence point the concentrations [MI], [MI_2] and [MI_3] and therefore the absorbance of the solution will be linearly dependent upon the added titrant volume.

EXPERIMENTAL CONDITIONS

The most convenient way to select experimental conditions is by means of diagrams similar to the pM–pH diagrams used by Reilley.[10] The following quantities are plotted *vs.* pH:

a. $\log K_{ML'(ML)'}$; side-reactions of M are not included,

b. $\log \alpha_{M(A)}$, $\log \alpha_{M(B)}$, *etc* for every side-reaction of M with A, B, and so on,

c. $\log \chi_I$ in which $\chi_I = C_I \cdot K_{MI'(MI)'} = Z_I \cdot \alpha_M$; ($\chi_I$ should be distinguished from $\alpha_{M(I)} = 1 + [I] \cdot K_{MI'(MI)'}$).

See for examples the diagrams of lead and zinc (Figs. 5 and 6).
Titration condition (17) can be written as

$$\log Z_I = \log \chi_I - \log \alpha_M > 1. \tag{18}$$

In (18) α_M is the overall side-reaction coefficient.[3] Titration condition (15) can be written as

$$\log \left(\frac{Z_M}{Z_I}\right) = \log \left(\frac{C_M \cdot K_{M'L'(ML)'}}{C_I \cdot K_{M'L'(MI)'}}\right) = \log (C_M) \cdot \left(\frac{K_{ML'(ML)'}}{\chi_I}\right) > 3{\cdot}5. \tag{19}$$

It is convenient to make a plot of $K_{ML'(ML)'}/\chi_I$ which will be denoted as ${}^{Ind}K$, *vs.* pH. For the calculation of $Z_M/Z_I = C_M \cdot {}^{Ind}K$ we need to know C_M. An approximate value of C_M generally serves in order to check equation (19).

The pH range for suitable titrations is found as the range where both conditions are satisfied. This range can simply be read from the diagram.

If no indicator giving a metal–indicator complex with sufficient absorptivity is available, back-titration will be necessary. This procedure is not essentially different from a direct titration. It will be discussed in a separate paper.

Limits of determination

Two separate conditions determine the limit of determination. First a spectrophotometer requires a minimum change in absorption for a given precision. In our experiments (Zeiss spectrophotometer PMQ II) titration with an accuracy of 1% could be performed with $\Delta A = 0{\cdot}1$. With a 20-mm pathlength and $\Delta\varepsilon \sim 2000$ l.mole^{-1}.mm^{-1} the minimum for C_M is about $3 \times 10^{-6} M$ and with $\Delta\varepsilon \sim 5000$ l.mole^{-1}.mm^{-1} C_M is even as low as $10^{-6} M$. Secondly C_M is restricted for theoretical reasons, because $\log C_M \cdot {}^{Ind}K > 3{\cdot}5$ implies a minimum for C_M.

Lead

The determinations of lead were carried out in solutions containing citric acid as this was the medium in which the ions were separated electrophoretically. Therefore

the influence of citric acid has been taken into account. The diagram for lead is presented in Fig. 5. Two indicators were suitable for our purpose: Xylenol Orange and PAR. First Xylenol Orange (XO) will be considered.

The first condition—equation (18)—$\log Z_I = \log \chi_{XO} - \log \alpha_{Pb} > 1$ is satisfied above pH 5·5. The indicator itself changes colour at pH above 6·5 so only a small pH-range (5·7–6·1) remains for practical use. ($\Delta\varepsilon \sim 4000$ l.mole^{-1}.mm^{-1}; $\lambda = 575$ nm). The conditional constant in that range is marked as ^{XO}K. As $\log {}^{XO}K = 8{\cdot}7$ the second titration condition—equation (19)—is satisfied for $C_M > 5 \times 10^{-6}M$. It was experimentally confirmed that $5 \times 10^{-6}M$ is the minimum concentration for the determination of lead in a solution buffered with hexamine. The reaction proceeds nearly instantaneously.

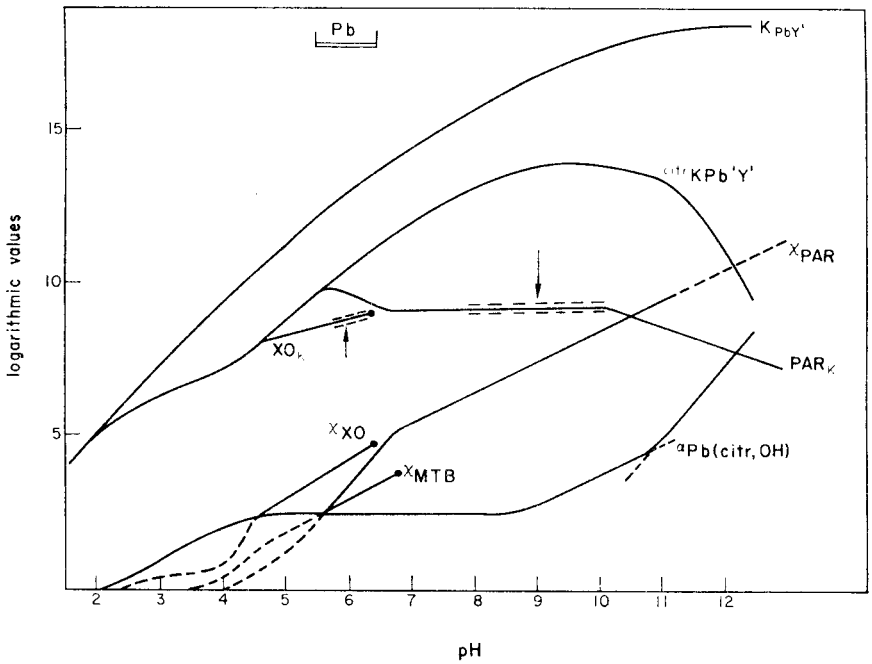

FIG. 5.—The influence of the medium on the K', χ and α-values of lead. The curves are constructed with the basic conditions: $C_I = 10^{-4}M$ and $C_{citr} = 2 \times 10^{-3}M$. In $\log K'$ only side-reactions in which ML and L are involved are taken into account.

In the introduction it was mentioned that the metal spots on the electrophoresis strips are located with the aid of a spray indicator. This indicator differs from the titration indicator mostly for practical reasons. A possible interference by the spray indicator has to be investigated. In the Pb–XO–EDTA titration PAR and oxine did not interfere. When no citric acid is present condition (18) is also satisfied for lower pH.

PAR can also be used as titration indicator. The condition $Z_{PAR} > 10$ [equation (18)] is satisfied above pH = 6·5. Experimentally, we found a nearly constant value for ^{PAR}K ($\sim$9·0) in the pH range 6·5–10 ($\Delta\varepsilon \sim 3500$ l.mole^{-1}.mm^{-1}; $\lambda = 510$ nm). The second titration condition [equation (19)] again determines the minimum of C_M

and is satisfied for $C_M > 3 \times 10^{-6}M$. In the given pH range the reaction proceeds instantaneously. Oxine did not interfere when used as spray indicator.

Zinc

In the case of zinc a larger number of side-reactions may interfere, resulting in a more complicated diagram (Fig. 6).

Many indicators have been described: Eriochrome Black T, PAN, dithizone, Xylenol Orange, Methylthymol Blue (MTB), zincon and PAR.

The zinc–Erio T complex dissociates slowly, resulting several minutes being required to reach equilibrium after each addition of titrant. Moreover, the absorbance drifts, presumably because of air oxidation of the indicator. This renders Erio T unsuitable.

Dithizone needs an alcoholic medium to remain in solution; so does PAN. This makes both dithizone and PAN less suitable.

The coefficients $\chi_{\text{Xylenol Orange}}$ and χ_{MTB} hardly exceed the other side-reaction coefficients. The inapplicability of these indicators has been confirmed experimentally.

Zincon is a very suitable indicator ($\Delta\varepsilon = 3000$; $\text{l.mole}^{-1}.\text{mm}^{-1}$; $\lambda = 615$ nm). From Fig. 6 it follows that the titration condition [equation (18)] $Z_{\text{zincon}} > 10$ is satisfied in the pH range 9·5–10·5 in the presence of citric acid under the conditions that $[NH_3] < 0{\cdot}05M$ and that cyanide is absent. The second titration condition [equation (19)] was always satisfied in our investigations. $\text{Log}\ {}^{\text{zincon}}K \sim 11$ is so large that the minimum of C_M was determined by $\Delta\varepsilon$ and the spectrophotometer used.

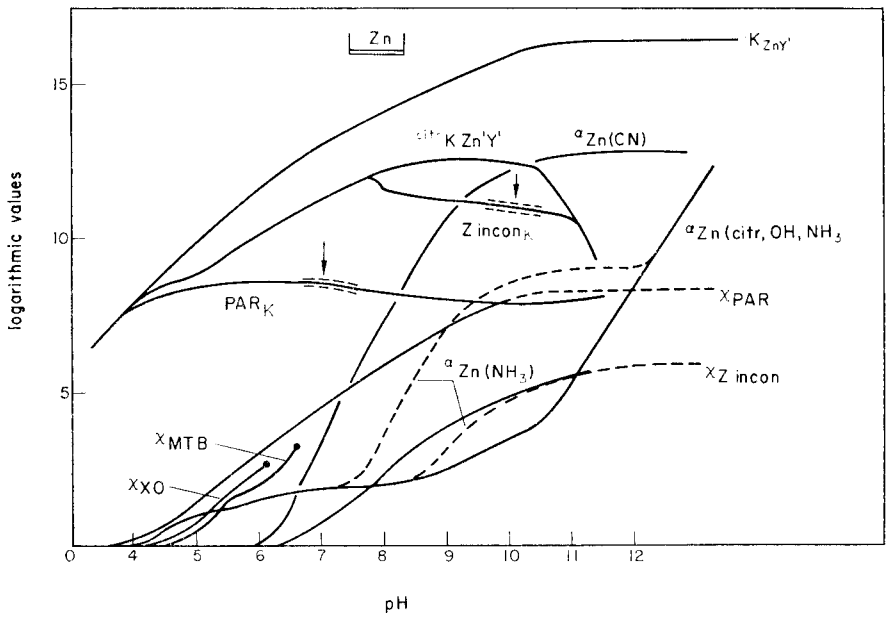

FIG. 6.—The influence of the medium on the K', χ and α-values of zinc. The curves are constructed with the basic conditions: $C_I = 10^{-4}M$ and $C_{citr} = 2 \times 10^{-3}M$. The dotted lines for ammonia correspond to 0·1 and $1M$ NH_3. The CN-line corresponds to $0{\cdot}1M$. In $\log K'$ onlyside-reactions in which ML and L are involved are taken into account.

PAR and oxine, if used for spraying the electrophoresis strips, both interfere as χ_{PAR} and χ_{oxine} amply exceed χ_{zincon}.

PAR can also be used as titration indicator and is very suitable ($\Delta\varepsilon \sim 5000$ l.mole^{-1}.mm^{-1}; $\lambda = 488$ nm). From the diagram it follows that $Z_{PAR} > 10$ is satisfied for pH $> 5{\cdot}5$ in the presence of citric acid. Oxine does not interfere if used as spray indicator. No data about PAR were available from the literature. We experimentally found $\log {}^{PAR}K$ to lie between 8·0 and 8·5 in the whole pH range, so the limit of determination follows from the second titration condition [equation (19)]. This condition is satisfied for $C_M > 10^{-5}M$.

Sometimes lead and zinc were not completely separated on the electrophoresis strips. A direct titration of both metals could then be performed in the following way. According to Fig. 5 lead can be titrated at pH = 9·0 with PAR as indicator, while according to Fig. 6 zinc can be masked with cyanide ($Z_{ZnY} < 1$). Zinc, however, is not masked by cyanide (0·1M) in the pH range 5·5–7·5. So in the same solution zinc could additionally be titrated at pH = 6·5 (hexamine buffer).

DISCUSSION

For the construction of the diagrams it is necessary to know the conditional constants and the side-reaction coefficients. For many metals the data are tabulated[11,12] as a function of pH. It must be emphasized that in the tables $\alpha_{M(OH)}$ is included and that consequently a correction has to be made for evaluating $K_{ML'(ML)'}$.

$\chi_I = C_I \cdot K_{MI'(MI)'}$ can be calculated from the metal–indicator stability constants, which are known for a few indicators. In the case of 1:1 complexation the values can also be found from the transition point tables[11] because $pM_{trans} = \log K_{MI'(MI)'}$.

When no data are available from the literature, satisfactory results can be obtained by estimating Z_I and (Z_M/Z_I) respectively from the curvature of the upper part of the titration curve (Fig. 1: $\log \delta/\beta) \sim -\frac{1}{2}\log Z_I$) and the curvature near the equivalence point (analogously: $\log mi_e \sim -\frac{1}{2}\log (Z_M/Z_I)$).

When a wide pH range is permitted according to the theory, it is generally preferable to choose a small pH value as the reaction velocity decreases in inverse proportion to χ_I and so mostly decreases with increasing pH. (This suggests that the reaction MI + L → ML + L occurs in two steps: MI → M → ML.)

In this paper we have restricted ourselves to lead and zinc in a citric acid medium. The method has also been applied in other fields then electrophoresis. In the author's laboratory several alloys (Mg–Mn, 1% V in Cr, Ni–Ga, rare earths in Ag–Au, Yb–In, Zn–Mn and many others) have successfully been titrated directly or indirectly with Bi, Pb, Ce and Mg as back-titrants and with EDTA and DCTA as complexing agents. Detailed procedures will be presented in separate publications.

Complexometric titration of μmole amounts of metals[13–15] have mostly been developed on an empirical basis (*cf.* ref. 1). This is remarkable in comparison with the relatively simple way in which the titration conditions can be selected and the easy way in which the titrations can be performed.

In only a few cases a systematic negative deviation or a smooth break unexpectedly arose. The smooth break turned out to disappear if a purified indicator was used. A systematic negative deviation can theoretically be expected if an indicator forms M_2I complexes in solution. It is advisable to take different commercially available indicators in these cases.

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Zusammenfassung—Die photometrische Titration des Metallindikatorkomplexes MI mit einem Liganden L wird diskutiert. Zur Bestimmung des Endpunktes wird ein Tangentenverfahren verwendet. In Verbindung mit einem angenommenen maximalen Titrationsfehler wurden aus diesem Verfahren die Titrationsbedingungen hergeleitet. Es wird ein Verfahren eingeführt, das in Verbindung mit den abgeleiteten Titrationsbedingungen die Auswahl eines geeigneten Titrationsmediums erlaubt. Dazu dient ein Diagramm, in dem log K, log α und log χ gegen den pH-Wert aufgetragen sind. Das Verfahren wird angewandt auf die Bestimmung von Blei und Zink in Gegenwart von Zitronensäure, dem Medium, das bei ihrer papierelektrophoretischen Trennung verwendet wird. Die Verwendung von Zitronensäure bedingt einige Einschränkungen; es wird gezeigt, daß das entwickelte Verfahren allgemein anwendbar ist.

Résumé—On discute du titrage photométrique du complexe indicateur de métal MI avec un ligand L. On adopte une technique de tangente pour la détermination du point de fin de dosage. De cette technique, en combinaison avec une erreur de titrage maximale supposée, on a déduit des conditions de titrage. On présente une méthode qui, conjointement avec les conditions de titrage déduits, permet la sélection d'un milieu de titrage convenable au moyen d'un diagramme dans lequel log K, log α et log χ sont tracés en fonction du pH. La méthode est appliquée à la détermination du plomb et du zinc en la présence d'acide citrique, le milieu utilisé pour leur séparation par électrophorèse sur papier. L'emploi d'acide citrique introduit quelques limitations; on montre que la méthode élaborée est généralement applicable.

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CHROMATOGRAPHIC SEPARATION AND COLORIMETRIC DETERMINATION OF GOLD*

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Summary—Gold(III) is selectively sorbed from 1*M* hydrochloric acid by a short column containing a special acrylate resin. Then the gold is eluted from the column with acetone–hydrochloric acid, and the absorbance of the effluent is measured at 340 nm. Gold(III) may be successfully separated and determined in samples containing many other metal ions.

COLORIMETRIC methods for the determination of gold have been reviewed by Beamish *et al.*[1] Some of the methods rely on co-precipitation[2,3] or batch extractions[4–6] to separate gold from interfering metal ions. Platinum metals interfere with a number of the methods.[4,6] Bravo and Iwamoto[7] extracted gold into chloroform as $Bu_4N^+AuCl_4^-$ and measured the absorbance at 321 nm. Strelow *et al.*[8] determined gold in cyanide wastes by atomic absorption after a concentration step in which gold(III) was extracted from dilute hydrochloric acid into isobutyl methyl ketone.

Examination of a new series of resins made by Rohm & Haas showed that a column containing XAD-7, a porous polyacrylate resin, sorbs gold(III) selectively from dilute hydrochloric or from dilute nitric acid solutions. After foreign metal ions have been washed from the column, gold(III) is stripped from the column with acetone and the gold content of the yellow solution is measured spectrophotometrically. A short column and a fast flow-rate are used so that separation, washing and elution of gold from the column can usually be completed within 10 min.

EXPERIMENTAL

Reagents

Ion-exchang eresin. Amberlyst XAD-7 polyacrilic resin (Rohm & Haas) crushed and screened to a mesh size of 80-100. Before use the resin should be washed alternately with 6*M* hydrochloric acid and acetone and then air-dried.

Hydrochloric acid, 1*M*. Prepared from reagent grade concentrated acid.

Organic solvent. J. T. Baker purified acetone was used throughout.

Acetone–1M hydrochloric acid solution. Prepared by mixing 2·5 volumes of acetone with 1 volume of aqueous 1*M* hydrochloric acid.

Metal ion solutions, 0·05*M*. When possible, these were prepared from the chlorides, dissolved in 1*M* hydrochloric acid. Sb(V) required evaporation in *aqua regia* to oxidize appreciable amounts of Sb(III) impurity. Ru(IV) was prepared by evaporation of $RuCl_3$ in *aqua regia*. U(VI) solution was prepared from $UO_2(ClO_4)_2 \cdot 4H_2O$ and diluted with 1*M* hydrochloric acid. Au(III), $2{\cdot}79 \times 10^{-3}M$ was made from "Baker Analyzed" $HAuCl_4 \cdot 3H_2O$ dissolved in 1*M* hydrochloric acid.

Distribution coefficients

Distribution coefficients were measured for various concentrations of hydrochloric acid by weighing accurately ~0·5 g of XAD-7 resin and equilibrating it in a stoppered container by shaking with a gold(III) solution. The gold(III) remaining in solution was determined spectrophotometrically.

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2768.

The distribution coefficients were calculated by using the equation

$$D = \frac{\text{mmole Au on resin}}{\text{mmole Au in solution}} \times \frac{\text{ml of solution}}{\text{g of resin}}.$$

Column preparation

Glass columns were used which had a top reservoir of 30 mm length of 20-mm o.d. tubing, a 0·10-m long middle section of 10-mm tubing, and a 10–20 mm section of 5-mm tubing at the bottom. Resin was held in the column by a plug of glass wool. There was no stop-cock, but flow could be shut off by placing a stopper over the bottom section. A column was packed by adding a slurry of 80–100 mesh XAD-7 resin in 1*M* hydrochloric acid until a resin bed 40–50 mm high was obtained. When packed, the column gave a flow-rate of ~2–3 ml/min.

Procedures

Separation. Take a sample that contains 1·5–5·5 μmole of gold(III) and is 1*M* in hydrochloric acid. Add this to the XAD-7 column and allow the liquid level to drop to the top of the resin bed. Rinse the walls of the reservoir with 1*M* hydrochloric acid and then add 8 ml of 1*M* hydrochloric acid to wash any foreign metal ions through the column and separate them from the gold. Strip the gold(III) from the column with 6–7 ml of acetone–1*M* hydrochloric acid (2·5:1). Collect this effluent in a 25-ml volumetric flask and dilute to volume with aqueous 1*M* hydrochloric acid.

Analysis. Determine the gold(III) spectrophotometrically at 340 nm against a solvent blank containing 4 ml of the acetone–hydrochloric acid mixture in 25 ml total volume (dilute with 1*M* hydrochloric acid).

RESULTS

Distribution coefficients for gold(III) on XAD-7 were determined as a function of hydrochloric acid concentration, and the results are summarized in Fig. 1. A

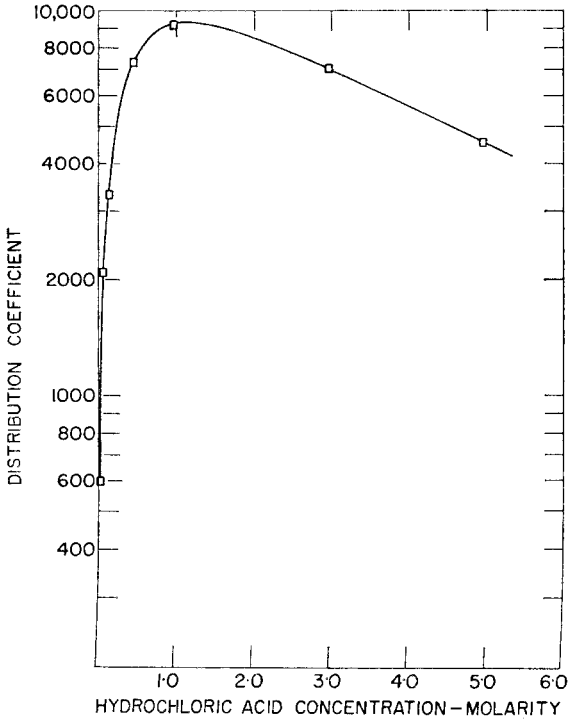

FIG. 1.—Distribution coefficients of gold(III) on Amberlyst XAD-M resin in various hydrochloric acid solutions.

hydrochloric acid concentration of 1*M* was selected for subsequent work, although the results show that gold(III) is absorbed quite well over a broad concentration range of hydrochloric acid.

Qualitatively it was observed that from 1*M* hydrochloric acid gold(III) is sorbed as a tight yellow band on a column of XAD-7. Gold(III) is quite rapidly eluted from the column by acetone. After further experimentation, a mixture of acetone and aqueous hydrochloric acid (2·5:1) was chosen to strip gold(III) from the column. This solution elutes gold(III) rapidly and avoids formation of gas bubbles in the resin (which happens when acetone alone is employed). After the gold(III) has been stripped, washing the column with a little aqueous 1*M* hydrochloric acid prepares it for the next sample.

To test the ability of the column to sorb gold(III) from very dilute solution, 1 litre of $2{\cdot}79 \times 10^{-6}M$ gold(III) in 1*M* hydrochloric acid was passed through a short column of XAD-7. On elution of the gold(III) with acetone–hydrochloric acid and measurement spectrophotometrically, a recovery of 100·8% was obtained for the gold.

Samples containing gold(III) and various foreign metal ions were separated on the XAD-7 column, and the gold(III) was stripped and determined spectrophotometrically. Quantitative separation and recovery of gold(III) was obtained in all cases (see Table I). Bismuth is slightly sorbed by the resin and required approximately 16 ml of 1*M* hydrochloric acid to wash it off before elution of the gold. Problems encountered when ruthenium was in more than one oxidation state were solved by prior

TABLE I.—SEPARATIONS OF GOLD(III) FROM OTHER METAL IONS

Metal ion	Metal added, *μmole*	Au added, *μmole*	Au found,* *μmole*	Difference, *μmole*
Al(III)	100	2·79	2·77	−0·02
Bi(III)	100	2·79	2·78	−0·01
Ca(II)	140	2·79	2·80	+0·01
Cd(II)	100	2·79	2·77	−0·02
Ce(IV)	100	2·79	2·78	−0·01
Co(II)	100	2·79	2·80	+0·01
Cr(III)	100	2·79	2·77	−0·02
Cu(II)	100	2·79	2·80	+0·01
Fe(III)	200	2·79	2·78	−0·01
Hg(II)	100	2·79	2·78	−0·01
Mn(II)	100	2·79	2·81	+0·02
Ni(II)	100	2·79	2·78	−0·01
Pb(II)	†	2·79	2·79	0·00
Pd(II)	100	2·79	2·79	0·00
Pt(IV)	100	2·79	2·80	+0·01
Ru(IV)	100	2·79	2·83	+0·04
Sb(V)	60	2·79	2·78	−0·01
Sn(IV)	100	2·79	2·78	−0·01
U(VI)	200	2·79	2·77	−0·02
Zn(II)	100	2·79	2·81	+0·02
Cu(II)	2800	2·79	2·79	0·00
Fe(III)	2800	2·79	2·78	−0·01
Zn(II)	2800	2·79	2·78	−0·01

* Average of 2 or 3 individual results.

† 2 ml of a concentrated solution of $PbCl_2$ in 1*M* hydrochloric acid.

boiling in *aqua regia*. The volume of the samples containing large amounts of iron, copper or zinc was larger (~11 ml), but the volume of additional 1*M* hydrochloric acid wash was no greater than that used for the other samples.

Several anions were tested for possible interference, by addition as the corresponding acid to the gold samples. The results in Table II show there is no interference. It was found, however, that bromide forms a strong complex with gold(III) which in the presence of acetone interferes with the spectrophotometric measurement.

TABLE II.—SEPARATION AND RECOVERY OF GOLD(III) IN THE PRESENCE OF OTHER ANIONS

Anion	Added, *mmole*	Au added, *μmole*	Au found, *μmole*	Difference, *μmole*
ClO_4^-	~3·0	2·79	2·76	−0·03
NO_3^-	~7·9	2·79	2·78	−0·01
PO_4^{3-}	~3·6	2·79	2·78	−0·01
SO_4^-	~3·6	2·79	2·76	−0·03

After stripping from the column with acetone–hydrochloric acid, the gold(III) is determined spectrophotometrically at 340 nm as its yellow complex. The spectrum of gold(III) in 1*M* hydrochloric acid, shown in Fig. 2, shows the absorption maximum at a shorter wavelength, but the strong absorption by acetone prevents the use of a wavelength much shorter than 330 nm; between 330 and 340 nm the absorbance of acetone in the solvent becomes negligible. In the acetone–hydrochloric acid mixture used the molar absorptivity of gold(III) at 340 nm is 234 $l.mole^{-1}.mm^{-1}$ and a plot of absorbance *vs.* concentration gives a linear plot.

Evaporation of the acetone before spectrophotometric measurement of the

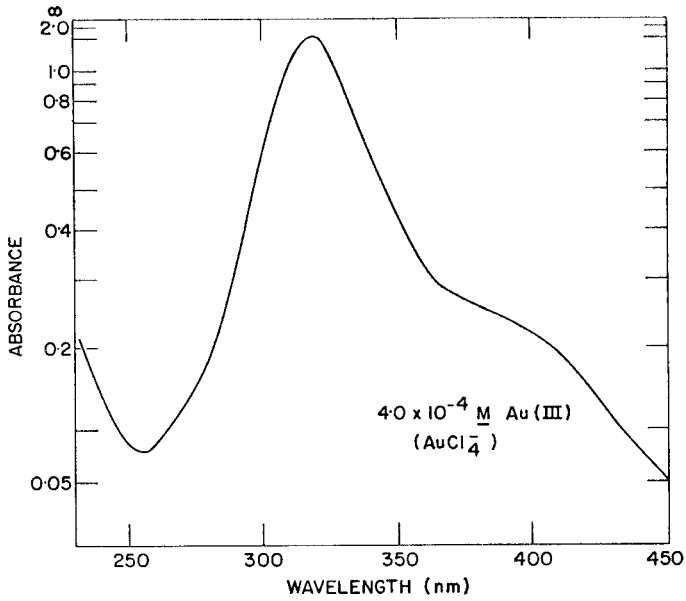

FIG. 2.—Absorption spectrum of gold(III) in 1*M* hydrochloric acid.

gold(III) was attempted and proved to be unsuccessful. Some gold(III) is reduced during the evaporation and requires that the sample be evaporated with *aqua regia*. Even then the recoveries of gold are low.

A method by McBride and Yoe,[4] based on the formation of a gold(III) tetrabromide complex, was investigated briefly. The formation constant for forming this complex from the gold(III) tetrachloride complex was reported as $3{\cdot}1 \times 10^6$, and the wavelength for maximum absorbance of the bromide complex is longer than for the chloride complex. However, tests of this method revealed that the bromide complex is destroyed by small amounts of acetone. Attempts to use methanol or ethanol as the eluent resulted in destruction of both the chloride and bromide complexes.

Notes on the analysis of practical samples

The work reported concerns the separation and determination of gold, starting with samples containing gold(III) and other metals in 1*M* hydrochloric acid. The treatment of most mineral or other commercial samples up to this point should be rather straightforward. A solid sample containing ~1·5 μmole or more of gold is dissolved in *aqua regia* (care must be exercised with cyanide precipitates) and then evaporated to near dryness. Then the sample is diluted with an appropriate volume of 1*M* hydrochloric acid. It is not necessary to evaporate again with hydrochloric acid, because nitrogen oxides, which interfere with many methods of analysis, are washed through the column and separated from the gold.

If a particular sample contains appreciable amounts of silicates or insoluble chlorides, the sample should be filtered before being introduced on to the column, to avoid a build-up of unwanted fine material on the top of the column.

Zusammenfassung—Gold(III) wird aus 1*M* Salzsäure an einer kurzen Säule mit einem besonderen Acrylatharz selektiv adsorbiert. Dann wird das Gold mit Aceton-Salzsäure von der Säule eluiert und die Extinktion der abfließenden Lösung bei 340 nm gemessen. Gold(III) kann in Proben, die viele andere Metallionen enthalten, mit Erfolg abgetrennt und bestimmt werden.

Résumé—L'or(III) est sélectivement adsorbé d'acide chlorhydrique 1 *M* par une courte colonne contenant une résine acrylique spéciale. L'or est alors élué de la colonne à l'acétone-acide chlorhydrique et l'on mesure l'absorption de l'effluent à 340 nm. L'or(III) peut être séparé avec succès et dosé dans des échantillons contenant de nombreux autres ions métalliques.

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ELECTROCHEMICAL BEHAVIOUR OF ISOPROPANOL AT PLATINUM ELECTRODES

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Summary—The accessible potential range of isopropanol was found to be from +1·1 to −1·2 V *vs.* Ag/AgCl in non-aqueous 0·01*M* LiCl, with acetone being formed at the anode and hydrogen at the cathode. Water was formed in a side-reaction, probably by ketal formation, the rate being proportional to the electrode area. Another side-reaction at the cathode produced an insoluble product after prolonged electrolysis. The coulometric current efficiency was nevertheless very high (99·6–99·97%) and almost independent of current density. The results indicate that the cathode reaction proceeded with somewhat less than theoretical current efficiency.

THE LONG-ESTABLISHED electrochemical use of aqueous or mixed aqueous–non-aqueous solutions to achieve adequate solubility has been extended in recent years as interest in non-aqueous solvents has increased, because the use of certain solvents significantly increases the variety of possible electrochemical reactions and also offers the possibility of varying reaction conditions to facilitate examination of mechanisms.

The use of non-aqueous solvents in analytical applications is documented in several monographs and review articles.[1–7] Among the alcohols, methanol has been used occasionally for polarography at the DME.[8] It is, however, not a suitable solvent for voltammetry at a platinum microelectrode, because relatively large background currents are observed. Ethanol is similar to water in many of its properties, which possibly accounts for the relative lack of interest in its use as an electrolytic solvent. Very little is known about higher alcohols, though isopropanol has been found to be the most suitable in many applications. It shows a convenient liquid range (from −89° to 82°), a rather low vapour pressure (177 mbar at 25°) and a fairly high viscosity ($2{\cdot}43 \times 10^{-3}$ N.sec.m^{-2} at 20°). Its dielectric constant is high enough (18·3 at 20°)[9] to make electrochemical measurements reasonably easy. Further, it is readily obtained in high purity and is soluble in water in all proportions. Isopropanol has been used for coulometric[10,11] and potentiometric titrations.[12]

General considerations show that the redox potential range accessible in isopropanol differs from that in water, but it has not been clearly defined. The aim of the present investigation was to study the reactions which limit the potential range of isopropanol at a platinum electrode, the effects of water upon this range, and the possibility of generating acids and bases quantitatively by oxidation and reduction of an isopropanol solution containing an indifferent electrolyte. The kinetics of the side-reactions were also studied.

EXPERIMENTAL

Chemicals

Solvent isopropanol was of Merck *p.a.* grade. Its water content was found to be 0·06% (Karl Fischer titration). Removal of water by distillation from phosphoric anhydride can introduce acidic impurities. The commercially available solvent was therefore used without further purification. The supporting electrolyte $NaClO_4 \cdot H_2O$ (Fluka *p.a.* grade) was dried at 130° for 3 hr. Solutions of sodium perchlorate (0·05*M*) were prepared from the dried salt. No increase in water content was observed.

Measuring technique

The current–potential curves were obtained by using the standard method with three electrodes, the potential of the indicator electrode being controlled with an AMEL model 551/SU potentiostat. The observed curves were automatically plotted with a Goerz Servogor recorder.

Cell and electrodes

The measuring cell was maintained at 25·0° and an atmosphere of dry nitrogen was provided. The working electrode comprised a platinum wire, 0·5 mm in diameter and 4 mm long, fused into a glass tube 6 mm in diameter. The active surface area was small (8 mm^2). High current densities were consequently obtained and yet enabled small currents to be measured. The electrode surface was regenerated by polishing after each measurement. Under these conditions measurements were found to be sufficiently reproducible.

The auxiliary electrode consisted of a platinum net immersed directly in the perchlorate solution. This avoids the disadvantages (diffusion, *etc*) inherent in a two-compartment cell.

An Ag/AgCl reference electrode[13,14] in 0·01*M* lithium chloride in isopropanol was used in order to obtain sufficiently high reproducibility and to avoid water contamination. The silver–silver chloride electrodes were prepared according to Ives and Janz.[15] Contact with the measuring solution was provided by a capillary containing the lithium chloride solution.

RESULTS

Accessible potential range

Oxidation limit. According to the method used by Kolthoff[16] the oxidation limit occurs at 1·1 V (with respect to the Ag/AgCl electrode in 0·01*M* lithium chloride), see Fig. 1. The effect of water is small, which can also be seen from Fig. 1. Displacement of the curve is relatively slight since the acidic character of isopropanol is less than that of water.[17]

Reduction limit. The cut-off potential was found to be −1·2 V (*vs*, Ag/AgCl). The effect of water was slightly more pronounced. The change in the shape of these curves when water is added to the solution gives an indication of the effect of an increase in the dielectric constant and the acidity of the medium. Water is known to be a stronger base than isopropanol. When the solution was buffered by a strong acid the addition of water altered the diffusion current profoundly (Fig. 2). This current was found to be proportional to the acid concentration (Fig. 3).

Reactions limiting the oxidation range

Anodic oxidation of isopropanol solutions containing sodium perchlorate results in an acidification of the medium. The principal reaction may be written:

$$3(CH_3)_2\overset{H}{\underset{OH}{C}} \rightleftharpoons 2\,(CH_3)_2\overset{H}{\underset{OH_2^+}{C}} + 2\,e^- + (CH_3)_2CO \qquad (1)$$

The presence of acetone was confirmed through its 2, 4-diphenylhydrazone, the melting point of which agreed (±1°) with a literature value of 126°.

Prigent *et al.*[18] obtained acetone and water as products in the oxidation of an alkaline isopropanol solution and showed the reaction to be quantitative. If reaction (1) is the only one occurring during oxidation it should be possible to generate the strongest acid capable of existence in this medium. The presence of water in the medium is not a prerequisite as Carson *et al.*[10] suggest. Attempts to produce this acid were made, the cell previously described[11] being used.

An amperostat constructed in this laboratory allowed generation of the acid at constant current. Titrations were performed in the following way.[19] For a given

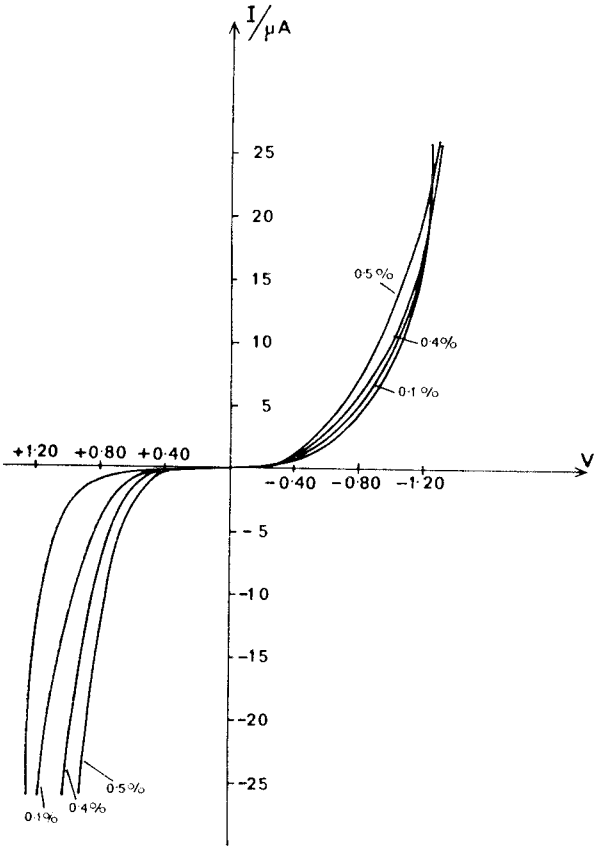

FIG. 1.—Current/voltage curves at a Pt-microelectrode in isopropanol, 0·05*M* in sodium perchlorate, with small amounts of water added. Scan rate 100 mV/min.

amount of the base diphenylguanidine, acid corresponding to about 95% neutralization was generated coulometrically in the titration cell before the base was added. Several drops of indicator (3% Thymol Blue in methanol) were also added and coulometric acid generation continued to the equivalence point. The results are contained in Table I. An alternative method provided additional information on this point (see section on current efficiency).

Reactions which limit the reduction range in isopropanol

During the electrolysis of 0·05*M* sodium perchlorate in isopropanol, gas evolution was observed at the platinum electrode. The reaction may be written:

$$2(CH_3)_2\overset{H}{\underset{OH}{C}} + 2\,e^- \rightleftharpoons 2(CH_3)_2\overset{H}{\underset{O^-}{C}} + H_2 \qquad (2)$$

This reaction has been used successfully for the coulometric titration of weak acids at constant current.[11] Besides the main reaction (2) a side-reaction was observed after electrolysis for sufficiently long times at high current density (corresponding to

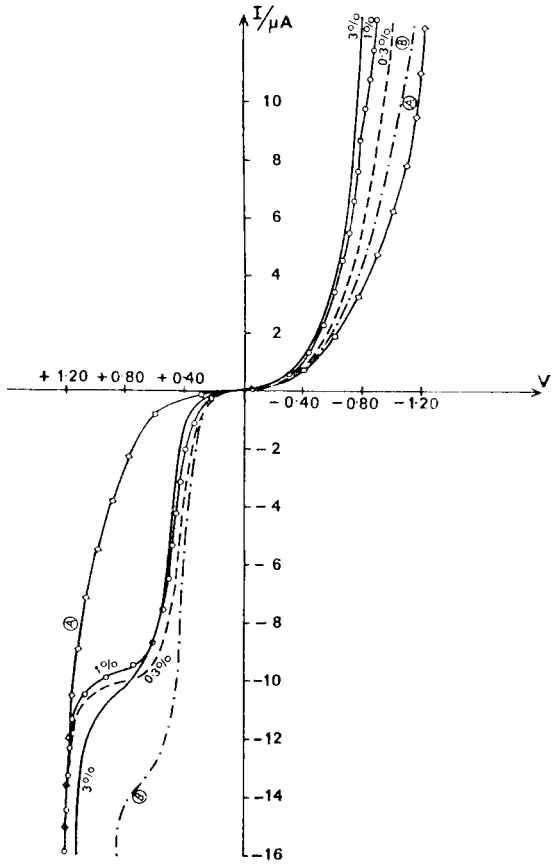

FIG. 2.—Current/voltage curves at a Pt-microelectrode in isopropanol, 0·05*M* in sodium perchlorate and 0·0004*M* in perchloric acid with small amounts of water added. Scan rate 100 mV/min.

approximately 10 mmole of base in 50 ml). A pale yellow insoluble product was formed on the electrode. The deposit was removed, dried and dissolved in water. The resulting solution was weakly basic, corresponding to pK = 9·8, the equivalent weight of the original solid being 460. The sodium content determined by flame photometry was found to vary between 10 and 30% in different electrolysis experiments. In one case the carbon corresponded to 24% and the hydrogen to 5·6%. When the current was reversed the deposit broke loose and fell to the bottom of the vessel. Replacement of sodium perchlorate with lithium perchlorate resulted in a more rapid formation of solid, which blocked the current.

Current efficiency

An assessment of the overall current efficiency was made with a cell in which both the anode and cathode were immersed in the same solution. If acid and base are generated solely according to equations (1) and (2) respectively and at identical rates no change in the acidity of the solution occurs. Excess of acid or base can be readily detected with an indicator system comprising a glass electrode and reference electrode

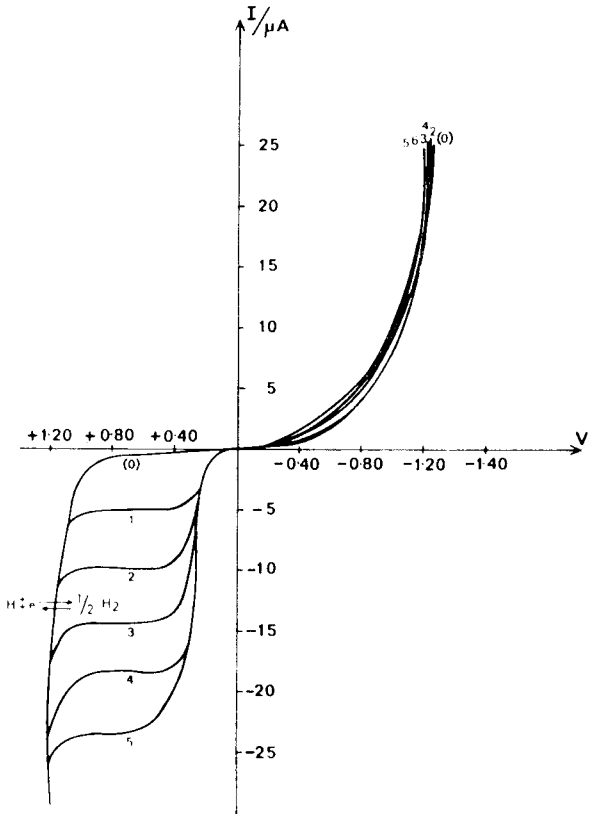

FIG. 3.—Current/voltage curves at a Pt-microelectrode in isopropanol, 0·05*M* in sodium perchlorate and with various amounts of perchloric acid. Scan rate 100 mV/min.
[$HClO_4$]: *1*—$2 \times 10^{-4}M$, *2*—$4 \times 10^{-4}M$, *3*—$6 \times 10^{-4}M$, *4*—$8 \times 10^{-4}M$, *5*—$1 \times 10^{-3}M$.

(Ag/AgCl, 0·01*M* lithium chloride in isopropanol) provided a sufficiently large number of coulombs is passed. A current efficiency of 100% may be assumed if the anode and cathode reactions balance exactly at several values of the current density. The procedure for determining the excess of acid or base in the solution was as follows.

The indicator electrodes were standardized in a picric acid–tetraethylammonium picrate buffer solution in isopropanol. The initial acidity of the solution (0·05*M* sodium

TABLE I.—COULOMETRIC TITRATION OF *N,N*-DIPHENYLGUANIDINE

Current, *mA*	Taken, *μmole*	Found, *μmole*	Error, %
0·250	4·31	4·27	−0·9
0·250	6·92	7·00	+1·2
0·300	5·82	5·75	−1·2
0·300	6·48	6·52	+0·6
0·300	10·87	10·91	+0·4
0·300	11·17	11·09	−0·7
0·900	16·47	16·40	−0·4

perchlorate in isopropanol) in the electrolysis cell was then measured. The electrodes were removed and stored in a solution of sodium perchlorate in isopropanol. A known amount of charge was then passed through the electrolysis cell. Standardization of the indicator electrodes was repeated and the final acidity of the electrolysed solution determined. Excess of acid or of base was estimated by potentiometric titration, the standardized electrode system being used. The end-point was taken as the potential corresponding to the initial acidity of the solution. Titrations to the equivalence point were also made and gave almost exactly the same results. The potentiometric measurements were made with a voltage follower, a compensating voltage source and a recorder. Readings were taken when the electrodes were at equilibrium (maximum allowable drift 0·1 mV/min). The titration curves were very steep with a jump of several hundred mV, indicating the presence of a strong acid. Table II summarizes the results and shows that generation efficiency was almost 100%. The largest deviations were found at low current densities. An excess of acid was found in the solution at all current densities.

TABLE II.—CURRENT EFFICIENCY

Current density, $\mu A/mm^2$	Generated acid or base, *mmole*	Excess of acid generated, *μmole*	Error, %
10	2·584	11·90	$0·4_4$
20	4·406	6·19	$0·1_4$
30	7·031	9·99	$0·1_4$
40	3·072	2·75	$0·0_9$
50	3·840	2·85	$0·0_7$
60	4·735	6·30	$0·1_3$
70	5·136	4·35	$0·0_8$
80	5·452	4·49	$0·0_8$
90	5·634	6·16	$0·1_1$
100	7·157	7·69	$0·1_1$
110	8·516	5·36	$0·0_6$
120	2·97	0·87	$0·0_3$

To investigate the possible consumption of water in the cell reaction, samples of the solution were analysed by gas chromatography. This method was more sensitive than Karl Fischer titration. An Aerograph 202 chromatograph was used with a column of Porapak Q at 190°. The water content of the solution was found unexpectedly to increase linearly with time during electrolysis (Fig. 4).

Variation of the current density did not affect the rate of water formation ($K = 3·6 \times 10^{-6}$ mole.l^{-1}.sec^{-1} for similar platinum electrodes of 100 mm^2 surface area, the values calculated according to Janata and Mark[20]).

On reduction of the area of the cathode (to 25 mm^2), and with an anode area of 100 mm^2, the rate of formation of water was found to be $K = 1·6 \times 10^{-6}$ mole.l^{-1}.sec^{-1}, but still to be independent of current density even at very low current densities. Reduction of the anode surface area to 25 mm^2 with a cathode area of 100 mm^2 caused the rate of water formation to be dependent on the current density (Fig. 5). The rate of water formation thus seems to be dependent on the total platinum surface area rather than on the area of only one of the electrodes. The surface can probably be activated by electrolysis as shown by the increase in rate reported in Fig. 5.

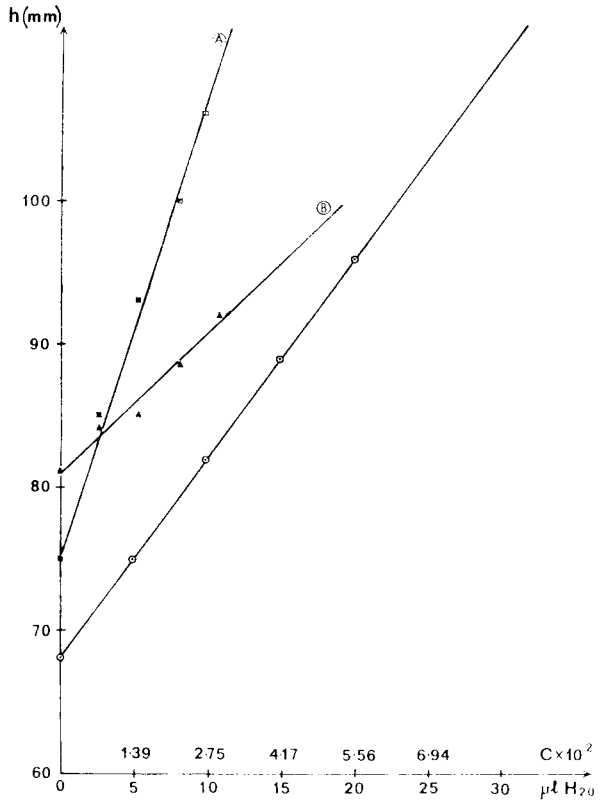

FIG. 4.—Peak height of water on a chromatogram plotted *vs.* the amount of water added (calibration curve ⊙) and *vs.* the amount calculated if 1 mole water had been found for each Faraday consumed.
Ⓐ anode area = cathode area = 100 mm²; Ⓑ anode area = 25 mm²; cathode area = 100 mm². Current 4·01 mA.

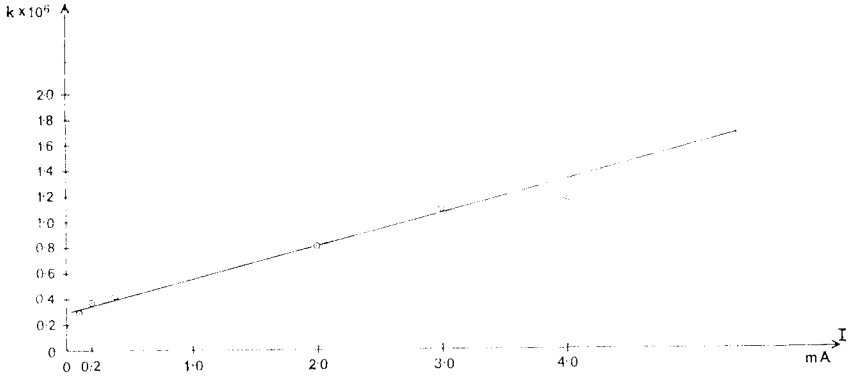

FIG. 5.—Rate constant of water formation as a function of current density. Cathode area = 100 mm², anode area = 25 mm².

DISCUSSION

When reactions (1) and (2) take place in the electrolysis cell, the net result is a decomposition of the solvent according to the reaction

$$(CH_3)_2C(H)(OH) \rightleftharpoons (CH_3)_2CO + H_2 \quad (3)$$

Formation of water arises from a chemical side-reaction which we assume to be

$$(CH_3)_2CO + 2(CH_3)_2CHOH \rightarrow (CH_3)_2C[OCH(CH_3)_2]_2 + H_2O$$

This ketal formation, a reaction known to be acid-catalysed, produces water.

As an electrochemical solvent isopropanol has several advantages. It has a larger accessible potential range than water and is well suited for voltammetry. The use of secondary alcohols avoids formation of acidic oxidation products, *i.e.*, carboxylic acids, which interfere with the acid-base system under investigation. Coulometric generation of reagents can be performed with high accuracy, which has been proved by titration of acids[10,11] and of bases (this report). A more accurate and direct test of current efficiency has also been made. The addition of water is not necessary in order to obtain quantitative generation of acid or base. Water is, however, formed spontaneously at the electrode in a side-reaction.

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Zusammenfassung—Der zugängliche Potentialbereich bei Isopropanol beträgt in nichtwäßriger 0,01 M LiCl-Lösung +1,1 bis −1,2 V gegen Ag/AgCl; an der Anode bildet sich Aceton, an der Kathode Wasserstoff. In einer Nebenreaktion bildet sich Wasser, wahrscheinlich durch Ketalbildung; das Ausmaß dieser Reaktion ist proportional zur Elektrodenfläche. Eine weitere Nebenreaktion an der Kathode ließ nach längerer Elektrolysendauer ein unlösliches Produkt entstehen. Die coulometrische Stromausbeute war gleichwohl sehr hoch (99,6–99,97%) und von der Stromdichte fast unabhängig. Die Ergebnisse weisen darauf hin, daß die Kathodenreaktion mit etwas kleinerer als der theoretischen Stromausbeute ablief.

Résumé—On a trouvé que le domaine de potentiel accessible de l'isopropanol est de +1,1 à −1,2 V par rapport à Ag/AgCl en LiCl 0,01*M* non aqueux, avec formation d'acétone à l'anode et d'hydrogène à la cathode. Il se forme de l'eau dans une réaction secondaire, probablement par formation de cétal, la vitesse étant proportionnelle à la surface d'électrode. Une autre réaction secondaire à la cathode forme un produit insoluble après électrolyse prolongée. L'éfficacité du courant coulométrique est néanmoins très élevée (99,6–99,97%) et presqu'indépendante de la densité de courant. Les résultats montrent que la réaction à la cathode se développe avec une efficacité de courant quelque peu inférieure à la théorie.

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INDIREKTE POLAROGRAPHISCHE BESTIMMUNGEN NACH KOMPLEXCHEMISCHEN VERDRÄNGUNGSREAKTIONEN

BESTIMMUNG DES ALUMINIUMS IN HALBLEITERMATERIALIEN

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(*Eingegangen am* 16. *April* 1970. *Angenommen am* 24. *Juli* 1970)

Zusammenfassung—Es wird eine indirekte Methode für die Bestimmung von Aluminium beschrieben, die auf der Bestimmung des Cadmiums beruht, das aus seinem ÄDTA-Komplex durch Aluminium verdrängt wird. Bei 80° wird das Gleichgewicht schnell erreicht, und nach Abkühlen wird die Lösung bei pH 4 polarographiert. Es können 0,1 μg/ml an der tropfenden Elektrode und 0,01 μg/ml Aluminium an der stationären Quecksilberelektrode bestimmt werden. Die Methode wird zur Bestimmung von Aluminium in Halbleiter-Galliumarsenid angewendet.

DIE DIREKTE POLAROGRAPHISCHE Bestimmung des Aluminiums ist wegen des stark negativen Reduktionspotentials kaum möglich. In saurer Lösung stört die Entladung der Wasserstoffionen die Bestimmung, in schwachsaurer bis neutraler Lösung schließt die Hydrolyse der Aluminiumsalze eine Bestimmung aus und Aluminate sind an der Tropfelektrode ohnehin inaktiv. Es wurden deshalb indirekte Bestimmungsmethoden erarbeitet, die auf den unterschiedlichen Reduktionspotentialen eines Aluminiumchelatkomplexes und des freien Komplexbildners beruhen. Als Komplexbildner wurden neben 8-Hydroxychinolin[1] vor allem Di-*o*-azoverbindungen[2] verwendet; der Reaktionsmechanismus wurde am Beispiel des Aluminiumkomplexes mit Solochromviolett RS von Holleck[3] genauer untersucht. Verschiedene Möglichkeiten der Aluminiumbestimmung durch Rücktitration eines ÄDTA-Überschusses mit Zink und Cadmium bei amperometrischer Endpunktsanzeige führten zum Versuch, Aluminium indirekt polarographisch zu bestimmen.

Prinzip der Methode

Ein Kation A bildet mit dem Komplexbildner Y den Komplex AY mit der Bildungskonstanten K_{AY}. Ein anderes Kation B bildet mit Y den Komplex BY, dessen Bildungskonstante K_{BY} ist. Wenn $K_{AY} \gg K_{BY}$ ist, verdrängt A das Kation B aus dessen Komplex nach der Gleichung

$$BY + A \rightarrow AY + B \qquad (1)$$

Die Gleichgewichtskonstante für diese Verdrängungsreaktion ist durch den Quotienten der Bildungskonstanten gegeben:

$$k = \frac{K_{AY}}{K_{BY}} . \qquad (2)$$

Ist A wegen seines stark negativen Reduktionspotentials polarographisch nicht bestimmbar, so kann es indirekt bestimmt werden, wenn es nach der Reaktion mit BY

die äquivalente Menge an B freigesetzt hat. B muß polarographisch gut bestimmbar sein; die Stufe von B muß ein deutlich positiveres Potential als die seines Komplexes BY haben. Das bedingt eine relative hohe Stabilität des Komplexes BY, dessen Konstante $K_{BY} > 10^6$ sein soll. Auch die Bestimmung sehr kleiner Konzentrationen von A setzt diese Mindestgröße von K_{BY} voraus, um zu große Blindwertstufen zu vermeiden, die durch einen zu hohen Dissoziationsgrad von BY auftreten würden.[4–9] Die Anwendung solcher Verdrängungsreaktionen zur indirekten polarographischen Analyse ist dabei nicht an die Bedingung $K_{AY} \gg K_{BY}$ gebunden. Durch die Gegenwart eines weiteren Komplexbildners X kann das Gleichgewicht (1) völlig zugunsten der Bildung von AY + B verschoben werden, wenn X nur mit B, nicht dagegen—oder nur in unbedeutendem Grade—mit A reagiert. Der Komplex BX muß polarographisch gut bestimmbar sein, seine Bildungskonstante muß wesentlich kleiner als die von BY sein, um die Stufenhöhe BX eindeutig bestimmen zu können. Auf diese Weise wurden Erdalkaliionen und Magnesium indirekt polarographisch bestimmt, indem Zink in ammoniakalischer Lösung durch Erdalkali- und Magnesiumionen aus seinem ÄDTA-Komplex verdrängt und polarographisch bestimmt wurde.[8,10]

Bestimmung des Aluminiums

Die Bestimmung beruht auf der Verdrängungsreaktion

$$CdY^{2-} + Al^{3+} \rightarrow AlY^{-} + Cd^{2+} \tag{3}$$

wobei als Komplexbildner Y^{4-} ÄDTA (Dinatriumsalz) verwendet wurde. Aus den thermodynamischen Bildungskonstanten ergibt sich im Gleichgewichtszustand ein Konzentrationsverhältnis $AlY^{-}:CdY^{2-}$ von weniger als 1:2. Zur Gleichgewichtsveränderung zugunsten der Bildung von AlY^{-} wurde die Reaktion in Acetatpufferlösung durchgeführt. Acetationen (ac) bilden mit Cadmiumionen komplexe Verbindungen des Typs $[Cd(ac)_x]^{2-x}$ für $1 \leqslant x \leqslant 4$. Vom Aluminium sind in den gegebenen Konzentrationen auch bei hoher Acetationenkonzentration keine entsprechenden Komplexe bekannt. Für das Gleichgewicht ergibt sich dann:

$$k' = \frac{K_{Al} \cdot \alpha_{Cd}}{K_{Cd} \cdot \alpha_{Al}} \tag{4}$$

wo α_{Al} und α_{Cd} Koeffizienten nach Schwarzenbach, sind die alle Nebenreaktionen dieser Ionen im Gleichgewicht berücksichtigen. Sie drücken die Konzentrationen aus, um die der Hilfskomplexbildner Acetat, sowie die OH^{-}-Ionen zur Bildung von Hydroxokomplexen mit ÄDTA konkurrieren.

pH-*Abhängigkeit des Verdrängungsgleichgewichts*

Aus Gleichung (4) geht hervor, daß sich die Konstante des Verdrängungsgleichgewichtes in dem Maße mit dem pH ändert, wie sich der Quotient α_{Cd}/α_{Al} mit dem pH ändert. Während die Bildung von Cadmiumhydroxokomplexen erst im alkalischen Bereich einsetzt, überlagert sich das Hydrolysegleichgewicht des Aluminiums dem Aluminium–ÄDTA-Gleichgewicht schon oberhalb pH 4 merklich. In Abb. 1 sind die Bildungsgleichgewichte der ÄDTA-Komplexe des Cadmiums und Aluminiums graphisch dargestellt. Kurve 3 der Abb. 1 zeigt die Bildungskonstante des Cadmium-ÄDTA-Komplexes in Acetatpufferlösungen, die aus polarographischen Konzentrationsmessungen bestimmt wurde. Die Differenz zwischen den Kurven 1 und 3

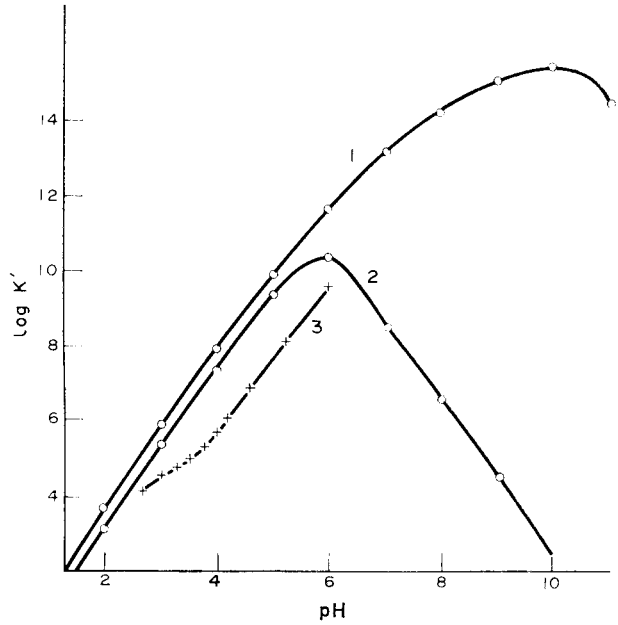

Abb. 1.—pH-abhängige Bildungskonstanten von Cd-ÄDTA (1), Al-ÄDTA (2)[2,11] und Cd-ÄDTA in Acetatlösungen (3).

entspricht dem Wert $\lg \alpha_{Cd}$, einer Größe, die der Bildung des Cadmiumacetatkomplexes entspricht.

Die Differenz zwischen den Kurven 2 und 3 ergibt nach Gleichung (4) den logarithmischen Wert für die Konstante des Verdrängungsgleichgewichts (Abb. 2). Der für die Verdrängungsreaktion günstigste pH-Bereich ist dadurch abgegrenzt: Bei pH $< 3{,}5$ ist die Bildung des Cadmiumacetat-Komplexes zu gering und die Dissoziation des Cadmium–ÄDTA-Komplexes zu hoch, um einen völligen Austausch zu bewirken, oberhalb pH 5 wird die Bildungskonstante des Aluminium–ÄDTA-Komplexes gegenüber der des Cadmium–ÄDTA-Komplexes zu klein. Da darüberhinaus die Verdrängungsreaktion mit steigendem pH langsamer verläuft, verbleibt für die Verdrängungsreaktion ein pH-Bereich von 3,5 bis 5,0.

Bestimmung der Konstanten des Verdrängungsgleichgewichts

Wird die Konzentration an vorgegebenem Cadmium-ÄDTA mit a und die zu bestimmende Aluminiumkonzentration mit b bezeichnet, so ergibt sich im Gleichgewicht

$$a = [CdY^{2-}] + [Cd^{2+}] \tag{5}$$

$$b = [AlY^{-}] + [Al^{3+}] \tag{6}$$

Da die Konzentration an Cd^{2+}-Ionen durch Verdrängung entstanden ist, gilt auch

$$[Cd^{2+}] = [AlY^{-}] = c \tag{7}$$

Für das Gleichgewicht (1) folgt dann

$$k' = \frac{K_{Al} \cdot \alpha_{Cd}}{K_{Cd} \cdot \alpha_{Al}} = \frac{c^2}{(a - c)(b - c)} \tag{8}$$

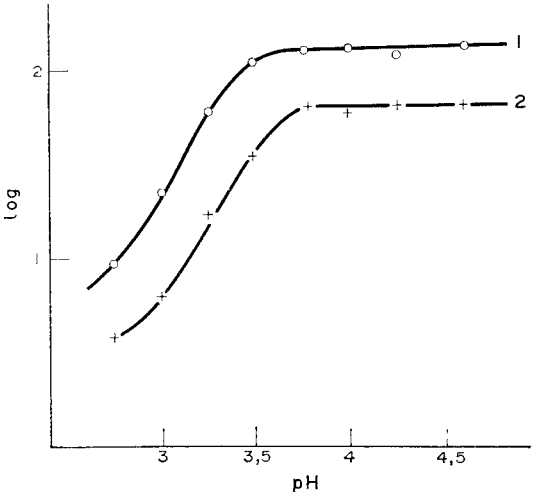

ABB. 2.—Kurve 1: pH-abbhängige Korrekturfunktion lg $\alpha_{Cd(ac)}$.
Kurve 2: Gleichgewichtskonstante der Verdrängungsreaktion unter den gegebenen Bedingungen (lg k).

Der Cd-ÄDTA-Überschuß wurde niedrig gehalten, um zu verhindern daß die Differenz $(b - c)$ in Gl. (8) zu klein wird. Die experimentell bestimmten Werte für k' bei verschiedenen Überschüssen an Cadmium–ÄDTA sind in Tabelle 1 zusammengefaßt, ihre Mittelwerte sind in Abb. 2 graphisch dargestellt. Sie stimmen mit den berechneten Werten im untersuchten pH-Bereich gut überein. Die Differenz lg α_{Cd} – lg k' ist im untersuchten Bereich konstant und zeigt dadurch, daß die Bildung von Aluminiumacetatkomplexen zu gering ist, um das Verdrängungsgleichgewicht merklich zu beeinflussen.

TABELLE I.—EXPERIMENTELL BESTIMMTE k-WERTE FÜR DAS VERDRÄNGUNGSGLEICHGEWICHT NACH GL. 8

pH	$a = 10^{-3}M$ $b = 4 \cdot 10^{-4}M$		$a = 6 \cdot 10^{-4}M$ $b = 4 \cdot 10^{-4}M$		$a = 5 \cdot 10^{-4}M$ $b = 4 \cdot 10^{-4}M$		$a = 4 \cdot 10^{-4}M$ $b = 4 \cdot 10^{-4}M$	
	10^4c	k	10^4c	k	10^4c	k	10^4c	k
2,75	3,50	3,77	3,10	3,68	2,90	3,64	2,62	3,61
3,25	3,80	11,62	3,55	11,43	3,38	11,41	3,10	11,75
3,5	3,92	31,66	3,80	32,8	3,68	32,0	3,40	32,1
3,75	3,96	64,8	3,89	65,3	3,80	60,0	3,55	61,6
4,0	3,96	64,8	3,90	71,9	3,81	64,2	3,56	65,4
4,25	3,96	64,8	3,89	65,3	3,81	64,2	3,56	65,4
4,6	3,96	64,8	3,89	65,3	3,81	64,2	3,57	68,7

Abhängigkeit des Verdrängungsgleichgewichts vom Cadmium–ÄDTA-Überschuß

Aus Abb. 2 ist ersichtlich, daß die Konstante des Verdrängungsgleichgewichts einen Maximalwert von etwa $k' = 65$ hat, den sie bei pH 3,8 erreicht. Bei einem zu geringen Überschuß an Cadmium–ÄDTA findet auch oberhalb pH 3,8 nur ein unzureichender Austausch statt. Für den Quotient $[AlY^-]/[Al^{3+}]$, der für die analytische Anwendung bedeutsam ist, folgt aus den Gleichungen (5) bis (8):

$$\frac{c}{(b-c)} = k' \frac{(a-c)}{c} = k'\left(\frac{a}{c} - 1\right). \qquad (9)$$

Bei einer weitgehenden Verdrängung wird $\lim_{c \to b} a/c = a/b$, $a/c - 1$ ist aber der Überschuß an vorgegebenem Cadmium–ÄDTA, der mit f bezeichnet, zur einfachen Beziehung führt:

$$\frac{[AlY^-]}{[Al^{3+}]} = \frac{c}{b - c} = k' \cdot f. \tag{10}$$

Für die Bedingungen der quantitativen Analyse muß $f \geqslant 2$ sein, die Konzentration an Cadmium–ÄDTA muß also größer als das Dreifache der zu bestimmenden Aluminiumkonzentration sein.

Temperaturabhängigkeit der Gleichgewichtseinstellung

Die Bildung des Aluminium–ÄDTA-Komplexes ist kinetisch gehemmt und verläuft erst bei erhöhter Temperatur genügend schnell und vollständig. Wie zu erwarten war, trifft das auch auf die vorliegende Verdrängungsreaktion zu (Abb. 3).

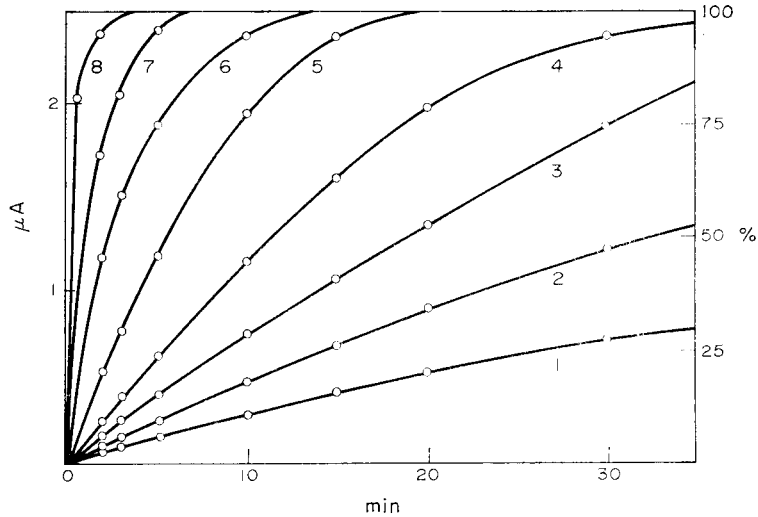

ABB. 3.—Zeitabhängigkeit der Verdrängungsreaktion bei verschiedenen Temperaturen.
1—30°C; *2*—40°C; *3*—50°C; *4*—60°C; *5*—70°C; *6*—80°C; *7*—90°C; *8*—100°C
Cd–ÄDTA: $10^{-3}M$, Al^{3+}: $3{,}6 \cdot 10^{-4}M$, pH 4,6.

Die Titration von Al^{3+}-Ionen mit ÄDTA zeigte, daß die direkte Bildung des Komplexes langsamer als die Verdrängungsreaktion verläuft, dagegen zeigt die Rücktitration eines ÄDTA-Überschusses einen schnelleren Ablauf der Komplexbildung als die Verdrängungsreaktion bei gleichem Überschuß. Mit steigendem Cadmium–ÄDTA-Überschuß erhöht sich die Geschwindigkeit der Verdrängungsreaktion (Abb. 4), bei steigendem pH wird sie vermindert.

EXPERIMENTELLER TEIL

Geräte

Gleichwechselstrompolarograph GWP 63 und Tropfzeitgeber TZG 1, beide Akademiewerkstätten Berlin; Kemula-Elektrode E 69, Radiometer Kopenhagen; pH-Meßverstärker MV 11, Meinsberg.

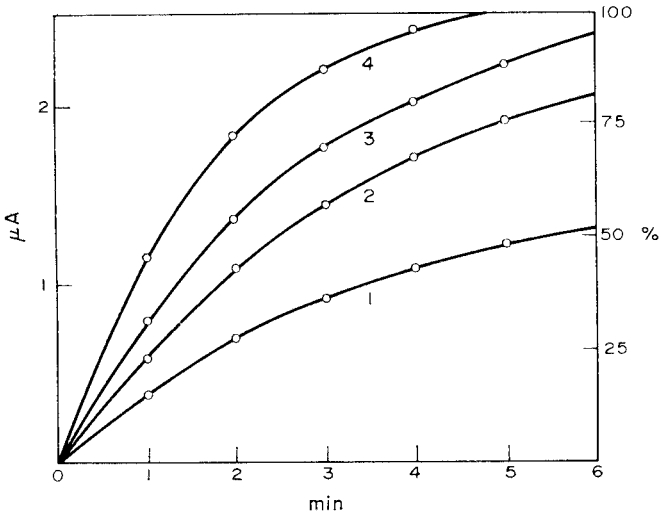

ABB. 4.—Zeitabhängigkeit der Verdrängungsreaktion bei verschiedenen Cd–ÄDTA-Konzentrationen:
1—$4 \cdot 10^{-4}M$; *2*—$10^{-3}M$; *3*—$2 \cdot 10^{-3}M$; *4*—$4 \cdot 10^{-3}M$; Al^{3+}: $3{,}6 \cdot 10^{-4}M$; 80°C; pH 4,6.

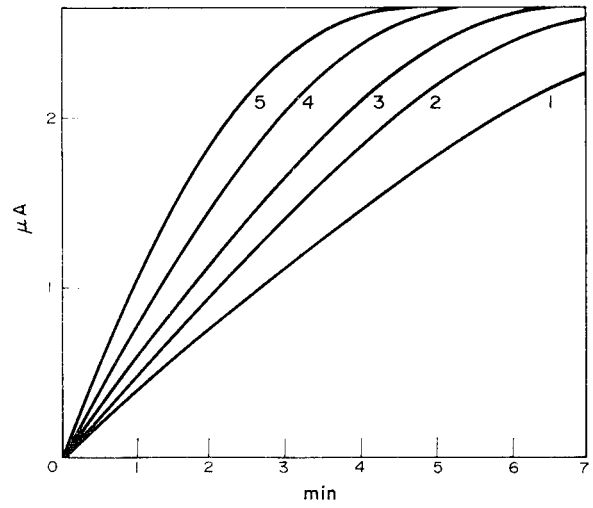

ABB. 5.—Zeitabhängigkeit der Verdrängungsreaktion bei verschiedenen pH-Werten.
1—5,6; *2*—4,6; *3*—4,25; *4*—3,75; *5*—3,25; Cd–ÄDTA: $2 \cdot 10^{-3}M$; Al^{3+}: $3{,}6 \cdot 10^{-4}M$; 80°C.

Reagentien und Lösungen

Cadmium–ÄDTA 0,01*M* in 0,5*M* Kaliumnitratlösung (Hergestellt aus Cadmiumnitrat (superrein), ÄDTA (Testal) und Kaliumnitrat *p.a.*). Die Genauigkeit der Äquimolarität lag bei 0,02%, Durch Verdünnung mit Kaliumnitratlösung wurden Lösungen geringerer Konzentration hergestellt.

Cadmiumnitrat 0,05*M* in 0,5*M* Kaliumnitratlösung *p.a.*

ÄDTA-Lösung 0,01*M*.

Aluminiumchloridlösungen verschiedener Konzentrationen durch Verdünnung einer 0,05*M* Lösung, deren Titer durch ÄDTA-Titration eingestellt wurde.

Pufferlösungen von Ammonium- und Natriumacetat/Essigsäure *p.a.*, die Gesamtacetatkonzentration war jeweils 2*M*.

Bestimmung der Konstanten des Verdrängungsgleichgewichts

Pufferlösungen mit den in Tabelle I aufgeführten Konzentrationen an Cadmium–ÄDTA und Al^{3+}-Ionen wurden 15 Minuten auf 80° erwärmt und nach Abkühlung polarographiert. Die Werte für $[Cd^{2+}]$ wurden aus den Eichkurven entnommen, die mit Cadmiumnitrat in den jeweils gleichen Pufferlösungen aufgenommen wurden.

Temperaturabhängigkeit der Verdrängungsreaktion

Eine Cadmium–ÄDTA-Lösung bestimmter Konzentration wurde in der bei konstanter Temperatur gehaltenen Meßzelle auf die Reaktionstemperatur gebracht (Genauigkeit $\pm$ 0,5°), dann wurde eine bestimmte Menge Al^{3+}-Lösung zugefügt und nach kurzer Durchmischung mit Stickstoff, bei konstantem Potential von $-1{,}0$ V gegen Bodenquecksilber das Polarogramm aufgenommen. Die in den Abbildungen 3 bis 5 aufgeführten Diffusionsströme sind um die Blindwertbeträge korrigiert. Sie wurden aus den Eichkurven entnommen, die bei der gegebenen Temperatur in den jeweils gleichen Pufferlösungen aufgenommen wurden. Zur Aufnahme der Eichkurven wurden Lösungen verwendet, in denen die Verdrängungsreaktion vollständig abgelaufen war.

Zur quantitativen Analyse

Aluminiumchloridlösungen (Gesamtaluminium 0,027 bis 0,27 mg) wurden in 100-ml Bechergläsern mit 10 ml Pufferlösung und 1 bis 5 ml 0,01*M* Cadmium–ÄDTA-Lösung versetzt, 10 Minuten erhitzt, nach Abkühlung mit der gleichen Pufferlösung auf 50 ml aufgefüllt. Dann wurden in der Meßzelle 10 ml dieser Lösungen 10 Minuten mit Stickstoff entlüftet und zwischen $-0{,}4$ und $-1{,}0$ V gegen Bodenquecksilber polarographiert. Die Stufe des Polarogramms hat ein Halbstufenpotential von $-0{,}62$ V (bezogen auf die gesättigte Kalomelelektrode). Jeder Lösung wurde ein Standardzusatz von Cadmiumnitrat zugesetzt, dann wurde erneut polarographiert. Die graphische Auswertung (Diffusionsstrom gegen Aluminiumkonzentration) zeigt eine Gerade, die von einer Cadmiumeichkurve (aufgenommen unter gleichen Bedingungen) um weniger als 1,5% abweicht. Nach der Standardzusatzmethode wurden Werte erhalten, die von den vorgelegten Aluminiumkonzentrationen um maximal 3% abweichen. Diese Versuche wurden mehrfach unter Veränderung des pH, der Reaktionsdauer und -temperatur, des Cadmium–ÄDTA-Überschusses sowie der Aluminiumkonzentrationen im Bereich $5 \cdot 10^{-6}$ bis $2 \cdot 10^{-3}M$ wiederholt.

Inversvoltammetrische Analyse

Es wurden 0,2 bis 2,5 ml einer $10^{-4}M$ Aluminiumchloridlösung mit 5 ml Pufferlösung (pH 4) und 1 bis 5 ml $10^{-4}M$ Cadmium–ÄDTA-Lösung versetzt und auf dem siedenden Wasserbad erhitzt. Dann wurde mit Ammoniumacetatlösung (Puffer hoher Kapazität) pH 6 eingestellt und nach dem Abkühlen, auf 25, 50 bzw. 100 ml aufgefüllt, so daß die Aluminiumkonzentration $2 \cdot 10^{-7}$ bis $10^{-5}M$ war, die Cadmium–ÄDTA-Konzentration wurde dadurch auf 10^{-6} bis $2 \cdot 10^{-5}M$ eingestellt. Zehn ml der jeweiligen Lösung wurden in der Meßzelle 10 Minuten mit Stickstoff entlüftet, wobei vor die Meßzelle eine Waschflasche mit dem Grundelektrolyten geschaltet war. Die Anreicherung fand bei $-0{,}9$ V (GSK) statt, die Elektrolysedauer wurde bei einer Elektrodenoberfläche von 3 bis 5 mm² zwischen 2 und 5 Minuten variiert. Die Rührgeschwindigkeit betrug 1200 U/min, der Potentiometervortrieb 0,4 V/min. Der Peak des Cadmiumblindwertes wurde jeweils am gleichen Quecksilbertropfen in analoger Lösung unter gleichen Bedingungen bestimmt. Im untersuchten Konzentrationsbereich ergab sich eine relative Standardabweichung von $\pm$10%.

ERGEBNISSE

Der nach der Verdrängungsreaktion gemessene Diffusionsstrom entspricht der Cadmiumkonzentration im Verdrängungsgleichgewicht. Er ist nach der Korrektur um den Blindwert der Aluminiumkonzentration im Bereich $5 \cdot 10^{-6}$ bis $10^{-3}M$ direkt proportional (Abb. 6). Die Größe des Blindwertes ist vom pH und der Cadmium–ÄDTA-Konzentration abhängig. Der Blindwert steigt bei Erniedrigung des pH und Erhöhung der Konzentration an. In Abb. 7 sind die bei vorgegebener Cadmium–ÄDTA-Konzentration bestimmten Cadmiumkonzentrationen in Abhängigkeit vom pH dargestellt; die gemessenen Werte stimmen mit den berechneten gut überein. Bei zu großem Cadmium–ÄDTA-Überschuß kann der Blindwert

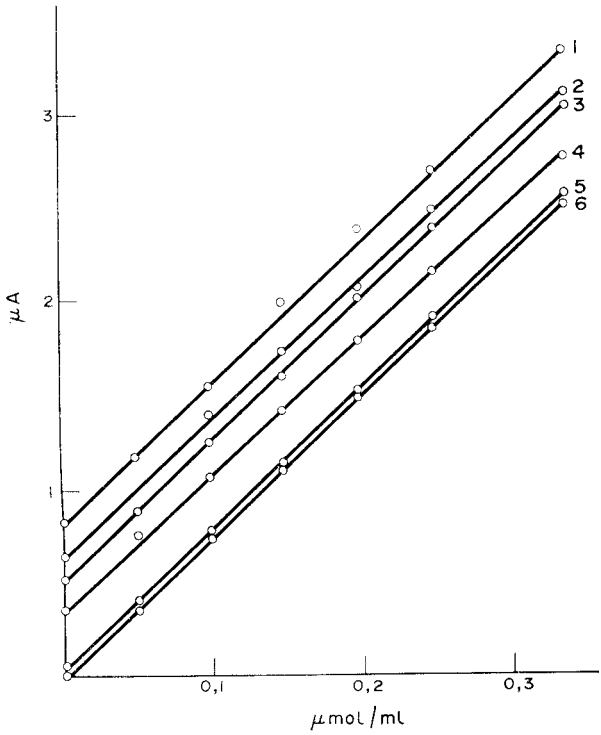

ABB. 6.—Aluminiumeichkurven bei verschiedenen pH-Werten und verschiedenen Cd–ÄDTA-Konzentrationen:
Cd–ÄDTA: $9 \cdot 10^{-4}M$; *1*—pH 3,25; *3*—pH 3,75; *5*—pH 4,6; *6*—pH 5,6
Cd–ÄDTA: $6{,}5 \cdot 10^{-4}M$; *2*—pH 3,25; *4*—pH 3,75.

wesentlich größer als der Meßwert sein; der Überschuß soll deswegen nicht größer als das 10 bis 20-fache der zu erwartenden Aluminiumkonzentration sein. Ein zu geringer Überschuß schränkt die lineare Proportionalität zwischen Diffusionsstrom und Aluminiumkonzentration ein (Abb. 6, Kurven 2 und 4). Für sehr geringe Aluminiumkonzentrationen ($c < 10^{-5}M$) muß die Diffusionsstrommessung bei höheren pH-Werten erfolgen, weil die Blindwerte des Komplexdissoziationsgleichgewichts zu groß werden. Da aber bei pH > 4,5 die Reaktionsgeschwindigkeit zu gering ist, wird die Verdrängungsreaktion bei pH 4 durchgeführt, das Polarogramm und bei pH 5 bis 6 aufgenommen. Überraschend ist die gute Reproduzierbarkeit der gemessenen Ströme bei pH > 5, denn es war zu befürchten, daß die Bildung polynuklearer Aluminiumhydroxokomplexe[12,13] mit ÄDTA das Verdrängungsgleichgewicht beeinträchtigt. Die Eichkurven für die polarographischen Bestimmung des Aluminiums zeigten einen Anstieg von 7,4 $\mu A \cdot \mu Mol^{-1}.ml$ mit Blindwerten von 0,0, 0,05, bzw. 0,16 μA bei pH 5,6, 4,6 und 3,75. Es ist somit möglich, an der tropfenden Elektrode eine Aluminiumkonzentration von 0,1 μg/ml und an der stationären Elektrode von 0,01 μg/ml zu bestimmen.

Arbeitsvorschrift für die Bestimmung des Aluminiums in Galliumarsenid

Galliumarsenid (1 bis 10 mg) wird in 2 bis 5 ml Salzsäure–Salpetersäure-Gemisch (3 : 1) gelöst, vorsichtig eingedampft und mit 5 bis 10 ml halbonzentrierter Salzsäure aufgenommen. Mit dem gleichen Volumen Methylisobutylketon wird zweimal im Scheidetrichter extrahiert, wobei das

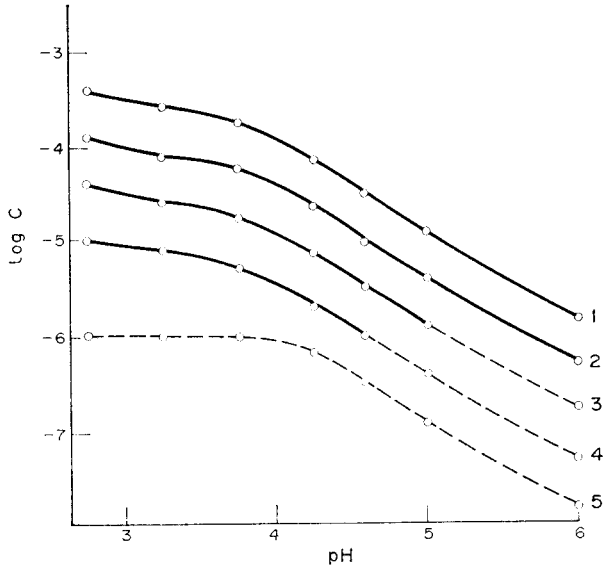

ABB. 7.—Cd^{2+}-Ionenkonzentration im Cd–ÄDTA-Komplexgleichgewicht in Acetatpufferlösungen.
Cd–ÄDTA-Konzentrationen: *1*—$10^{-2}M$; *2*—$10^{-3}M$; *3*—$10^{-4}M$; *4*—$10^{-5}M$; *5*—$10^{-6}M$.

Gallium quantitativ als Chlorogalliumsäure in die organische Phase geht. (Soll eine anschließende Galliumbestimmung erfolgen, so darf nach der Lösung des Galliumarsenids nicht eingedampft werden. Die klare Lösung wird nach Zugabe von 5 bis 10 ml Salzsäure sofort extrahiert.) Die wäßrige Phase wird eingedampft und in 2 ml 0,1*M* Salzsäure aufgenommen. Nach Hinzufügen von 1 bis 5 ml 0,01*M* Cadmium–ÄDTA-Lösung wird kurz zum Sieden erhitzt und mit Acetatpuffer (pH 4) versetzt. Nach dam Abkühlen wird die Lösung mit der gleichen Pufferlösung auf 10 bzw. 25 ml aufgefüllt. Ein aliquoter Teil wird in der Meßzelle 10 Minuten mit Stickstoff entlüftet und von −0,4 bis −1,0 V polarographiert. Die Aluminiumkonzentration wird aus einer Eichkurve entnommen, die mit Aluminiumchloridlösungen in gleicher Arbeitsweise aufgenommen wurde. Bei der Analyse geringfügig dotierten Galliumarsenids ist die Cadmium–ÄDTA-Konzentration entsprechend zu verringern. Vor der Aufnahme des Polarogramms wird die Lösung auf pH 5 bis 6 gebracht.

Für die inversvoltammetrische Bestimmung an der stationären Elektrode wird die Analysenprobe in gleicher Weise vorbereitet. Die Anreicherung findet bei −0,9 V (GSK) statt. Die Elektrolysedauer, Größe der Elektrodenoberfläche und Empfindlichkeit der Registrierung werden den vorhandenen Aluminiumkonzentrationen angepaßt, ebenso die Rührgeschwindigkeit und die Geschwindigkeit des Potentiometerablaufs den apparativen Möglichkeiten. Bei einer Ausgangsmenge von 10 mg Galliumarsenid können mit Hilfe dieser Methode 10^{-4}% Aluminium bestimmt werden.

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Summary—An indirect polarographic method is described for the determination of aluminium, based on the determination of cadmium displaced from its EDTA-complex by the aluminium. The exchange reaction is done at 80° so that equilibrium is reached rapidly, and the measurements are made on solution at pH 4. At the dropping mercury electrode, 0.1 μg of aluminium per ml can be determined, and by using inverse voltammetry at a stationary electrode, 0.01 μg/ml. The method has been applied to the estimation of aluminium in semi-conductor grade gallium arsenide.

Résumé—On décrit une méthode polarographique indirecte pour le dosage de l'aluminium, basée sur le dosage du cadmium déplacé de son complexe-EDTA par l'aluminium. La réaction d'échange est faite à 80°, de sorte que l'équilibre est atteint rapidement, et les mesures sont faites sur des solutions à pH 4. A l'électrode à goutte de mercure, on peut doser 0,1 μg d'aluminium par ml, et en utilisant la voltammétrie inverse sur électrode stationnaire, 0,01 μg/ml. On a appliqué la méthode à l'estimation de l'aluminium dans l'arséniure de gallium qualité semi-conducteur.

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EXTRACTIONS WITH LONG-CHAIN AMINES—III*

COLORIMETRIC DETERMINATION OF MOLYBDENUM AS THIOGLYCOLLATE

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Summary—A highly selective and sensitive colorimetric determination of molybdenum(VI) based on its extraction with a chloroform solution of trioctylamine from solutions of acetic and thioglycollic acid (TGA) is described. The yellow chloroform extract containing the molybdenum–TGA complex is measured at 370 nm. With a single extraction it is possible to determine small amounts of molybdenum in the presence of very large concentrations of almost all metals. Only bismuth, mercury and tungsten interfere.

THE YELLOW COLOUR formed by molybdenum(VI) with thioglycollic acid (TGA) was proposed by Will and Yoe[1] for colorimetric determination of molybdenum in aqueous solutions. The sensitivity of the reaction (0·15 ppm) is high but the method is unselective and cannot be used in the presence of copper, tin, nickel, cobalt, bismuth and higher concentrations of iron. In addition, close control of the amount of reagent added and of other conditions is necessary.

Solvent extraction of molybdenum with tributylammonium thioglycollate has been used by Ziegler and Horn[2], prior to gravimetric determination of molybdenum as lead molybdate. Busev and co-workers[3] used diphenylguanidinium thioglycollate for the extraction of molybdenum into an isopentanol–chloroform mixture and measured the absorbance at 400 nm. Ray and co-workers[4] have also used thioglycollic acid for the extraction of molybdenum from 1*M* hydrochloric acid into isopentanol.

We have found that the TGA–molybdenum complex is extracted very easily into chloroform solutions of high molecular-weight amines such as Aliquat and Alamine, practically without interference from very large concentrations of iron and other elements, with the exception of bismuth, mercury and tungsten. In addition the absorbance of the extract is stable and independent of the amount of added TGA; there is a pronounced absorption maximum at 370 nm.

EXPERIMENTAL

Reagents

A 0·05*M* solution of molybdenum was prepared by dissolution of 8·822 g of $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ in 1 litre of water, and standardized complexometrically.[5] A $5 \times 10^{-4}M$ solution was prepared by appropriate dilution.

A 5% solution of trioctylamine was prepared by dissolution of 50 g of Alamine 336-S (General Mills, Chemical Division, Kankakee, Illinois) in 1 litre of pure chloroform and used without further purification.

Other reagents such as 1*M* thioglycollic acid, 0·05*M* solutions of various metals, solids, and solutions of sodium chloride *etc*, were prepared from reagent-grade chemicals.

* Part II: Talanta 1971, **18**, 91.

RESULTS AND DISCUSSION

Absorption spectrum

Preliminary experiments have shown that the reaction of molybdenum with thioglycollic acid and the extraction of the product is very dependent on the acidity when various amounts of dilute sulphuric acid are used, whereas acidification of nearly neutral molybdenate solutions with glacial acetic acid is largely independent of the acid concentration. The explanation is relatively simple. Acetic acid is a weak acid and the hydrogen ion concentration varies roughly as the square root of the acid concentration. Because the pK is about 4·7, acetic acid of concentration between 1 and 6M will yield a pH of 2·2 $\pm$ 0·2. To achieve a similar control of pH with a strong acid such as sulphuric acid would need much more careful control. The measurements were made as follows: 2 ml of 5 $\times$ $10^{-4}M$ molybdenum were diluted with various amounts of acetic acid, 0·5 ml of 1M thioglycollic acid was added and the solution was diluted to 25 ml with water. After extraction with 5 ml of 5% Alamine solution by shaking for 2 min, the organic phase was filtered through dry filter paper into a 10-mm cell and the spectrum recorded between 350 and 500 nm. As seen from Fig. 1, a range of 5–10 ml of acetic acid in 25 ml of final solution is practically without effect on the absorption maximum at 370 nm. For further study, 5 ml of acetic acid in 25 ml of the solution were used.

The effect of TGA concentration was similarly investigated, and it was found

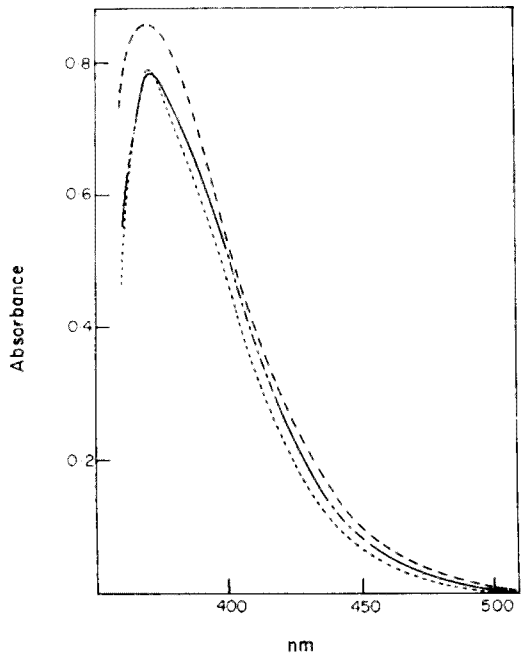

FIG. 1.—Absorption spectrum of molybdate—TGA complex.
2 ml of 5 $\times$ $10^{-4}M$ Mo(VI) + 1 ml of satd. Na_2SO_4 solution + 0·5 ml of 1M thioglycollic acid + x ml of glacial acetic acid, diluted to 25 ml and extracted with 5% solution of Alamine in chloroform. Measured in 10-mm silica cells after 1 hr.
CH_3COOH: ------ 0 ml; ····· 1 ml;
——— 5 ml; ·–·–·– 10 ml.

that 0·5–5·0 ml of 1 *M* TGA gave the same absorbance for a fixed amount of molybdate. The molar absorptivity was calculated to be $1{\cdot}95 \times 10^3$ l. mole^{-1}.mm^{-1}.

Unlike aqueous solutions,[1] the Alamine solution had an absolutely stable absorbance for at least 4 hr.

Influence of anions

Molybdenum was similarly determined in solutions containing various amounts of sodium chloride and fluoride, potassium acetate, dipotassium hydrogen phosphate, and EDTA. The results are summarized in Table I. The extraction is relatively sensitive to the presence of chloride and nitrate. Less than 1 % of sodium chloride, potassium nitrate and sodium fluoride is tolerable. EDTA and phosphate are without effect.

TABLE I.—INFLUENCE OF ANIONS ON MOLYBDENUM EXTRACTION

Added	*A*	Added	*A*
No salt added	0·780		
Satd. NaCl soln. 1 ml	0·790	0·05*M* EDTA 5 ml	0·782
2 ml	0·760	10 ml	0·780
5 ml	0·636	1*M* KNO_3 1 ml	0·780
10 ml	0·246	2 ml	0·776
4 % NaF soln 0·5 ml	0·763	5 ml	0·710
1·0 ml	0·730	K_2HPO_4 0·2 g	0 777
2·0 ml	0·685	0·5 g	0·782
5·0 ml	0·655	1·0 g	0·780

Influence of volume

Under otherwise optimal conditions molybdenum was extracted from various volumes of aqueous phase. For 2 ml of 5×10^{-4}*M* molybdenum in 25, 50, 100 and 150 ml of aqueous phase the absorbances of the extracts were 0·784, 0·782, 0·782, 0·780, showing that volumes of analysed sample between 25 and 150 ml had no effect on the extraction.

Determination of molybdenum in the presence of foreign metals

Large amount of salts of those elements which can interfere because of their reaction with thioglycollic acid were dissolved in a minimum amount of water or sulphuric acid, transferred into a 150-ml separatory funnel, mixed with 2 ml of 5×10^{-4}*M* molybdenum, neutralized if necessary, mixed with 1 ml of saturated sodium sulphate solution, 5 ml of glacial acetic acid and 5 ml of 1 *M* thioglycollic acid, diluted to 25–30 ml and extracted as before. Measurement was made in silica cells at 370 nm. Most elements (see Table II) did not interfere, but further explanation is needed for some, as follows.

On addition of TGA to a solution of molybdenum and iron the first few drops produce an intense blue colour which fades rapidly. Further addition of TGA finally leads to non-appearance of the blue colour, *i.e.*, all the iron has been reduced. After addition of 0·5 ml of 1*M* TGA in excess and neutralization of the solution, the procedure can be applied without interference. Vanadium(V) is also reduced by TGA, forming a blue compound which is partly extracted into the Alamine solution. Because this blue compound has maximum absorption at 600 nm it does not effect the

molybdenum measurement at 370 (Fig. 2). Only a small amount of vanadium is extracted and the aqueous phase remains intensely blue.

Chromate is reduced by TGA to green chromium(III), but a sufficiency of TGA must be added, and this makes the solution too acid for the molybdenum determination. It is therefore better to add the TGA first and then to neutralize the solution nearly to pH 7 with sodium hydroxide, make acid with 10 ml of glacial acetic acid, add 1 ml of saturated sodium sulphate solution, dilute to 50 ml, and extract with 10 ml of Alamine solution. It can happen that after this procedure a small amount of unreduced chromate is co-extracted into the Alamine solution and gives rise to a certain absorbance. It is recommended that the organic layer be separated into another funnel, 30 ml of water and 10 ml of acetic acid be added, and then TGA dropwise with shaking until the maximum green colour is achieved. The organic layer is then separated and measured as before.

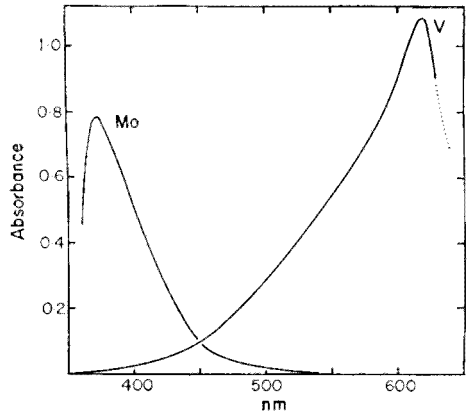

FIG. 2.—Absorption spectrum of 99·6 μg of Mo(VI) and 0·44 g of V(V) (1 g of NH_4VO_3). Procedure as for Fig. 1; solution contained 10 ml of glacial acetic acid per 25 ml.

Bismuth, tungsten and mercury interfere. Tungsten and larger amounts of lead can easily be removed by opening-out the sample by evaporation with sulphuric acid. Mercury can be volatilized from hydrochloric acid solutions. In special cases bismuth can be previously extracted with Alamine as the BiI_4^- complex or removed by other methods.

PRACTICAL APPLICATIONS

Determination of molybdenum in alloys

Dissolve a suitable amount of the sample in 10 ml of *aqua regia*. After dissolution is complete, add 1 ml of conc. sulphuric acid and evaporate to white fumes. Dilute somewhat, neutralize with potassium hydroxide nearly to pH 7, transfer the solution without filtration into a 100-ml volumetric flask, and dilute to the mark. Take an aliquot (5–20 ml) in a 150-ml separatory funnel, add 1 ml of saturated sodium sulphate solution and 1*M* thioglycollic acid as described before, and then 0·5 ml of the acid in excess. Neutralize the solution nearly to pH 7, add 5 ml of glacial acetic acid, dilute to around 25 ml, and extract with 5 ml of 5% Alamine solution. Measure in a 10-mm silica cell at 370 nm.

Some results of the analysis of two alloys which were available are given in Table III.

TABLE II.—DETERMINATION OF 99·6 μg OF MOLYBDENUM IN PRESENCE OF OTHER ELEMENTS

Compound added	Metal, *g*	Me:Mo	Absorbance
None	—	—	0·782
$FeNH_4(SO_4)_2.12H_2O$	Fe 0·407	4000	0·780
	Fe 2·09	21000	0·784
$CoCO_3$ + Ni dissolved in sulphuric acid	Co 0·99 Ni 1·00	9900 10000	0·776
Mg, Mn, Zn sulphates	Mg 0·09 Mn 0·23 Zn 0·22	900 2300 2200	0·779
$UO_2(C_2H_3O_2)_2.2H_2O$ + 1 ml of satd. NaCl soln.	U 0·540	5500	0·768
$K_2Cr_2O_7$	Cr 0·170 Cr 0·800	1800 8000	0·786 0·391*
NH_4VO_3	V 0·025 V 0·440	250 4500	0·787 0·782
Synthetic solution of 0·11 g Fe + 0·45 g Co + 0·5 g Ni + 0·09 g Mg + 0·27 g Cr	Total 1·420	14000	0·388*
Synthetic solution of 0·27 g U + 0·080 g Cr + 0·44 g V	Total 0·790	7900	0·390*

* Extracted into 10 ml of Alamine solution instead of 5 ml.

TABLE III.—DETERMINATION OF MOLYBDENUM IN ALLOYS.

Composition of the alloy, %	Weight of sample, *mg*	Aliquot from 100 ml,	Mo found, %	Mo present, %
Cr 12·76 Ni 14·07 W 2·68 Co 10·31 Nb 1·26 Al 0·11 Fe 55·13*	38	10 ml 5 ml	1·94 1·89	1·91
Co 65·30 Cr 27·10 Ni 3·44 Fe 1·20	33	10 ml 5 ml	2·78 2·65	2·75

* Contains also C 0·40, Si 1·04, P 0·01, S 0·016.

Acknowledgement—The authors wish to thank Mr. J. E. House (General Mills Inc. Minneapolis, U.S.A.) for providing Alamine 336-S.

Zusammenfassung—Eine sehr selektive und empfindliche Bestimmung von Molybdän(VI) wird beschrieben, die auf seiner Extraktion aus Essigsäure und Thioglykolsäure (TGA) enthaltenden Lösungen mit einer Lösung von Trioctylamin in Chloroform beruht. Der gelbe Chloroform-Extrakt, der den Molybdän-TGA-Komplex enthält, wird bei 370 nm gemessen. Mit einer einzigen Extraktion kann man kleine Molybdänmengen in Gegenwart sehr großer Konzentrationen fast aller Metalle bestimmen. Nur Wismut, Quecksilber und Wolfram stören.

Résumé—On décrit une détermination colorimétrique hautement sélective et sensible du molybdène(VI), basée sur son extraction par une solution chloroformique de trioctylamine de solutions d'acide acétique et thioglycolique (TGA). L'extrait chloroformique jaune contenant le complexe molybdène-TGA est mesuré à 370 nm. Avec une seule extraction il est possible de doser de petites quantités de molybdène en la présence de très grandes concentrations de presque tous les métaux. Seuls les bismuth, mercure et tungstène interfèrent.

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SHORT COMMUNICATION

Spektrophotometrische Untersuchung der Umsetzung von Wismut(III) mit Ascorbinsäure

(*Eingegangen am* 13. *Februar* 1970. *Angenommen am* 30. *Juni* 1970)

DURCH systematische spektrophotometrische Untersuchungen über die Fähigkeit der Ascorbinsäure, mit mehreren Elementen Komplexbildungen einzugehen, wurde festgestellt,[1,2] daß sie je nach dem pH-Wert in unterschiedlichem Grade die Absorption von Wismut(III) im Wellenlängenbereich 220–280 nm beeinflußt.

Die Entwicklung einer Methode zur Trennung von Uran als Ascorbinsäurekomplex am Amberlite IRA-400 beruht auf der Annahme,[3] daß Wismut(III) einen positiv geladenen gelben Komplex bildet, der am Anionenaustauscher nicht absorbiert wird.

Es wird ferner festgestellt,[4] daß Wismut(III) in 0,5*N* Ascorbinsäurelösung bei pH 4 einen Komplex bildet, dessen polarographische Stufe für analytische Zwecke sehr geeignet ist.

Da die angeführten Verfasser die Zusammensetzung und Stabilität des Komplexes nicht bestimmten, halten wir es für angebracht, diese Lücke auszufüllen und somit unser Wissen um die Umsetzung von Wismut(III) mit Ascorbinsäure zu vervollständigen.

EXPERIMENTELLER TEIL

Reagenzien und Apparatur

$Bi(ClO_4)_3$ erhielten wir durch Auflösen von metallischem Wismut (Reinheitsgrad 99,999%) in konz. Perchlorsäure. Verwendet wurde medizinische Ascorbinsäure (AS). Alle übrigen Reagenzien waren analysenrein. Die Ascorbinsäurelösungen wurden stets frisch bereitet.[5–9] Die angesetzte Ascorbinsäure wurde durch Titration mit Kaliumjodat in regelmäßigen Zeiträumen überprüft. Unter den nachstehend angegebenen Versuchsbedingungen sind die Ascorbinsäurekomplexe erwiesenermaßen bis 4 Stdn. nach ihrer Herstellung beständig.

Die Ionenstärke sämtlicher Lösungen hielten wir durch Zusatz der erforderlichen Menge an Natrium-perchlorat konstant ($\mu = 0{,}5$). Die Messung der pH-Werte der Lösungen erfolgte mittels Glaselektrode auf dem pH-Meter Seibold, Typ GV 53 ($\pm 0{,}05$ pH).

Die Extinktion wurde gegen Ascorbinsäurelösungen von geeigneter Konzentration oder doppeldestilliertes Wasser mit Hilfe der Spektrophotometer VSU-2p, VSU-1 und CO-4A (10-mm Kuvetten) gemessen.

ERGEBNISSE

Im Wellenlängenbereich 275–185 nm wurde die Extinktion von Wismut(III)- und Ascorbinsäurelösungen einzeln und im Gemisch aus beiden bei unterschiedlichen Konzentrationen und pH-Werten bestimmt. Die Ergebnisse stimmen mit den Aussagen in Zitat 2 überein. In diesem Spektralbereich liegen die Absorptions maxima von Wismut(III), Ascorbinsäure und dem Komplex, was die mathematische Auswertung der Versuchsergebnisse erschwert und unduns veranlaßte, vollständigere Untersuchungen auf den Bereich 295–400 nm, in dem Wismut(III) nicht absorbiert, einzuschränken.

In Abb. 1 sind die Spektren der reinen Ascorbinsäure und ihres Gemisches mit Wismut(III) für unterschiedliche pH-Werte dargestellt, die an den betreffenden Kurven durch Ziffern (für die Ascorbinsäure eingekreist) angegeben sind. Wie die Voruntersuchungen zeigten, ist der Komplexbildungsgrad in saurem Medium nicht hoch und bei pH > 5 deutet die Trübung der Lösungen auf die eingetretene Hydrolyse hin.

Zur Erforschung der Komplexverbindung wurden deren Absorptionsspektren im pH-Bereich 1–5, steigend um 1 pH, für Konzentrationen der Ausgangskomponenten aufgenommen, die sich, wie die Voruntersuchungen ergaben, als die geeignetsten erwiesen haben: $C_{Bi} = 1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$, $3 \cdot 10^{-4}$, $4 \cdot 10^{-4} M$; $C_{AS} = 0{,}03, 0{,}06, 0{,}09, 0{,}15, 0{,}18 M$. Für jede Wismut(III)-Konzentration in Anwesenheit von Ascorbinsäure wurden innerhalb des angegebenen Konzentrationsbereichs Spektren aufgenommen, die den in Abb. 1 dargestellten ähnlich sind.

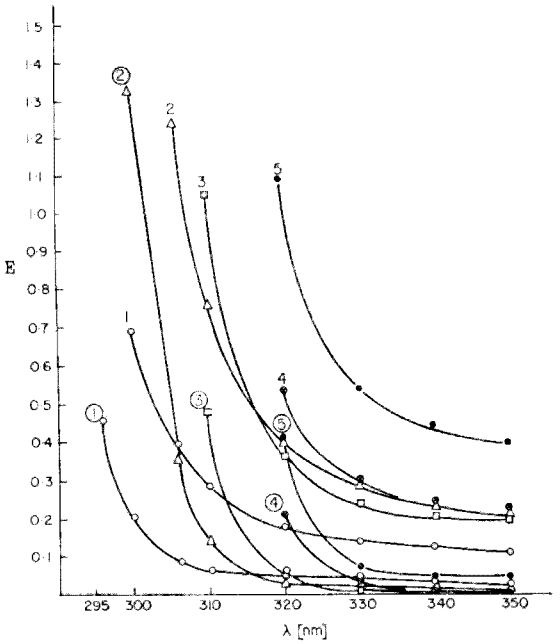

ABB. 1.—Absorptionsspektren von Wismut ($3 \cdot 10^{-4}M$) mit Ascorbinsäure ($0{,}015M$) und Lösungen reiner Ascorbinsäure derselben Konzentrationen. Die Kurven ①, ②, ③, ④, ⑤ beziehen sich auf die reine AS und *1*, *2*, *3*, *4*, *5* auf das Bi-AS-Gemisch; die Zahlen geben den pH-Wert der Lösungen an.

Auswertung der Ergebnisse

Wir nehmen an, daß Wismut(III) und AS einen Komplex mit der Allgemeinformel $Bi_q(AS)_n$ bilden. Nach Zitat 11 weist das Abhängigkeitsverhältnis $\log \Delta E/\log C_{Bi}$ auf die Einkernigkeit des Komplexes im gesamtem pH-Bereich hin. Zur Bestimmung der Anzahl (n) der im Komplex koordinierten AS-Moleküle wurde die Beziehung $\log \Delta E/(\varepsilon_n C_{Bi} - \Delta E)/\log C_{AS}$ bei unterschiedlichen Wellenlängen, pH-Werten der Lösungen und Wismutkonzentrationen untersucht. Die ermittelten Werte von ε_n (Extinktionskoeffizient) wurden in erster Näherung nach Zitat 12 berechnet. Die Diagramme der vorstehenden Beziehung stellen Geraden dar, deren Neigung für n Werte ergibt, die 1 naheliegen. Die Zusammensetzung des Komplexes entspricht demgemäß der Beziehung Bi/AS = 1:1. Die gesamte Bestimmung der Zusammensetzung erfordert auch die Ermittlung der Anzahl der im Komplexmolekül enthaltenen OH^-- und H^+-Ionen.[15] Nimmt man schlechthin an, daß

$$Bi^{3+} + jOH^- + iH^+ + A^{2-} \rightleftarrows Bi(OH)_j \cdot H_iA, \tag{1}$$

so ist die Gesamtstabilitätskonstante des Komplexes

$$\beta = \frac{[Bi(OH)_jH_iA]}{[Bi][A] \cdot K_w{}^j[H]^{(i-j)}}, \tag{2}$$

wo A^{2-} das Anion der Ascorbinsäure und K_w das Ionenprodukt des Wassers bedeuten.

Die konditionelle Stabilitätskonstante des Komplexes ist durch die nachstehende Beziehung bestimmt:

$$\beta' = \frac{[Bi(OH)_j \cdot H_iA]}{C_{Bi} \cdot C_{AS}}. \tag{3}$$

Aus (2) und (3) ergibt sich durch Einsatz der jeweiligen α-Koeffizienten der Nebenreaktionen die Gleichung

$$\beta = \frac{\beta' \cdot \alpha Bi(OH)\alpha A(H)}{K_w{}^j \cdot [H]^{(i-j)}} = \frac{\gamma}{K_w{}^j[H]^{(i-j)}}, \tag{4}$$

die in logarithmischer Form

$$\log \gamma = \log \beta \cdot K_w^j + (j - i)\,\mathrm{pH} \qquad (5)$$

den Zusammenhang zwischen dem pH und der Komplexzusammensetzung aufdeckt. Die Komplexverbindung weist nur dann eine konstante Zusammensetzung auf, wenn die zu bestimmende Größe $\log \gamma$ eine lineare Funktion von pH ist. Aus dem Abb. 2 ist der nichtlineare Charakter dieser Abhängigkeit mit einem deutlich ausgeprägten Minimum ersichtlich. Die Zusammensetzung der Komplexverbindung wechselt innerhalb des zu untersuchenden pH-Bereichs, und die Neigungen der Tangenten in den beiden Kurvenabschnitten sind es, die $(j - i)$ bestimmen.

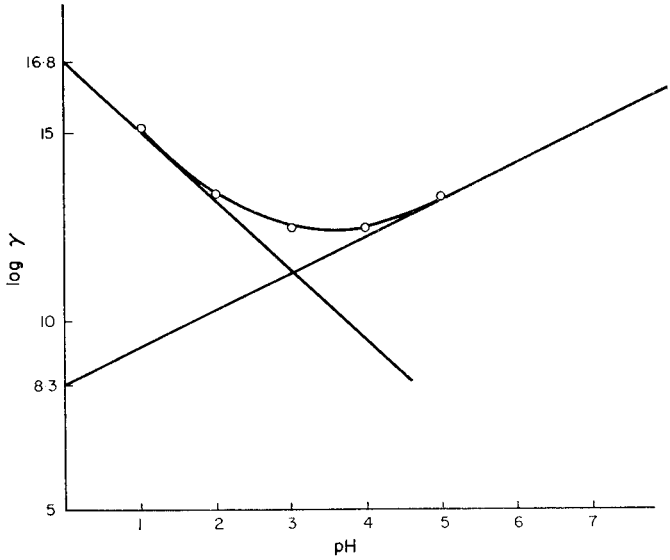

ABB. 2.—Abhängigkeitsverhältnis $\log \gamma$/pH.

Bei pH $< 2{,}0$, $(j - i) = -2$, infolgedessen ist $[BiH_2(H_2O)A]^{3+}$ die einfachste Formel für den in saurem Medium vorhandenen Komplex I.

Aus der Voraussetzung für das Minimum der Funktion (5) folgt, daß bei pH $\sim 3{,}0$, $i = j$. Bei diesem pH ist die möglichst einfache Zusammensetzung des Komplexes II: $[Bi(H_2O)A]^{+}$.

Für pH $> 4{,}0$ ist $(j - i) = 1$, was besagen will, daß die Anzahl der Wasserstoffionen um 1 kleiner ist als die der OH-Ionen im Molekül der Komplexverbindung III: $[Bi(H_2O)(OH)A]$.

Die konditionelle Stabilitätskonstante des Komplexes wurde für unterschiedliche Wellenlängen und pH-Werte nach einigen vorgeschlagenen Methoden[14–16] berechnet, wobei es sich herausstellte, daß man diese Konstante ohne systematischen Fehler, doch mit Streuungen nach den verschiedenen Methoden und innerhalb der Grenzen ein und derselben Methode, erhält. Aus diesem Grunde wurden die Versuchsergebnisse nach der Methode der kleinsten Quadrate[17] ausgewertet, wobei als unbekannt die konditionelle Stabilitätskonstante und der molare Extinktionskoeffizient des Komplexes gelten.

TABELLE I.—KONDITIONELLE STABILITÄTSKONSTANTEN

pH	Anzahl der konditionellen Gleichungen	λ, *nm*	β'	ε, $l.mole^{-1}.mm^{-1}$
1,0	6	310	13,4 ± 0,3	170
2,0	24	320	12,3 ± 0,7	192
3,0	24	320	22,0 ± 1,0	178
4,0	18	330	42,0 ± 2,0	120
5,0	6	350	55,0 ± 7,0	151

In der Tabelle sind die für unterschiedliche pH-Werte und Wellenlängen erhaltenen β'- und ε Werte wiedergegeben.

Die Bestimmung der gesamten Stabilitätskonstanten erfolgte anhand der Gleichung (4), wobei zur Berechnung der α-Koeffizienten Literaturangaben sowohl über die erste und zweite Dissoziationskonstanten der Ascorbinsäure als auch über die Hydrolysekonstanten für Bi-Ion herangezogen

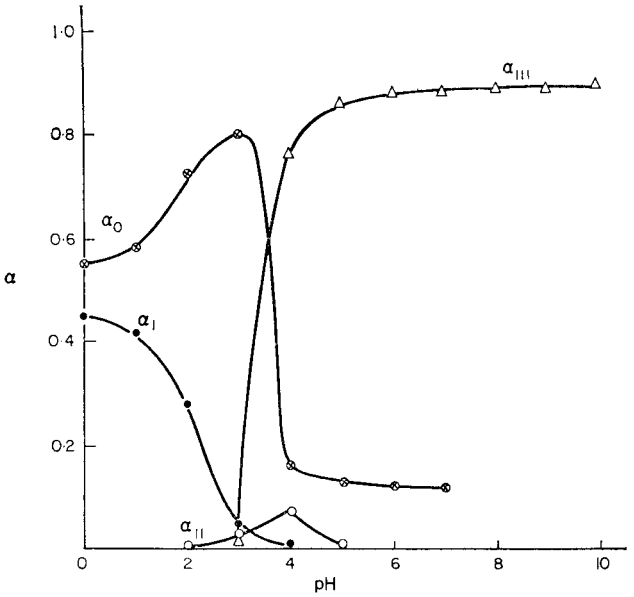

ABB. 3.—Verteilungskurven der Komplexe in Abhängigkeit vom pH des Mediums: α_0 von dem an AS nicht gebundenem Bi, α_I von $[BiH_2(H_2O)A]^{3+}$, α_{II} von $[Bi(H_2O)]^{+}$ und α_{III} von $[Bi(H_2O)OHA]$.

wurden.[18,19] Für log β der Komplexe I, II und III erhielt man: $\log\beta_I = 30{,}8$; $\log\beta_{II} = 25{,}3$; $\log\beta_{III} = 22{,}3$. Aus diesen Werten wurde der Bildungsgrad für jeden einzelnen Komplex bei unterschiedlichen pH-Werten berechnet. In Abb. 3 sind die Verteilungskurven der besagten Komplexe als Funktionen von pH dargestellt. Es ist daraus ersichtlich, daß in dem von uns untersuchten pH-Bereich im System die drei Komplexe annähernd die gleiche Konzentration aufweisen.

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Zusammenfassung—Die Bildung von Komplexen vom BA-Typ zwischen Wismut(III) und Ascorbinsäure im pH-Bereich 1–5 wurde bei spektrophotometrischen Messungen beobachtet. Eine pH-Änderung bewirkt eine Änderung der Anzahl von Protonen, die an den Komplex gebunden sind, sodaß drei Spezies im Gleichgewicht miteinander stehen: $[BiH_2O{\cdot}H_2A]^{3+}$, $[BiH_2O{\cdot}A]^{+}$ und $[BiH_2O{\cdot}OH{\cdot}A]$. Für diese Spezies wurden die Stabilitätskonstanten unter den einschlägigen Bedingungen ermittelt.

Summary—The formation of BA-type complexes between bismuth(III) and ascorbic acid in the pH range 1–5 has been observed from spectrophotometric measurements. A change in the pH results in a change in the number of protons attached to the complex, so that three species are in equilibrium: $[BiH_2O{\cdot}H_2A]^{3+}$, $[BiH_2O{\cdot}A]^{+}$ and $[BiH_2O{\cdot}OH{\cdot}A]$, for which conditional stability constants have been determined.

Résumé—On a observé, à partir de mesures spectrophotométriques, la formation de complexes de type BA entre le bismuth(III) et l'acide ascorbique dans le domaine de pH 1–5. D'une variation du pH résulte un changement dans le nombre de protons attachés au complexe, de sorte que trois espèces sont en équilibre: $[BiH_2O{\cdot}H_2A]^{3+}$, $[BiH_2O{\cdot}A]^{+}$ et $[BiH_2O{\cdot}OH{\cdot}A]$, pour lesquelles on a déterminé les constantes de stabilité conditionnelles.

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ANNOTATION

An analytical study of the vanadium(IV)–chromium(VI) reaction

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IT IS WELL KNOWN that for a reaction to form the basis of a quantitative procedure the equilibrium constant must be large enough and the reaction fast enough. The equilibrium constant of the reaction

$$6VO^{2+} + Cr_2O_7^{2-} + 2H^+ \rightleftharpoons 6VO_2^+ + 2Cr^{3+} + H_2O \quad (1)$$

calculated from the standard potentials[1] of the two half-cell reactions

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\circ = 1{\cdot}33\ V \quad (2)$$

$$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O \qquad E^\circ = 0.999\ V \quad (3)$$

is large enough ($K = 3{\cdot}6 \times 10^{33}$) to signify that the reaction takes place from left to right almost to completion. However, in practice, such a conclusion may sometimes be far from reality because the standard potentials used above in the calculation always refer to ideal conditions and never take into account the actual experimental conditions. A more meaningful and practical conclusion may be expected if formal potentials are used. The calculation of the equilibrium constant K' for the reaction

$$Cr(VI) + 3V(IV) \rightleftharpoons Cr(III) + 3V(V) \quad (4)$$

based on the formal potentials[2,3] of the two systems Cr(VI)/Cr(III) (1·08 V) and V(V)/V(IV) (0.99 V) in 1*N* sulphuric acid yields a value of $\times 3{\cdot}8 \times 10^4$ which corresponds only to about 90% oxidation of vanadium(IV) (K' must be $\sim 10^{12}$ for 99.9% reaction). Perhaps this kind of approach, with too much credence given to the reported formal potential of Cr(VI)/Cr(III), has been responsible for the analytical importance of the vanadium(IV)–chromium(VI) reaction being neglected so far.

Someya[4,5] appears to have been the first to attempt to use this reaction quantitatively. He first proposed and later discarded a method of oxidizing vanadium by potassium dichromate in sulphuric acid solution and titrating the vanadium with iron(II) sulphate, in hot solution, using diphenylamine as indicator. Although he also reports[6] that vanadium(IV) can be titrated with potassium dichromate, with diphenylamine as indicator, the method seems fallacious because the same indicator is used in titrations with vanadium(V) as oxidant under similar conditions of acidity. It is reported that although vanadium(IV) interferes with permanganate titration of iron(II) because of its oxidation to vanadium(V), it does not interfere and is *not* oxidized when dichromate is the titrant.[7] Recently a method of determining lower oxides of vanadium by reacting them with an excess of potassium dichromate or ferric alum in acid medium has been described.[8] The excess of dichromate is titrated with Mohr's salt or the iron(II) formed is titrated with dichromate. The authors, however, believe that even with excess of dichromate the lower oxides of vanadium are oxidized only to vanadium(IV). But in such determinations, even if vanadium(IV) is further oxidized to vanadium(V) by chromium(VI), the analytical result is unaffected because the iron(II) titration (visual or potentiometric) does not differentiate between chromium(VI) and vanadium(V) in the solution.

In a recent communication, Ottaway and Fuller[9] reported their investigation into the cause of errors in the determination of iron(III) by the tin(II) chloride–mercury(II) chloride–dichromate method when vanadium was present. The positive errors were originally believed to be due to the partial oxidation of vanadium(IV) to vanadium(V) in the titration. To show that this is not the source of error, these authors have undertaken a study of the influence of vanadium on the iron(II)–dichromate titration and made some interesting observations. They report that although partial oxidation of vanadium(IV) by chromium(VI) is thermodynamically feasible and certainly occurs to some extent, the potentiometric titration of a mixture of iron(II) and vanadium(IV) with potassium, dichromate gives a clear potential break at a volume within 0·1% of that for iron(II) alone. There is apparently no oxidation of vanadium(IV) before the indicator, barium diphenylaminesulphonate; changes colour, so the indicator indicates the iron(II) end-point accurately. But it is not known from their paper whether vanadium is without effect for thermodynamic or kinetic reasons. This paper seeks to resolve the point.

EXPERIMENTAL

Reagents

Potassium dichromate, 0·01*M*.

Cerium(IV) and vanadium(IV) sulphate solutions. Prepared and standardized as already described.[10]

Exploratory titrations

In potentrometric titrations, no sharp potential break was observed for either direct or reverse titrations (Fig. 1), and a derivative curve made no improvement since $\Delta E/\Delta V$ was nearly constant over a 1-ml range near the expected equivalence point. In the reverse titration potential equilibration was sluggish and there was a difference of at least 5–10 mV when the null-point was approached from opposite directions, but in general fairly stable potentials were obtained in 1–2 min after each addition of titrant. Both 0·5 and 1·0*N* sulphuric acid media were used. The total volume was adjusted to be about 25 ml at the equivalence point. The titration curve around the equivalence point was flatter when the dilution was higher, possibly indicating that the reaction was more incomplete under these conditions but the volume could not be reduced further if perfect electrical continuity in the cell was to be ensured.

Ferroin (E° 1·06 V) and *N*-phenylanthranilic acid (E° 1·08 V) were tried as indicators but as is to be expected from the potentials, were useless.

The alternative procedure of adding an excess of vanadium(IV) to chromium(VI) was adopted to

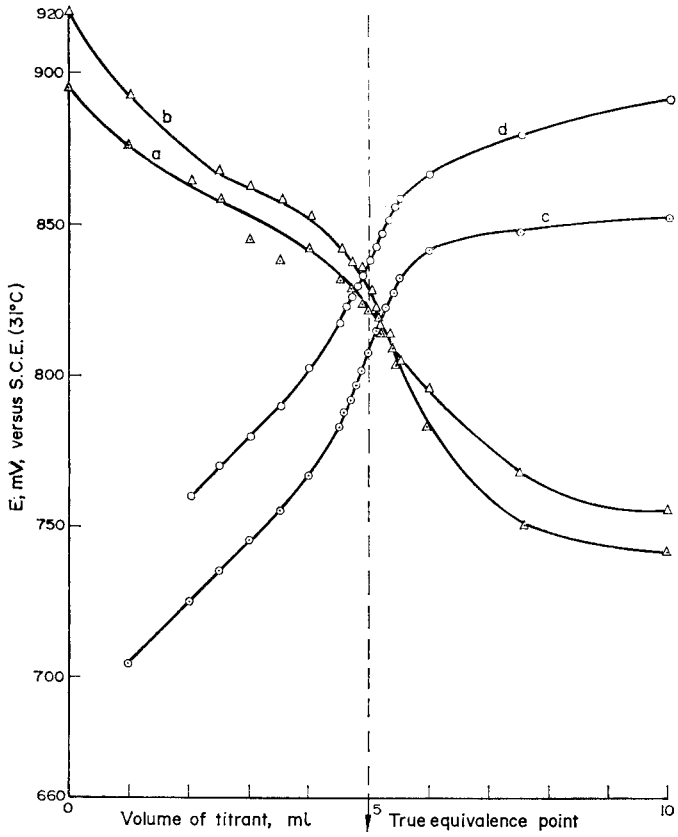

FIG. 1.—Potentiometric titrations with 0·0500*N* Cr(VI) or V(IV).
(a) 5 ml of 0·0500*N* Cr(VI) in ~20 ml of 0·5*N* H_2SO_4;
(b) 5 ml of 0·0500*N* Cr(VI) in ~20 ml of 1·0*N* H_2SO_4;
(c) 5 ml of 0·0500*N* V(IV) in ~20 ml of 0·5*N* H_2SO_4;
(d) 5 ml of 0·0500*N* V(IV) in ~20 ml of 1·0*N* H_2SO_4.

test whether the reaction really goes to completion. Since there is no simple titrimetric procedure in which vanadate is differentiated from dichromate, the unreacted vanadium(IV) was determined. The reaction of vanadium(IV) with permanganate in strong acid solution is slow at room temperature but quite rapid in hot solutions. However, the chromium(III) present in the mixture is increasingly oxidized by permanganate as the temperature rises above room temperature.[11] Under these conditions, titration at room temperature is inevitable and the end-point is usually less sharp. The other commonly used titrant for vanadium(IV) is cerium(IV) and the defects of this have been investigated by Rechnitz and Rao.[12] The potentiometric titration of vanadium(IV) with cerium(IV) sulphate[13,14] or with ferroin as indicator in 7·0–8·5*M* acetic acid medium[10] was found to give theoretically correct and consistent results. The latter titration was reported to be free from interference from chromium(III), and was therefore used to determine the unreacted vanadium(IV). It was found that even with a moderate excess of vanadium(IV) the reduction of chromium(VI) is complete in 2–5 min and the results are correct to within 0·2%.

Recommended procedure

To 4–10 ml of ~0·02*M* chromium(VI), add 10·00 ml of 0·10*N* vanadium(IV) sulphate in 1·0*N* sulphuric acid (previously standardized[10]), stir the mixture well and allow it to stand for 2–5 min. Add 20–25 ml of glacial acetic acid and dilute to about 50 ml, and titrate with cerium(IV) sulphate at room temperature, using 1–2 drops of 0·01*M* ferroin as indicator.

DISCUSSION

The large excess of vanadium might be thought to shift the equilibrium towards complete reaction, but during the back-titration with cerium(IV) the excess of vanadium(IV) is being removed and the equilibrium will shift back again if the reaction of vanadium(IV) and chromium(VI) is rapid and reversible. The implication is that the reaction is slow in one direction and fairly rapid in the other, so that a kinetic effect prevents reversal of the reduction of chromium(VI), during the time taken to back-titrate the vanadium(IV).

An alternative explanation is supplied by the work of Smith,[2,15] which shows that there is complete lack of symmetry in the potential curves for the direct and reverse titration of iron(II) with dichromate. It is therefore not correct to use the formal potential of the nearly irreversible Cr(VI)/Cr(III) system for calculation of the equilibrium constant of dichromate reactions. Further, the platinum electrode is known to respond sluggishly in dichromate systems, so the potential indicated may not be the true potential. The potential is also insensitive to changes in the concentration of chromium(III), and it is evident that this system is a peculiar one, the behaviour of which cannot be predicted from the formal potential. Based purely on thermodynamic considerations, a formal potential of 1·23 V is required for the system for completion (99·9%) of the reaction with vanadium(IV) when chemically equivalent amounts of the reactants are mixed in a 1*N* sulphuric acid medium.

In the light of this arguement, the observations of Ottaway and Fuller on the behaviour of vanadium in the iron(II)–dichromate titration after the iron(II) end-point, and the failure of the present author to achieve a direct or reverse titration of vanadium(IV) with dichromate may both be looked on as due to lack of proper response of the platinum electrode to the Cr(VI)/Cr(III) system, which results in no true potentials and no significant potential break at the end-point.

This explanation seems more attractive than the one based on an unusually slow rate for the vanadium(IV)–chromium(VI) reaction, but it implies that the reaction is sufficiently fast in the direct titration and is thermodynamically feasible, and that the whole difficulty lies in the methods used for locating the end-point. Similar reasoning applies to the visual or potentiometric titration of a mixture of chromate and vanadate with iron(II), the end-point being indicated for the total only.

However, when chemically equivalent amounts of the reactants were mixed and the extent of reaction was determined by titrating[10] the unreacted vanadium(IV), it was found that the reaction is 95% complete in about 5 min, and that there is not much further progress in the reaction even after 30 min more which would imply a thermodynamic reason for the failure of the direct titration. further experimentation showed that if the reaction mixture was kept for 24 hrs or heated for at least 30 min on a boiling water-bath, the reaction was 99·7 ± 0·1% complete. Furthermore, if a 100% excess of either reagent is used, the reaction 99·8% complete in 5 min. It therefore appears to be fairly certain that the reaction fails for kinetic reasons.

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Summary—Experimental conditions for reduction of chromium(VI) by vanadium(IV) are described. An excess of vanadium(IV) is necessary. The evidence indicates that the direct titration fails for kinetic rather than thermodynamic reasons, but that the back-titration procedure is made quantitative by the slow rate of the reverse reaction between vanadium(V) and chromium(III).

Zusammenfassung—Die Versuchsbedingungen zur Reduktion von Chrom(VI) mit Vanadium(IV) werden beschrieben. Ein Überschuß von Vanadium(IV) ist notwendig. Die Ergebnisse zeigen, daß die Titration eher aus kinetischen als aus thermodynamischen Gründen fehlschlägt; das Rücktitrationsverfahren geht jedoch quantitativ, da die Rückreaktion zwischen Vanadium(V) und Chrom(III) langsam verläuft.

Résumé—On décrit les conditions expérimentales pour la réduction du chrome(VI) par le vanadium(IV). Un excès de vanadium(IV) est nécessaire. L'expérience montre que le titrage direct ne marche pas pour des raisons cinétiques, plutôt que thermodynamiques mais que la technique de titrage en retour est rendue quantitative par la faible vitesse de la réaction inverse entre vanadium(V) et chrome(III).

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Talanta, 1971, Vol. 18, p. i. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Tables for Use in High Resolution Mass Spectrometry: R. BINKS, J. S. LITTLER and R. L. CLEAVER, Heydon, London, 1970. Pp. xx + 160, £10·80.

This is a collection of tables which will be of interest mainly to the practising mass spectrometrist and more specifically to those members of the group using a double focussing instrument of high resolving power. There are six separate tables which list the precise masses of ions containing carbon, fluorine and nitrogen, the mass ratios of such ions to ions of adjacent mass, the mass ratios of ions of such composition to those one mass unit higher and the characteristic mass spectral patterns produced by including within the ions polyisotopic hetero-atoms. There is also included with each collection a booklet containing additional tables. This permits the rapid identification of the atomic constitution of ions containing C, H, N and O from their measured precise mass. The introduction is written in English, in French and in German.

Chocolate, Cocoa and Confectionery: Science and Technology: BERNARD W. MINIFIE, Churchill, London, 1970. Pp. viii + 624. £6.

The chapter on quality control and the appendix on analytical methods will be of interest to most analysts; the whole book is a mine of information for food chemists, and at today's prices is remarkably good value.

Talanta, 1971, Vol. 18, p. iii. Pergamon Press. Printed in Northern Ireland

NOTICE

85th Annual Meeting of the Association of Official Analytical Chemists

This meeting will be held at Marriott Motor Hotel, Twin Bridges, Washington D.C. 20010, 11–14 October 1971 on the theme of methods of analysis for materials and products important to health and agriculture, *i.e.*, drugs, pesticides, foods, beverages, food additives, cosmetics, feeds, fertilizers, *etc.* Details may be obtained from L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington D.C. 20044.

Talanta, 1971, Vol. 18, p. iv. Pergamon Press. Printed in Northern Ireland

NOTE

It has been brought to our attention that the term "Kryptonates" used in the Talanta Review by Tölgyessy and Varga (*Talanta*, 1970, **17**, 659) is a registered trademark of Panametrics, Waltham, Massachusetts 02154, and should be used with a capital initial and in inverted commas.

SUMMARIES FOR CARD INDEXES

Titration curves in complexometric titrations with the redox system Fe(III)/Fe(II): ADAM HULANICKI and REGINA KARWOWSKA, *Talanta*, 1971, **18**, 239. (Institute of Chemistry, University, Warsaw, Poland.)

Summary—Potentiometric titrations of metal ions with EDTA have been carried out with a platinum or graphite electrode and the Fe(III)/Fe(II) redox system. In the absence of oxygen and for pH <2 the titration curves may be described by an equation similar to that given previously for titrations with silver and mercury electrodes. Titration curves for bismuth and indium, which are more strongly complexed than iron, are asymmetrical and useful for analytical purposes. When the titrated ions are complexed less strongly than iron(III) ions the kinetics of metal complexation have a pronounced effect. The titration curves of thorium and copper, which react more rapidly than iron, are analytically useful. The curves recorded rapidly after titrant additions have a better end-point break than those which correspond to thermodynamic equilibrium. When a metal, *e.g.*, nickel, is weakly bound by EDTA, and reacts more slowly than iron, a very small end-point break or none at all is observed.

An induction furnace for the determination of cadmium in solutions and zinc-base metals by atomic-absorption spectroscopy: J. B. HEADRIDGE and DAVID RISSON SMITH; *Talanta*, 1971, **18**, 247. (Department of Chemistry, The University, Sheffield, U.K.)

Summary—An induction furnace coupled to a Unicam SP90 atomic-absorption spectrophotometer is described for the determination of traces of volatile elements in solutions and volatile matrices. The apparatus has been used to obtain calibration graphs for 1–20 and 50–750 ng of cadmium in μl-volumes of solution, the 228·8 and 326·2-nm resonance lines respectively being used, and to determine cadmium in 5-mg samples of zinc-base metals within the concentration range 5–400 μg/g by using the less sensitive 326·2-nm line. A furnace temperature of 1350° was used. Data on accuracy and precision are presented. The apparatus could readily be used to determine trace elements in volatile materials at concentrations of 10–1000 ng/g.

Colour changes of chemical indicators—III. Colour specification and its accuracy: STANISLAV KOTRLÝ and KAREL VYTŘAS, *Talanta*, 1971, **18**, 253. (Department of Analytical Chemistry, College of Chemical Technology, Pardubice, Slov. povstání 565, Czechoslovakia.)

Summary—The systematic deviations involved in methods for computation of chromaticity co-ordinates have been studied for the specification of indicator colour changes. The weighted ordinate method ($\Delta\lambda$ = 10 nm) has proved to be satisfactory for evaluation both of C.I.E. and complementary co-ordinates. The C.I.E. colour specification should be included among basic data about chemical indicators.

КРИВЫЕ КОМПЛЕКСОНОМЕТРИЧЕСКИХ ТИТРАЦИЙ ОКИСЛИТЕЛЬНОВОССТАНОВИТЕЛЬНОЙ СИСТЕМОЙ Fe(III)/Fe(II):

ADAM HULANICKI and REGINA KARWOWSKA, *Talanta*, 1971, **18**, 239.

Резюме—Проведены комплексонометрические титрации ионов металлов с ЭДТА, с использованием платинового или графитового элекродов и окислительно-восстановительной системы Fe(III)/Fe(II). В отсутствии кислорода и при pH < 2 титрационные кривые можно описать при помощи уравнения, подобного уравнению данному для титраций с использованием серебрового и ртутного электродов. Титрационные кривые для висмута и индия, которые металлы образуют комплексы сильнее железа, имеют асимметрическую форму и ими можно пользоваться для анализа. В случае когда титрируемые ионы образуют комплексы слабее железа(III), кинетика комплексообразования показывает резко выраженное влияние. Титрационные кривые тория и меди, которые металлы реагируют быстрее железа, применимы в анализе. Кривые записанные быстро после добавления титрованного раствора показывают лучше выраженный конец титрования чем кривые соответствующее термодинамическому равновесию. В случае металла слабо связанного с ЭДТА и реагирующего медленнее железа—в том качестве никеля—получается только небольшой сгиб кривой в конце титрования или сгиб совсем не обнаруживается.

ИНДУКЦИОННАЯ ПЕЧЬ ДЛЯ ОПРЕДЕЛЕНИЯ КАДМИЯ В РАСТВОРАХ И МЕТАЛЛАХ НА ОСНОВЕ ЦИНКА МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

J. B. HEADRIDGE and DAVID RISSON SMITH, *Talanta*, 1971, **18**, 247.

Резюме—Описана индукционная печь, соединенная с атомно-абсорбционным спектрометром Юникам СП90, для определения следов летучих элементов в растворах и летучих веществах. Прибором пользовались для получения калибровочных кривых для 1–20 и 50–750 нг кадмия в микролитрах раствора, с использованием резонансных линий при 228,8 и 326,2 нм, и кадмия в 5 мг пробы металлов на основе цинка с использованием менее чувствительной линии при 326,2 нм. Температура печи была 1350°. Приведены данные для точности и воспроизводимости. Прибор может быть применен для определения следов элементов в летучих веществах при концентрациях 10–1000 нг/г.

ПЕРЕМЕНЫ ЦВЕТА ХИМИЧЕСКИХ ИНДИКАТОРОВ—III. СПЕЦИФИКАЦИЯ ЦВЕТА И ЕЁ ТОЧНОСТЬ:

STANISLAV KOTRLÝ and KAREL VYTŘAS, *Talanta*, 1971, **18**, 253.

Резюме—Изучены систематические ошибки обнаруживаемые в методах расчета координат хроматичности для спецификации перемены цвета индикаторов. Метод утяжелённой ординаты ($\Delta\lambda = 10$ нм) оказался удовлетворительным как для определения С.I.E. так и для определения дополнительных координат. Надо включить спецификацию цвета С.I.E. в основные данные химических индикаторов.

Comparison of a modified Kjeldahl and a vacuum fusion technique for determination of nitrogen in tantalum alloys: WARREN F. DAVIS, JUDSON W. GRAAB and EMERY J. MERKLE, *Talanta*, 1971, **18**, 263. (Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio, U.S.A.)

Summary—Results obtained for the determination of nitrogen in the tantalum alloys T-111 (Ta–8W–2Hf) and T-222 (Ta–10W–2·5Hf–0·1C) by Kjeldahl and vacuum fusion procedures are compared. Results obtained by each technique are shown for the determination of nitrogen in the MAB T-111 sample, two commercial T-111 samples and a commercial sample of T-222 alloy. In the 5–25 ppm range, the relative standard deviation was 3–9% by the Kjeldahl procedure and 4–8% by vacuum fusion. This is a measure of the homogeneity of the material as well as of the reproducibility of the results. The agreement of the results obtained by these two techniques increases confidence in the vacuum fusion results for nitrogen in tantalum.

Polarographische Bestimmung von Beryllium mit *o*-(2-Hydroxy-5-methyl-phenylazo) benzoesäure: E. BLASIUS, K.-P. JANZEN and W. FALLOT-BURGHARDT, *Talanta*, 1971, **18**, 273. (Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 6600 Saarbrücken, BRD.)

Summary—Beryllium can be determined polarographically in aqueous methanol solutions as its complex with *o*-(2-hydroxy-5-methylphenylazo)benzoic acid. As little as 10^{-9} mole/ml can be determined. Aluminium interferes when present in a molar concentration five times that of the beryllium or greater, though larger amounts may be separated by using a chelate-exchanger based on *o*-(hydroxyphenylazo)-benzoic acid.

Extraction of tungsten with 8-hydroxyquinoline and some of its derivatives: K. AWAD, N. P. RUDENKO, V. I. KUZNETSOV and L. S. GUDYM, *Talanta*, 1971, **18**, 279. (Institute of Nuclear Physics, Moscow State University, Moscow, U.S.S.R.)

Summary—The extraction of tungsten by chloroform solutions of 8-hydroxyquinoline(**I**), 2-methyl-8-hydroxyquinoline(**II**), 5,7-dibromo-8-hydroxyquinoline(**III**) and 8-mercaptoquinoline(**IV**), as a function of the concentration of tungsten and reagent and the acidity of the aqueous phase, has been studied. Evidence was obtained for the quantitative extraction of tungsten over a wide range of acidity. The degree of extraction of tungsten at $10^{-5}M$ concentration with **I**, **III** and **IV** gives two maxima when plotted against acidity. The extraction maximum for the more acidic solutions lies in the region where the reagents exist in the protonated form and its position depends on the reagent used. It is suggested that different tungsten complexes are extracted, depending on the acidity of the aqueous phase.

СРАВНЕНИЕ ИЗМЕНЕННОГО МЕТОДА КЬЕЛДАЛЯ С МЕТОДОМ ПЛАВЛЕНИЯ В ВАКУУМЕ ДЛЯ ОПРЕДЕЛЕНИЯ АЗОТА В СПЛАВАХ ТАНТАЛА:

WARREN F. DAVIS, JUDSON W. GRAAB and EMERY J. MERKLE, *Talanta*, 1971, **18**, 263.

Резюме—Сравнены результаты полученные в определении азота в сплавах тантала Т-111 (Ta-8W-2Hf) и Т-222 (Ta-10W-2,5Hf-0,1C) методами Кьелдаля и плавления в вакууме. Результаты полученные каждым из методов для определения азота приведены для образца МАБ Т-111, двух коммерческих образцов Т-111 и для одного коммерческого образца сплава Т-222. В области 5–25 мкг/г относительная стандартная ошибка составляла 3–9 % для метода Кьелдаля, а 4–8 %—для метода плавления в вакууме. Это представляет собой меру как для гомогенности материала так и для воспроизводимости результатов. Согласность полученных этими методами результатов повышает поверие в результаты, полученные методом плавления в вакууме для азота в тантале.

ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ БЕРИЛЛИЯ *о*-(2-ОКСИ-5-МЕТИЛФЕНИЛАЗО) БЕНЗОЙНОЙ КИСЛОТОЙ:

E. BLASIUS, K.-P. JANZEN and W. FALLOT-BURGHARDT, *Talanta*, 1971, **18**, 273.

Резюме—Бериллий определен полярографическим методом в водных растворах метанола в форме его комплекска с *о*-(2-окси-5-метилфенилазо) бензойной кислотой. Метод позволяет определять до 10^{-9} молей/мл. Алюминий мешает определению если присутствует в пятикратной или больше молярной концентрации бериллия. Большие количества можно отделять с использованием хелатообменника, основывающегося на *о*-(оксифенилазо) бензойной кислоте.

ИЗВЛЕЧЕНИЕ ВОЛЬФРАМА 8-ОКСИХИНОЛИНОМ И НЕКОТОРЫМИ ИЗ ЕГО ПРОИЗВОДНЫХ:

K. AWAD, N. P. RUDENKO, V. I. KUZNETSOV and L. S. GUDYM, *Talanta*, 1971, **18**, 279.

Резюме—Изучено извлечение вольфрама растворами в хлороформе 8-оксихинолина (I), 2-метил-8-оксихинолина (II), 5,7-дибромо-8-оксихинолина (III) и 8-меркаптохинолина (IV), в зависимости от концентрации вольфрама и реагента и кислотности водной фазы. Полученные данные указывают количественное извлечение вольфрама в широком диапазоне кислотностеи. Степень извлечения вольфрама при концентрации $10^{-5}M$ с I, III, и IV дает два максимума в зависимости от кислотности. Максимум извлечения для более кислых растворов находится в области в которой реагент существует в протонированной форме и его положение зависит от использованного реагента. Это объясняется извлечением различных комплексов вольфрама, в зависимости от кисолотности водной фазы.

Differential thermal analysis of transitions in finely-divided solids suspended in liquid media: D. A. BLACKADDER and T. L. ROBERTS, *Talanta*, 1971, **18**, 287. (Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge.)

Summary—The experimental difficulties associated with differential thermal analysis (DTA) are reviewed. Quantitative work has always required calibration of the equipment, and conventional solid diluents have serious disadvantages. It is shown that calibration is not strictly necessary, given appropriate conditions. Dilute suspensions of polymer crystals in organic liquids provide ideal media for DTA when used as diluent and as reference material. Convection currents are suppressed and the medium can support fine particles of the solid under test, even when the solid has a relatively high specific gravity. The new theory and techniques have been tested experimentally by measuring the heats of fusion of two inorganic salt hydrates. The results are in excellent agreement with literature values. A novel arrangement with a double thermocouple junction is shown to have considerable potentialities as a means of making precise measurements quite simply.

An indirect atomic-absorption method for the determination of selenium: HERBERT K. Y. LAU and PETER F. LOTT, *Talanta*, 1971, **18**, 303. (Department of Chemistry, University of Missouri-Kansas City, Missouri 64110, U.S.A.)

Summary—Because of the difficulty in determining selenium directly, an indirect atomic-absorption method has been developed, based on two selective reactions that lead to the formation of the $Pd(DanSe)_2Cl_2$ complex and measurement of the palladium absorption. Reaction conditions, separation techniques, effect of foreign ions, instrumental conditions and sample analysis in the sub-ppm range are described. The method is more sensitive than existing atomic-absorption methods for selenium.

Photometric complex-formation titrations of submicromole amounts of metals in the presence of an approximately equivalent amount of indicator: J. KRAGTEN, *Talanta*, 1971, **18**, 311. (Natuurkundig Laboratorium, Universiteit van Amsterdam, The Netherlands.)

Summary—The photometric titration of the metal indicator complex MI with a ligand L is discussed. A tangent procedure is adopted for the determination of the end-point. From this procedure, in combination with an assumed maximum titration error, titration conditions have been derived. A procedure is introduced which, in conjunction with the derived titration conditions, permits the selection of a suitable titration medium by means of a diagram in which log K, log α and log χ are plotted *vs.* pH. The procedure is applied to determination of lead and zinc in the presence of citric acid, the medium used for their paper-electrophoretic separation. The use of citric acid introduces some limitations; it is shown that the method developed is generally applicable.

ДИФФЕРЕНЦИАЛЬНЫЙ ТЕРМИЧЕСКИЙ АНАЛИЗ ПРЕВРАЩЕНИЙ В ПОРОШКОВИДНЫХ ТВЁРДЫХ ВЕЩЕСТВАХ, СУСПЕНДИРОВАННЫХ В ЖИДКИХ СРЕДАХ:

D. A. Blackadder and T. L. Roberts, *Talanta*, 1971, **18**, 287.

Резюме—Обсуждены экспериментальные затруднения в связи с дифференциальным термическим анализом (ДТА). Применение метода в количественном анализе всегда изыскивало калибровку прибора, а твёрдые разбавители имеют серьёзные недостатки. Показано что не совсем нужно провести калибровку в подходящих условиях. Разбавленные суспензии кристаллов полимеров в органических жидкостях оказались совершенными средами для ДТА если они использованы в качестве разбавителя и эталонного вещества. Конвекционные токи подавлены, среда может поддерживать мелкие частицы испытуемого вещества, даже в случае большого удельного веса этого вещества. Новая теория и методы испытаны экспериментальным путем, измерением теплот плавления гидратов двух неорганических солей. Результаты находились в отличном согласии с опубликованными данными. Показано что новый способ, включающий двойное соединение термопар, имеет хорошие возможности для несложного выполнения прецизионных измерений.

КОСВЕННЫЙ МЕТОД АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ ДЛЯ ОПРЕДЕЛЕНИЯ СЕЛЕНА:

Herbert K. Y. Lau and Peter F. Lott, *Talanta*, **18**, 1971, 303.

Резюме—Непосредственное определение селена трудно, потому разработан косвенный метод атомно-абсорбционной спектрометрии, основывающийся на двух селективных реакциях, ведущих к образованию комплекса $Pd(DanSe)_2Cl_2$ и измерению поглощения палладия. Описаны условия реакции, методы разделения, влияние посторонних ионов, условия прибора и анализ проб содержащих субмикрограммовые количества селена. Метод является более чувствительным чем настоящие методы атомно-абсорбционной спектрометрии для селена.

ФОТОМЕТРИЧЕСКИЕ-КОМПЛЕКСООБРАЗУЮЩИЕ ТИТРАЦИИ СУБМИКРОМОЛЕВЫХ КОЛИЧЕСТВ МЕТАЛЛОВ В ПРИСУТСТВИИ ПРИБЛИЗИТЕЛЬНО ЭКВИВАЛЕНТНОГО КОЛИЧЕСТВА ИНДИКАТОРА:

J. Kragten, *Talanta*, 1971, **18**, 311.

Резюме—Обсуждено фотометрическое титрование комплекса металла с индикатором MI лигандом L. Процедура на основе тангенса применена для определения конца титрования. Условия титрации выработаны из этой процедуры и предположенной максимальной ошибки титрации Предложена процедура которая, вместе с выработанными условиями титрации, позволяет отобрать подходящую титрационную среду, пользуясь диаграммой показывающей $\lg K$, $\lg \alpha$ и $\lg \chi$ в зависимости от pH. Метод применен в определении свинца и цинка в присутствии лимонной кислоты—среды использованной при разделении методом электрофореза на бумаге. Использование лимонной кислоты вводит некоторые ограничения; показана общая применимость разработанного метода.

Chromatographic separation and colorimetric determination of gold: JAMES S. FRITZ and WILLIAM G. MILLEN, *Talanta*, 1971, **18**, 323. (Department of Chemistry and Institute for Atomic Research, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Gold(III) is selectively sorbed from 1*M* hydrochloric acid by a short column containing a special acrylate resin. Then the gold is eluted from the column with acetone–hydrochloric acid, and the absorbance of the effluent is measured at 340 nm. Gold(III) may be successfully separated and determined in samples containing many other metal ions.

Electrochemical behaviour of isopropanol at platinum electrodes: A. REHIOUI and G. JOHANSSON, *Talanta*, 1971, **18**, 329. (Department of Analytical Chemistry University of Umeå, 901 87 Umeå, Sweden.)

Summary—The accessible potential range of isopropanol was found to be from +1·1 to −1·2 V *vs.* Ag/AgCl in non-aqueous 0·01*M* LiCl, with acetone being formed at the anode and hydrogen at the cathode. Water was formed in a side-reaction, probably by ketal formation, the rate being proportional to the electrode area. Another side-reaction at the cathode produced an insoluble product after prolonged electrolysis. The coulometric current efficiency was nevertheless very high (99·6–99·97%) and almost independent of current density. The results indicate that the cathode reaction proceeded with somewhat less than theoretical current efficiency.

Indirekte polarographische Bestimmungen nach komplexchemischen Verdrängungsreaktionen: Bestimmung des Aluminiums in Halbleitermaterialien: KARL SCHÖNE, *Talanta*, 1971, **18**, 339. Sektion Chemie der Karl-Marx-Universität, Leipzig, DDR.)

Summary—An indirect polarographic method is described for the determination of aluminium, based on the determination of cadmium displaced from its EDTA-complex by the aluminium. The exchange reaction is done at 80° so that equilibrium is reached rapidly, and the measurements are made on solution at pH 4. At the dropping mercury electrode, 0.1 μg of aluminium per ml can be determined, and by using inverse voltammetry at a stationary electrode, 0·01 μg/ml. The method has been applied to the estimation of aluminium in semi-conductor grade gallium arsenide.

ХРОМАТОГРАФИЧЕСКОЕ ОТДЕЛЕНИЕ И КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЗОЛОТА:

JAMES S. FRITZ and WILLIAM G. MILLEN, *Talanta*, 1971, **18**, 323.

Резюме—Золото(III) сорбируется селективно из 1*M* соляной кислоты на краткой колонке наполненной специальной акриловой смолой. Золото элюируют из колонки смесью ацетона и соляной кислоты и измеряют светопоглощение элюата при 340 нм. Метод позволяет успешно отделять и определять золото(III) в образцах, содержащих многочисленные другие ионы металлов.

ЭЛЕКТРОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ ИЗОПРОПАНОЛА НА ПЛАТИНОВОМ ЭЛЕКТРОДЕ:

A. REHIOUI and G. JOHANSSON, *Talanta*, 1971, **18**, 329.

Резюме—Определенный диапазон напряжения изопропанола составляет +1,1 до −1,2 *В* в сравнении с Ag/AgCl в неводном растворе 0,01*M* LiCl, с образованием ацетона на аноде и водорода на катоде. Вода образуется в результате побочной реакции, вероятно путем образования кетала, а скорость реакции пропорциональная площади электрода. Другая побочная реакция на катоде дала нерастворимый продукт после длительного электролиза. Однако кулонометрическая эффективность тока была очень высокая (99,6–99,97 %) и почти независима от плотности тока. Полученные результаты указывают что реакция на катоде поступает с эффективностью тока, до некоторой степени ниже чем теоретической.

КОСВЕННЫЕ ОПРЕДЕЛЕНИЯ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ, ОСНОВЫВАЮЩИЕСЯ НА РЕАКЦИЯХ ЗАМЕЩЕНИЯ КОМПЛЕКСОВ: ОПРЕДЕЛЕНИЕ АЛЮМИНИЯ В ПОЛУПРОВОДНИКАХ:

KARL SCHÖNE, *Talanta*, 1971, **18**, 339.

Резюме—Описан косвенный полярографический метод определения алюминия, основывающийся на определении кадмия, вытесненного алюминием из его комплекса с ЭДТА. Реакция замещения проведена при 80° для быстрого получения равновесия, а измерения выполнены в растворах при pH 4. Использование капельного ртутного электрода позволяет определить 0,1 мкг/мл алюминия, а применение обратной вольтамперометрии на стационарном электроде—0,01 мкг/мл. Метод применен в определении алюминия в арсениде галлия полупроводниковой чистоты.

Extractions with long-chain amines—III. Colorimetric determination of molybdenum as thioglycollate: R. PŘIBIL and J. ADAM, *Talanta*, 1971, **18**, 349. (Analytical Laboratory, Heyrovský Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—A highly selective and sensitive colorimetric determination of molybdenum(VI) based on its extraction with a chloroform solution of trioctylamine from solutions of acetic and thioglycollic acid (TGA) is described. The yellow chloroform extract containing the molybdenum–TGA complex is measured at 370 nm. With a single extraction it is possible to determine small amounts of molybdenum in the presence of very large concentrations of almost all metals. Only bismuth, mercury and tungsten interfere.

Spektrophotometrische Untersuchung der Umsetzung von Wismut(III) mit Ascorbinsäure: N. ELENKOVA, Č. PALAŠEV and L. ILČEVA, *Talanta*, 1971, **18**, 355. (Lehrstuhl für analytische Chemie, Höheres chemisch-technologisches Institut, Sofia 56, Bulgaria.)

Summary—The formation of BA-type complexes between bismuth(III) and ascorbic acid in the pH range 1–5 has been observed from spectrophotometric measurements. A change in the pH results in a change in the number of protons attached to the complex, so that three species are in equilibrium: $[BiH_2O{\cdot}H_2A]^{3+}$, $[BiH_2O{\cdot}A]^{+}$ and $[BiH_2O{\cdot}OH{\cdot}A]$, for which conditional stability constants have been determined.

An analytical study of the vanadium(IV)–chromium(VI) reaction: K. SRIRAMAM, *Talanta*, 1971, **18**, 361. (Department of Chemistry, Andhra University Postgraduate Centre, Guntur-5, Andhra Pradesh, India.)

Summary—Experimental conditions for reduction of chromium(VI) by vanadium(IV) are described. An excess of vanadium(IV) is necessary. The evidence indicates that the direct titration fails for kinetic rather than thermodynamic reasons, but that the back-titration procedure is made quantitative by the slow rate of the reverse reaction between vanadium(V) and chromium(III).

ЭКСТРАКЦИИ С АМИНАМИ С ДЛИННОЙ ЦЕПЬЮ—III. КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МОЛИБДЕНА В ФОРМЕ ТИОГЛИКОЛАТА:

R. Přibil and J. Adam, *Talanta*, 1971, **18**, 349.

Резюме—Описан высокоизбирательный и чувствительный метод определения молибдена(VI), основанный на его экстракции раствором триоктиламина в хлороформе из растворов уксусной или тиогликоленой кислотах (ТГК). Хлороформовый экстракт желтого цвета, содержащий комплекс молибдена с ТГК измеряют при 370 нм. Только одная экстракция позволяет определять небольшие количества молибдена в присутствии больших концентраций практически всех металлов. Только висмут, ртуть и вольфрам мешают определению.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ РЕАКЦИИ ВИСМУТА(III) С АСКОРБИНОВОЙ КИСЛОТОЙ:

N. Elenkova, Č. Palašev and L. Ilčeva, *Talanta*, 1971, **18**, 355.

Резюме—Обнаружено на основе спектрофотометрических измерений образование комплексов висмута(III) с аскорбиновой кислотой типа BA в области pH 1–5. Перемена pH вызывает перемену числа протонов связанных с комплексом. Этим образом три комплекса находятся в равновесии: $[BiH_2O{\cdot}H_2A]^{3+}$, $[BiH_2O{\cdot}A]^{+}$ и $[BiH_2O{\cdot}OH{\cdot}A]$, для которых определены условные константы стабильности.

АНАЛИТИЧЕСКОЕ ИЗУЧЕНИЕ РЕАКЦИИ ВАНАДИЯ(IV)—ХРОМА(VI):

K. Sriramam, *Talanta*, 1971, **18**, 361.

Резюме—Описаны экспериментальные условия восстановления хрома(VI) ванадием(IV). Нужно иметь избыток ванадия(IV). Данные указывают что непосредственное титрование не удавнется вследствие термодинамических лучше чем кинетических причин, но что метод оттитровывания избытка количественный только вследствие медленной оборотной реакции ванадия(V) с хромом(III).

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