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PART II

Mixtures of amines can be separated by elution chromatography on cation-exchange resins loaded with nickel ions or other cations capable of forming amine complexes. The cations are complexed with ammonia beforehand, and amine molecules exchange with ammonia molecules as ligands. Aqueous ammonia is used as the eluant. The method has proved particularly effective for separating diamines.

J. J. LATTERELL AND H. F. WALTON,
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Anal. Chim. Acta, 32 (1965) 191–194.

SEPARATION OF AMINES BY LIGAND EXCHANGE. PART II*

J. J. LATTERELL AND H. F. WALTON
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(Received June 14th, 1964)

The term "ligand exchange" was introduced by HELFFERICH[1] to describe the exchange of electron-donating ligands coordinated to metal ions held by a cation-exchange resin. He showed that ammonia molecules coordinated with ions of nickel and copper in a resin could be exchanged reversibly for molecules of an amine, and that such exchanges could be used for column separations. He recovered 1,3-diamino-2-propanol from a dilute aqueous solution containing ammonia by passing the solution through a column of cation-exchange resin loaded with nickel–ammonia complex ions. The diamine was selectively adsorbed from the dilute solution, but could displaced by passing concentrated aqueous ammonia. Two ammonia molecules displaced one diamine molecule, so that the displacement was favored by high concentration[2].

Ligand exchange has the practical advantage that one equivalent of resin can bind up to 3 moles of ammonia or amine: $(RSO_3)_2Ni(NH_3)_6$. By varying the nature of the metal ions and the functional groups of the resin many variations in selectivity should be possible. For ligand exchange to be practical, however, the metal ions must be held fast by the resin and not displaced by the ammonium ions in the aqueous ammonia solutions used as eluants. HELFFERICH used a carboxylate resin, arguing that the carboxyl groups of the resin bind Ni(II) and Cu(II) more strongly than sulfonate ions of a sulfonic acid resin. This has the drawback, however, that the capacity of the metal ions to bind ammonia or amine molecules is reduced by their coordination with the $-COO^-$ groups of the resin.

In a preliminary report[3] we described the application of ligand exchange to elution chromatography. Experiments were made with sulfonated polystyrene resins using silver(I) as the metal ion. Displacement of silver from the resin by aqueous ammonia was excessive, so these tests were abandoned. (We later found that the cation-exchange displacement of $Ag(NH_3)_2^+$ could be greatly reduced by using isopropanol as the solvent.) Nickel(II), on the other hand, was strongly held; the concentration of nickel(II) eluted by passing 1 *M* ammonia through a column of nickel-loaded 8%-crosslinked sulfonated polystyrene resin hardly exceeded 1 mg/l. Using a column of this resin we separated benzylamine and pyridine by elution. We studied several ligand exchange distributions by equilibrium shaking tests. Hydrazine and 1,2-diamines were held very strongly.

This paper describes a continuation of this work.

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* Part I, see reference 3.

EXPERIMENTAL

Materials

Most of the experiments were done with sulfonated crosslinked polystyrene cation-exchange resins, Dowex-50W, 50–100 mesh, with various degrees of crosslinking (8% unless otherwise specified). These were obtained from the Bio-Rad Corporation, as were two other resins, Bio-Rex 70, with functional carboxyl groups, and Bio-Rex 63, with functional phosphoric acid groups. The amines used were purified by distillation, except for ethylenimine, which was supplied by the Dow Chemical Company and used as received, and certain ^{14}C-labelled amines.

Columns

The columns used had diameter 0.7–1 cm and bulk bed volume about 10–15 ml. Flow rates were 0.2–0.5 ml/min. A Vanguard fraction collector (siphon type) was used. In many experiments the ammonia solutions used as eluants were passed through a small column of strong-base anion-exchange resin just ahead of the main column in order to remove carbonate.

Equilibrium shaking tests

A number of equilibrium distributions were measured by shaking weighed quantities of resins with measured volumes of aqueous solutions containing amines and ammonia, and analyzing the solution after shaking for 8 h or more. Because of analytical difficulties and the fact that the resin compositions were found by difference from the solution compositions, these results were not very accurate.

Analytical methods

A major difficulty in studying and using ligand exchange is that of detecting and measuring small concentrations of amines in the presence of relatively high concentrations of ammonia (about 1–5 *M*). The following methods were used in this study.

(*a*) *Ultraviolet absorption*, for aromatic amines; piperazine and piperidine can also be determined, but ammonia interferes significantly[4].

(*b*) *Absorption, in the visible region, by copper(II) complex.* This was applicable to 1,2- and 1,3-diamines. A small, measured amount of copper sulfate solution was added, and the absorbance measured in a 5-cm cell at 475–500 mμ ,where the copper–diamine complexes absorb considerably more strongly than the copper–ammonia complex. The diamine complexes are much more stable than the ammonia complex, and it is possible to measure 10^{-3} *M* ethylenediamine in 1 *M* ammonia.

(*c*) *Reaction with potassium 1,2-naphthoquinone-4-sulfonate.* This reagent forms red colored compounds with ethylenimine and certain primary and secondary amines[5,6]. Ammonia reacts with the reagent too, but the amine adducts are selectively extracted with chloroform. Thus 10^{-4} *M* ethylenimine could be easily detected in 1 *M* ammonia.

(*d*) *Flame photometry.* In an oxygen–hydrogen flame, amines produce C-H and C-N emission bands with a peak intensity at 388 mμ. Ammonia gives a little emission too, and the method is not as sensitive as one wishes, but 0.02–0.05 *M* amines could be detected in 1 *M* ammonia.

(*e*) *Liquid scintillation counting*, using ^{14}C-labelled amines. Obviously this is only of value as an exploratory method. Amines studied in this way were ethylenediamine, ethanolamine and dimethylamine. Difficulties were experienced with the adsorption of amines on glass (at low ammonia concentrations) and the influence of ammonia on the counting efficiency.

Infrared absorption in the 1–2 μ region was investigated but was not sufficiently sensitive. Longer wavelength infrared was also studied using calcium fluoride cells, but again the sensitivity was inadequate.

Expression of data

The distribution of amines between the resins and aqueous ammonia solutions was expressed by two numbers, as follows:

$$D = \left(\frac{\text{amount of amine in resin}}{\text{amount of amine in solution}}\right) \text{ per unit column segment}^{7}$$

$$\lambda = \left(\frac{\text{amine in resin}}{\text{NH}_3 \text{ in resin}}\right) \times \left(\frac{\text{NH}_3 \text{ in solution}}{\text{amine in solution}}\right)$$

These two quantities are related as follows: $\lambda = D \cdot \dfrac{\alpha[\text{NH}_3]}{cn}$

where α = void fraction of packed column; c = mmoles metal ions per ml packed column; and n = mmoles NH_3 per mmole metal ion. The quantity D is directly and simply related to the elution volume for trace amounts of amine in a column. It equals the number of void column volumes that must pass by the peak of the band to elute it from the column[7].

The *void fraction*, α, is in a sense fictional. For uniform, close-packed, impermeable spheres it equals 0.39, but it is impossible to evaluate *a priori* in this case, since dissolved ammonia does penetrate the resin beads to some extent. The numerical value of D calculated from the elution volume depends inversely on the value of α chosen, but α cancels again when λ is calculated, except for the one void column volume that is swept out by the front of the eluant as it passes down the column. Formally a value $\alpha = 0.4$ was used in this work.

The quantity c is determined analytically. It was about 1.07 for the nickel-loaded, 8%-crosslinked polystyrene resin used in this work.

The quantity n would equal 6 for this nickel-loaded resin if the nickel ions were fully coordinated and if the proportion of amine were very small. In 1 *M* aqueous ammonia, n for nickel ions[8] is 5.3. For simplicity a value of 6 was used throughout this work for nickel-loaded sulfonated polystyrene resin.

RESULTS

Binding of ammonia by metal ions in cation-exchange resins

Previous work by one of us[9] had shown that metal–ammonia complexes in sulfonic acid resins were just as stable as they were in aqueous solutions. In carboxylic acid resins the complexes were less stable, by one or two powers of ten, but there was no evidence of a decreased maximum coordination number. In view of HELFFERICH's suggestion[1,2] that the carboxylate groups of the resin "blocked" two of the coordination sites of the metal ions we repeated these experiments over a wider concentration range. The formation curves obtained with copper(II) and ammonia in sulfonic, carboxylic and phosphoric resins are shown in Fig. 1. It will be noted that the maximum coordination number in the carboxylic resin is still 4, though all formation constants are less by a factor of 20 than they are in water. In the phosphoric resin the maximum coordination number may well be reduced to 2.

One or two tests were made with a commercial zirconium phosphate exchanger. Here the mole ratio of coordinated ammonia to nickel(II) was about 2 in 1 *M* ammonia. Contrary to our earlier report[3], these exchangers do not release significant phosphate ions into 1 *M* ammonia. The first tests were made with a bad batch of material.

Experiments with ammonium-form resins

The simplest kind of ligand exchange, and one which completely avoids any ion-exchange displacement of the cation, is that in which the proton is the cation. One takes a column of resin loaded with ammonium ion as the counter-ion, places a small amount of amine at the top of the column and displaces this down the column by passing aqueous ammonia.

A number of monoamines, diamines and polyamines were investigated by column elution, and values of the distribution quotient were calculated. They are summarized in Table I. Most of the values are close to the ratios of base strengths of the amines to that of ammonia, as would be expected, and the crosslinking of the resin has little or no effect. The aromatic amines are bound much more strongly than their base strengths would imply. They seem to be attracted by the polystyrene matrix of the resin[10].

Experiments with phosphoric resin: effect of metal ion

Equilibrium distributions were measured with ethanolamine and ethylenediamine, ^{14}C-labelled, using both copper(II) and nickel(II) as the counter-ion. The data are shown in Fig. 2. Because of analytical difficulties they are not very accurate, but suffice to show that the nature of the counter-ion does have a significant effect. The diamine is much more strongly adsorbed than the monoamine. Because of the low coordination capacity of the metal ions in the phosphoric acid resin, no other tests were made with this material.

Experiments with carboxylic resin: effect of resin type

Figure 3 shows the effect of the resin matrix on the partition of two amines, ethanolamine and dimethylamine, with ammonia on nickel-loaded resins. These data were obtained from column tests. Good separation of these amines was obtained on the sulfonic resin but not on the carboxylic resin. The order of binding, incidentally, was the reverse of the order of the formation constants of the nickel complexes in aqueous solution. For nickel(II) and ethanolamine[11], $K_1 = 950$. An attempt was made to measure K_1 for nickel(II) and dimethylamine using the CALVIN–BJERRUM

TABLE I

AMINE–AMMONIA DISTRIBUTIONS ON AMMONIUM-LOADED SULFONATED POLYSTYRENE RESINS

Amine	*Resin crosslinking*	*Ammonia concn. (M)*	λ	*Base strength ratio (amine: NH_3)*
Ethylenediamine	4	4.4	6.1	9
	8	4.4	4.0	
	12	1.1	4.2	
		2.2	4.2	
		4.4	4.1	
1,2-Propanediamine	12	4.4	3.7	7.5
1,3-Propanediamine	4	4.4	24.2	32
		8.8	19.0	
	8	4.4	20.4	
		8.8	14.3	
	12	4.4	26.6	
1,4-Butanediamine	8	8.8	26.0	40
		15	22.0	
Diethylenetriamine	8	1.1	6.0	3.5
		2.2	3.2	
		4.4	1.8	
Piperazine	8	1.1	2.4	2.8
		4.4	2.5	
Ethylamine	8	Var.	16	28
Ethanolamine	8	Var.	1.2	1.8
Benzylamine	8	2.2	12.2	1.5
		8.8	12.9	
Pyridine	8	0	(D= 5)	10^{-4}
		4.4	2.1	
Aniline	8	0	(D= 8)	10^{-5}
		4.4	4.0	

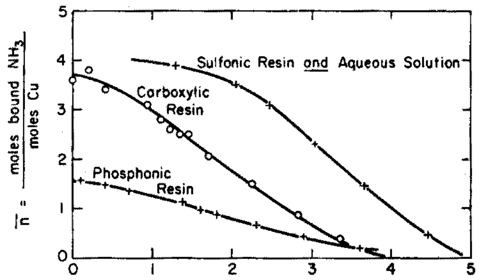
titration method; the constant was about 50, too small to measure accurately. Yet, in elution, ethanolamine was displaced from the column ahead of dimethylamine (Fig. 4).

Diamines and nickel–sulfonic acid resin

Equilibrium shaking tests were made with 5 diamines, ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, 1,4-butanediamine and 1,6-hexanediamine. Column elution tests were made with the last three of these. The 1,2-diamines were held so strongly that elution from a column by aqueous ammonia was virtually impossible. The data are shown in Table II. The result of a column separation of the 1,3-, 1,4- and 1,6-diamines is shown in Fig. 5.

Ethylenimine and nickel–sulfonic acid resin

By column elution tests, two values of the distribution coefficient, λ, were obtained: in 0.77 M ammonia, $\lambda = 0.48$; in 1.55 M ammonia, 0.52. It would thus be very difficult to separate ethylenimine from ethanolamine on this resin (see Fig. 3). The significance of these experiments, however, lies in the fact that ethylenimine was recovered from the column almost completely. This compound is rapidly hydrolyzed in acidic solutions and must be handled in alkaline solutions to prevent decomposition. Derivatives of ethylenimine are important in natural product chemistry, and ligand exchange presents a promising way of analyzing mixtures of these substances.



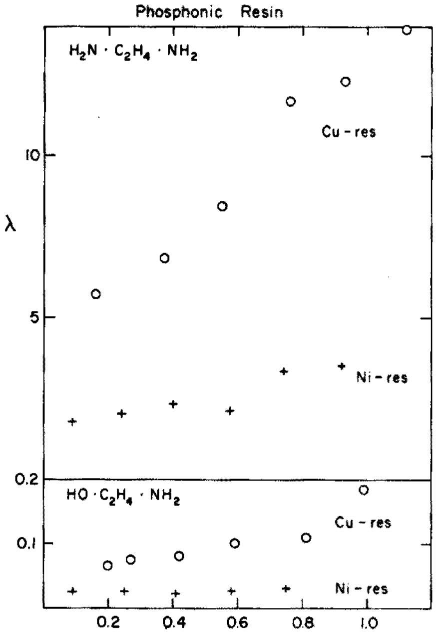


Fig. 1. Formation curves for Cu–NH_3 complexes in aqueous solution and 3 cation-exchange resins.

Fig. 2. Distribution coefficients for ethylenediamine and ethanolamine in a phosphoric acid cation-exchange resin; Cu and Ni as cations. Abscissae are molar concentrations of ammonia.

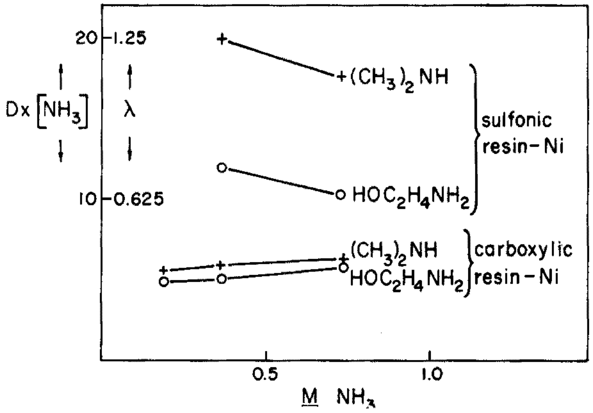


Fig. 3. Distribution coefficients for diethylamine and ethanolamine in sulfonic and carboxylic acid resins, with nickel(II). Values of λ refer to sulfonic resin only.

DISCUSSION

It is evident that ligand exchange has considerable potential in the elution chromatography of amines. The separation of diamines is perhaps the most striking separation reported in this paper, and Fig. 5 illustrates the very high column loadings

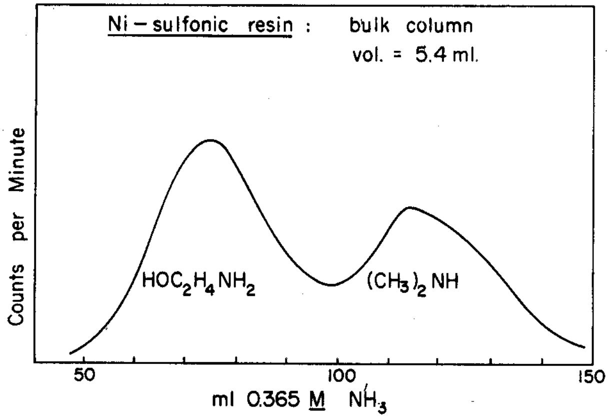


Fig. 4. Elution curve for diethylamine and ethanolamine, ^{14}C-labelled.

TABLE II

DIAMINE–AMMONIA DISTRIBUTIONS ON NICKEL-LOADED 8%-CROSSLINKED SULFONATED POLYSTYRENE RESIN[a]

Amine	*Ammonia concn. (M)*	λ
Ethylenediamine	1.27	200
	2.65	210
	5.32	360
	7.82	290
1,2-Propanediamine	2.86	90
	3.96	140
1,3-Propanediamine	1.22	3.6[b]
	3.60	5.0
	4.45	4.2
	7.20	2.9
1,4-Butanediamine	1.22	0.67[b]
	1.55	1.3
	1.88	2.1
1,6-Hexanediamine	1.22	0.23[b]
	4.45	0.78

[a] The 1,2-diamines were measured by equilibrium shaking tests, the others by column elution.
[b] These values were obtained at high column loading and are, therefore, too small.

that are possible with this technique; a total of 7 mmoles of the diamines was loaded on a column of bulk volume 10 ml, containing only 11 mmoles of nickel ions.

The big hindrance to the use of ligand exchange as an analytical tool has been the lack of a good general method for analyzing and monitoring the column effluents. A possibility now under study is to use a recording differential refractometer for continuous monitoring. This should be especially effective with amines of relatively high molecular weight, and it is these amines for which the technique has most to offer. They are difficult to analyze by gas chromatography.

The data presented in this paper are still quite rough. Attempts were made to measure ligand exchange distributions over a range of amine: ammonia ratios by equilibrium shaking tests, but as was mentioned above, these measurements are not

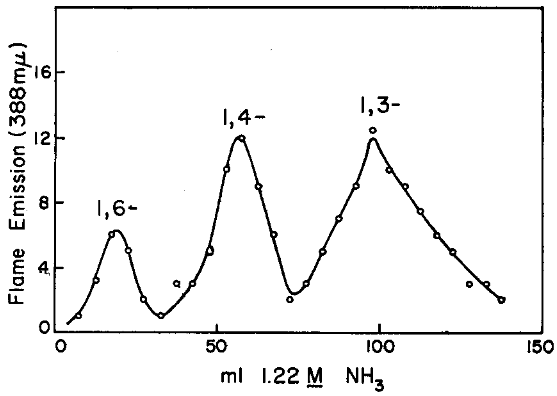


Fig. 5. Elution curve for a mixture of 3 diamines. Flame photometry used to analyze effluent. Loading: 3 mmoles 1,4-butanediamine, 2 mmoles each of 1,3-propanediamine and 1,6-hexanediamine. Bulk column volume, 10 ml.

very reliable. Thus far we feel that elution volumes give much more accurate distribution coefficients than do shaking tests. Such data as we have, however, show several points of interest. The lack of correlation between ligand exchange selectivities and the stabilities of the metal–amine complexes in aqueous solution was noted above for the case of ethanolamine and dimethylamine, and another striking case is the comparison of the binding of ethylenediamine and 1,3-propanediamine by nickel–sulfonic acid resin. The ratio of the distribution coefficients is about 40 (Table II); the ratio of the formation constants, K_1, of the nickel–diamine complexes in aqueous solution[12] is only 16, and these constants refer to bidentate, chelated complexes, whereas the effect of ammonia concentration on ligand exchange distributions (Table II) indicates that at low diamine : ammonia ratios the diamines act as monodentate ligands in the resin. There must be a special reason for the very strong binding of 1,2-diamines. The strong binding of hydrazine was previously noted[4].

By studying ligand exchange equilibria it may be possible to learn something about the stability of mixed complexes containing two different ligands, such as ammonia and an amine.

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This paper is based on the Ph.D. thesis of J. J. LATTERELL, University of Colorado, 1964.

SUMMARY

Mixtures of amines can be separated by elution chromatography on cation-exchange resins loaded with nickel ions or other cations capable of forming amine complexes. The cations are complexed with ammonia beforehand, and amine molecules exchange with ammonia molecules as ligands. Aqueous ammonia is used as the eluant. The method has proved particularly effective for separating diamines.

RÉSUMÉ

Des mélanges d'amines peuvent être séparées par élution chromatographique sur résines (échangeurs de cations), chargées d'ions nickel ou d'autres cations pouvant former des complexes aminés. Les cations sont complexés au préalable avec l'ammoniaque. Cette méthode s'est montrée particulièrement efficace pour la séparation de diamines.

ZUSAMMENFASSUNG

Es lassen sich Mischungen von Aminen trennen durch Elutionschromatographie am Kationenaustauscher der mit Nickelionen oder anderen Kationen beladen ist, die im Stande sind, Aminkomplexe zu bilden. Die Kationen werden vorweg mit Ammoniak in die Komplexe überführt und dann die Ammoniakmoleküle gegen die Aminmoleküle ausgetauscht. Als Eluierungsmittel dient wässrige Ammoniaklösung. Die Methode hat sich besonders wirksam für die Trennung der Diamine bewährt.

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ANION-EXCHANGE SEPARATION OF CADMIUM IN ORGANIC SOLVENT–NITRIC ACID MEDIA

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Since cadmium is not adsorbed on strongly basic anion-exchange resins from pure aqueous nitric acid systems[1], no attempts have hitherto been made to develop methods for the isolation and separation of cadmium in such media. In contrast, several anion-exchange separation methods of cadmium in hydrochloric acid solutions containing iodide or methanol have been reported[2,3].

Investigations recently carried out by **FRITZ AND GREENE**[4] as well as by **KORKISCH AND ARRHENIUS**[5] have shown, however, that in nitric acid solutions containing isopropanol[4] or acetic acid[5] there are rather large differences between the adsorbabilities of cadmium and zinc, which might be employed for their chromatographic separation. The latter medium and three others were therefore closely investigated, and equilibrium studies were made in these and other mixtures of organic solvents with nitric acid, in order to develop suitable methods for the separation of cadmium from zinc, aluminium, and several other elements.

The separation of cadmium from aluminium is of special importance because of its high absorption cross-section for thermal neutrons; hence the concentration of cadmium in aluminium which is to be used in reactor cores must be carefully controlled.

EXPERIMENTAL

Reagents and solutions

The resin used for the separation and equilibrium studies was Dowex 1-X8 (100–200 mesh, nitrate form). The resin was soaked in solutions consisting of 90% organic solvent–10% 5 *N* nitric acid, transferred to the ion-exchange columns and pretreated with mixtures of the same composition as that used to slurry the resin.

Stock solutions of cadmium, zinc, aluminium, and other elements were made by dissolving the reagent-grade nitrates in 5 *N* nitric acid. Also used were chemically pure organic solvents such as ethanol, methyl glycol, glacial acetic acid, propionic acid, and others.

Apparatus

Columns of 50 and 85 cm length with a diameter of 1 cm were used throughout this work. For the analysis of copper and aluminium base alloys, the columns of 85 cm length were employed. For gradient elution a device with a constant-volume mixing chamber similar to that described by SCHWAB *et al.*[6] was used.

Procedures

Separation of cadmium from zinc and aluminium. The sorption solution consisted of 20 ml of a 90% organic solvent–10% 5 *N* nitric acid mixture containing known amounts of cadmium, zinc and/or aluminium. This solution was passed through the column at a flow rate of 0.5 ml/min. During this operation cadmium, zinc, and aluminium were adsorbed.

After sorption the resin was washed with a wash solution of the same composition as that used for pretreatment and sorption. Each 5-ml fraction of the effluent was collected and its metal content determined by a suitable titration, *e.g.* with 0.01 or 0.001 *M* EDTA (disodium salt) in presence of a suitable indicator as for instance of xylenol orange.

Results obtained by this procedure are recorded in Fig. 1. For the experimental results shown in Table I, however, only zinc and aluminium were washed out with the organic solvent–nitric acid wash solution; cadmium was removed from the columns by means of 1 *N* nitric acid in order to shorten the rather lengthy time of eluting cadmium with the wash solution.

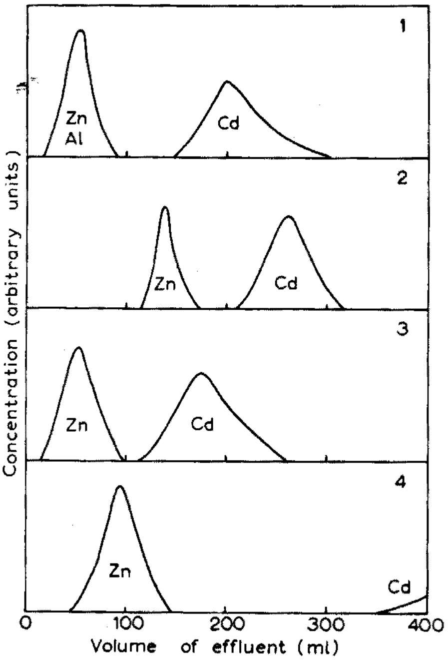

Fig. 1. Separation of cadmium from zinc in several 90% organic solvent–10% 5 *N* nitric acid mixtures on a 50 cm × 1 cm column of Dowex 1-X8, at a flow rate of 0.5 ml/min. (1) ethanol; (2) gradient elution with ethanol following adsorption from propionic acid; (3) methyl glycol; (4) acetic acid.

Analysis of copper and aluminium base alloys. Usually 0.5–1.0 g of the alloy

TABLE I

SEPARATION OF CADMIUM FROM ZINC AND ALUMINIUM IN 90% ORGANIC SOLVENT–10% 5 *N* NITRIC ACID MEDIA ON DOWEX 1-X8

Organic solvent (90%)	*Added (mg)*			*Found (mg)*		
	Cadmium	*Zinc*	*Aluminium*	*Cadmium*	*Zinc*	*Aluminium*
Ethanol	5.0	5.0		5.01	4.97	
Ethanol	10.0	10.0	10.0	10.0	10.01	10.03
Ethanol	50.0	50.0	50.0	49.9	50.0	50.05
Ethanol	5.0	100.0	100.0	5.01	99.8	99.7
Ethanol	5.0	500.0	500.0	4.97	501.6	501.9
Methyl glycol	5.0	5.0		5.0	5.03	
Methyl glycol	10.0	10.0	10.0	9.7	10.6	10.1
Methyl glycol	50.0	50.0	50.0	38.5	50.1	50.2
Acetic acid	5.0	5.0		5.04	5.07	
Acetic acid	10.0	10.0	10.0	9.98	10.1	10.2
Acetic acid	50.0	50.0	50.0	50.0	50.8	49.7
Acetic acid	5.0	500.0	500.0	5.03	497.8	495.4
Propionic acid–ethanol (gradient elution)	5.0	5.0		4.98	5.02	
Propionic acid–ethanol (gradient elution)	10.0	10.0	10.0	9.96	10.2	10.5
Propionic acid–ethanol (gradient elution)	50.0	50.0	50.0	49.7	50.09	50.4
Propionic acid–ethanol (gradient elution)	5.0	500.0	500.0	5.0	498.9	501.3

was dissolved in nitric acid and the solution was evaporated to dryness on a water bath. The residue was taken up in 5 ml of 5 *N* nitric acid and an aliquot of 1 ml together with 1 ml of a cadmium stock solution containing 5, 10, or 20 mg of cadmium was diluted to 20 ml with ethanol. This solution was then passed through the column (85 cm × 1.0 cm) as described above. After the last traces of copper or aluminium had been washed out, cadmium was eluted with 100 ml of 1 *N* nitric acid. The cadmium in the eluate was then titrated with EDTA. In Fig. 2 an example of such a separation is given.

Separation by gradient elution. Cadmium and zinc were adsorbed on the resin as described above from 20 ml of a mixture of 90% propionic acid and 10% 5 *N* nitric acid. After sorption, elution was started by means of a 90% ethanol–10% 5 *N* nitric acid solution which was added at a rate of 0.5 ml/min (same rate as flow rate of column) to 50 ml of 90% propionic acid–10% 5 *N* nitric acid solution agitated by means of a magnetic stirrer. Thus a differential exchange of propionic acid against ethanol was achieved, effecting the separation without change of any other experimental conditions such as acid concentration and volume of wash solution.

Determination of distribution coefficients. For the determination of batch distribution coefficients, 2 ml of a stock solution containing 5 mg of the metal ion were diluted to 20 ml with the solvent in question. To this solution 1 g of the resin was added and the mixture was agitated mechanically for 12 h. The resin was then filtered off and the element was determined titrimetrically in an aliquot of the filtrate.

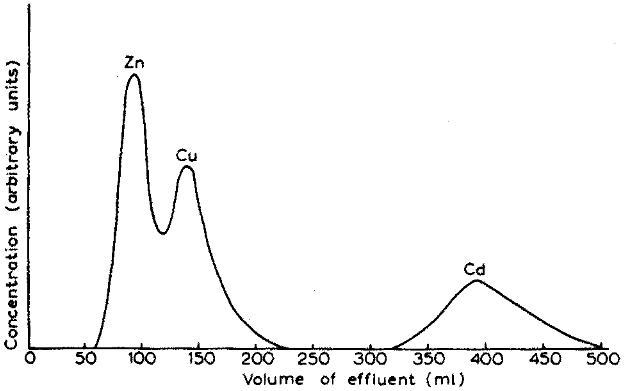

Fig. 2. Separation of cadmium from zinc and copper in 90% ethanol–10% 5 N nitric acid mixture (analysis of a copper base alloy) on a 85 cm × 1 cm column of Dowex 1-X8, at a flow rate of 0.5 ml/min.

RESULTS AND DISCUSSION

In Table II distribution values for cadmium, zinc and aluminium in the investigated media are recorded. From these results it is seen that for quantitative separation of cadmium from zinc and aluminium especially, media containing ethanol or acetic acid are the most promising. To demonstrate the possibility of separating cadmium from zinc in a medium in which the separation factor of these two elements is much less suitable, the system methyl glycol–nitric acid was also investigated. The propionic acid–nitric acid medium from which both cadmium and zinc are adsorbed to a more or less high degree was selected to investigate gradient elution in respect to its applicability in mixed organic aqueous solutions.

TABLE II

DISTRIBUTION COEFFICIENTS OF CADMIUM, ZINC AND ALUMINIUM IN SEVERAL 90% SOLVENT–10% 5 N NITRIC ACID MEDIA

Solvent	*Cadmium*	*Zinc*	*Aluminium*
Water	1.0	1.0	1.0
Methanol	5.0	1.0	1.0
Ethanol	14.0	1.0	1.0
n-Propanol	42.1	8.5	4.4
Isopropanol	95.2	16.1	2.6
n-Butanol	42.0	21.2	11.3
Isobutanol	70.8	35.5	17.0
Acetone	57.0	12.1	37.0
Dioxan	27.0	12.4	13.3
Tetrahydrofuran	16.5	18.5	18.0
Methyl glycol	4.0	1.0	1.0
Ethyl glycol	6.2	1.0	1.0
Acetic acid	83.0	8.2	1.0
Propionic acid	173.0	37.0	3.0

Distribution coefficients of copper, iron, nickel, and lead were also determined and were found in 90% ethanol–10% 5 *N* nitric acid to be 3.2, 1.0, 2.0 and 1,900, respectively, showing that except for lead their separation from cadmium can easily be effected in this medium.

The effect of varying the concentration of nitric acid on the distribution coefficients of cadmium and zinc in ethanol, methyl glycol, acetic acid, and propionic acid media containing 10% (v/v) of the nitric acid was studied; except in the case of cadmium practically no increase of the distribution values with increasing overall acidity of nitric acid was noticed.

Investigations of the influence of varying the organic solvent concentrations on the distribution coefficients of cadmium and zinc showed that in all cases the adsorption increased linearly with increasing percentage of organic solvent.

From studies of the effect of the concentration of cadmium on its distribution coefficient in the 4 selected media (ethanol, methyl glycol, acetic acid, and propionic acid containing 10% 5 *N* nitric acid) it was evident that the loading capacities of the resin in the various media were very much dependent on the distribution coefficient of cadmium, *i.e.* the higher this coefficient the greater is the loading capacity. This general trend has earlier been described in detail by KORKISCH AND ARRHENIUS[5].

Based on these investigations, several separations of cadmium from zinc and aluminium were performed with the working procedure described above (Table I). Except for separations performed in methyl glycol–nitric acid medium, separation of cadmium from zinc and aluminium was always quantitative. Separation in methyl glycol was only quantitative when the concentration of cadmium did not exceed 5 mg. Typical elution curves are shown in Fig. 1 to demonstrate the effectiveness of the various separation methods.

Because the most suitable conditions for separation were found in 90%

TABLE III

ANALYSES OF COPPER AND ALUMINIUM BASE ALLOYS

Composition of alloy (major constituents)	*Cadmium added (mg)*	*Cadmium found (mg)*
Cu (65%), Zn (34%)	5.0	4.98
	10.0	10.06
	20.0	20.08
Cu (64%), Zn (16%), Ni (16%)	5.0	5.03
	10.0	10.03
	20.0	19.89
Cu (62%), Zn (30%), Ni (8%)	5.0	5.0
	10.0	9.93
	20.0	20.08
Al (99%)	5.0	5.02
	10.0	10.04
	20.0	19.94
Al (97%)	5.0	5.01
	10.0	9.96
	20.0	20.10
Al (95%)	5.0	5.02
	10.0	9.98
	20.0	19.94

ethanol–10% 5 *N* nitric acid medium, this mixture was selected for the isolation of cadmium from solutions of copper and aluminium base alloys. The results recorded in Table III show that in all cases a quantitative recovery of the added cadmium could be achieved. In Fig. 2 a typical result obtained on applying this procedure to the analysis of a brass sample to which cadmium has been added is shown.

In conclusion, the present method is well suited for the quantitative and accurate separation of milligram amounts of cadmium from zinc and aluminium even if the latter is present in excess by two orders of magnitude. Attempts to separate cadmium from uranium under these or similar conditions proved unsuccessful because of the small difference in adsorbabilities of these two elements.

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SUMMARY

The anion-exchange separation of cadmium from zinc and aluminium in organic solvent–nitric acid mixtures was studied. The distribution coefficients of the 3 elements in various 90% organic solvent–10% 5 *N* nitric acid media were determined for Dowex 1-X8 resin. A 90% ethanol–10% 5 *N* nitric acid medium was most satisfactory for the quantitative separation of cadmium from zinc and aluminium. The method was applied to the analysis of some copper and aluminium base alloys. Methyl glycol or acetic acid could be used instead of ethanol. Both cadmium and zinc were strongly adsorbed from a 90% propionc acid–10% 5 *N* nitric acid medium; separation was then effected by gradient elution.

RÉSUMÉ

Les auteurs ont examiné la séparation du cadmium d'avec le zinc et l'aluminium, en milieu solvant organique–acide nitrique (90% éthanol–10% acide nitrique 5 *N*) au moyen d'un échangeur d'anions (résine Dowex 1-X8). Ce procédé a été appliqué à l'analyse d'alliages à base cuivre et aluminium. L'éthanol pourrait être remplacé par le méthylglycol ou l'acide acétique. Le cadmium et le zinc, en milieu acide propionique 90%–acide nitrique 5 *N* 10%, sont tous deux fortement adsorbés.

ZUSAMMENFASSUNG

Die Trennung des Cadmiums vom Zink und Aluminium mit einem Anionenaustauscher aus einem Gemisch von organischen Lösungsmitteln und Salpetersäure wurde untersucht. Die Verteilungskoeffizienten von 3 Elementen für den Austauscher Dowex 1-X8 wurden in verschiedenen Medien von 90% organischen Lösungsmitteln und 10% 5 *N* Salpetersäure bestimmt. Eine 90%ige Äthanol–10% 5 *N* Salpetersäurelösung erwies sich als vorteilhafter für die quantitative Trennung des Cadmiums vom Zink und Aluminium als eine Lösung, die 90% Methylglycol und 10% 5 *N* Salpetersäure enthielt. Die Anwendung der Äthanol–Salpetersäure-Mischung wurde für die Analyse einiger Kupfer- und Aluminiumlegierungen angewandt. Sie ergab befriedi-

gende und leicht zu reproduzierende Ergebnisse. Anstelle von Äthanol oder Methylglycol, kann Essigsäure ebenfalls erfolgreich angewandt werden. Aus einer Mischung von 90% Propionsäure und 10% 5 *N* Salpetersäure werden sowohl Cadmium als auch Zink vom Harz stark adsorbiert. Die Trennung dieser 2 Elemente in diesem Medium wird verbessert mittels der Gradientenelution, die auf den allmählichen Austausch der Propionsäure durch Äthanol beruht.

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SYSTEMATIC ANALYSIS BY SOLVENT-EXTRACTION METHODS

PART II. QUANTITATIVE ANALYSIS

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In Part I[1] we presented a scheme or qualitative analysis by solvent-extraction methods. We found that many of the reactions used to achieve separations could also be used for the determination of the elements concerned, usually by spectrophotometry. One of the usual difficulties — that of interference by other cations — was, of course, virtually eliminated by the extraction methods used. The scheme of separation was described in Part I. The same apparatus was used in the work described in the present paper.

Since it was known that the group separations were clean and essentially quantitative, only the determination of the elements within groups was investigated. Standard methods were generally found to work excellently for our purposes if they were modified to take into account the nature of the extract forming the starting material. The methods were checked by carrying various amounts of standard solutions of the elements concerned through the separation and determination procedure. Elements within a group were determined both alone and in the presence of other members of the group.

EXPERIMENTAL

Analysis of group II — iron and copper

The thiocyanate method for iron is very sensitive but subject to several interferences and the colour fades. The elements that normally interfere are removed by the extraction method, and the colour is stable long enough for measurements to be reliable. For copper the diethyldithiocarbamate method is suitable, provided that any iron present is completely removed first.

Reagents. Thiocyanate reagent. Saturate 650 ml of acetone with potassium thiocyanate and add 350 ml of water.

Sodium diethyldithiocarbamate. A 1% solution in water.

Procedure. Take 5 ml of sample solution containing not more than 500 μg each of iron(III) and copper(II), add 50 mg of citric acid and adjust the pH of the solution to about 1.5. Extract with three 5-ml portions of a 20% solution of acetylacetone in chloroform, and finally with 5 ml of chloroform. Shake the combined extracts with

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three 4-ml portions of 6 N hydrochloric acid and discard the organic phase. To the acid solution add *cautiously* 4 ml of concentrated sulphuric acid and cool. Extract with three 4-ml portions of amyl acetate and retain the aqueous phase for the copper determination. Dilute the organic phase to 100 ml in a standard flask with thiocyanate reagent, mix, and after 5 min measure the optical density at 496 mμ in a 1-cm cell against a reagent blank. The colour is stable for at least 2 h and Beer's law is obeyed. To the acid solution add concentrated ammonia to raise the pH to about 10. Add sodium diethyldithiocarbamate solution dropwise until all the copper has been precipitated and then extract it completely with 5-ml portions of a 5:2 mixture of chloroform and acetone. Dilute the combined extracts to 100 ml with solvent, mix, and measure the optical density in 1-cm cells at 440 mμ against a blank. The colour is stable for at least 2 h and Beer's law is obeyed.

Analysis of group III — silver, bismuth and mercury(II)

The reversion method of IRVING *et al.*[2] is very useful for this group. In this method the metal ion is extracted as its dithizone complex and the optical density of the excess dithizone is measured. The metal is then back-extracted as an inorganic complex and the increase in optical density due to the release of dithizone is measured and is equivalent to the amount of metal originally present as its complex with dithizone. Until the present work the reversion method had been used only for the determination of single metals, but we found that successive determinations could be made by our back-extraction method of separation. Furthermore a single calibration curve sufficed for all three metals if the metal ion concentration was expressed in gram equivalents per litre.

Reagents. The carbon tetrachloride must be of analytical reagent grade. Potassium iodide solution must be freshly prepared to prevent the formation and extraction of iodine.

Procedure. Take 5 ml of sample solution containing not more than 500 μg of each of the metals in the group, add 50 mg of citric acid, and remove Groups I and II[1]. Then extract with 5-ml portions of a saturated solution of dithizone in carbon tetrachloride until no further colour change occurs in the extract. Dilute the combined extracts to 250 ml with carbon tetrachloride (Solution A). Shake 25 ml of the solution with two 20-ml portions of 0.2 N nitric acid, run off the organic phase through glass wool to dry it, and measure the optical density again (d_1) against Solution A in 1-cm cells at 600 mμ. Shake the same or a fresh portion of solution with 20 ml of M sodium chloride at pH 1, run off the organic phase through glass wool and measure the optical density again against Solution A (d_2). Finally shake the same (or a new) portion of solution with 20 ml of M potassium iodide at pH 1, separate, and measure the optical density (d_3) as before. The optical densities d_1, ($d_2 — d_1$) and ($d_3 — d_2$) are the reversion values for bismuth, silver and mercury(II) respectively. A calibration graph can be plotted empirically or the slope reported by IRVING *et al.*[2] can be used to evaluate the results. Our value of $26.7 \cdot 10^3$/l/gmole/cm is in exact agreement.

Analysis of groups IV and I — chromium(VI) and chromium(III)

The method of GLASNER AND STEINBERG[3] can be used for the determination of chromium in both oxidation states.

Procedure. Collect the precipitate of chromium hydroxide (Group I) on a filter stick, wash it with water and dissolve it in 2 ml of dilute sulphuric acid. Add a drop of 0.01% silver nitrate solution and 0.25 g of potassium persulphate and heat until all the chromium has been oxidised. Cool, adjust the pH to just less than 2 with dilute ammonia solution, add 5 ml of ethyl acetate and 1 ml of 0.1 *M* hydrogen peroxide and shake. Separate the organic phase and extract twice more with 5-ml portions of ethyl acetate. Dilute the combined extracts to 25 ml with solvent and measure the optical density at 580 mμ in 1-cm cells against a blank. To determine chromium(VI) the procedure is the same from the point at which the pH is adjusted, and is applied directly in the separation of Group IV in the scheme[1]. If the original sample was dissolved in concentrated nitric acid so that chromium(III) is present as a nitrato complex, the chromium(III) will appear in the residual Group VIII and could be determined there by a similar method. We found the ethyl acetate solution of the peroxide complex to be stable for about 2 h, longer than the period reported by BROOKSHIRE AND FREUND[4].

Analysis of group V — lead, cadmium, zinc, nickel, antimony, cobalt and manganese

These elements are separated into three sub-groups as in the qualitative scheme. The sub-groups can then be analysed for each of their constituents.

Procedure. Take 5 ml of sample solution containing no more than 500 μg of any constituent, add 50 mg of citric acid and remove Groups I to IV. Extract the diethyldithiocarbamates of the metals in Group V of the scheme by extraction with a 5:2 mixture of chloroform and acetone. Back-extract with two 5-ml portions of *N* hydrochloric acid and reserve the extracts for the determination of lead, zinc and cadmium. Back-extract the organic phase again with two 5-ml portions of 10% potassium cyanide solution and determine nickel and antimony in the aqueous phase. The organic phase contains any cobalt and manganese.

Lead, zinc and cadmium. To the combined acid extracts add 8 ml of 2 *N* sodium hydroxide and 5 ml of *M* sodium tartrate, transfer to a 25-ml standard flask, dilute to the mark and mix. Transfer a portion of this solution to a polarographic cell, de-oxygenate, and polarograph from −0.3 to −1.3 V. Read off the results from a calibration curve. The zinc wave is not as good as the lead and cadmium waves. The half-wave potentials are −0.5, −0.7 and −1.1 V for lead, cadmium and zinc respectively.

Nickel and antimony. Make the cyanide extract slightly acidic and add enough formaldehyde to react with the cyanide. Make the solution slightly ammoniacal, add dimethylglyoxime and extract the nickel complex into chloroform. Dilute to a convenient standard volume and measure the optical density at 366 mμ in a 1-cm cell. Beer's law is obeyed and up to 500 μg of nickel can be determined.

We have not yet found a reliable method for the determination of antimony.

Cobalt and manganese. Evaporate to dryness the organic phase remaining after the extraction of the first two sub-groups. Dissolve the residue in about 1 ml of concentrated nitric acid, transfer to a 25-ml standard flask, dilute to the mark and mix. Take a 10-ml portion and neutralise with concentrated ammonia solution. Add 1 ml of 2 *M* nitric acid and dilute to 50 ml in a standard flask with a saturated solution of ammonium thiocyanate in acetone. Mix and measure the optical density at 620 mμ against a blank.

Take a second 10-ml portion, neutralise it with ammonia, add 4 ml of 2 *M* nitric acid and 0.25 g of potassium periodate and boil the solution for several minutes. Add another 0.25 g of periodate and boil for a few minutes after the permanganate colour appears. Cool, dilute to 50 ml and measure the optical density against a blank at 525 mμ.

Analysis of group VI — tin and arsenic

The tin(IV) diethyldithiocarbamate is bright orange and can be used directly to determine tin. The colour fades slowly, however, and measurements must be made at some specific time after the complex has been formed. No suitable method has been found for the determination of arsenic.

Procedure. After removal of Groups I to V of the scheme adjust the pH to about 5, precipitate the tin(IV) and arsenic(V) diethyldithiocarbamates and extract them into a 5:2 chloroform–acetone mixture. Dilute the extract to 50 ml with chloroform and 15 min after the initial addition of extractant measure the optical density in a 1-cm cell at 355 mμ against a blank. Beer's law is obeyed up to 500 μg of tin per 50 ml of chloroform solution.

RESULTS

The results obtained when single salts and mixtures were carried through the procedure are presented in Tables I to V.

TABLE I

DETERMINATION OF COPPER AND IRON

Copper		*Iron*	
Taken (μg)	*Found (μg)*	*Taken (μg)*	*Found (μg)*
400	404		
29	31		
509	510		
		429	420
		247	245
		88	83
232	215	165	158
33	35	445	435
447	445	28	31

DISCUSSION

The results presented show a maximum error of about 10% and an average error of just over 3%. For the quantities involved this is not unreasonable; it could undoubtedly be improved by careful attention to detail and technique. The main

TABLE II

SILVER, BISMUTH AND MERCURY(II)

Silver		*Bismuth*		*Mercury*	
Taken (µg)	*Found (µg)*	*Taken (µg)*	*Found (µg)*	*Taken (µg)*	*Found (µg)*
				396	393
				115	115
				468	468
		416	413		
		75	63		
		248	228		
582	590				
88	90				
480	460				
		192	196	370	385
294	295	122	130		
254	258			178	171
152	150	122	125	307	320
243	248	252	260	117	105

TABLE III

COBALT AND MANGANESE

Cobalt		*Manganese*		*Also present*
Taken (µg)	*Found (µg)*	*Taken (µg)*	*Found (µg)*	*250 µg each of*
281	278			
462	450			Fe, Hg, Zn, Ni
		236	228	
		474	495	Fe, Hg, Zn, Ni
370	377	205	190	
200	203	100	100	Fe, Hg, Zn, Ni
500	504	500	510	Fe, Hg, Zn, Ni

TABLE IV

CHROMIUM(III) AND CHROMIUM(VI)

Chromium(III)		*Chromium(VI)*		*Also present*
Taken (µg)	*Found (µg)*	*Taken (µg)*	*Found (µg)*	
400	410			
300	305			Fe, Bi, Hg
200	205			Fe, Bi, Hg
		472	482	Fe, Bi, Hg
		95	100	Fe, Bi, Hg
		284	283	

TABLE V

LEAD, CADMIUM AND ZINC

Lead		*Cadmium*		*Zinc*	
Taken (µg)	*Found (µg)*	*Taken (µg)*	*Found (µg)*	*Taken (µg)*	*Found (µg)*
334	332	289	296	172	183
186	170	520	521	172	188
371	381	116	128		
742	735	289	296	172	165
		289	263	172	165
371	348	289	272	172	163
186	170	520	534	172	181
149	136	231	252	309	336

advantage of the method is that many of the interferences that can occur are eliminated by the separation methods used. The scheme is capable of being extended to cover a greater range of elements. It promises to be useful in rock and mineral analysis, especially for the determination of minor constituents that may be of geochemical interest. We are doing further work in this direction.

SUMMARY

Methods are suggested for the systematic separation and determination of 12 metals by a combination of solvent-extraction and spectrophotometric methods.

RÉSUMÉ

Quelques méthodes sont suggérées pour la separation systématique et le dosage de 12 métaux par une combinaison d'extraction par solvants et de spectrophotométrie.

ZUSAMMENFASSUNG

Methoden für die systematische Trennung und Bestimmung von 12 Metallen durch Lösungsextraktionsmittel und Spektrophotometrie sind beschrieben.

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GENERAL CONSIDERATIONS IN COMPLEXIMETRIC TITRATIONS

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Many factors, such as pH, auxiliary complexing agents, the presence of a second metal, etc., are critical in the compleximetric determination of a metal. It is thus important to consider the matter on a sound theoretical basis, when a compleximetric titration is to be elaborated. The theory of compleximetric methods has been dealt with by several authors[1-5]. SCHMID AND REILLEY[6], extending the expressions proposed by FORTUIN *et al.*[2] and FLASCHKA AND KHALAFALLAH[3], have treated theoretically the indicator transition near the equivalence point by means of the end-point index. The present authors have proposed an expression for the indicator transition in titrations using an indicator system NY–HA[7]. These theories, however, have been restricted in application, and it is seldom[8-12] that a method has been developed on the basis of quantitative theoretical considerations. The present authors[13] have demonstrated that theory and experiment agree well for the indicator transition near the equivalence point of compleximetric titrations of some alkaline earths in the presence and absence of sodium.

In the present paper, general expressions for [M] and [Y] in the presence and absence of a second metal are derived and interpretation of these expressions is attempted by means of the concept of ligand buffer[14]. The sharpness of potentiometric and amperometric end-point indication in compleximetric titrations is also discussed. Some general expressions for the indicator transition using an HA or NY–HA indicator system are derived and it is shown that the sharpness of photometric or visual end-point indication can be quantitatively accounted for in a similar way to that proposed by SCHMID AND REILLEY[6]. Provided that the constants of all the species involved in a particular system are available, it is thus possible to establish a compleximetric method on a sound theoretical basis by means of the following general theory.

VARIATION OF $[M_I]$ AND $[Y]$ IN THE ABSENCE OF A SECOND METAL M_{II}

Variation of $[M_I]$

During the titration the following stoichiometric relationships hold (omitting charges for simplicity):

$$C_{\mathrm{M_I}} = [\mathrm{M_I Y}]' + [\mathrm{M_I}]' \qquad (1)$$

$$C_{\mathrm{Y}} = [\mathrm{M_I Y}]' + [\mathrm{Y}]' \qquad (2)$$

where $[\mathrm{M_I}]' = [\mathrm{M_I}]\beta_{(\mathrm{M_I})}$, $[\mathrm{Y}]' = [\mathrm{Y}]\alpha_{\mathrm{H(Y)}}$, $[\mathrm{M_I Y}]' = [\mathrm{M_I HY}] + [\mathrm{M_I Y}] + [\mathrm{M_I Y(OH)}]$*. The formation constants of $\mathrm{M_I Y}$, $\mathrm{M_I HY}$ and $\mathrm{M_I Y(OH)}$ are given as follows:

$$K_{\mathrm{M_I Y}} = \frac{[\mathrm{M_I Y}]}{[\mathrm{M_I}]\,[\mathrm{Y}]} \qquad (3)$$

$$K_{\mathrm{M_I HY}} = \frac{[\mathrm{M_I HY}]}{[\mathrm{M_I}]\,[\mathrm{HY}]} = \frac{[\mathrm{M_I HY}]}{[\mathrm{M_I}]K_{\mathrm{HY}}[\mathrm{Y}]\,[\mathrm{H}]} \qquad (4)$$

$$K_{\mathrm{M_I Y(OH)}} = \frac{[\mathrm{M_I Y(OH)}]}{[\mathrm{M_I Y}]\,[\mathrm{OH}]} = \frac{[\mathrm{M_I Y(OH)}]\,[\mathrm{H}]}{K_{\mathrm{M_I Y}}[\mathrm{M_I}]\,[\mathrm{Y}]K_{\mathrm{W}}}$$

where K_{HY} is the formation constant of HY.

Combining eqns. (1) and (2), we have:

$$C_{\mathrm{Y}} = C_{\mathrm{M_I}} - [\mathrm{M_I}]' + [\mathrm{Y}]'$$

or

$$C_{\mathrm{Y}} = C_{\mathrm{M_I}} - [\mathrm{M_I}]\beta_{(\mathrm{M_I})} + [\mathrm{Y}]\alpha_{\mathrm{H(Y)}} \qquad (6)$$

By appropriate substitution and rearrangement of eqns. (1) through (5),

$$[\mathrm{M_I Y}]' = C_{\mathrm{M_I}} - [\mathrm{M_I}]' = C_{\mathrm{Y}} - [\mathrm{Y}]' = [\mathrm{M_I}]\,[\mathrm{Y}]\gamma_{\mathrm{M_I,Y}} \qquad (7)$$

where $\gamma_{\mathrm{M_I,Y}} = K_{\mathrm{M_I HY}}K_{\mathrm{HY}}[\mathrm{H}] + K_{\mathrm{M_I Y}} + K_{\mathrm{M_I Y(OH)}}K_{\mathrm{M_I Y}}K_{\mathrm{W}}/[\mathrm{H}]$.

Combining eqns. (6) and (7) and designating $C_{\mathrm{Y}}/C_{\mathrm{M_I}}$ (fraction titrated) as a, we get:

$$a = 1 - \frac{[\mathrm{M_I}]\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}} + \frac{\alpha_{\mathrm{H(Y)}}}{[\mathrm{M_I}]\gamma_{\mathrm{M_I,Y}}} - \frac{\alpha_{\mathrm{H(Y)}}\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}\gamma_{\mathrm{M_I,Y}}} \qquad (8)$$

This expresses the change in $[\mathrm{M_I}]$ during the titration; the last term on the right side of eqn. (8) can be neglected under conditions favorable for titration. Thus:

$$a = 1 - \frac{[\mathrm{M_I}]\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}} + \frac{\alpha_{\mathrm{H(Y)}}}{[\mathrm{M_I}]\gamma_{\mathrm{M_I,Y}}} \qquad (9)$$

In eqn. (9) the second term on the right side is mainly concerned with the change in $[\mathrm{M_I}]$ before the equivalence point, and the third term is mainly concerned with that after the equivalence point. At the equivalence point, $a = 1$, thus from eqn. (9):

$$[\mathrm{M_I}]_{\mathrm{e.p.}} = \left(\frac{C_{\mathrm{M_I}}\alpha_{\mathrm{H(Y)}}}{\beta_{(\mathrm{M_I})}\gamma_{\mathrm{M_I,Y}}}\right)^{\frac{1}{2}} \qquad (10)$$

Variation of [Y]

From eqns. (6) and (7), we have:

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* $\alpha_{\mathrm{H(Y)}}$ and $\beta_{(\mathrm{M_I})}$ are the side-reaction coefficients of protonation of Y and of complexation of $\mathrm{M_I}$ respectively[1,5].

$$C_Y = C_{M_I} - \frac{(C_Y - [Y]\alpha_{H(Y)})\beta_{(M_I)}}{[Y]\gamma_{M_I,Y}} + [Y]\alpha_{H(Y)}$$

which by arrangement leads to:

$$a = \left(1 + \frac{\beta_{(M_I)}}{[Y]\gamma_{M_I,Y}}\right)^{-1} + \frac{[Y]\alpha_{H(Y)}}{C_{M_I}} \tag{11}$$

Equation (11) is an expression for [Y] over the entire range of titration. In the vicinity of the equivalence point, $\beta_{(M_I)}/[Y]\gamma_{M_I,Y}$ is much smaller than unity, and eqn. (11) can be rewritten as follows:

$$a = 1 - \frac{\beta_{(M_I)}}{[Y]\gamma_{M_I,Y}} + \frac{[Y]\alpha_{H(Y)}}{C_{M_I}} \tag{12}$$

The similarity of eqns. (9) and (12) may be noted. Analogously to the preceding section, [Y] at the equivalence point is given by:

$$[Y]_{e.p.} = \left(\frac{C_{M_I}\beta_{(M_I)}}{\alpha_{H(Y)}\gamma_{M_I,Y}}\right)^{\frac{1}{2}} \tag{13}$$

VARIATION OF $[M_I]$ AND [Y] IN THE PRESENCE OF A SECOND METAL M_{II}

Variation of $[M_I]$

In the presence of a second metal M_{II}, the following stoichiometric relationships hold:

$$C_{M_I} = [M_IY]' + [M_I]' \tag{14}$$

$$C_{M_{II}} = [M_{II}Y]' + [M_{II}]' \tag{15}$$

$$C_Y = [M_IY]' + [M_{II}Y]' + [Y]' \tag{16}$$

where

$$[M_{II}Y]' = C_{M_{II}} - [M_{II}]' = [M_{II}]\,[Y]\gamma_{M_{II},Y}\,. \tag{17}$$

Combining eqns. (16) and (17), we have:

$$\begin{aligned} C_Y &= [M_IY]' + [M_{II}]\,[Y]\gamma_{M_{II},Y} + [Y]\alpha_{H(Y)} \\ &= [M_IY]' + [Y]\,([M_{II}]\gamma_{M_{II},Y} + \alpha_{H(Y)}) \end{aligned} \tag{18}$$

Substituting eqn. (14) into (18),

$$C_Y = C_{M_I} - [M_I]\beta_{(M_I)} + [Y]\,([M_{II}]\gamma_{M_{II},Y} + \alpha_{H(Y)}) \tag{19}$$

which upon rearrangement leads to:

$$a = 1 - \frac{[M_I]\beta_{(M_I)}}{C_{M_I}} + \frac{[M_{II}]\gamma_{M_{II},Y} + \alpha_{H(Y)}}{[M_I]\gamma_{M_I,Y}} - \frac{\beta_{(M_I)}([M_{II}]\gamma_{M_{II},Y} + \alpha_{H(Y)})}{C_{M_I}\gamma_{M_I,Y}} \tag{20}$$

in which the last term can be neglected. Near the equivalence point, $[M_{II}]$ may be replaced by $C_{M_{II}}/\beta_{(M_{II})}$. Then we have:

$$a = 1 - \frac{[M_I]\beta_{(M_I)}}{C_{M_I}} + \frac{\alpha_{H,M_{II}(Y)}}{[M_I]\gamma_{M_I,Y}} \tag{21}$$

where $\alpha_{\mathrm{H,M_{II}(Y)}}$ is the side-reaction coefficient taking into account the protonation of Y as well as the chelation of Y by $\mathrm{M_{II}}$, and $\alpha_{\mathrm{H,M_{II}(Y)}} = C_{\mathrm{M_{II}}}\gamma_{\mathrm{M_{II},Y}}/\beta_{(\mathrm{M_{II}})} + \alpha_{\mathrm{H(Y)}}$ in the vicinity of the equivalence point*. Equation (21) is an expression for $[\mathrm{M_I}]$ in the vicinity of the equivalence point, taking into consideration the presence of a second metal $\mathrm{M_{II}}$.

At the equivalence point, we have:

$$[\mathrm{M_I}]_{\mathrm{e.p.}} = \left(\frac{C_{\mathrm{M}}\,\alpha_{\mathrm{H,M_{II}(Y)}}}{\beta_{(\mathrm{M_I})}\gamma_{\mathrm{M_I,Y}}}\right)^{\frac{1}{2}} \tag{22}$$

Variation of [Y]

Combining eqns. (7) and (19):

$$C_{\mathrm{Y}} = C_{\mathrm{M_I}} - \frac{[\mathrm{M_IY}]'\beta_{(\mathrm{M_I})}}{[\mathrm{Y}]\gamma_{\mathrm{M_I,Y}}} + [\mathrm{Y}]\alpha_{\mathrm{H,M_{II}(Y)}} \tag{23}$$

Near the equivalence point $[\mathrm{M_IY}]'$ may be regarded as $C_{\mathrm{M_I}}$. Thus:

$$a = 1 - \frac{\beta_{(\mathrm{M_I})}}{[\mathrm{Y}]\gamma_{\mathrm{M_I,Y}}} + \frac{[\mathrm{Y}]\alpha_{\mathrm{H,M_{II}(Y)}}}{C_{\mathrm{M_I}}} \tag{24}$$

Equation (24) relates *a* with [Y] near the equivalence point in the presence of a second metal $\mathrm{M_{II}}$.

At the equivalence point, $a = 1$, and thus:

$$[\mathrm{Y}]_{\mathrm{e.p.}} = \left(\frac{C_{\mathrm{M_I}}\beta_{(\mathrm{M_I})}}{\gamma_{\mathrm{M_I,Y}}\alpha_{\mathrm{H,M_{II}(Y)}}}\right)^{\frac{1}{2}} \tag{25}$$

Comparing eqns. (9) and (12) with eqns. (21) and (24), it can be seen that $\alpha_{\mathrm{H(Y)}}$ in the former is replaced by $\alpha_{\mathrm{H,M_{II}(Y)}}$ in the latter. Thus the effect of a second metal can be easily understood by means of the "ligand buffer" concept[14]: in the presence of a second metal and after the equivalence point, we are concerned with a ligand buffer containing $\mathrm{M_{II}}$ in excess, pY being buffered at a higher level than in the absence of $\mathrm{M_{II}}$. Correspondingly, after the equivalence point $\mathrm{pM_I}$ is buffered at a lower level in the presence of a second metal than in its absence.

When $C_{\mathrm{M_{II}}} = 0$ or interaction of $\mathrm{M_{II}}$ with Y is not appreciable ($\gamma_{\mathrm{M_{II},Y}}/\alpha_{\mathrm{H(Y)}}\beta_{(\mathrm{M_{II}})} \simeq 0$), eqns. (21) and (24) become identical with eqns. (9) and (12), respectively.

By means of eqns. (9), (12), (21) and (24), we can consider and predict quantitatively the changes in [M] or [Y] in the vicinity of the equivalence point in potentiometric or amperometric titrations.

SHARPNESS OF END-POINT INDICATION

End-points in compleximetric titrations can be indicated by various methods (*e.g.* amperometric, potentiometric, photometric or visual). In this section the ease of

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* $\alpha_{\mathrm{H,M_{II}(Y)}} = \dfrac{[\mathrm{M_{II}Y}]' + [\mathrm{Y}]'}{[\mathrm{Y}]} = [\mathrm{M_{II}}]\gamma_{\mathrm{M_{II},Y}} + \alpha_{\mathrm{H(Y)}}$.

recognition of end-points in compleximetric titrations will be considered, and the definition of a sharpness index will be given for each case as a quantitative measure of the transition at the equivalence point.

Amperometric end-point indication

Provided that there is no appreciable current due to the dissociation of MY, amperometric titration is based on the measurement of either M′ (M not combined with Y) or Y′ (Y not combined with M)*. The equations (9) and (12) allow the construction of a–$[\mathrm{M_I}]'$ and a–$[\mathrm{Y}]'$ diagrams, which are fundamental amperometric titration curves**. The sharpness index of an amperometric titration is defined as $C_{\mathrm{M_I}}/[\mathrm{M_I}]'_{\mathrm{e.p.}}$ or $C_{\mathrm{M_I}}/[\mathrm{Y}]'_{\mathrm{e.p.}}$ and given as:

$$C_{\mathrm{M_I}}/[\mathrm{M_I}]'_{\mathrm{e.p.}} = (C_{\mathrm{M_I}}\gamma_{\mathrm{M_I,Y}}/\beta_{(\mathrm{M_I})}\alpha_{\mathrm{H(Y)}})^{\frac{1}{2}} \tag{26}$$

$$C_{\mathrm{M_I}}/[\mathrm{Y}]'_{\mathrm{e.p.}} = (C_{\mathrm{M_I}}\gamma_{\mathrm{M_I,Y}}/\beta_{(\mathrm{M_I})}\alpha_{\mathrm{H(Y)}})^{\frac{1}{2}} \tag{27}$$

It may be noted that the numerical values of $C_{\mathrm{M_I}}/[\mathrm{M_I}]'_{\mathrm{e.p.}}$ and $C_{\mathrm{M_I}}/[\mathrm{Y}]'_{\mathrm{e.p.}}$ are identical. The greater the sharpness index, the sharper the end-point indication; that is, the higher the values of $C_{\mathrm{M_I}}$ and $\gamma_{\mathrm{M_I,Y}}/\alpha_{\mathrm{H(Y)}}\beta_{(\mathrm{M_I})}$, the more distinct is the end-point indication***.

In the presence of a second metal $\mathrm{M_{II}}$, we have from eqn. (22):

$$C_{\mathrm{M_I}}/[\mathrm{M_I}]'_{\mathrm{e.p.}} = (C_{\mathrm{M_I}}\gamma_{\mathrm{M_I,Y}}/\beta_{(\mathrm{M_I})}\alpha_{\mathrm{H,M_{II}(Y)}})^{\frac{1}{2}} \tag{28}$$

Since the concentration of free Y is buffered at a lower level after the equivalence point in the presence of a second metal $\mathrm{M_{II}}$ ("ligand buffer"), the greater the values of $C_{\mathrm{M_{II}}}$ and $\alpha_{\mathrm{H,M_{II}(Y)}}$, the less distinct is the end-point.

Potentiometric end-point indication

pM–a and pY–a diagrams constructed by the use of eqns. (9), (12), (21) or (24) allow the quantitative consideration of potentiometric titration, in which the greater the jump of pM or pY at the equivalence point, the more distinct is the end-point.

Equations (9), (12), (21) and (24) can be rewritten as follows:

$$a = 1 - [\mathrm{M}]\mathrm{f_1} + \frac{\mathrm{f_2}}{[\mathrm{M}]} \tag{29}$$

$$a = 1 - \frac{\mathrm{f_1}}{[\mathrm{Y}]} + [\mathrm{Y}]\mathrm{f_2} \tag{30}$$

where $\mathrm{f_1}$ and $\mathrm{f_2}$ are constants depending on such experimental conditions as $\gamma_{\mathrm{M_I,Y}}$,

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* A versatile method of amperometric titration has been proposed[15] which utilizes the oxidation wave of Hg in the presence of Y.

** Titration is supposed to be carried out at a potential at which only $\mathrm{M_I}'$ or Y′ gives a polarographic wave.

*** The sharpness of a photometric end-point with no indicator (*e.g.* titration of copper, measuring the change of absorbance due to CuY) can be discussed by means of eqn. (26) or (27).

C_{M_I}, $\alpha_{H,M_{II}(Y)}$, $\beta_{(M_I)}$, etc. It should be noted that $f_1f_2 = (C_{M_I}\gamma_{M'_I,Y'})^{-1} = \alpha_{H,M_{II}(Y)}\,\beta_{(M_I)}/C_{M_I}\gamma_{M_I,Y}$.

A calculation of the buffer capacity* $\pi_{pM} = |d(C_Y/C_M)/dpM|$ (absolute value) or $\pi_{pY} = |d(C_Y/C_M)/dpY|$ (absolute value) leads to the consideration of end-point sharpness[14].

$$\pi_{pM} = 2.3[M]\left(f_1 + \frac{f_2}{[M]^2}\right) \tag{31}$$

$$\frac{d\pi_{pM}}{dpM} = -(2.3)^2[M]\left(f_1 - \frac{f_2}{[M]^2}\right)$$

Thus it is evident that π_{pM} is minimal at a point where $[M] = (f_2/f_1)^{\frac{1}{2}}$**.

From eqn. (29) [M] at the equivalence point is given by:

$$[M]_{e.p.} = (f_2/f_1)^{\frac{1}{2}} \tag{32}$$

Therefore $(\pi_{pM})^{-1}$ becomes maximal at the equivalence point. Then it can be said that, in potentiometric titrations, regardless of the presence of a second metal, the equivalence point is found at the point where the pM or pY jump is a maximum.

$(1/\pi_{pM})_{e.p.}$ or $(1/\pi_{pY})_{e.p.}$ is a measure of the end-point sharpness and is called the "potentiometric sharpness index" designated as $S_{pot.}$. Differentiation of eqn. (30) with respect to pY yields an expression for π_{pY} from which:

$$S_{pot.} = (\pi_{pM})_{e.p.}^{-1} = (\pi_{pY})_{e.p.}^{-1}$$

or

$$\begin{aligned} S_{pot.} &= 0.217(f_1f_2)^{-\frac{1}{2}} \\ &= 0.217(C_{M_I}\gamma_{M_I,Y}/\alpha_{H,M_{II}(Y)}\beta_{(M_I)})^{\frac{1}{2}} \end{aligned} \tag{33}$$

Thus in order to obtain a distinct end-point, it is necessary to realize smaller values of f_1 and f_2, namely larger values of C_{M_I} and $\gamma_{M_I,Y}$ and smaller values of $\alpha_{H,M_{II}(Y)}$ and $\beta_{(M_I)}$.

REILLEY *et al.*[11,12] proposed a method of compleximetric titration with a mercury electrode as the indicator electrode. The potential of the mercury electrode is determined by $[Hg^{2+}]$ and given as follows:

$$E = E_0 + \frac{RT}{2F}\ln[Hg^{2+}] \tag{34}$$

Thus, if HgY is added, since $\gamma_{Hg,Y}$*** is very high, $\gamma_{Hg,Y}[Hg][Y]$ will equal C_{Hg} in a suitable pH range where neither the formation of mercury(II) hydroxide nor the release of Hg^{2+} ions is appreciable. Then:

$$[Hg^{2+}] = \frac{C_{Hg}}{\gamma_{Hg,Y}[Y]} \tag{35}$$

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* For a correction to the previous paper[14], see Appendix.

** Differentiation of the more general equation (11) shows the existence of inflection point at $C_Y/C_M = 0.5$. At this point π_{pY} become maximal. In titrations of Y with M, π_{pM} becomes maximal at the point $C_M/C_Y = 0.5$.

*** $\gamma_{Hg,Y} = K_{HgHY}K_{HY}[H] + K_{HgY} + K_{HgY(OH)}K_{HgY}K_W/[H]$. $\gamma_{Hg,Y}$ is a function of [H] but constant for a certain pH (for a certain pH range where HgY prevails, $\gamma_{Hg,Y} = K_{HgY}$).

Substituting eqn. (35) into eqn. (34),

$$E = E_0 + 0.0296 \log \frac{C_{Hg}}{\gamma_{Hg,Y}} + 0.0296\ pY \tag{36}$$

In other words, the potential E is determined solely by pY for definite experimental conditions (for a certain value of C_{Hg} and pH): E varies with the change in pY. Therefore in this case, the titration can be discussed by means of the afore-mentioned pY–*a* diagram.

PHOTOMETRIC OR VISUAL TITRATION

Methods of photometric titration can be conveniently divided into two classes: one method based on the measurement of the absorbance due to MY or titrant Y (no metal indicator) and the other using a metal indicator.

The former method can be considered fully in much the same way as in the amperometric titration (see the preceding section). In the following only the latter case will be discussed.

In general the concentration of metal indicator C_A is about 10^{-5} *M* and may be negligibly small compared with C_M. Thus it is assumed that the stoichiometric relationships (1) and (2) hold throughout the titration*. The following two cases will be discussed separately: (*a*) the use of HA as an indicator, and (*b*) the use of an indicator system NY–HA as an indicator.

HA as an indicator

(*a*) *Formation of a 1:1 chelate M_IA.* Combining the formation constant of M_IA (37) and the stoichiometric relationship (38), we obtain eqn. (39).

$$K_{M_IA} = \frac{[M_IA]}{[M_I][A]} \tag{37}$$

$$C_A = [M_IA] + [A]' \tag{38}$$

$$[M_I] = \frac{(C_A - [A]')\alpha_{H(A)}}{[A]'K_{M_IA}} \tag{39}$$

The indicator transition ϕ is given by

$$\phi = \frac{[A]'}{C_A} \tag{40}$$

Substituting eqn. (40) into eqn. (39),

$$[M_I] = \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}}{K_{M_IA}} \tag{41}$$

$$\text{If } \phi = 0.5,\ [M_I]_{\phi=0.5} = \frac{\alpha_{H(A)}}{K_{M_IA}} \tag{42}$$

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* For a more general treatment taking the effects of the indicator concentration into account, see ref. 13.

Substitution of eqn. (41) into eqns. (9) and (21) leads to:

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}\beta_{(M_I)}}{K_{M_IA}C_{M_I}} + \frac{\phi}{1-\phi}\,\frac{K_{M_IA}\alpha_{H(Y)}}{\alpha_{H(A)}\gamma_{M_I,Y}} \tag{43}$$

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}\beta_{(M_I)}}{K_{M_IA}C_{M_I}} + \frac{\phi}{1-\phi}\,\frac{K_{M_IA}\alpha_{H,M_{II}(Y)}}{\alpha_{H(A)}\gamma_{M_I,Y}} \tag{44}$$

Equations (43) and (44) relate a with ϕ in the vicinity of the equivalence point in the absence and in the presence of a second metal M_{II} respectively.

(*b*) *Formation of M_IA, M_IA_2 ..., M_IA_j.* Now the effects of successive complex formation will be discussed. The over-all formation constant of M_IA_j is given by:

$$K_{MA_j} = \frac{[M_IA_j]}{[M_I]\,[A]^j} \tag{45}$$

From the stoichiometric relationship for C_A, it follows that:

$$\begin{aligned} C_A - [A]' &= [M_IA] + 2[M_IA_2] + \ldots + j[M_IA_j] \\ &= [M_I]\,[A]\,\{K_{M_IA} + 2K_{M_IA_2}[A] + \ldots + j\,K_{M_IA_j}[A]^{j-1}\} \end{aligned} \tag{46}$$

$$[M_I] = \frac{C_A - [A]'}{[A]'}\,\frac{\alpha_{H(A)}}{\sum\limits_{j=1}^{j} j\,K_{MA_j}[A]^{j-1}} \tag{47}$$

The molar absorbance of a metal chelate of a metallochromic indicator is generally proportional to the number of indicator molecules bound to the metal. Thus designating the molar absorbance of M_IA as ε,

$$\phi = \frac{\varepsilon[A]'}{\varepsilon C_A} = \frac{[A]'}{C_A} \tag{48}$$

This means that, even in the case where successive complex formation is appreciable, ϕ can be defined in the same way as in the case where only the 1:1 chelate M_IA must be considered.

Substituting eqn. (48) into eqn. (47),

$$[M_I] = \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}}{\sum\limits_{j=1}^{j} j\,K_{M_IA_j}[A]^{j-1}} \tag{49}$$

In most cases $j \leqslant 2$, and if $j = 2$, then:

$$[M_I] = \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}}{K_{M_IA} + 2K_{M_IA_2}[A]} \tag{50}$$

When $\phi = 0.5$

$$[M_I]_{\phi=0.5} = \frac{\alpha_{H(A)}}{K_{MA} + 2K_{MA_2}[A]} = \frac{\alpha_{H(A)}}{K_{MA} + K_{MA_2}C_A/\alpha_{H(A)}} \tag{51}$$

Thus we can see that $[M_I]_{\phi=0,5}$ is a function of pH and C_A. Substituting eqn. (50) into eqns. (9) and (21),

$$a = 1 - \frac{1-\phi}{\phi} \frac{\alpha_{\mathrm{H(A)}}\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}(K_{\mathrm{M_IA}} + 2K_{\mathrm{M_IA_2}}[\mathrm{A}])} + \frac{\phi}{1-\phi} \frac{\alpha_{\mathrm{H(Y)}}(K_{\mathrm{M_IA}} + 2K_{\mathrm{M_IA_2}}[\mathrm{A}])}{\gamma_{\mathrm{M_I,Y}}\alpha_{\mathrm{H(A)}}} \tag{52}$$

$$a = 1 - \frac{1-\phi}{\phi} \frac{\alpha_{\mathrm{H(A)}}\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}(K_{\mathrm{M_IA}} + 2K_{\mathrm{M_IA_2}}[\mathrm{A}])} + {} + \frac{\phi}{1-\phi} \frac{\alpha_{\mathrm{H,M_{II}(Y)}}(K_{\mathrm{M_IA}} + 2K_{\mathrm{M_IA_2}}[\mathrm{A}])}{\gamma_{\mathrm{M_I,Y}}\alpha_{\mathrm{H(A)}}} \tag{53}$$

By the aid of these equations photometric or visual end-point detection with HA as an indicator can be quantitatively accounted for in the presence as well as in the absence of a second metal $\mathrm{M_{II}}$.

Use of a system NY–HA as an indicator

When there is no appropriate metal indicator for $\mathrm{M_I}$, a NY–HA system may be considered as an indicator. The case can be confined to one where only N reacts with A to form a colored chelate and the formation of such colored chelates as $\mathrm{M_IA}$, $\mathrm{M_{II}A}$, etc. is not appreciable.

Discussions on the use of the NY–HA system may be conveniently divided into two cases: (a) $\gamma_{\mathrm{N',Y'}} > \gamma_{\mathrm{M',Y'}}$, *e.g.* the indicator system Mg–EDTA–Erio T in the titration of barium[16], Cu–EDTA–PAN in the titration of aluminum[17] and Zn–EGTA–Zincon[8,9] or Zn–EGTA–PAN[10,18] in the titration of calcium; (b) $\gamma_{\mathrm{N',Y'}} < \gamma_{\mathrm{M',Y'}}$, *e.g.* Mg–EDTA–Erio T in the titration of calcium[16] (so-called partial replacement titration).

Case a: $\gamma_{\mathrm{N',Y'}} > \gamma_{\mathrm{M',Y'}}$. In most cases A forms a 1:1 chelate with N. Constant $K_{\mathrm{NY-A}}$ for the replacement equilibrium (54) is given by eqn. (55):

$$\mathrm{NY'} + \mathrm{A'} \rightleftharpoons \mathrm{NA'} + \mathrm{Y'} \tag{54}$$

$$K_{\mathrm{NY-A}} = \frac{[\mathrm{NA}]'[\mathrm{Y}]'}{[\mathrm{NY}]'[\mathrm{A}]'} = \frac{\gamma_{\mathrm{N,A'}}}{\gamma_{\mathrm{N,Y'}}} \tag{55}$$

Stoichiometric relationships for C_{A} and C_{N} are as follows:

$$C_{\mathrm{A}} = [\mathrm{NA}]' + [\mathrm{A}]' \tag{56}$$

$$C_{\mathrm{N}} = [\mathrm{NA}]' + [\mathrm{NY}] + [\mathrm{N}]' \tag{57}$$

From eqn. (55):

$$[\mathrm{Y}] = \frac{[\mathrm{A}]'[\mathrm{NY}]'\gamma_{\mathrm{N,A'}}}{[\mathrm{NA}]'\alpha_{\mathrm{H(Y)}}\gamma_{\mathrm{N,Y'}}} = \frac{[\mathrm{A}]'[\mathrm{NY}]'\gamma_{\mathrm{N,A}}}{[\mathrm{NA}]'\alpha_{\mathrm{H(A)}}\gamma_{\mathrm{N,Y}}} \tag{58}$$

Ordinarily it may be assumed that $C_{\mathrm{N}} \gg C_{\mathrm{A}}$. So substituting eqns. (56) and (57) into eqn. (58), we obtain:

$$[\mathrm{Y}] = \frac{\phi}{1-\phi} \frac{C_{\mathrm{N}}\gamma_{\mathrm{N,A}}}{\alpha_{\mathrm{H(A)}}\gamma_{\mathrm{N,Y}}} \tag{59}$$

where $\phi = [A]'/C_A$ by definition. It follows that

$$[Y]_{\phi=0.5} = \frac{C_N \gamma_{N,A}}{\alpha_{H(A)} \gamma_{N,Y}} \tag{60}$$

It should be noted that $[Y]_{\phi=0.5}$ depends on pH and C_N. Substituting eqn. (59) into eqns. (12) and (24):

$$a = 1 - \frac{1-\phi}{\phi} \frac{\beta_{(M_I)} \alpha_{H(A)} \gamma_{N,Y}}{\gamma_{M_I,Y} C_N \gamma_{N,A}} + \frac{\phi}{1-\phi} \frac{\alpha_{H(Y)} C_N \gamma_{N,A}}{C_{M_I} \alpha_{H(A)} \gamma_{N,Y}} \tag{61}$$

$$a = 1 - \frac{1-\phi}{\phi} \frac{\beta_{(M_I)} \alpha_{H(A)} \gamma_{N,Y}}{\gamma_{M_I,Y} C_N \gamma_{N,A}} + \frac{\phi}{1-\phi} \frac{\alpha_{H,M_{II}(Y)} C_N \gamma_{N,A}}{C_{M_I} \alpha_{H(A)} \gamma_{N,Y}} \tag{62}$$

When successive complex formation, NA_1, NA_2 ... NA_j, must be considered, then from the formation constants of the species involved and the stoichiometric relationships for C_A and C_N, we have:

$$[Y] = \frac{\phi}{1-\phi} \frac{C_N \sum_{j=1}^{j} j\, K_{NA_j} [A]^{j-1}}{\alpha_{H(A)} \gamma_{N,Y}} \tag{63}$$

In most cases $j \leqslant 2$. In this case, eqn. (63) simplifies to:

$$[Y] = \frac{\phi}{1-\phi} \frac{C_N (K_{NA} + 2K_{NA_2}[A])}{\alpha_{H(A)} \gamma_{N,Y}} \tag{64}$$

and

$$[Y]_{\phi=0.5} = \frac{C_N (K_{NA} + 2K_{NA_2}[A])}{\alpha_{H(A)} \gamma_{N,Y}} = \frac{C_N (K_{NA} + K_{NA_2} C_A/\alpha_{H(A)})}{\alpha_{H(A)} \gamma_{N,Y}} \tag{65}$$

From eqn. (65) it is evident that $[Y]_{\phi=0.5}$ is a function of pH, C_N and C_A.

Substituting eqn. (64) into eqns. (12) and (24):

$$\begin{aligned} a = 1 &- \frac{1-\phi}{\phi} \frac{\gamma_{N,Y} \alpha_{H(A)} \beta_{(M_I)}}{C_N \gamma_{M_I,Y} (K_{NA} + 2K_{NA_2}[A])} + \\ &+ \frac{\phi}{1-\phi} \frac{C_N \alpha_{H(Y)} (K_{NA} + 2K_{NA_2}[A])}{C_{M_I} \alpha_{H(A)} \gamma_{N,Y}} \end{aligned} \tag{66}$$

$$\begin{aligned} a = 1 &- \frac{1-\phi}{\phi} \frac{\gamma_{N,Y} \alpha_{H(A)} \beta_{(M_I)}}{C_N \gamma_{M_I,Y} (K_{NA} + 2K_{NA_2}[A])} + \\ &+ \frac{\phi}{1-\phi} \frac{C_N \alpha_{H,M_{II}(Y)} (K_{NA} + 2K_{NA_2}[A])}{C_{M_I} \alpha_{H(A)} \gamma_{N,Y}} \end{aligned} \tag{67}$$

Case b: $\gamma_{N',Y'} < \gamma_{M',Y'}$. The following stoichiometric relationships hold:

$$C_M = [MY]' + [M]' \tag{68}$$

$$C_Y = [MY]' + [NY]' + [Y]' \tag{69}$$

$$C_N = [NY]' + [N]' \tag{70}$$

If N is added as NY, it follows that:

$$C_Y' = C_Y - C_N \tag{71}$$

where C_{Y}' refers to the total concentration of titrant used.

By appropriate substitutions and rearrangements of eqns. (68), (69), (70) and the formation constants of the involved species, we obtain:

$$C_{Y}' = C_M - [N]\left(\frac{\gamma_{N',Y}[MY]'}{\gamma_{M',Y}[NY]'} + 1\right)\beta_{(N)} + \frac{[NY]'}{\gamma_{N',Y'}[N]\beta_{(N)}} \qquad (72)$$

In the vicinity of the equivalence point, [MY] and [NY] may be regarded as C_M and C_N respectively. Then:

$$a = 1 - [N]\left(\frac{\gamma_{N',Y}C_M}{\gamma_{M',Y}C_N} + 1\right)\frac{\beta_{(N)}}{C_M} + \frac{C_N}{\gamma_{N,Y'}C_M[N]} \qquad (73)$$

If only the formation of a 1:1 chelate NA has to be taken into account, from the formation constant of NA and the indicator transition ϕ:

$$[N] = \frac{1-\phi}{\phi}\,\frac{\alpha_{H(A)}}{\gamma_{N,A}} \qquad (74)$$

Combining eqns. (73) and (74), we obtain:

$$a = 1 - \frac{1-\phi}{\phi}\left(\frac{\gamma_{N',Y}C_M}{\gamma_{M',Y}[NY]'} + 1\right)\frac{\alpha_{H(A)}\beta_{(N)}}{\gamma_{N,A}C_M} + \frac{\phi}{1-\phi}\,\frac{\gamma_{N,A}[NY]'}{\gamma_{N,Y'}\alpha_{H(A)}C_M} \qquad (75)$$

where $[NY]'$ may be regarded as C_N if $a \simeq 1$.

When $\gamma_{N',Y}C_M/\gamma_{M',Y}][NY]'$ is sufficiently greater than unity, eqns. (75) and (61) become identical. Even if successive complex formation of N with A must be considered, the indicator transition can easily be dealt with in much the same way as in the case where only the formation of a 1:1 chelate has to be taken into account (as to the effect of a second metal, see preceding section).

End-point sharpness of photometric or visual titration

By means of eqns. (43), (44), (52), (53), (61), (62), (66), (67) and (75), various equilibria involved in compleximetric titrations can be discussed quantitatively.

Now a is related to ϕ by means of the following general expression:

$$a = 1 - \frac{1-\phi}{\phi}f_1 + \frac{\phi}{1-\phi}f_2 \qquad (76)$$

where f_1 and f_2 are constants dependent on $\gamma_{M,Y}$, $\gamma_{M,A}$ and on experimental conditions such as pH, auxiliary complexing agents, etc. As noted above, the second term on the right side of eqn. (76) is mainly concerned with the indicator transition before the equivalence point and the third term is mainly concerned with that after the equivalence point. Although the following discussions are based on eqn. (76), each result can be easily translated for practical purposes by substituting the numerical values of which f_1 and f_2 are composed.

At the equivalence point,

$$\phi_{e.p.} = \frac{(f_1)^{\frac{1}{2}}}{(f_1)^{\frac{1}{2}} + (f_2)^{\frac{1}{2}}} \qquad (77)$$

It follows that $\phi_{\mathrm{e.p.}}$ is a function of f_1 and f_2 and that $\phi = 0.5$ at the equivalence point *only when* $f_1 = f_2$. Differentiation of eqn. (76) with respect to a leads to:

$$\frac{d\phi}{da} = \left(\frac{da}{d\phi}\right)^{-1} = \left(f_1 \frac{1}{\phi^2} + f_2 \frac{1}{(1-\phi)^2}\right)^{-1} \tag{78}$$

$$\frac{d^2a}{d\phi^2} = -2\, f_1 \frac{1}{\phi^3} + 2\, f_2 \frac{1}{(1-\phi)^3} \tag{79}$$

Thus $d\phi/da$ becomes a maximum with the following value of ϕ:

$$\phi_{(d\phi/da)\,\mathrm{max.}} = \frac{(f_1)^{\frac{1}{3}}}{(f_1)^{\frac{1}{3}} + (f_2)^{\frac{1}{3}}} \tag{80}$$

$(d\phi/da)_{\mathrm{max.}}$ is given by the following:

$$(d\phi/da)_{\mathrm{max.}} = (f_1^{\frac{1}{3}} + f_2^{\frac{1}{3}})^{-3} \tag{81}$$

When the end-point is located at a point where $d\phi/da$ is a maximum, then the greater the value of $(d\phi/da)_{\mathrm{max.}}$, the sharper will be the end-point. In order to obtain a sufficiently large value of $(d\phi/da)_{\mathrm{max.}}$, it is necessary to realize sufficiently low values of f_1 and f_2. Under conditions where the value of f_1 is low, the indicator is not appreciably discolored until very near the equivalence point; if the value of f_2 is low, the indicator transition after the equivalence point is very sharp*. From the practical point of view, it may be said that visual detection of a point with $(d\phi/da)_{\mathrm{max.}}$ is possible when f_1 and f_2 are both less than 10^{-3} **.

From the definition of f_1 and f_2:

$$f_1 f_2 = \frac{\alpha_{\mathrm{H,M_{II}(Y)}}\beta_{(\mathrm{M_I})}}{C_{\mathrm{M_I}}\gamma_{\mathrm{M_I,Y}}}$$

Thus it follows that the product $f_1 f_2$ is independent of indicator characteristics. For a certain value of $f_1 f_2$, $(d\phi/da)_{\mathrm{max.}}$ is greatest when $f_1 = f_2$.

Now we consider the titration error involved in the end-point location at a point with $(d\phi/da)_{\mathrm{max.}}$. Putting eqn. (80) into eqn. (76), the fraction titrated at a point with $(d\phi/da)_{\mathrm{max.}}$ is given by the following:

$$a_{(d\phi/da)\mathrm{max.}} = 1 - (f_1^2 f_2)^{\frac{1}{3}} + (f_1 f_2^2)^{\frac{1}{3}} \tag{82}$$

This means that a point with $(d\phi/da)_{\mathrm{max.}}$ is not always the equivalence point. The end-point with $(d\phi/da)_{\mathrm{max.}}$ comprises a theoretical error given by the following:

$$\text{Theoretical error} = (f_1 f_2^2)^{\frac{1}{3}} - (f_1^2 f_2)^{\frac{1}{3}} \tag{83}$$

Thus it is only when $f_1 = f_2$ that an end-point with $(d\phi/da)_{\mathrm{max.}}$ coincides with the equivalence point. $d\phi/da$ becomes maximal before the equivalence point when $f_1 > f_2$, and after the equivalence point when $f_1 < f_2$.

However when f_1 and f_2 are both sufficiently low, the theoretical error given by eqn. (83) is negligibly small.

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* A second metal does not alter f_1 but makes f_2 large, consequently the indicator transition after the equivalence point becomes more or less obscure in its presence.

** When $f_1 = f_2 = 10^{-3}$, we obtain $\phi = 0.1$ for $a = 0.99$ and $\phi = 0.9$ for $a = 1.01$, so a visual titration can be successfully carried out within an error of ± 1%.

When $f_1 = f_2$, $\phi_{e.p.} = 0.5$. Thus $[M]_{\phi=0.5}$ and $[Y]_{\phi=0.5}$ given by eqns. (42) and (60) are equal to $[M]_{e.p.}$ and $[Y]_{e.p.}$ given by eqns. (22) and (25) respectively.

$$\left(\frac{C_{M_I}\alpha_{H\,M_{II}(Y)}}{\beta_{(M_I)}\gamma_{M_I,Y}}\right)^{\frac{1}{2}} = \frac{\alpha_{H(A)}}{\gamma_{M_I,A}} \tag{84}$$

$$\left(\frac{C_{M_I}\beta_{(M_I)}}{\alpha_{H,M_{II}(Y)}\gamma_{M_I,Y}}\right)^{\frac{1}{2}} = \frac{C_N\gamma_{N,A}}{\alpha_{H(A)}\gamma_{N,Y}} \tag{85}$$

When $f_1 < f_2$, $[M]_{e.p.} > [M]_{\phi=0.5}$ or $[Y]_{e.p.} < [Y]_{\phi=0.5}$, and when $f_1 > f_2$, $[M]_{e.p.} < [M]_{\phi=0.5}$ or $[Y]_{e.p.} > [Y]_{\phi=0.5}$.

From the above considerations, it may be concluded that, in order to obtain a sharp and correct end-point in visual compleximetric titrations, it is necessary: (*a*) to realize a sufficiently high value of $C_{M_I}\gamma_{M_I,Y}/\alpha_{H,M_{II}(Y)}\beta_{(M_I)}$ and (*b*) to choose an indicator and experimental conditions which fulfil the requirement $[M]_{\phi=0.5} = [M]_{e.p.}$ or $[Y]_{\phi=0.5} = [Y]_{e.p.}$ as satisfactorily as possible.

For an indicator system NY–HA, $[Y]_{\phi=0.5}$ can be modified to some extent for a certain set of N, A and pH, because $[Y]_{\phi=0.5}$ is a function of C_N. This is why the NY–HA system is advantageous in some cases of selective titrations especially when the value of $C_{M_I}\gamma_{M_I,Y}/\alpha_{H,M_{II}(Y)}\beta_{(M_I)}$ is not sufficiently high. Sometimes the titration must be carried out with a fairly low value of $C_{M_I}\gamma_{M_I,Y}/\alpha_{H,M_{II}(Y)}\beta_{(M_I)}$. When $C_{M_I}\gamma_{M_I,Y}/\alpha_{H,M_{II}(Y)}\beta_{(M_I)} \leqslant 10^5$, photometric determination of the end-point is preferable.

Although, if $f_1 = f_2$, a point with $(d\phi/da)_{max.}$ is theoretically the equivalence point, it is not always possible to obtain experimental conditions which lead to $f_1 = f_2$, and, for an insufficiently low value of $f_1 f_2$, a small difference between f_1 and f_2 may produce a considerable error as shown in eqn. (83).

Therefore in photometric titrations, the end-point is usually obtained by a graphical method making either f_1 or f_2 sufficiently low (see Fig. 1).

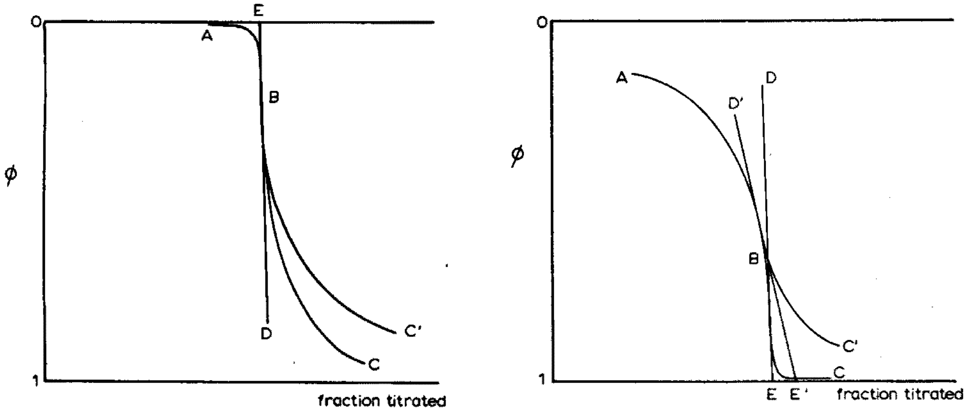

Fig. 1. Graphical determination of end-points. a, making f_1 low; b, making f_2 low. Curves ABC, in the absence of a second metal; curves ABC', in the presence of a second metal; E, E', end-points. For Fig. 1a (left), DE: tangent at the inflection point of the curve ABC or ABC'. For Fig. 1b (right), DE: tangent at the inflection point of the curve ABC; D'E': tangent at the inflection point of the curve ABC'.

The graphical method represented in Fig. 1a always gives rise to a negative error and that in Fig. 1b always gives a positive error.

When the end-point is located at the intersection of the tangent at the inflection point ($d\phi/da$ = max.) with the horizontal line $\phi = 0$ ($1 - \phi = 1$) (Fig. 1a), the theoretical error is given by formula (86); when the end-point is taken at the intersection of the tangent at the inflection point with the horizontal line $\phi = 1$ ($1 - \phi = 0$) (Fig. 1b), the theoretical error is given by formula (87):

$$- f_1^{2/3}(f_1^{1/3} + 3f_2^{1/3}) \tag{86}$$

$$f_2^{2/3}(f_2^{1/3} + 3f_1^{1/3}) \tag{87}$$

In both cases the error involved is negligibly small if either f_1 or f_2 is adequately low. Although the presence of a second metal does not appreciably affect f_1, it makes f_2 high. Therefore in the graphical determination of the end-point, it is strongly desirable to adopt the method given in Fig. 1a, making f_1 low.

In the photometric titration, graphical determination of the inflection point is not always easy, but it is not difficult to find the point $\phi = 0.05$. Thus from a practical point of view, it will be more convenient to trace the tangent at the point $\phi = 0.05$. When the end-point is taken as the intersection of this tangent and the horizontal line $\phi = 0$, the theoretical error involved is given by the following:

$$- 39f_1 - 0.002f_2 \tag{88}$$

When $f_1 < 10^{-4}$, the error is low enough for practical purposes, even with a value of f_2 of unity.

In Table I the theoretical errors are given for various sets of f_1 and f_2.

TABLE I

THEORETICAL ERRORS INVOLVED IN THE GRAPHICAL DETERMINATION OF END-POINT IN THE PHOTOMETRIC TITRATION

(A) End-point: intersection of the tangent at the inflection point and the horizontal line $\phi = 0$
Theoretical error (%)

f_1 f_2	10^{-5}	10^{-4}	10^{-3}
10^{-2}	−0.03	−0.16	−0.7
10^{-1}	−0.07	−0.32	−1.5
1	−0.15	−0.67	−3.1

(B) End-point: intersection of the tangent at the point $\phi = 0.05$ *and the horizontal line* $\phi = 0$
Theoretical error (%)

f_1 f_2	10^{-5}	10^{-4}	10^{-3}
10^{-2}	−0.04	−0.4	−4
10^{-1}	−0.06	−0.4	−4
1	−0.24	−0.6	−4.2

As can be seen from the above discussions, the optimum conditions and end-point sharpness as well as theoretical errors for a given compleximetric titration, can easily be predicted by means of f_1 and f_2. Thus the determination of the various constants involved in the calculation of f_1 and f_2 is of great importance in fundamental research on compleximetric titrations.

Since end-point sharpness can be objectively given as a function of f_1 and f_2, it may be preferable to give this expression in papers dealing with a new method of titration. Thus the somewhat ambiguous expressions such as obscure, sluggish or sharp end-point, can be avoided. Even if some constants are not available for the exact calculation of f_1 and f_2, approximate values of f_1 and f_2 can easily be found from photometric titration curves.

APPENDIX

Note on the buffer capacity of a ligand buffer

The concept of ligand buffer was proposed in ref. 14 in which the buffer capacity of a ligand buffer was defined and calculated. An error was made in differentiation and eqns. (10) and (11) of the previous paper should read:

$$\pi = \frac{2.3K_{MA}[A]}{(K_{MA}[A] + 1)^2} \tag{10}$$

and

$$\pi = 2.3(\alpha - 1)/\alpha^2 \tag{11}$$

respectively. Accordingly calculated values of buffer capacity given in the same paper should be revised as follows:

BUFFER CAPACITY OF THE LIGAND BUFFER FOR VARIOUS VALUES OF C_M/C_A

$a = C_M/C_A$	*Buffer capacity*
1.1	0.191
2	0.578
5	0.371
11	0.191

SUMMARY

Some general theoretical expressions are proposed for various titration curves involved in compleximetric titrations. The effects of some critical factors, such as pH, auxiliary complexing agents and presence of a second metal, are all taken into account in these expressions. The sharpness and errors of potentiometric, amperometric and photometric (visual) indication of end-points are also theoretically discussed.

RÉSUMÉ

Les auteurs proposent quelques expressions théoriques générales, pouvant s'appliquer à diverses courbes de titrages compleximétriques, tenant compte de l'influence de facteurs tels que pH, agents complexants et présence d'un second métal. Les auteurs examinent également la netteté et la précision d'indications potentiométriques, ampérométriques et photométriques de points finals.

ZUSAMMENFASSUNG

Es werden einige allgemeine theoretische Ausdrücke für verschiedene Titrationskurven einschliesslich komplexometrischer Titrationen vorgeschlagen. Der Einfluss des pH-Wertes, von Hilfskomplexbildnern und die Gegenwart eines zweiten Metalls wird in diesen Ausdrücken berücksichtigt. Die Schärfe und die Fehler der potentiometrischen, amperometrischen und photometrischen (sichtbaren) Anzeige des Endpunktes werden ebenfalls theoretisch diskutiert.

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THE DETERMINATION OF ALUMINIUM IN AQUEOUS SOLUTION BY ATOMIC ABSORPTION SPECTROSCOPY

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The literature concerning the determination of aluminium by atomic absorption is small in volume, and for the most part dates from early 1963. ROBINSON[1] described a technique which utilised a spark discharge in the flame and achieved a reasonable sensitivity, but this method and the equipment required do not appear very satisfactory for routine laboratory use. GILBERT[2] in a review article stated that "aluminium is undetectable in air–gas . . . or air–acetylene or oxyhydrogen or oxyacetylene . . .". SLAVIN AND MANNING[3] reported the use of a Zeiss total consumption atomizer-burner with a fuel-rich oxyacetylene flame and obtained a sensitivity (p.p.m. for 1% absorption) of 6 p.p.m.; they used a solution containing ethanol in unspecified concentration.

CHAKRABARTI, LYLES AND DOWLING[4] have published the only paper to appear (at the time of writing), which could be said to describe the practical determination of aluminium by atomic absorption spectroscopy. Their method involved the prior extraction of the aluminium into 4-methyl-2-pentanone, and this detracted somewhat from the normal simplicity of atomic absorption methods. Further, although the sensitivity obtained (1% absorption) was estimated at 8 p.p.m., this was hardly a practical sensitivity limit as the standard deviation found at low levels was 13 p.p.m.

This paper describes a completely different approach to the problem; a true pre-mixed flame is used rather than the total consumption-type burners used by other workers for aluminium work. The results are felt to be of some importance, not only in supplying a rapid and accurate method for aluminium determination, but also in extending the rather meagre knowledge of reaction processes in flames.

EXPERIMENTAL

Apparatus

The apparatus used for the work described consisted of a Zeiss M4 QIII monochromator together with a modulated power supply (100 cycles) and a broadband a.c. amplifier, the latter units being supplied by Techtron Appliances Pty. Ltd. The photomultiplier used was an E.M.I. type 6256, and the aluminium hollow-cathode was supplied by Atomic Spectral Lamps Pty. Ltd. The spray chamber used (Fig. 1) was of the authors' own design and was made by a local glass technician. It features a ground-glass cone (B24) onto which the ground-glass socket of the burner fits. The atomizer used was a standard type (Evans Electroselenium Ltd.).

Epoxy resin cement was used to seal the end plug into the spray chamber, and the atomizer into this end plug, to avoid the possibility of gas leaks.

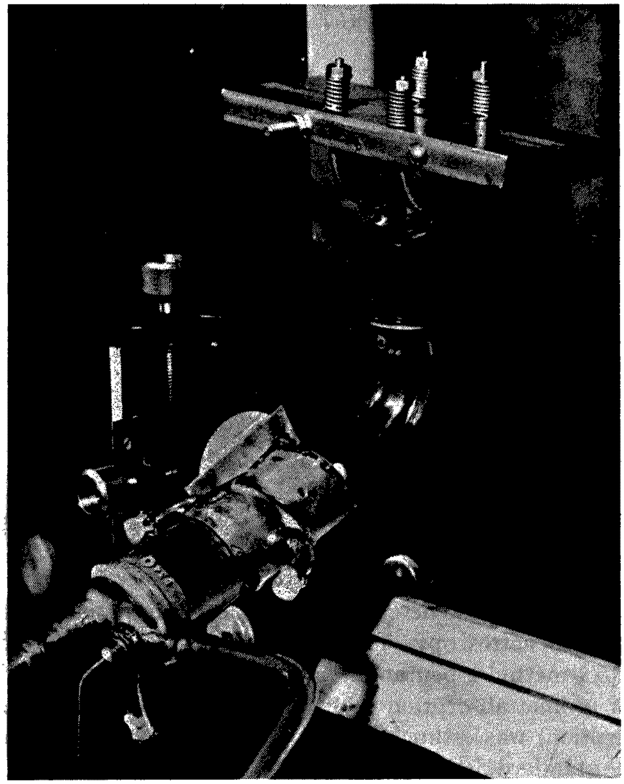


Fig. 1. Burner and spray chamber.

Initial development

The equipment was assembled as shown schematically in Fig. 2. By means of the flow-meters, F1, F2 and F3, the flows of nitrogen, oxygen and acetylene respectively could be varied. However, it should be pointed out that when the pressures of nitrogen and oxygen delivered to the flow-meters are kept equal, a decrease in oxygen flow will cause an increase in nitrogen flow and *vice versa*, as the flow of gas at a given pressure is governed by the fixed geometry of the atomizer.

The initial experimental work was carried out using a burner top of steel plate, 0.125 in. thick, mounted on a glass base. The burner geometry found most effective at this time was a single row of 14 holes of 1 mm diameter spaced at 2 mm centres. With this burner, it was found that atomic absorption by aluminium commenced at an oxygen concentration in the nitrogen–oxygen stream of about 40%, with the acetylene flow adjusted to give a slightly fuel-rich flame.

Absorption for a given aluminium concentration was found to increase as the oxygen content of the atomizing stream was increased, the acetylene being adjusted at each oxygen level to keep the flame still slightly fuel-rich. The best sensitivity obtained using this type of burner was 0.8 p.p.m. (1% absorption), using an oxygen content of 85% in the atomizing stream and a completely aqueous solution. However, overheating of the relatively thin plate used for the burner top caused detonation of the pre-mixed gases in the spray chamber, and this design was then abandoned. The above work has been previously described by the authors[5].

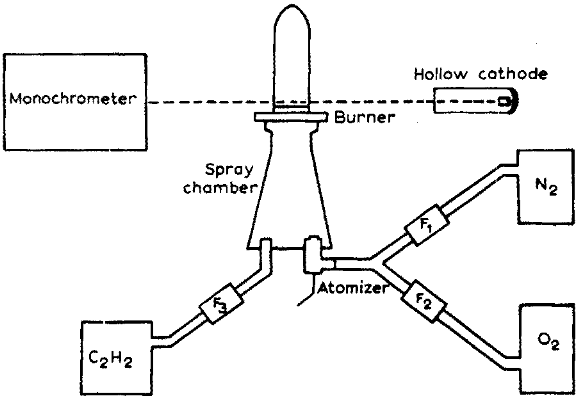


Fig. 2. Schematic diagram of apparatus.

Later development

A considerable amount of investigation was then directed to the design of water-cooled burners of the same basic type as that previously described, and also of slotted types. However, considerable difficulty was experienced due to blockage of the holes and slots by condensed spray particles and precipitated salts. It was therefore decided to use a rather massive metal top so that in use it would become heated to a temperature sufficient to prevent condensation, but low enough to prevent any danger of detonation. After considerable experimentation, the design described below was arrived at, and when operated with a gas mixture of suitable composition (see below), this burner reached an equilibrium temperature of 130–150°. This temperature is considered quite safe, the minimum ignition temperature for air–acetylene mixtures having been stated as 350° and that for oxygen–acetylene mixtures[6] as 335°. Provided that the burner is allowed to heat to near 100° before any aspiration of solution, condensation does not take place.

The burner

The burner, which is shown in Fig. 1, consists of two pieces of 1 in. × 0.5 in.

stainless steel, 6 in. long, joined together with 2 stainless steel spacers so placed as to produce a slot of 0.45 × 30 mm. The lower side of this stainless steel portion is ground flat and fitted to the glass base with the spring clips shown.

Determination of optimum operating conditions

Resonance line used. It was discovered quite early in the investigations described above, that the resonance line at 3093 Å (actually a doublet: 3092.7, 3092.8 Å) was more sensitive in absorption than the line at 3961 Å which has been used by other workers. In addition it was in a region of the spectrum which was much less subject to flame noise with the burner described. Consequently all of the work described below was concentrated on the line at 3093 Å; the relative sensitivities of the various aluminium lines are shown in Fig. 3.

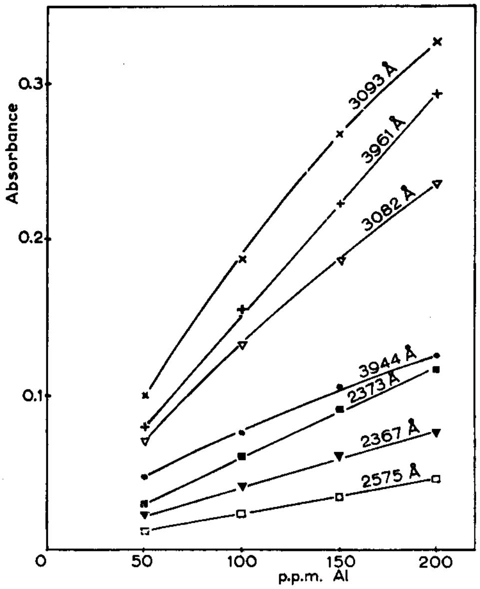
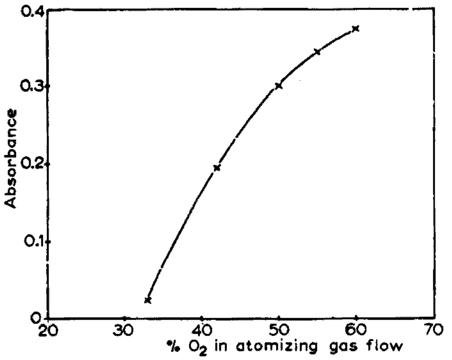


Fig. 3. Relative sensitivities of aluminium resonance lines.

Flame composition. Figure 4 illustrates the variations which occurred in absorbance of a 200 p.p.m. aluminium solution as the percentage of oxygen in the total flow of nitrogen plus oxygen in the atomizing gas stream was varied; the acetylene flow was adjusted to the optimum for each composition. The total flow of oxygen plus nitrogen, was maintained constant at about 10 l/min for this and all succeeding work, by maintaining the pressure of the gases at 15 p.s.i.

Figure 5 illustrates the variation in absorbance for a 200 p.p.m. aluminium solution when the percentage of oxygen in the atomizing gas stream was held constant at 50% while the acetylene flow was varied. In practice the optimum flame condition is readily achieved by adjustment of the acetylene flow to produce a white "feather" about 1.5–2 in. high above the blue cone. The upper limit of oxygen concentration shown in Fig. 4 was the greatest used, as this was considered to be a safe limit for the burner described. Higher concentrations produced a lower blue cone with greater risk of striking back.



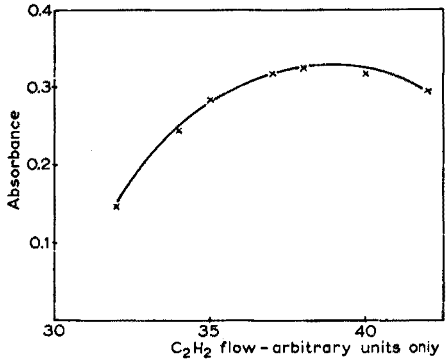
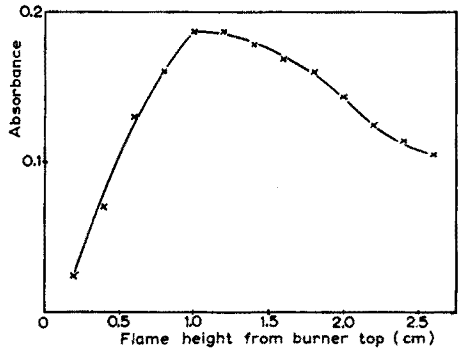


Fig. 4. Variation of absorbance with oxygen flow.

Fig. 5. Variation of absorbance with acetylene flow.

The chosen level of around 50% oxygen in the atomizing stream was safe and offered reasonable sensitivity, but it appears quite likely from the results obtained that better sensitivities could be obtained with other combinations of gas composition and burner design.

Position of the flame. Figures 6 and 7 illustrate the variations in absorbance for a 100 p.p.m. aluminium solution as the position of the flame was varied relative to the path of the light beam from the hollow cathode. Figure 6 shows the effect of



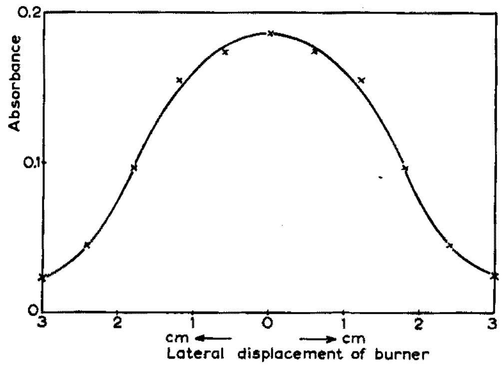


Fig. 6. Aluminium absorption at different flame heights.

Fig. 7. Aluminium absorption at different lateral positions of the flame.

variation of the height of the flame, 0 corresponding to the point where the burner top first starts to interrupt the light beam. Figure 7 shows the effect of variations in the lateral adjustment of the flame, the height being set at the optimum of 1.0 cm; here, 0 corresponds to the centre of the light beam. It can be seen that adjustment is not notably more critical than for other elements when an elongated burner is used. These measurements were made with a relatively undefined light path focussed in the centre of the flame.

Lamp current and slit-width. With a gas composition of 50% oxygen in the atomizing stream and with the optimum acetylene flow, the effects on absorbance of various lamp currents and monochromator slit-widths were examined for a 100 p.p.m. aluminium solution. It can be seen from Fig. 8 that for the lamp and monochromator used, the sensitivity tends to fall with increased slit-width, particularly at low (4 mA) and high (16–20 mA) lamp currents. As a result, for all ensuing work, conditions were stabilized at a lamp current of 10 mA and a slit-width of 0.05 mm.

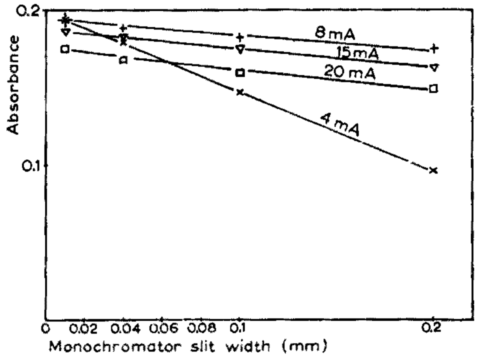


Fig. 8. Effects of lamp current–slit-width on absorption.

RESULTS AND DISCUSSION

Sensitivity and precision

It has been quite common in atomic absorption work to define the limit of detection as that concentration of an element which will produce an absorption of 1%. However, this is not always a practical figure, particularly if the noise level exceeds 0.5%; Chakrabarti, Lyles and Dowling[4] adopted the method of defining the limit of detection as twice the standard deviation found at very low levels of concentration.

In the work described here, it was found that the noise level (flame plus lamp) was very low, certainly less than 0.5%, so that the usual method has been employed. The concentration of aluminium needed to produce 1% absorption in aqueous solution was found to be about 1.7 p.p.m. with an atomizing gas stream containing 50% oxygen. It appears certain that a different burner design and gas composition could produce higher sensitivities but it seems doubtful that such changes would improve the sensitivity beyond a factor of 2 or 3.

Suggested reaction mechanism

Since other workers have not been able to achieve absorption for aluminium with oxyacetylene flames in the absence of organic solvents, it does seem reasonable to ask why the burner described has proved so successful (relatively). Firstly, it is considered quite important that the burner described is a true pre-mix burner. The major consequences of this are: (*a*) higher temperatures are produced, and (*b*) a considerable amount of free carbon is produced in the flame.

The latter is probably the most important and aids the production of neutral aluminium atoms by the reaction

$$AlO + C \rightleftharpoons Al + CO$$

This mechanism has been already suggested by GIBSON, GROSSMAN AND COOKE[7]. The possibility that nitrogen took part in the reaction and aided the production of aluminium by the formation of unstable cyanide molecules was considered. However, the replacement of nitrogen in the atomizing stream by an equal volume of argon produced an identical sensitivity.

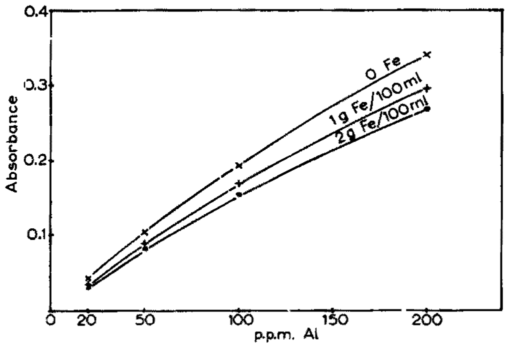
The time available to achieve some degree of equilibrium in the flame is also considered to be important. The average total-consumption burner delivers the flame gases at a velocity several times greater than the burning velocity. In the case of the burner described the velocity through the burner opening probably does not exceed the burning velocity for the composition used by more than 40–50%.

The results obtained with this type of burner also naturally lead to a re-examination of the mechanisms proposed by others for total-consumption burners fed with organic solutions. Possibly the main function of the organic material is to promote the production of carbon in the flame, and not merely to raise the temperature. Further experimental work is obviously required to elucidate the nature of such flame reactions, about which too little is currently known, and it is hoped that this paper may encourage further work along these lines.

Investigation of interferences

A widespread investigation was made of potential interferences in an effort to encompass the analysis of a wide range of sample types. The types of samples for which standard samples were available were non-ferrous metals and alloys, iron ores, steels, and phosphate rock. In addition to the cations and anions which would be naturally introduced from these sample types, an investigation was also made of the anions which would be introduced in various acid digestions, and also of high concentrations of sodium such as would be introduced from peroxide fusions.

Up to 2 g/100 ml of the following ions caused no interference: Ca^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Na^{+}, PO_4^{3-}, SO_4^{2-}. Serious interference effects were found in the presence of iron and chloride; the magnitudes of these interferences are shown in Figs. 9 and 10 where calibration graphs are shown for aluminium in the presence of various concentrations of iron and chloride ion respectively. No method of eliminating these interferences has been devised to date. It is therefore necessary to eliminate the use of hydrochloric acid or other chloride-containing material, and to compensate for iron interference by preparing standards containing a similar amount of iron to that expected in the sample. This is not very difficult in most cases; it can be seen from the graphs that if the concentration of iron is less than 10 times the concentration of aluminium in the sample its effect can be ignored. In the case of such samples as iron ore and steel, the iron content is either known or is determined in any case. If a series of standards containing different levels of iron is used, the true aluminium content can be calculated by numerical interpolation between the appropriate standards. The concentration of nitric acid has no detectable effect on the aluminium absorption and it was therefore chosen as the preferred medium, a concentration of 2–5% being used.



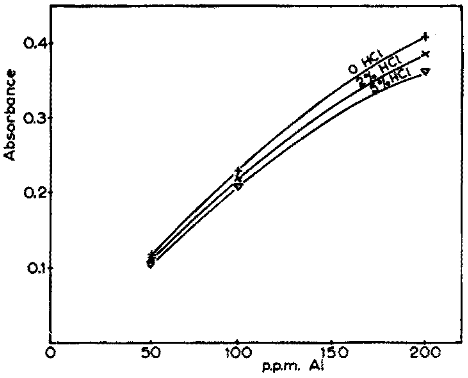


Fig. 9. Effect of iron on aluminium absorption.

Fig. 10. Effect of chloride on aluminium absorption.

Analysis of standard samples

The analytical results obtained, together with the analyses supplied, are shown for a number of standard samples in Table I. The results for iron ore and steel samples were obtained by calibrating with reference to standards containing known amounts of iron, and interpolating between these graphs from the (known) iron content of the sample.

TABLE I

ANALYTICAL RESULTS OBTAINED

Sample	*Atomic absorption result found (A) (%)*	*Standard result (B) (%)*	*Difference (A – B) (%)*
Aluminium Bronze NBS 164	6.30	6.21	+ 0.09
Zinc die casting alloy NBS 94a	3.98	3.90	+ 0.08
Iron Ore B.H.P. S1	2.04	2.03	+ 0.01
Iron Ore B.C.S. 175/1	1.06	1.10	– 0.04
Steel NBS 22c	0.12	0.116	—
Steel NBS 125	0.25	0.261	– 0.01
Steel NBS 106a	1.10	1.08	+ 0.02
Steel NBS 65d	0.06	0.059	—
Phosphate Rock A.M.D.L. 1	0.25	0.25	—
Phosphate Rock A.M.D.L. 2	3.48	3.49	– 0.01
Phosphate Rock A.M.D.L. 3	0.25	0.255	— 0.01

It can be seen from Table I that agreement obtained between the atomic absorption method and the standard methods used is quite reasonable. At the lower levels determined (less than 0.2%), sensitivity tends to be a limiting factor.

The authors wish to thank the management of Sulphide Corporation Pty. Limited for permission to publish this paper.

SUMMARY

A special burner is proposed for the atomic absorption spectrophotometric determination of aluminium. With a suitable mixture of nitrogen, oxygen and acetylene, a limit of detection of less than 2 p.p.m. was achieved in aqueous solution. The experimental variables and potential interferences were studied. Iron and chloride interfered in high concentrations, and must be either absent or allowed for in the preparation of standards. Several standard samples of various types were analysed for aluminium with satisfactory results.

RÉSUMÉ

Un brûleur spécial est proposé pour le dosage spectrophotométrique par absorption atomique de l'aluminium. En utilisant un mélange approprié d'azote, d'oxygène et d'acétylène, on peut arriver à une limite de détection de moins de 2 p.p.m. Le fer et les chlorures gênent en fortes concentrations. Plusieurs dosages d'aluminium, dans des types variés d'échantillons ont donné des résultats satisfaisants.

ZUSAMMENFASSUNG

Ein Spezialbrenner wird für die atomare Absorptionsspektrometrie zur Bestimmung von Aluminium vorgeschlagen. Mit einer geeigneten Mischung von Stickstoff, Sauerstoff und Acetylen wurde in wässriger Lösung eine Nachweisgrenze von weniger als 2 p.p.m. erreicht. Es wurden experimentelle Veränderungen und mögliche Störungen untersucht. Eisen und Chlorid störten in hohen Konzentrationen und müssen entweder abwesend oder auch in den Eichproben enthalten sein. In mehreren unterschiedlichen Eichproben wurde Aluminium mit befriedigenden Ergebnissen bestimmt.

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ETUDE SUR LE DOSAGE DU CARBONE TOTAL DANS LE MONOCARBURE D'URANIUM

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Compte tenu de certaines de ses excellentes caractéristiques physiques, l'emploi du monocarbure d'uranium comme combustible nucléaire est de plus en plus envisagé. Les difficultés de fabrication, alliées à une certaine sensibilité à l'air humide, rendent nécessaire un contrôle très strict de ce matériau avant sa transformation en élément de combustible. Le dosage du carbone total est l'un des éléments essentiels de ce contrôle, car il peut fournir des indications valables sur la stoechiométrie du monocarbure.

Les méthodes de dosage du carbone, tant dans les composés organiques que dans les métaux et alliages, sont très largement décrites dans la littérature. Beaucoup d'entr'elles ont donné naissance à des appareils commerciaux qui ont fait leurs preuves. Toutefois, l'aspect un peu original du contrôle précis en routine d'une production de monocarbure d'uranium nous a amené à comparer les méthodes les plus courantes. Les appareils commerciaux ont été employés sans modification particulière.

Si toutes les techniques reposent sur un même principe à savoir: combustion de l'échantillon dans un courant d'oxygène et mesure de l'anhydride carbonique dégagé, elles diffèrent par la méthode de mesure du CO_2: (*a*) gravimétrie (micro ou macro), (*b*) conductimétrie électrique, (*c*) conductibilité thermique, (*d*) coulométrie, (*e*) volumétrie, (*f*) manométrie.

PARTIE EXPÉRIMENTALE

Préparation et combustion des échantillons

Les échantillons de monocarbure d'uranium à contrôler, se présentent dans notre cas, sous forme de morceaux grossiers ou de disques de 25 mm de diamètre et 5 mm d'épaisseur. Ils sont homogénéisés par broyage à 50–100 mesh en atmosphère sèche et inerte (argon). Des contrôles, effectués avant et après cette opération, ont donné les mêmes valeurs en carbone total.

Conservé sous argon, dans de petits flacons de verre, le monocarbure n'est mis au contact de l'air que pendant le temps nécessaire à la pesée, temps trop court pour permettre une altération sensible[1].

Les données de la littérature[2–6] et notre expérience (voir Tableau I) montrent que l'on obtient une combustion complète de l'UC vers 900°. Pour plus de sécurité, nous brûlons les échantillons vers 1000–1100°, sauf dans le cas du dosage du CO_2 par conductibilité thermique, où le four est porté à 1500–1600°, l'appareil LECO utilisant un four à haute fréquence.

Le monocarbure d'uranium commençant à réagir d'une manière appréciable avec l'oxygène dès 200–300°[3,5,7], on introduit en général l'échantillon dans un tube de combustion froid.

TABLEAU I

TAUX DE CARBONE TROUVÉ DANS UC EN FONCTION DE LA TEMPÉRATURE DE COMBUSTION (MACROGRAVIMÉTRIE)

Température (°)	*% de C trouvé dans UC*
575	4.86
690	4.87
800	4.88
900	4.91
975	4.93
1050	4.92
1100	4.93
1270	4.92

On purifie au préalable l'oxygène par passage dans des absorbeurs contenant successivement de l'acide sulfurique concentré, de l'ascarite et de l'anhydrone. Pour la méthode (*a*) une purification supplémentaire vis-à-vis d'éventuelles matières organiques est obtenue par contact préalable de l'oxygène avec un fil de platine irridié (10%) chauffé au rouge sombre[8,9].

Toutes les pesées sont effectuées à l'aide d'une semi-microbalance Mettler S 6, d'une portée de 80 g, et de 0.005 mg de sensibilité dans le domaine de mesure optique (jusque 100 mg).

Description des méthodes

Macro- et microgravimétrie[2,4,10–12]. Le dosage est effectué à l'aide d'appareils classiques de détermination du carbone et de l'hydrogène dans les substances organiques de la firme Janke et Kunkel modèles D5 et MU 101 munis de tubes de combustion en quartz de 18 et 7 mm de diamètre intérieur. L'échantillon, pesé dans une nacelle de platine calcinée, est introduit dans la zone du four mobile. La température du four fixe contenant le tube rempli d'oxyde de cuivre, est maintenue à 900°. Le débit d'oxygène, contrôlé par un débitmètre placé à la sortie de l'appareil, est réglé à 50–70 ml/min pour la macrogravimétrie et 10–15 ml/min pour la microgravimétrie, tandis que la température du four mobile est lentement élevée à 1000–1100°.

Les temps de combustion sont respectivement de 60 et 30 min. Le CO_2 produit est capté dans des macro ou micro absorbeurs tarés, remplis d'ascarite et d'anhydrone. Parmi les divers absorbants essayés, seuls, l'ascarite et l'amiante sodée donnent des blancs reproductibles. Avec la purification supplémentaire de l'oxygène (voir ci-dessus), ils sont inférieurs à 0.1 mg pour la macrogravimétrie et 0.02 mg pour la microgravimétrie.

Conductimétrie électrique. L'appareil Wösthoff O. H. G. no. 556-11, utilisé dans la gamme de mesure la plus élevée est conçu pour le dosage simultané du carbone et du soufre dans les aciers. Son étalonnage préalable peut être effectué à l'aide de graphite "Specpure" ou d'échantillons standards de fonte ou mieux de monocarbure d'uranium analysés par macrogravimétrie.

Un échantillon de 50 à 200 mg est pesé dans une nacelle en platine calcinée; celle-ci est introduite rapidement à l'intérieur du tube de combustion et le débit d'oxygène est porté à 3 l/min. La réaction est terminée en 1–2 min.

Une prise aliquote des gaz produits, purifiés de l'anhydride sulfureux éventuellement présent, à l'aide d'une colonne de perhydrite est introduite dans une cellule conductimétrique, remplie de 18 ml d'une solution de NaOH $N/400$ et maintenue à la même température que la cellule de référence par un bain d'huile agité. La mesure de la variation de conductibilité de la solution, due à l'absorption du CO_2, permet le calcul de la teneur en carbone de l'échantillon[13–15]. Pour le volume de solution utilisée, cette variation n'est proportionnelle à la quantité de CO_2 que pour des quantités de carbone comprises entre 0 et 250 μg[14]. La mesure n'est donc possible que sur une prise aliquote des gaz provenant de la combustion.

L'oxygène est purifié par passage dans un tube chauffé à la température de combustion. Compte tenu de la brièveté de la réaction, le blanc est négligeable; l'appareil permet, d'ailleurs, de le compenser automatiquement.

Conductibilité thermique. Nous utilisons l'appareil "LECO 598-10-50 second Carbon Analyzer", muni d'un four à induction no. 521-300 et étalonné à l'aide de fontes ou de monocarbures d'uranium standards.

Un échantillon de 0.2 à 0.5 g est placé dans un creuset spécial en céramique, contenant 1 g de fer et 1 g d'étain, et introduit dans le four à induction. Le débit d'oxygène lors de la combustion est de 1.5 l/min. Le dosage repose sur la mesure, par une cellule de conductibilité à thermistors, de la différence de conductibilité thermique entre l'oxygène et l'anhydride carbonique produit lors de la combustion, débarrassé de l'eau et l'anhydride sulfureux qui peuvent être formés lors de la réaction. Les valeurs des conductibilités thermiques relatives de l'anhydride carbonique et de l'argon sont très voisines*[16].

Le monocarbure d'uranium étant synthétisé et conservé en atmosphère d'argon, l'on peut craindre une interférence due à cet élément. Un contrôle[17] par extraction sous vide et à haute température (environ 2000°) a montré l'absence de ce gaz dans les échantillons analysés.

La valeur du blanc due à l'oxygène est éliminée lors de la mise à zéro de l'appareil.

Coulométrie. Le titrateur automatique coulométrique CTA-5C, de la firme R. Schoeps, a été utilisé pour toutes les mesures. Une prise aliquote du CO_2 de combustion

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* Conductibilités thermiques relatives par rapport à l'air, de différents gaz.

	0°	*100°*		*0°*	*100°*
O_2:	1.01	1.032	H_2:	7.004	6.94
N_2:	1.003	0.998	CO:	0.96	0.92
Ar:	0.685	0.695	SO_2:	0.344	—
CO_2:	0.590	0.690			

est absorbée dans une solution basique de perchlorate de baryum. La précipitation de $BaCO_3$ amène une diminution du pH par formation d'ions hydrogène. Le pH est ramené à sa valeur initiale par production électrolytique d'ions OH^-. La mesure de la quantité de courant utilisée dans cette opération permet le calcul par la loi de Faraday de la teneur en carbone de l'échantillon analysé. Cette méthode est donc absolue et ne nécessite aucun étalonnage[18,19].

Volumétrie. Les mesures sont effectuées à l'aide de l'appareil commercial Ströhlein, bien connu pour le dosage rapide du carbone dans l'acier et la fonte. Son principe repose sur la mesure de la différence, ramenée aux conditions normales de pression et de température, entre le volume total $O_2 + CO_2$ et le volume après absorption du CO_2, provenant de la combustion, dans une solution de potasse.

Manométrie. Cette technique est décrite par COOK ET SPEIGHT[20], et CROSSLEY, FOSTER ET PHILLIPS[6,21]. Le CO_2 de combustion est condensé dans des pièges refroidis par l'oxygène liquide. On le vaporise ensuite dans un volume connu d'environ 100 ml, et l'on mesure sa pression à la température ambiante à l'aide d'une jauge de McLeod. N'ayant pas expérimenté nous-mêmes cette méthode, nous avons repris pour notre comparaison les résultats donnés par CROSSLEY ET FOSTER[21].

RÉSULTATS OBTENUS ET COMPARAISON DES MÉTHODES

En se basant sur les valeurs reportées dans la littérature et les mesures que nous avons effectuées, les résultats obtenus par les techniques décrites sont résumés dans le Tableau II et comparés dans les Tableaux III et IV. Les symboles utilisés signifient:

n = nombre de mesures
X = valeur d'une mesure
$\bar{X}$ = valeur de la moyenne arithmétique calculée sur n mesures
a b c ... n = indices des différents échantillons

$$\sigma = \sqrt{\frac{\Sigma(X-\bar{X})^2}{n-1}} = \text{écart type estimé à l'aide de } n \text{ mesures sur le même échantillon}$$

$$\sigma\,\% = \frac{\sigma \cdot 100}{\bar{X}} = \text{coefficient de variation de la méthode}$$

$$\sigma_{\text{total}} = \sqrt{\frac{\Sigma(X_a-\bar{X}_a)^2 + \Sigma(X_b-\bar{X}_b)^2 + \ldots + \Sigma(X_n-\bar{X}_n)^2}{(n_a-1)+(n_b-1)+\ldots+(n_n-1)}} =$$

écart type estimé à l'aide de l'ensemble des résultats

$$F = \frac{\sigma_1^2}{\sigma_2^2} = \text{test } F \text{ pour la comparaison des écarts types}$$

Le Tableau IV donne les valeurs du rapport

$$f = \frac{F \text{ expérimental}}{F \text{ théorique}}$$

TABLEAU II

RÉSULTATS OBTENUS PAR LES DIFFÉRENTES TECHNIQUES

Echantillons	*Macrogravimétrie*			*Microgravimétrie*			*Cond. électrique*			*Cond. thermique*		
C	*n*	$\bar{X}$ % − *C*	*σ*	*n*	$\bar{X}$ % − *C*	*σ*	*n*	$\bar{X}$ % − *C*	*σ*	*n*	$\bar{X}$ % − *C*	*σ*
1	12	4.80	0.018	12	4.77	0.040	18	4.82	0.110	6[b]	4.84	0.042
2	6	4.95	0.017	—	—	—	6	4.95	0.070	16[b]	4.97	0.036
3	8	4.73	0.017	5	4.76	0.039	9	4.76	0.090	—	—	—
4	5	4.97	0.016	4	5.07	0.040	7	5.02	0.100	—	—	—
5	4	4.60	0.011	—	—	—	—	—	—	6	4.62	0.016
6	4	4.66	0.010	—	—	—	—	—	—	6	4.68	0.020
7	18	4.80	0.008	—	—	—	—	—	—	—	—	—
8	18	4.65	0.008	—	—	—	—	—	—	—	—	—
9	18	4.66	0.008	—	—	—	—	—	—	—	—	—
10	5	4.61	0.010	—	—	—	12	4.63	0.090	—	—	—
11	4	4.77	0.011	—	—	—	—	—	—	6	4.79	0.016
12	4	4.89	0.010	—	—	—	—	—	—	6	4.92	0.018
13	18	4.87	0.006	—	—	—	—	—	—	—	—	—
14	18	4.88	0.006	—	—	—	—	—	—	—	—	—
15	18	4.78	0.006	—	—	—	—	—	—	—	—	—
Monocristaux	—	—	—	4	4.76	0.010	—	—	—	—	—	—
UC	—	—	—	—	—	—	—	—	—	—	—	—
Σn		160			25			52			46	
σ_{total} (%C)		0.010			0.038			0.097			0.029	
σ%		0.21			0.79			2.02			0.59	

[a] A l'exception de l'échantillon 3, les valeurs données pour cette technique ont été obtenus par le laborato de contrôle de fabrication.
[b] Résultats obtenus par le laboratoire LECO.
[c] Température de combustion de 900–1000°.
[d] Résultats tirés de CROSSLEY ET FOSTER[21].

pour la comparaison des écarts types des méthodes prises deux à deux et avec une probabilité de 95%. Si *f* est supérieur à 1, le test est significatif, si *f* est inférieur à 1, il ne l'est pas. En lisant le Tableau dans le sens vertical, la méthode est plus précise, si la valeur de *f* est suivie du signe (+), moins précise si elle est suivie du signe (—). Plus les valeurs de *f* supérieures à 1 sont élevées, plus le test est significatif.

L'écart type que nous avons trouvé pour la macrogravimétrie est, d'une manière générale, en accord avec la valeur donnée par CROSSLEY ET PHILLIPS[6].

L'écart type trouvé pour la microgravimétrie est supérieur à celui donné par TASSINARI[10]. Cependant, le calcul de *F*, compte tenu de la différence de degré de liberté, ne donne pas une différence significative.

Des valeurs de *f* (Tableau IV) calculées à partir des résultats du Tableau II, il ressort significativement, à 95% de probabilité, que:

la macrogravimétrie est la méthode la plus précise,
la conductimétrie électrique la moins précise,
la manométrie est plus précise que la microgravimétrie.

A notre connaissance, il existe actuellement peu de données dans la littérature sur le dosage du carbone dans le monocarbure d'uranium par conductimétrie électrique et thermique, coulométrie et manométrie. Il nous a cependant paru intéressant

Coulométrie			*Volumétrie*[a]			*Manométrie*		
n	$\bar{X}$ % − *C*	σ	*n*	$\bar{X}$ % − *C*	σ	*n*	$\bar{X}$ % − *C*	σ
6[c]	4.78	0.041	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
5[c]	4.74	0.042	5	4.74	0.070	—	—	—
5[c]	4.98	0.043	—	—	—	—	—	—
9	4.63	0.016	2	4.70	—	—	—	—
3	4.67	0.015	2	4.75	—	—	—	—
—	—	—	18	4.88	0.020	—	—	—
—	—	—	18	4.73	0.020	—	—	—
—	—	—	18	4.72	0.020	—	—	—
—	—	—	—	—	—	—	—	—
3	4.78	0.016	2	4.70	—	—	—	—
3	4.89	0.017	2	4.87	—	—	—	—
—	—	—	18	4.82	0.034	—	—	—
—	—	—	18	4.86	0.034	—	—	—
—	—	—	18	4.83	0.034	—	—	—
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	7[d]	4.84	0.017
	34			113			7	
	0.031			0.031			0.017	
	0.65			0.64			0.33	

de résumer dans le Tableau V les valeurs trouvées pour d'autres matériaux à teneur en carbone voisine.

Les appareils mentionnés pour conductimétrie électrique, conductibilité thermique, et coulometrie ont des performances supérieures pour des teneurs en carbone moins élevées. Ils sont, en effet, conçus pour le dosage du carbone dans les métaux et alliages ayant des teneurs très souvent inférieures à 1%. Dans le cas du monocarbure d'uranium, on doit donc travailler avec des poids relativement faibles d'échantillon (influence plus marquée de l'hétérogénéité) et ne prélever qu'une partie des gaz de combustion, ce qui dans les deux cas est préjudiciable à la précision.

Les résultats obtenus par ces appareils doivent cependant être considérés, comme très satisfaisants, eu égard à la rapidité d'une mesure par rapport à la macrogravimétrie. Ils pourraient vraisemblablement être améliorés par une étude plus approfondie des paramètres pouvant influencer la mesure.

La macrogravimétrie reste actuellement, selon nous, la méthode la plus sure en raison de l'aisance des manipulations, de la précision et du caractère absolu de la mesure. Elle nécessite toutefois une quantité d'échantillon et un temps plus importants. La coulométrie mise à part, le désavantage principal des méthodes physiques de mesure réside dans le fait que l'exactitude du résultat final est liée à un étalonnage préalable à l'aide d'echantillons de référence. Cet étalonnage d'ailleurs augmente légèrement le temps d'analyse. Il faut signaler l'intérèt de la microgravimétrie lorsqu'on ne dispose que de très peu d'échantillon, son écart type n'étant que de 0.038% de carbone pour des prises de l'ordre de 10 à 50 mg.

TABLEAU III

COMPARAISON DES MÉTHODES

Méthodes	*Pour une mesure*		*Données statistiques*				*Auteurs*	*Référence*
	Poids (mg)	*Temps total estimé (min)*	*n*	*%C des échantillons analysés*	σ_{total} *(%C)*	*Intervalle de confiance pour 1 mesure à 95%*		
Macrogravimétrie	2000	100 environ	160	de 4.60 à 4.97	0.010	± 0.020	CCR-Ispra	Tableau II
	200–2000	100 environ	9	4.785	0.022	± 0.050	EMRICK *et al.*	12
	1500	100 environ	—	4.64	0.015	—		2
	500	100 environ	6	4.87	0.015	± 0.038	CROSSLEY *et al.*	6
Microgravimétrie	10–50	45 environ	25	de 4.76 à 5.07	0.038	± 0.078	CCR-Ispra	Tableau II
	5–10	45 environ	7	4.78	0.020	± 0.049	TASSINARI	10
Conductimétrie électrique	50–200	10 environ	52	de 4.63 à 5.02	0.097	± 0.200	CCR-Ispra	Tableau II
Conductibilité thermique	200–500	5 environ	46	de 4.62 à 4.97	0.029	± 0.058	CCR-Ispra	Tableau II
Coulométrie	100–200	5 environ	34	de 4.63 à 4.98	0.031	± 0.062	CCR-Ispra	Tableau II
Volumétrie	250	15 environ	113	de 4.70 à 4.88	0.031	± 0.062		Tableau II
	200–400		—	de 5.00 à 10.00	0.050	—	ATODA *et al.*	3
Manométrie	80–100	30 environ	7	4.84	0.017	± 0.033	CROSSLEY ET FOSTER	21

TABLEAU IV

COMPARAISON DES MÉTHODES: TEST *f* À 95% DE PROBABILITÉ[a]

Méthodes	*Macrogravimétrie*	*Microgravimétrie*	*Cond. électrique*	*Cond. thermique*	*Coulométrie*	*Volumétrie*	*Manométrie*
Manométrie	1.34(+)	1.30(−)	8.68(−)	0.78	0.87	0.89	
Volumétrie	7.17(+)	0.92	6.62(−)	0.74	0.63		0.89
Coulométrie	6.24(+)	0.81	5.73(−)	0.67		0.63	0.87
Cond. thermique	5.96(+)	0.97	6.90(−)		0.67	0.74	0.78
Cond. électrique	65.27(+)	3.50(+)		6.90(+)	5.73(+)	6.62(+)	8.68(+)
Microgravimétrie	9.62(+)		3.50(−)	0.97	0.81	0.92	1.30(+)
Macrogravimétrie		9.62(−)	65.27(−)	5.96(−)	6.24(−)	7.17(−)	1.34(−)

[a] Lecture dans le sens vertical: (+) = significativement plus précise; (−) = significativement moins précise.

TABLEAU V

DONNÉES POUR D'AUTRES MATÉRIAUX

Méthodes	*Nature de l'échantillon*	*% C*	*Données indiquées*	*Références*
Conductibilité électrique	Carbure de tungstène	6.31	$\sigma = 0.14$ % C	15
	Carbure de tungstène [a]	6.42	$\sigma = 0.084$% C	
	Fer brut	3.76	$\sigma = 0.033$% C	
Conductibilité thermique	Ferro-chrome	de 6 à 9	± 0.08%	22
	Ferro-chrome	6.85	$\sigma = 0.022$ ($n = 6$)	Résultats trouvés par les auteurs
	Fonte	2.55	$\sigma = 0.015$ ($n = 12$)	
Manométrie	Carbure de plutonium	4.72	σ % = 0.30	21

[a] Combustion effectuée dans un micro-creuset de platine.

Il semble que dans la plupart des cas il y ait une erreur systématique entre la volumétrie et les autres méthodes pour lesquelles la concordance entre les moyennes d'un même échantillon est satisfaisante compte tenu des coefficients de variation.

En conclusion, les Tableaux III et IV permettent de choisir la technique la plus adéquate suivant la quantité d'échantillon disponible, la précision souhaitée, le nombre d'analyses à effectuer dans un temps donné.

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RÉSUMÉ

Cette étude compare les reproductibilités obtenues pour le dosage du carbone total dans le monocarbure d'uranium par différentes techniques analytiques: macro- et microgravimétrie, conductimétrie électrique, conductibilité thermique, coulométrie, volumétrie gazeuse et manométrie.

SUMMARY

A comparative study is made of the reproducibilities obtained for the determination of total carbon in uranium monocarbide by different analytical techniques: macro- and microgravimetry, electrical conductivity, thermal conductivity, coulometry, gaseous volumetry and manometry.

ZUSAMMENFASSUNG

Die Bestimmung des Gesamtkohlenstoffs in Uranmonocarbid mit verschiedenen analytischen Methoden wurde untersucht, um die Reproduzierbarkeiten der einzelnen Methoden miteinander zu vergleichen. Folgende Methoden wurden geprüft: Makro- und Mikrogravimetrie, elektrische Leitfähigkeit, thermische Leitfähigkeit, Coulometrie, Volumetrie und Manometrie.

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A RAPID RADIOCHEMICAL METHOD FOR ANTIMONY AND ARSENIC

PART II. DEVELOPMENT AND TESTING OF THE METHOD

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Previous radiochemical methods, based on the electrolytic generation of stibine, have been successfully applied to the separation of antimony from a fission product mixture by COOK[1] and WILKINSON AND GRUMMITT[2]. Chemical yields of 60–80% were obtained in 15–30 min.

In the present paper, the use of a fast electrolytic cell[3] for the rapid separation of antimony and arsenic from a mixture of fission products is described. It is confirmed that antimony and arsenic can be cleanly separated from one another by the difference in thermal stabilities of their hydrides, as demonstrated previously by GREENDALE AND LOVE[4]. Decontamination factors for possible contaminants have been measured and these are also reported. The use of the method in the laboratory for separating antimony and arsenic, and in a nuclear reactor for separating antimony, has been demonstrated.

EXPERIMENTAL

Tracers

Antimony and arsenic tracers were prepared as described previously[3]. Bromine tracer was obtained by irradiating potassium bromide with thermal neutrons. After cooling for several days only ^{82}Br (36 h) remained. All other tracers were received from the Radiochemical Centre, Amersham, England. These were: ^{131}I in carrier-free form in dilute sodium hydroxide solution; ^{132}Te as sodium tellurite in aqueous solution; ^{75}Se as sodium sellenite in aqueous solution; ^{113}Sn as stannic chloride in hydrochloric acid solution (two different specific activities were used: 0.136 C/g Sn and 5.1 C/g Sn).

Counting

The counting techniques and procedures were described previously[3]. The γ-scintillation counter was used in all cases except for a few experiments with antimony and arsenic tracers when a liquid β-counter was employed.

Apparatus

Stibine and arsine are generated in the 5.5-ml electrolytic cell[3] containing 5 *N* hydrochloric acid as the electrolyte and antimony and arsenic carriers in the cathode compartment. In general the gases leaving the cell pass initially through a column of anhydrous calcium sulphate (10 cm × 1.1 cm diam.; −7 + 12 mesh B.S.S.). This column is tightly packed and the solids held firmly in position by a coil spring under the rubber bung. The gases then pass into a silica tube (4 mm diam.) heated to 480° followed by a sintered glass filter. Here the stibine is decomposed and the antimony metal collects on the cool region of the silica tube and on the sinter. Finally, a second silica tube heated to 950° and a second filter are used to decompose the arsine and collect the arsenic metal.

Procedure

After the porous diaphragm has been allowed to stand in 5 *N* hydrochloric acid for about 30 min, the solution of inactive carriers together with radioactive tracers or fission products is added to the cathode compartment and the cell assembled. The solution of inactive carriers consists of 0.25 mg of antimony(III), 0.25 mg of antimony(V) and 0.50 mg of arsenic(III) in 5 *N* hydrochloric acid. All air is then removed from the cell by allowing helium to flow through at 250 ml/min for several minutes before electrolysis. For the electrolysis itself, a current of approximately 50 A is passed for 10 sec. After a short time to ensure that all the stibine and arsine have passed through the system, the antimony and arsenic deposits can be counted *in situ* or the apparatus dismantled and the active deposits dissolved and counted in the liquid form. If the quantity of arsenic is small and insignificant compared to the antimony, then instead of decomposing the stibine thermally, it can be passed into silver nitrate solution, and the precipitated silver antimonide rapidly filtered and counted under standard conditions[1].

Chemical yields are determined as follows. The separated element is first brought into solution and the quantity determined either by spectrophotometric methods or by using a long-lived radioactive isotope as a tracer. In the latter case any short-lived isotopes separated from the fission product mixture are first allowed to decay away before the yield is determined.

If it is desired to study very short-lived isotopes, then a more rapid method of adding the solution of carriers and fission products to the cathode compartment of the cell is required. In some experiments, this was achieved by passing the liquid via a funnel directly into the cathode compartment of a fully assembled cell. (Very high speed methods of transfer using "rabbits" with a rubber diaphragm can also be employed[5-7]. The "rabbit" contains an aqueous solution of carriers and uranium and on returning from the reactor a hypodermic needle punctures the diaphragm and the liquid is drawn by suction into any desired separation apparatus.)

An alternative procedure for separating short-lived isotopes was also tested. The electrolytic cell containing uranium and antimony and arsenic carriers in solution, is placed in a nuclear reactor and irradiated with a pulse of neutrons. Stibine and arsine are then generated either during or after the irradiation and swept from the reactor by a flow of helium to a silica decomposition tube situated some 15 feet from the cell.

RESULTS AND DISCUSSION

Effects of antimony and arsenic valency states

It has been shown[3] that in 5 N hydrochloric acid, stibine is generated at the same rate from separate solutions containing antimony(III) and antimony(V). In order to confirm that in a mixture containing equal quantities of antimony(III) and antimony(V), stibine is also formed from the two valency states at the same rate, the technique of labelling each valency state with a different antimony isotope[4] was used. A mixture of 0.5 mg of ^{125}Sb(III) and 0.5 mg of ^{124}Sb(V) was made up immediately before use. In two experiments, the γ-spectra of the mixture before electrolysis and of the separated antimony were compared and found to be of identical shape.

The two valency states thus behave in a mixture in the same manner as they do separately. It is therefore not necessary to carry out the usual oxidation–reduction procedure on fission-product antimony to ensure equal separation of the two valency states. In the case of arsenic, however, the method as it stands can only be used for qualitative and not for quantitative separations of arsenic because of the different rates of arsine formation from the two valency states[3] and the very slow rate of exchange between them[8].

Interferences

One primary requirement for obtaining a high yield of stibine and arsine is to ensure that all oxidising substances are absent from the cell. For example, GRANT[9] states that air and nitric acid must be absent. It was demonstrated in the present work that traces of chlorine completely inhibit stibine formation. In one experiment with a low-current (5 A) cell, the current was passed for a very short time in the opposite direction to that normally used, thus liberating chlorine in the cathode compartment. The current was then reversed and passed in the correct direction for several minutes, but no trace of stibine could be detected in the gases leaving the cell. In the absence of chlorine, 30% of 1 mg of antimony in the cell was converted into stibine under the same conditions.

The electrolytic formation of stibine and arsine probably involves two steps, the first of which is the deposition of antimony and arsenic on the cathode[3,10]. Any other metal which deposits on the cathode during electrolysis will cover part of the antimony/arsenic deposit and would therefore be expected to lower the yield of hydride. This is the probable reason why COOK[1] found that tin, rhodium, ruthenium and platinum reduced the yield of electrolytic stibine. Metals such as uranium which are not deposited from aqueous solutions, should not interfere. It has been shown that this is so in a low-current (5 A) cell with amounts of uranium up to 0.1 g[11]. Quantities of uranium up to 0.2 g in the form of uranyl chloride and uranyl sulphate have been added to the high-current (50 A) cell, without any noticeable effect on the quantities of stibine and arsine produced—as determined by the visual appearance of the antimony and arsenic mirrors.

Decontamination factors

Possible contaminants of the separated antimony and arsenic are fission products which are either gases or which may be converted into gases in the electrolytic cell. These include bromine, iodine, antimony, arsenic, tellurium, selenium, tin and germanium. Decontamination factors for all these elements have been determined—except for germanium which was neglected because of its low fission yield. The decontamination factor is defined as the activity of the added contaminant divided by the amount of this activity found on the separated antimony or arsenic.

The conditions required for good separation of antimony and arsenic from one another were first determined. Contamination of the separated antimony by arsenic was studied as a function of furnace temperature and quantity of arsenic carrier used. It was thought that the latter parameter would be of importance because of the findings of TAMARU[12] who has shown that a clean antimony metal surface acts as a catalyst for the decomposition of arsine. When this surface becomes covered with a layer of arsenic, the rate of arsine decomposition rapidly decreases to one quarter of its initial value. If it is assumed that in the present experiments, most of the arsenic contamination is a result of this catalytic decomposition of arsine, then increasing the weight of arsenic carrier should reduce the *fraction* which contaminates the arsenic. The *weight* of arsenic which contaminates the antimony would be expected to be about the same because of the nature of the catalytic reaction. The experimental findings (Fig. 1) support this general conclusion. Increasing the decomposition temperature (Fig. 1) was found to increase the amount of arsenic contamination, due no doubt to the greater amount of arsine being decomposed. As a minimum temperature of 480° was found to be necessary for the complete decomposition of stibine, the use of this temperature together with 0.5 mg of arsenic carrier, gave the cleanest separation of antimony.

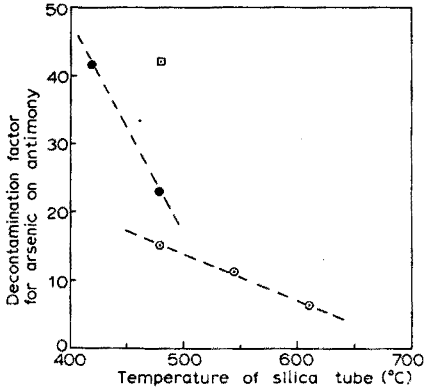

Fig. 1. Effect of stibine decomposition temperature and arsenic carrier concentration on the contamination of antimony by arsenic. ⊙ 0.10 mg arsenic carrier; ● 0.25 mg arsenic carrier; ⊡ 0.50 mg arsenic carrier.

A temperature of 890° was necessary to decompose arsine completely. The temperature of the second silica tube was therefore maintained at 950° to ensure that none of the arsine escaped. Under these conditions, the decontamination factor for antimony on the separated arsenic was found to be $2.5 \cdot 10^3$ using the following quantities of carrier: 0.25 mg antimony(III), 0.25 mg antimony(V), 0.50 mg arsenic(III).

The conditions given above for the clean separation of antimony and arsenic are only valid if the experimental conditions are maintained exactly as described. Changes in such parameters as gas flow-rate, diameter of the silica tube, length of the heated region, rate of electrolysis, etc., will naturally affect the temperatures necessary for optimum separation of antimony and arsenic. This is illustrated by the findings of GREENDALE AND LOVE[4], who, using a higher gas flow-rate and shorter heated region than in the present work, required a temperature of 600° to decompose stibine completely.

Decontamination factors for other elements apart from tin are listed in Table I. It can be seen that no significant contamination of either the antimony or arsenic occurs with these elements.

TABLE I

DECONTAMINATION FACTORS

Contaminant	*Decontamination factors*	
	Sb	*As*
Br	$>3 \cdot 10^3$	$>3 \cdot 10^3$
I	$>4 \cdot 10^4$	$>4 \cdot 10^4$
Te	$3 \cdot 10^4$	$2 \cdot 10^5$
Se	$7 \cdot 10^4$	$9 \cdot 10^4$

TABLE II

DECONTAMINATION FACTORS FOR TIN

Weight of Sn used (μg)	*$CaSO_4$ column*			*Decontamination factors*	
	Length(mm)	*Diam.(mm)*	*Mesh size (B.S.S.)*	*Sb*	*As*
75	43	11	$-7+12$	40	$2 \cdot 10^2$
75[a]	43	11	$-7+12$	40	$2 \cdot 10^2$
7.5	43	11	$-7+12$	80	$5 \cdot 10^2$
7.5	100	11	$-7+12$	$3 \cdot 10^2$	$2 \cdot 10^3$
0.4	100	11	$-7+12$	$3 \cdot 10^2$	$2 \cdot 10^3$
0.4	120	8.5	$-12+17$	80	$6 \cdot 10^2$

[a] In this experiment the electrolyte was a 4 *N* H_2SO_4/1 *N* HCl mixture, instead of the usual 5 *N* HCl.

Decontamination factors for tin are given in chronological order in Table II. In the first experiment, using a short calcium sulphate column, a fair amount of contamination occurred. This could be due either to vaporisation of tin(IV) chloride or to the electrolytic formation of tin hydride. Tin(IV) chloride is reported as being volatile from boiling hydrochloric acid solutions but not from mixed hydrochloric–sulphuric acid solutions[13]. A hydrochloric–sulphuric acid electrolyte was therefore used in the next experiment, but no reduction in tin contamination was noted. It is concluded therefore that tin is being volatilised from the cell as tin hydride. Some improvement was observed when the quantity of tracer was reduced by a factor of 10. It had been noticed previously that the tin hydride was adsorbed on calcium sulphate. The length of the calcium sulphate column was therefore doubled and a marked reduction in contamination occurred (Table II). Reducing the tin level to 0.4 μg or using small particles of calcium sulphate gave no further advantage.

Applications

The method was tested under normal laboratory conditions and also in a nuclear reactor. In order to confirm that pure antimony and arsenic are separated from a mixture of fission products, the γ-spectra of the separated isotopes were compared with published spectra. However, comparison was only possible with the longer-lived isotopes, as the γ-spectra of the shorter-lived species have not been published.

In the first experiment, antimony and arsenic were separated by the method described above from mixed fission products prepared by irradiating uranyl sulphate in a nuclear reactor for 10 min and then allowing to cool for 2 h. The observed γ-spectrum of antimony, when compared to the published spectra[14], showed that the major isotopes present were ^{129}Sb (4.6 h) and ^{130}Sb (37 min) with small amounts of ^{128}Sb (9.6 h) and ^{128}Sb (10 min) also being present. No impurities were detected.

The activity of the separated arsenic was considerably smaller than that of the antimony. The major γ-peak was at 0.6 MeV and decayed with a half-life of about 90 min. This was almost certainly ^{78}As (91 min). The heights of the other γ-peaks were too low to be measured accurately, but no contamination from antimony or any other elements was discernible.

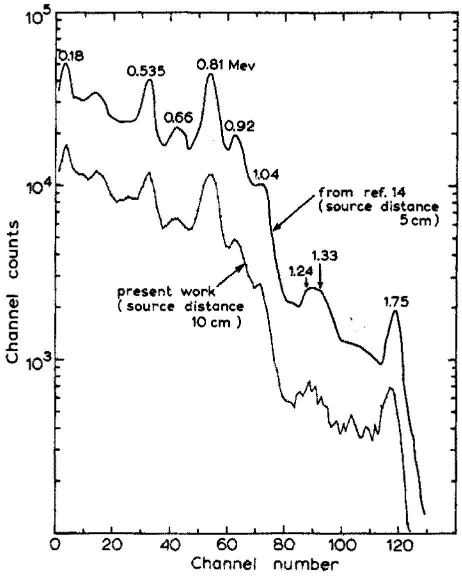

Fig. 2. Comparison of the γ-spectrum of ^{129}Sb (4.6 h) separated by this method with that published previously (ref. 14). The detector was a 3″ × 3″ NaI crystal in each case.

In a second experiment, the electrolytic cell containing uranium in solution, was irradiated with a pulse of neutrons in a nuclear reactor. In order to allow the shorter-lived isotopes to decay away, antimony was not separated until after a 5-h cooling period. The γ-spectra and total β-activity of the separated antimony were then measured at intervals during an 18-h decay period. The β-decay curve showed a maximum due to the growing-in of ^{129}Te (74 min) and then decayed with a half-life of 4.7 h due to ^{129}Sb (4.6 h). The first γ-spectrum showed that ^{129}Sb (4.6 h) was the major isotope present together with a small amount of ^{128}Sb (10 min). The ^{128}Sb (10 min) had decayed away when the second γ-spectrum (Fig. 2) was measured 40 min later. The published spectrum for ^{129}Sb is plotted on the same energy scale for comparison. It can be seen that the two spectra are identical—when the low statistical accuracy of our points at the higher energies is taken into consideration.

Further improvements

Two future modifications which are clearly possible and should enable the speed and efficiency of the method to be considerably improved are as follows.

(*a*) Replacement of the graphite cathode with a hollow-cathode constructed of copper or platinum. By having water flowing through this cathode at a high rate, it should be possible to use much higher currents than have been used hitherto.

(*b*) Coating the cathode with mercury should also increase the yield of hydride[10].

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SUMMARY

The formation of stibine and arsine by flash electrolysis is applied to the rapid separation of radioactive isotopes of antimony and arsenic from a mixture of fission products. A chemical yield of 45% for both antimony and arsenic was achieved in 10 sec. The conditions necessary for the clean separation of antimony and arsenic from one another and from other fission products are described. The method proved successful both in the laboratory and in a nuclear reactor.

RÉSUMÉ

Une méthode rapide est proposée pour la séparation radiochimique de l'antimoine et de l'arsenic, d'avec d'autres produits de fission. Un rendement chimique de 45% est obtenu en 10 sec, pour As et Sb. Ce procédé a été appliqué avec succès, soit au laboratoire, soit dans un réacteur nucléaire.

ZUSAMMENFASSUNG

Die Bildung von Stibin und Arsin durch Elektrolyse wird zur Trennung der radioaktiven Isotopen des Antimons und Arsens aus einer Mischung von Spaltpro-

dukten angewandt. Sowohl für Antimon als auch für Arsen wurde eine chemische Ausbeute von 45% in 10 Sek erreicht. Die Bedingungen, die für eine saubere Trennung des Antimons und Arsens voneinander und von den Spaltprodukten notwendig ist, werden beschrieben. Die Methode hat sich sowohl im Laboratorium als auch im Kernreaktor bewährt.

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THE RAPID DETERMINATION OF SILICA IN ROCKS AND MINERALS

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It is a remarkable fact that the second most abundant element of the lithosphere has proved to be one of the most difficult to determine rapidly and accurately by normal chemical methods. Compared with the other elements, there are remarkably few methods of determination. One of the first difficulties encountered is the large quantity of silicon present in normal rocks and minerals, so that employment of micromethods introduces sampling errors unless great care is taken. Silicon has normally been determined either by the classical gravimetric procedure involving dehydration and evaporation of silica[1], or by the colorimetric method via reduced silicomolybdic acid[2-5]. The first method is very time-consuming, while the second involves the constant replenishment of solutions, some of which have a very short shelf-life.

The use of the method whereby silicon is precipitated as potassium fluorosilicate, filtered, washed and titrated with a standard sodium hydroxide solution has been only scantily used because of the interference from elements such as aluminium, titanium and zirconium. Originally suggested by TRAVERS[6] and KORDON[7], the method has been utilised by SAJO[8] for slags and ceramic materials. The latter author made the interesting observation that when excess of calcium was present in solution and when the precipitation procedure was completed within 10 min, interference from aluminium and titanium was suppressed. SAJO's procedure[8] has been modified, for it has been observed that with many minerals difficulties may be encountered in fusion of the specimen to obtain a solution. SAJO[8] used potassium hydroxide fusion to render the sample soluble, but while this method is applicable to most minerals, there are some, such as sillimanite, zircon, etc., which are very intractable. For this reason we have preferred to use sodium peroxide fusion; an ancillary advantage is that during the subsequent acidification the solution does not precipitate silica whereas one obtained by hydroxide fusion is less reliable. There was found to be no essential difference between the results obtained by sodium peroxide fusion or potassium hydroxide fusion, provided that the mineral could be solubilized.

EXPERIMENTAL

Reagents

Analar quality reagents were used apart from alcohol and indicator.

Procedure

Mix 0.1000 g of finely ground sample with 1 g of sodium peroxide (measured by scoop) in a nickel crucible, sinter for 5 min and then fuse at dull red heat for a further 5 min. During this process leave the crucible lid slightly open. Normally most rocks passing 60–100 mesh B.S.S. will dissolve with such treatment, but some minerals such as zircon and tourmaline require very fine grinding to 300 mesh to enable complete dissolution to take place. The fusion is effected over a Bunsen or Mekèr burner, but the temperature must be kept low or considerable attack of the nickel crucible results. When fusion is complete, swirl the melt gently while cooling so that it is spread over the walls in a thin layer, thus ensuring a greater surface for subsequent dissolution. When cool, place the crucible, and lid if any spattering has occurred, in a 250-ml beaker. Add 10 ml of water to the upright crucible and *ca.* 5 ml to the beaker, cover the beaker with a watch glass and heat gently until all effervescence ceases (*ca.* 1 min.). Then transfer the contents of the crucible quantitatively to the beaker; the final volume of solution and washings should not exceed *ca.* 50 ml. Then add 10 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid by tilt measure and boil the solution for 1 min.

Cool the beaker and solution in a water trough to 30–40° and then transfer the liquid to a 200-ml plastic beaker using the minimum amount of distilled water to wash the glass beaker. Add 5 ml of 20% calcium chloride solution by tilt measure and 1 g of sodium fluoride by scoop measure, stir with a magnetic stirrer until all the sodium fluoride dissolves, add solid potassium chloride until an excess of 2–3 g over saturation point is present (*ca.* 25 g) and continue stirring for 2–3 min. Filter the precipitate on a Buchner funnel with No. 42 filter paper and wash thoroughly with a solution of 70 g of potassium chloride in 1 l of 1:1 ethanol–water. Wash 6–10 times with *ca.* 10-ml portions of solution, in order to ensure removal of all excess acid. Transfer the washed precipitate, filter paper and stirring bar to a 1-l beaker containing 500 ml of boiled and still very hot distilled water. Wash the Buchner funnel with hot distilled water to remove any adhering precipitate and add this to the beaker. Titrate with 0.15 *N* sodium hydroxide using 1% phenolphthalein as indicator. Determine blanks with each fresh batch of reagents used. 1 ml of 0.15 *N* sodium hydroxide corresponds to 2.252 mg of SiO_2.

RESULTS AND DISCUSSION

The method outlined gives very rapid dissolution of rocks and minerals and is superior to carbonate or hydroxide fusions in this respect. Furthermore, the initial sintering operation causes almost all of the material to react with sodium peroxide[9] so that very little, if any, spattering occurs on fusion. The silicate solution obtained by this method is quite stable and silica does not precipitate during acidification.

The solubility of the potassium fluorosilicate is reduced by the strongly acidic medium and the excess of potassium chloride added during precipitation, to such an extent that precipitation is almost instantaneous. It must be stressed that during the precipitation procedure, all operations after the addition of sodium fluoride up to the filtration and washing, must be concluded within 10 min or high values due to coprecipitation of aluminium and titanium occur. It appears that in any competition

TABLE I

DETERMINATION OF SILICA BY VARIOUS METHODS

Material	*Other oxides present (%)*			*Results by gravimetric method*			*Fluorosilicate results*		
	Al_2O_3	*TiO_2*	*Fe_2O_3*	*No. of analyses*	*SiO_2 (%)*	*Deviation (%)*	*No. of analyses*	*SiO_2 (%)*	*Deviation (%)*
Granodiorite[a]	15.22	0.57	3.71	2	69.3	±0.05	6	69.6	−0.13 + 0.11
Biotite[b]	18.56	3.24	19.88	2	38.8	±0.08	4	38.85	±0.14
Granite[c]	15.00	0.65	4.21	12	65.6	—	1	65.5	—
Granite[d]	15.07	0.59	5.09	6	67.2	−0.12 + 0.23	5	67.3	±0.06
Felspar[e]	20.20	<0.01	0.25	1	66.05	—	2	66.3	±0.06
Felspar[f]	19.06	0.02	0.07	6	68.7	−0.04 + 0.09	1	68.6	—
Dolerite[g]	14.45	1.40	8.43	2	40.5	±0.07	4	40.8	−0.06 + 0.09
Dolerite[h]	14.82	0.56	10.66	2	53.0	±0.00	3	53.2	0.00
Basic slag[i]	1.72	0.70	12.11	5	14.7	−0.09 + 0.16	2	14.6	±0.05
Firebrick[j]	33.9	1.48	3.50	7	56.7	−0.2 + 0.1	7	56.7	−0.29 + 0.15
Silica brick[k]	1.96	0.16	0.66	8	93.9	−0.09 + 0.08	2	93.9	0.00
Silicified wood[l]	0.2	<0.01	0.1	2	99.65	±0.03	2	99.4	±0.05

[a] Granodiorite from Mt. Alexander, Victoria, Australia.

[b] Biotite extracted from granodiorite.

[c] Granite from Centre National de la recherche scientifique – Roche etalon GR. (colorimetric SiO_2 = 64.9%), spread of gravimetric SiO_2 results not stated on material.

[d] Granite used at Australian National University for standard ASGl. (colorimetric SiO_2 = 68.1%).

[e] Felspar (anorthoclase) from Mt. Franklin, Victoria, Australia.

[f] Soda felspar – U.S. National Bureau of Standards, sample No. 99.

[g] Dolerite from N. rise 17th level, Morning Star gold mine, Woods Point, Victoria, Australia.

[h] Dolerite dyke, W. margin of N. end, Black Range, Marble Bar District, W. Australia.

[i] Basic slag – British chemical standard No. 174/1 from Bureau of analysed samples, Middlesborough, England.

[j] Firebrick – British chemical standard No. 269 from Bureau of analysed samples, Middlesborough, England.

[k] Silica brick from U.S. National Bureau of Standards, sample No. 102.

[l] Silicified wood from Frankston, Victoria, Australia.

for fluoride ions calcium is temporarily slightly stronger than aluminium or titanium. With volumes in excess of *ca.* 50 ml a longer time is taken to precipitate the fluorosilicate and contamination errors are therefore increased. Obviously it is equally possible to titrate the washed precipitate with a cerium(IV) solution using a Ce^{3+}/Ce^{4+} couple[10] and such a procedure would have several advantages; the necessary washing of the precipitate would be reduced, and the solution would be stable and would not require protection from atmospheric carbon dioxide. A disadvantage would be the occasional occlusion of calcium fluoride in the precipitate and hence titration with sodium hydroxide was used, the normality of 0.15 *N* being chosen to give conveniently large titres. A further point is that the addition of an indicator such as methyl red to the wash solution makes it possible to note when all the acid has been washed out. During the titration of the potassium fluorosilicate the solution should be maintained close to boiling, for the reaction is reversible to a certain extent. Normally at temperatures in excess of 75° the equilibrium is well to the right.

$$K_2SiF_6 + 4\ NaOH \rightleftharpoons SiO_2 + 4\ NaF + 2\ KF + 2\ H_2O$$

The results for a wide variety of materials are given in Table I. The figures for alumina, titania and total iron as ferric oxide have been tabulated to demonstrate the effect of variation of subsidiary elements. The results obtained for a specimen high in alumina (firebrick) and another high in titania (biotite) show that any interference by these oxides is very small. The agreement between the silica figures obtained by the classical gravimetric procedure and those obtained by the rapid method outlined above, indicates that generally the precipitation procedure gives higher results. However, it is normally considered that most results for silica by the classical gravimetric procedure are low[11,12] for a variety of reasons; accordingly, the accuracy of the fluorosilicate procedure would seem to be excellent and at least equivalent to, if not better than, the older method. Further great advantages in the utilisation of this newer method lie in its rapidity, the possibility of the introduction of batch procedures, and the relative simplicity of the apparatus required.

SUMMARY

A method is described for the rapid determination of silica in various substances by precipitation of potassium fluorosilicate; calcium ions are used to repress coprecipitation of aluminium and titanium. Solubility is reduced by low pH and excess potassium chloride. The separated precipitate is titrated with standard sodium hydroxide solution using phenolphthalein as indicator.

RÉSUMÉ

Une méthode est décrite pour le dosage rapide de la silice dans diverses substances, par précipitation du fluosilicate de potassium. Une addition d'ions calcium permet d'empêcher la coprécipitation de l'aluminium et du titane. Le précipité est finalement titré par une solution étalon d'hydroxyde de sodium, en utilisant la phénolphtaléine comme indicateur.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur schnellen Bestimmung von SiO_2 in verschiedenen Substanzen durch Fällung von Kaliumfluorosilikat. Calciumionen werden angewandt, um die Mitfällung von Aluminium und Titan zurückzudrängen. Die Löslichkeit wird durch einen niedrigen pH-Wert und einen Überschuss an Kaliumchlorid verringert. Der abgetrennte Niederschlag wird mit Natriumhydroxid und Phenolphthalein als Indikator titriert.

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THE DETERMINATION OF GLYCEROL

PART I. GENERAL INTRODUCTION: VOLUMETRIC DETERMINATION AS THE COPPER COMPLEX

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The determination of glycerol is very difficult, especially in technical materials where the number of interfering species present is often large. The commonly used procedures involving oxidation with dichromate or acetylation, are unsatisfactory as they are not specific for glycerol and the determination must often be performed in the presence of organic compounds which also undergo oxidation or acetylation. Improved oxidation procedures using potassium periodate have been described[1,2] and interfering substances have been separated before oxidation by paper chromatography[3]. Such methods, however, do not provide a means for determining glycerol in the presence of large concentrations of interfering substances and they are restricted to narrow concentration ranges.

Another approach to this problem, in which use is made of the copper–glycerol complex, was first described by BERTRAM AND RUTGERS[4,5]. Complexes of copper with organic compounds, such as glycerol, which have hydroxyl groups in adjacent and favourable positions, are well-known and a stable copper–glycerol compound was isolated from alkaline solution by BULLENHEIMER[6]. BERTRAM AND RUTGERS[4] made further studies of this compound and confirmed that the composition of the isolated crystals was $C_3H_5O_3CuNa \cdot 1.5\ H_2O$. The complex was found to hydrolyse rapidly in aqueous solution and early attempts to employ it in an analytical procedure were unsuccessful[7].

In this paper studies designed to overcome these difficulties are described and a volumetric method for the determination of glycerol is developed.

EXPERIMENTAL

Attempts to repress the hydrolysis of the copper–glycerol complex were made by BERTRAM AND RUTGERS[4] by the use of reagents in alcoholic solution. This was generally successful, but in their procedure a precipitate of copper(II) hydroxide was formed and this had to be separated from the complex. They encountered serious difficulties at this point because the complex itself is adsorbed to a small

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extent by the copper(II) hydroxide and very much more strongly by the oxi- or hemicellulose of the filter paper. It appeared to us that this problem might be overcome by filtration through a glass-fibre filter disc. Experiments were therefore made to see if a successful filtration could be carried out, which would allow the development of a volumetric procedure for glycerol.

Preliminary experiments were made using an approximately *M* solution of B.P. quality glycerol, prepared by dilution with water. The concentration was determined and adjusted by careful density determination and reference to tables[8].

A series of 10-ml aliquots of glycerol solution, with glycerol concentrations in the range 0.1 to 2.0% (w/v) (10 mg to 200 mg) were placed in 250-ml stoppered conical flasks and treated with 10 ml of 7.5 *M* sodium hydroxide solution and 60 ml of ethanol. Small volumes of *M* copper (II) chloride were then run in from a burette, the flasks being stoppered and shaken after each addition. This was continued until a permanent precipitate remained after shaking. Approximately 20 ml of ethanol was then added and each solution shaken as before. It was noticed that in some cases the addition of alcohol caused the precipitate to re-dissolve and when this occurred a further aliquot of copper(II) chloride was added and the shaking repeated. The solution was then filtered through a Buchner funnel fitted with a glass-fibre filter disc, under light suction from a water pump. Whatman filter discs type GF/A were found to be very suitable, giving rapid filtration without clogging. The filter was washed with a few ml of ethanol and the filtrate and washings transferred quantitatively to a 500-ml conical flask.

The most satisfactory method of determining glycerol volumetrically appeared to be the liberation of the copper in the complex, followed by reaction with potassium iodide and titration of the liberated iodine. This procedure has been employed by some other workers. The filtrate was therefore diluted with about 150 ml of water and made acid with 10% (v/v) sulphuric acid; 3 g of solid potassium iodide was then added and the liberated iodine titrated with 0.1 *N* sodium thiosulphate. The end-point was detected as usual by the addition of starch, and 2 g of solid ammonium thiocyanate was added near the end of the titration.

Initial results obtained by this method were disappointing. There were serious fluctuations and replicates often showed considerable discrepancies. It was considered that this might be due to adsorption on the filter disc or, more probably, on the copper(II) hydroxide precipitate. The experiments were therefore repeated, but after filtration the filter disc and residue were washed with three 5-ml portions of a solution of 0.75 *M* sodium hydroxide in ethanol containing not more than 10% water. The washings were added to the filtrate. A blank determination was also made exactly as before, but with glycerol absent. It was found, unexpectedly, that in the absence of glycerol the copper(II) hydroxide darkened very rapidly. Immediate filtration was therefore necessary in order to ensure that its behaviour in terms of solubility etc. was as similar as possible to that of the sample solution.

Results obtained by this modified procedure were much more satisfactory. The concentration range was therefore extended in both directions from 0.04 to 5.0% (w/v) (2 mg to 500 mg) glycerol. It was, however, found inconvenient to handle amounts of glycerol substantially above 400 mg, so that in such cases it is necessary to take an aliquot of the initial glycerol solution. The results obtained are presented in Table I. In these results correction for the blank was made and the glycerol content was calculated by means of the factor: 1 ml 0.1 *N* sodium thiosulphate = 9.2 mg glycerol.

TABLE I

DETERMINATION OF GLYCEROL

Glycerol taken (mg)	*Glycerol found (mg)*	*Glycerol taken (mg)*	*Glycerol found (mg)*
490	485	43.5	42.5
490	484	21	19.0
433	433	21	18.5
433	434.5	10	8.5
216.5	217.0	10	8.0
216.5	216.5	8.5	6.0
110	111.5	8.5	7.0
110	110.5	4.5	3.0
43.5	43.0	4.5	2.0

Recommended method

Place a 10-ml aliquot of a solution of the sample (adjusted to have a glycerol content within the range 50–400 mg) in a 250-ml stoppered flask and add 10 ml of 7.5 *M* sodium hydroxide and 60 ml of ethanol. Run in successive small volumes of *M* copper(II) chloride solution, stoppering and shaking the flask for 1 min after each addition. Continue until a slight permanent precipitate of copper(II) hydroxide remains. Add 20 ml of ethanol, stopper the flask and shake for 1 min; add more copper(II) solution if necessary (see p. 171).

Filter under light suction through a Buchner funnel fitted with a Whatman GF/A glass-fibre filter disc. Collect the filtrate in a 500-ml conical flask. Rinse out the flask and wash the residue with three 5-ml portions of a 0.75 *M* solution of sodium hydroxide in ethanol containing not more than 10% of water. Add the washings to the filtrate. Dilute the filtrate with 50 ml of water and make acid to litmus paper with 10% (v/v) sulphuric acid. Add 3 g of solid potassium iodide. Titrate the liberated iodine with 0.1 *N* sodium thiosulphate solution, using starch as indicator, and with addition of 2 g of solid ammonium thiocyanate near the end-point.

Carry out a blank determination exactly as described above, but without addition of glycerol; filter without delay (see p. 171). Apply any necessary correction to the volume of 0.1 *N* sodium thiosulphate required for titration of the sample.

TRIALS OF THE METHOD

In order to test the reproducibility of the method a number of determinations were made with "unknown" solutions of glycerol, prepared by dilution of B.P. quality glycerol. Replicate determinations were made with each solution (Table II). These results were obtained by 3 independent operators without prior knowledge of concentration level or batch identity. No difficulties were encountered and each determination was made in about 30 min.

TABLE II

REPRODUCIBILITY OF THE RECOMMENDED METHOD

Solution	*Glycerol content (%, w/v)*	
	By density measurement	*By copper complex titration*
A	3.80	3.78
A		3.79
A		3.79
B	2.26	2.25
B		2.25
B		2.24
C	1.23	1.24
C		1.24
C		1.22
D	0.55	0.53
D		0.52
D		0.51

Interferences

Previous methods for the determination of glycerol, particularly oxidation and acetylation methods, are often subject to serious interference from other organic compounds present as impurities. The specificity of the present procedure is much greater, as few of the impurities likely to be present in significant amounts form complexes with copper under the conditions adopted.

The nature of the impurities in "pure" and commercial glycerols is not known with certainty, but some attempts at qualitative separation by paper chromatography were made, similar to those reported by other workers[3]. After development of the chromatogram, it was treated with copper(II) chloride under alkaline conditions. In all cases only one spot, that of glycerol, showed appreciable blue coloration. This is not conclusive but indicates that the possibility of interference from impurities normally present in glycerol is remote.

In spite of the above, it was considered that other polyhydroxy compounds might also form copper complexes under the experimental conditions and so would interfere. Ethylene glycol instead of glycerol was therefore analysed by the recommended procedure; some complex formation took place, but recoveries were only about 35%. Significant amounts of such compounds are unlikely to be present in ordinary samples of glycerol, but care must be exercised if their presence is suspected, since they will enhance the apparent glycerol concentration.

DISCUSSION

The results in Table I show that this method is capable of giving accurate results within the range 40–400 mg of glycerol in the aliquot taken. At higher concentrations the spread of results becomes more serious. Below 40 mg the dilution is too great for satisfactory titration. The major drawback of previous methods, the adsorption of the copper complex onto the filter paper is evidently overcome by the use of glass-fibre filters. The rapid darkening of copper(II) hydroxide in the absence of glycerol is not fully understood. Experiments indicate that this does not affect the magnitude of the blank, but as a precaution rapid filtration is recommended.

The good results obtainable in routine analysis are indicated by the recoveries given in Table II. The reproducibility makes the method suitable for the assay of 99% pure glycerol solution and for commercial glycerols. The lower limit of the method is about 0.4% glycerol and it becomes progressively less accurate when used for concentrations below this level.

SUMMARY

A method for the determination of glycerol by means of the copper–glycerol complex is described; the complex is filtered free of excess copper(II) hydroxide and the copper is determined iodimetrically. Earlier difficulties due to adsorption of the complex are overcome by the use of glass-fibre filter discs. The method gives accurate results in the range 40–4% glycerol in the solution (400 to 40 mg glycerol in the aliquot taken).

RÉSUMÉ

Les auteurs décrivent une méthode de dosage volumétrique du glycérol, au moyen d'une solution de chlorure de cuivre, dont l'excès est précipité sous forme d'hydroxyde et filtré, en utilisant des disques filtrants en fibre de verre, pour éviter des adsorptions. On traite le filtrat par l'acide sulfurique et on dose finalement le cuivre du complexe par iodométrie. Résultats précis sont obtenus pour des teneurs en glycérol de 40 à 4%.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Glycerin mit Hilfe des Kupfer–Glycerin-Komplexes beschrieben. Der Komplex wird durch Filtration vom überschüssigen Kupfer(II)-hydroxyd befreit und das Kupfer jodometrisch bestimmt. Frühere Schwierigkeiten, die durch Adsorption des Komplexes hervorgerufen wurden, werden durch die Anwendung von Glasfiberfilterscheiben vermieden. Die Methode gibt genaue Ergebnisse im Bereich von 40–4% Glycerin in der Lösung.

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SHORT COMMUNICATIONS

X-ray spectrochemical analysis of tungsten in nickel

The use of nickel–tungsten alloys in electron tubes has resulted in a demand for a quick, reliable analysis to determine whether materials comply with specifications. Spectrographic analysis has served this purpose for most alloy constituents, but certain alloys have had to be determined by wet-chemical analysis. These methods are time-consuming and require several samples of each batch for complete analysis. A determination of tungsten by the emission spectrograph is difficult because of its refractory properties, since in an arc, tungsten oxide and carbide form and are incompletely volatilized. Furthermore, the spectra of nickel and tungsten are very intense giving a photographic background problem. X-Ray fluorescence techniques provide a simple direct determination and eliminate the need for complex chemical analysis.

The method described here is suitable for determining 0.5–3.0% tungsten in nickel; it requires the use of a platinum (or molybdenum) target tube. A tungsten target tube was originally used but had to be abandoned because of excessive scattering of duplicate wavelengths in the primary X-ray beam.

Experimental

Instrumentation. The method was developed using a General Electric Fluorescence Spectrometer. The instrumental conditions are detailed in Table I.

Preparation of samples and standards. Standard nickel–tungsten alloys were prepared in ingot form and rolled sheet form, covering a concentration range of 0–3% tungsten in 0.5% increments. They were analyzed by the conventional wet-chemical method[1–3] of precipitation as tungstic oxide. Because of the alloys being prepared in two forms, samples exhibited different surface conditions. To minimize this effect, selected standards from the ingot form were cut into 1-in. squares, wet ground to a flat surface, and given a 400-grit finish on wet Aloxite paper. Their surfaces were then cleaned in trichloroethylene to remove residual oil and other possible surface contaminants. Smooth flat surfaces, such as on rolled sheet, were cleaned in trichloroethylene.

TABLE I

INSTRUMENTAL CONDITIONS

Spectrograph	General Electric XRD-3 Fluorescence Spectrometer
X-ray tube	Machlett AEG-50X platinum target
Detector	General Electric No. 6 SPG counter
Crystal	Lithium fluoride (100 plane, 2d = 4.0267 Å)
Detector slit	Soller slit (0.010 in.)
Filter	Aluminum (0.010 in.)
X-ray tube voltage	50 kVP
X-ray tube current	50 mA
Counting time	100 sec
Emission lines	K_β for nickel L_β for tungsten and background

To check the effect of the orientation of the polishing marks, the standards were rotated a total of 180° at 90° intervals and measurements made in each position. The results are shown in Table II. These results show that the reproducibility is not appreciably affected by the polishing marks.

TABLE II

VARIATIONS IN TUNGSTEN COUNTS WITH ROTATION OF SAMPLES

Standard sample	*Sample initial position*	*Counts/sec*	
		Sample rotated 90°	*Sample rotated 180°*
0.5% W–Ni	292	294	295
1.0% W–Ni	463	470	464
1.5% W–Ni	642	649	640
2.0% W–Ni	847	843	837
2.5% W–Ni	1011	1002	1019
3.0% W–Ni	1192	1204	1184

Measurement of samples and standards. The intensities of the tungsten L_β line and nickel K_β line were measured by the fixed time technique. Counting times of 100 sec were used and recorded as counts/sec. One or two standards were run with each group of samples being analyzed to check on any instrumental drift.

A 0.010-in. aluminum filter covering the entire Soller slit aperture was used while counting the nickel K_β line to keep counting rates within limits imposed by the pulse resolution of the detector system.

Background intensity was measured from a pure nickel standard by counting for 100 sec at the tungsten L_β line. The net tungsten intensity was obtained by subtracting background intensity from individual tungsten intensity. The background for the nickel K_β was ignored, because it was negligible compared with the large nickel count.

Intensity ratios of the standards were calculated by dividing the net tungsten intensity by the corresponding nickel intensity.

$$\text{intensity ratio} = \frac{\text{net tungsten } L_\beta \text{ intensity}}{\text{nickel } K_\beta \text{ intensity}}$$

A calibration graph was plotted of intensity ratios against known tungsten concentrations over the range 0.5–3% tungsten. The plot was linear and the line intercepted the ordinate at zero intensity. The percentage of tungsten in samples was determined graphically by reading sample intensity ratios on the calibration curve. The linearity of the plot indicates that higher concentrations of tungsten could readily be determined.

Discussion

The results were checked by analyzing a group of samples by the present X-ray technique and comparing the values obtained with those of a chemical method[4] (Table III). These results are identical and within the reproducibility of the methods.

TABLE III

TYPICAL ANALYSIS OF Ni–W ALLOYS

Sample	*Tungsten found (%)*	
	Volumetric method	*X-ray method*
1	0.49	0.47
2	0.98	0.98
3	1.49	1.49
4	2.00	2.00
5	2.44	2.45
6	2.94	2.94

In certain early development assays, there were discrepancies in the concentrations found by X-ray and chemical methods which could not be attributed to variations of sample preparation or counting. One source of variation was found to be concentration gradients within the gross sample. This was detected by scanning across a sample using a lead mask with a 3/16-in. square opening which showed a 1% to 4% concentration variation. The concentration variation between different portions of the ingot sample was evident and the latter confirmed by chemical analysis. A second source of error was caused by using a tungsten target tube as the primary source of X-rays.

With a tungsten tube, the total intensity measured is the sum of the scattered radiation and the fluorescent radiation since the tungsten tube generates X-rays of the same wavelengths as the tungsten in the sample. Radiation is scattered irregularly, depending on the sample grain structure and surface, and consequently gives variable intensity measurements. Reproducible results were obtained with a platinum target tube, as should be expected with other target tubes given short enough X-rays to excite the tungsten L_β radiation.

Two principal sources of error affect the technique. They are the statistical variations in the counting plus any fluctuations in the electrical circuitry and the interpolation from the chemical calibration curve. The agreement is good and the accuracy is estimated to be ±1% of the tungsten concentration.

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Determination of molybdenum and tungsten in copper

Toluene-3,4-dithiol[1-6] can be used as a reagent for the determination of molybdenum and tungsten in copper after removal of the copper. The molybdenum complex is formed first and a small correction made for the effect of tungsten present. The tungsten is then determined on the aqueous solution obtained from the molybdenum extraction.

Reagents

All organic reagents were of analytical-reagent grade.

Toluene-3,4-dithiol (0.5%). Dissolve 20 g of sodium hydroxide in 500 ml of water. Cool to room temperature. Break a 5.0-g vial of reagent under the surface of the solution. Stir until solution is complete, warming to 35° if necessary. Add 10 ml of 80% mercaptoacetic acid in water. Dilute to 1 l with water and mix well. Store in a polyethylene bottle in a refrigerator.

Molybdenum stock solution, 1.00 mg/ml. Dissolve 1.00 g of high-purity molybdenum metal in 10 ml of sulfuric acid and a few drops of nitric acid. Fume to remove oxides of nitrogen. Cool, transfer to a 1-l volumetric flask and dilute to volume with water.

Molybdenum standard solutions. (1) 10 μg/ml. Transfer 10.0 ml of the stock solution to a 1-l volumetric flask. Dilute with about 500 ml of water, add 10 ml of sulfuric acid and dilute to volume with water. *(2) 1 μg/ml.* Transfer 50.0 ml of the 10 μg/ml standard solution to a 500-ml volumetric flask, dilute with about 250 ml of water, add 5 ml of sulfuric acid and dilute to volume with water.

Tungsten stock solution, 100 μg/ml. Dissolve 0.1794 g of sodium tungstate dihydrate in water and dilute to 1 l in a volumetric flask.

Tungsten standard solutions. (1) 10 μg/ml. Transfer 50.0 ml of tungsten stock solution to a 500-ml volumetric flask and dilute to volume with water. *(2) 1 μg/ml.* Transfer 50.0 ml of the 10 μg/ml stock solution to a 500-ml volumetric flask and dilute to volume with water.

Apparatus

A Beckman Model DU spectrophotometer with 1-cm and 5-cm quartz cells and an Eberbach electroanalyzer were used.

Procedures

Determination of molybdenum. Place a 1-g sample of copper in a 200-ml tall-form beaker and dissolve in a controlled amount of concentrated nitric acid. When the sample is completely in solution add 10 ml of 1 : 1 sulfuric acid and dilute to 100 ml. Place on the electroanalyzer and remove the bulk of the copper. Remove the beaker from the analyzer, washing off the electrodes with water. Evaporate to fumes of sulfur trioxide and cool. Dilute to 40 ml with water, add 1 ml of 20% (w/v) hydroxylamine hydrochloride solution and 10 ml of a 0.1% solution of neocuproine in 95% ethanol. Allow to stand for 15 min, adjust the pH to 5.0–5.5 with 28% ammonia, and allow to stand for 30 min. Transfer the solution to a 125-ml separatory funnel and extract

TABLE I

RESULTS FOR MOLYBDENUM

Cu present (g)	*Total present*		*In aliquot*		*Average Abs.*	*Corrected Abs.*	*Total Mo recovered (µg)*
	µg Mo	*µg W*	*µg Mo*	*µg W*			
					5-cm cell		
1	—	—	—	—	0.010		
1	20	20	8	8	0.350	0.331[a]	19.9
						0.340[b]	20.4
1	20	50	8	20	0.360	0.328[a]	19.7
						0.350[b]	21.0
1	20	100	8	40	0.368	0.314[a]	18.9
						0.358[b]	21.5
1	50	20	20	8	0.865	0.846[a]	50.8
						0.855[b]	51.3
1	50	50	20	20	0.870	0.838[a]	50.3
						0.860[b]	51.6
1	—	50	—	20	0.026		
—	—	—	—	—	0.004		
—	—	—	10	—	0.420	0.416	24.0[d]
					1-cm cell		
1	—	50	—	20	0.007		
1	100	50	40	20	0.346	0.339[c]	104
						0.343[b]	106
1	250	50	100	20	0.827	0.820[c]	252
						0.824[b]	254
—	—	—	—	—	0.003		
—	—	—	100	—	0.815	0.812	123.15[d]

[a] Correction of 0.0011 Abs./µg W present, from data obtained with W only.
[b] No correction made for the effect of W.
[c] Correction made for W present from data obtained in sample containing W only.
[d] µg/unit Abs. factor.

TABLE II

RESULTS FOR TUNGSTEN

Cu present (g)	*Total present*		*In aliquot*		*Average Abs.*	*Corrected Abs.*	*Total W recovered (µg)*
	µg Mo	*µg W*	*µg Mo*	*µg W*			
1	—	—	—	—	0.005		
1	20	20	8	8	0.177	0.172	20.0
1	20	50	8	20	0.427	0.422	49.0
1	20	100	8	40	0.869	0.864	100.2
1	50	20	20	8	0.156	0.151	17.5
1	50	50	20	20	0.443	0.438	50.8
1	100	50	40	20	0.456	0.451	52.3
1	250	50	100	20	0.437	0.432	50.1
1	20	50	8	20	0.451	0.446	51.7
1	—	50	—	20	0.436	0.431	46.4[a]

[a] µg/unit Abs. factor. This sample carried through the entire procedure.

with three 10-ml portions of chloroform, discarding the chloroform layer after each extraction. Transfer the aqueous layer to a 250-ml beaker and evaporate to fumes. Add 3 ml of concentrated nitric acid and 1 ml of 30% hydrogen peroxide, wash down the cover and wall of the beaker and take to fumes. Cool, rinse and fume again. Depending on the amount of molybdenum and tungsten present, take the total sample or aliquots at this point. Add a small quantity of water to dissolve salts, cool and transfer to a 50-ml volumetric flask. Place appropriate aliquots into 150-ml beakers, and add sulfuric acid so that the aliquot contains 5 ml of concentrated acid in a 30-ml volume. Add water to adjust the final volume. Cool to room temperature, then add 5 ml of dithiol solution and allow to stand for 15 min. Transfer the solutions to 125-ml separatory funnels with two 5-ml portions of chloroform. Shake for 1 min and allow the layers to separate. Collect the chloroform layer in dry 25-ml volumetric flasks. Make a second extraction with 10 ml of chloroform and add to the volumetric flasks. Dilute to volume with chloroform, mix and read in 5-cm cells at a wavelength of 680 mμ against chloroform in the reference cell.

Determination of tungsten. Transfer the aqueous solutions obtained after the molybdenum extraction back to the original 150-ml beakers. Wash out the separatory funnels into the original beakers. Take to fumes of sulfur trioxide, add 3 ml of nitric acid and 1 ml of 30% hydrogen peroxide; wash down the covers and walls of the beakers. Take to fumes of sulfur trioxide and then cool. Rinse and fume again. Allow to cool, then add 40 ml of water and 3 ml of titanium(III) chloride solution and place the beakers in a water bath. Heat at 80–90° for 15 min. Remove from the heat and add 5 ml of dithiol solution; replace the beakers in the bath and heat for 15 min at 80–90°. Remove from the heat and allow the solutions to stand for 2 h. Transfer to 125-ml separatory funnels with two 5-ml portions of chloroform. Shake for 1 min and allow the layers to separate. Collect the chloroform layer in a dry 25-ml volumetric flask. Make a second chloroform extraction with 10 ml and add to the flasks. Make to volume with ethanol, mix and read in 5-cm cells at 640 mμ with chloroform in the reference cell.

The method is suitable for the determination of microgram quantities of molybdenum and tungsten in copper. Molybdenum has no effect on the results for tungsten but there is a small positive effect on the results for molybdenum when tungsten is present. Typical results obtained by the method are shown in Tables I and II.

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Paper solubilization chromatography. Part II. Alcohols (C_7—C_{12})

The first paper in this series[1] described the chromatographic separation of various phenols on filter paper impregnated with ion-exchange resin by development with aqueous solutions of acetic acid. This technique is applied here to the separation of a series of water-insoluble aliphatic monohydric alcohols.

Solution chromatography of uncombined monohydric alcohols has rarely been used. MARUTA AND IWAMA[2] attempted to identify some monohydric alcohols containing more than five carbon atoms by development with aqueous acetic acid on filter paper. Their detecting reagent was a solution of vanadium oxinate. Even though they studied only alcohols with even numbers of carbon atoms (C_6–C_{18}), their separations were not highly successful.

Experimental

Essentially the same apparatus and procedures as reported earlier[1] were employed for the downward development of chromatograms. Amberlite SA-2 ion-exchange papers (batch No. 7802) in the sodium form (Scientifica Co., Clifton, N.J.) were used in sheets 18 in. long, of which about 15.5 in. (39 cm) was available for migration. Some ion exchange undoubtedly occurred between the acid developers and the paper, but previous results[1] showed this to be relatively unimportant.

All alcohols used were of the best grade commercially available and were used without further purification. Normal aliphatic alcohols from *n*-heptyl alcohol through *n*-dodecyl alcohol (C_7 through C_{12}) were studied; lower alcohols were too volatile for convenience.

Initial zones were approximately 5 µl of pure undiluted alcohol, applied by means of a few dabs from a Peerless wood applicator stick (Diamond Match Co., New York). Because of the limits of sensitivity of the detection tests, this amount of each alcohol was needed to allow certain detection after development and accompanying dilution of the zones. The spots were placed one inch apart across the origin.

The procedure for development was exactly as reported before[1], except that the chamber was equilibrated with each solvent for at least 1 h before development. The distance of migration was approximately 36.0 cm for every chromatogram. When mixtures were chromatographed, they were prepared on the paper by successively applying 5 µl of each alcohol to the same area of paper, with drying in between. Reference spots of each alcohol were run on the same sheet of paper.

Two reagents were employed for detecting the developed alcohol zones. (*1*) Vanadium oxinate solution was prepared similarly to a previous method[2]: 0.40 g of 8-hydroxyquinoline was dissolved in 25 ml each of xylene and glacial acetic acid and heated on a steam bath to 55°; 0.20 g of ammonium metavanadate was added with stirring, and the resultant blue-black solution was filtered through Whatman No. 42 filter paper after cooling. The reagent was prepared fresh every three days. Decreasing sensitivity toward alcohols was noted on ageing. Before spraying the dried chromatograms, the reagent was heated to 35°. The alcohol zones became light red while the background turned blue-black. (*2*) A 0.50% solution of potassium permanganate in approximately 0.1 *M* sulfuric acid was prepared. The dried chromatogram was drawn through this solution, and after the excess reagent had dripped back into the tray, the paper was steamed. All alcohol zones turned red, but the test was not so sensitive as (*1*); further, permanganate reacted identically with impurities in the paper which collected at the solvent front. Vanadium oxinate reacted with these impurities to give a black color, darker than the surrounding paper. Detection method (*1*) was used routinely throughout this work.

Results and discussion

Frequent reproducibility runs showed that the R_F values and spot sizes obtained were exceptionally constant. R_F values never differed by more than ±0.02 units from the values reported. The distances given (between the leading edge of the slower zone and the trailing edge of the faster zone) are the average of triplicate runs.

TABLE I

Alcohol	*Values of R_F for [HAc]*							
	3.0 M	*6.0 M*	*6.5 M*	*8.0 M*	*8.5 M*	*9.0 M*	*9.5 M*	*12.0 M*
C_7	0.00	0.00	0.45	0.93	0.97	1.00	1.00	1.00
C_8	0.00	0.00	0.38	0.88	0.95	0.98	0.98	1.00
C_9	0.00	0.00	0.34	0.86	0.92	0.92	0.95	1.00
C_{10}	0.00	0.00	0.23	0.66	0.73	0.90	0.95	1.00
C_{11}	0.00	0.00	0.13	0.21	0.33	0.87	0.95	1.00
C_{12}	0.00	0.00	0.10	0.15	0.29	0.58	0.71	1.00

Table I shows the R_F values obtained when development was performed with different molarities of acetic acid. The zones ranged from 1.7 to 4.6 cm in length and from 0.9 to 1.6 cm in width, and tended to enlarge as the molarity of acid increased. As was expected, with a given concentration of developer, the R_F values decreased as the homologous series of alcohols was ascended. This increase in affinity for the resin with increase in molecular weight was noted also in the column solubilization chromatography of these alcohols[3] and is explained by the increased solute–resin interactions (mainly London dispersion forces) which are possible as the solutes become more hydrocarbon in nature. The series of developers had a parallel solubilizing effect on each alcohol: plots of R_F *vs.* M gave a series of approximately parallel rising curves which were more or less uniformly displaced from each other. Thus, separations obtained with any one developing solution could not be enhanced by changing to another solution during the separation. These results are similar to those for the paper[1] and column[3] solubilization chromatography of phenols.

Table II shows results for development of the alcohols with various methanol solutions. The sizes of the developed zones were smaller with methanol than with acetic acid, ranging from 1.2 to 4.0 cm in length and from 0.7 to 1.4 cm in width. R_F values for a given alcohol increased with an increase in methanol and for a given concentration of solvent decreased down the homologous series. Plots of R_F *vs.* M were again a series of rising non-crossing lines. A solution which is 70.0% methanol by volume is

17.4 *M*; it obviously takes two to three times more moles of methanol than acetic acid to have a similar solubilizing effect on the alcohols (*cf.* ref. 4).

Acetic acid (8.0 *M*) and 75.0% methanol were the best developing solutions for the separations attempted. Methanol was chosen because a very faint forward trail (detected only with vanadium oxinate) was noted with every zone developed with acetic acid, although the main spots were clearly defined; this was never noted for methanol migrations.

TABLE II

Alcohol	*Values of R_F for various methanol concentrations*		
	70.0%	*75.0%*	*80.0%*
C_7	0.63	0.93	1.00
C_8	0.50	0.92	1.00
C_9	0.16	0.75	0.81
C_{10}	0.090	0.45	0.66
C_{11}	0.070	0.25	0.40
C_{12}	0.050	0.17	0.30

Development of a mixture of all six alcohols with 75.0% methanol yielded a separation of all except the C_7 and C_8 alcohols. C_{12} was separated from C_{11} by 0.90 cm; C_{11} from C_{10} by 5.2 cm; C_{10} from C_9 by 8.7 cm; C_9 from C_8 plus C_7 by 2.5 cm. The oval spot lengths were uniformly about 2.0 cm in this solvent. The two lower alcohols were separated in a separate experiment by development of a binary mixture with 70.0% methanol, the distance between zones being 2.7 cm.

Chromatographing derivatives is often superior to trying to separate uncombined organic compounds. For example, the derivatives are usually easier to detect and often easier to separate. However, it will usually be more convenient to separate the compounds directly if a selective chromatographic system and a reliable detection method such as those described above are available.

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Note. While this paper was in press, we became aware of the earlier separation of uncombined normal alcohols by thin-layer chromatography[5].

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Determination of aluminium in silicates with DCTA

PŘIBIL AND VESELÝ[1] showed that 1,2-diaminocyclohexanetetraacetic acid (DCTA), unlike EDTA, reacts quantitatively with aluminium in the cold even in concentrated solutions of neutral salts (*e.g.* 1 *M* NaCl). The reagent was used by BURKE AND DAVIS[2] to determine aluminium in a variety of alloys. It is here applied to the determination of aluminium in silicate materials after fusion with sodium hydroxide and extraction of the melt with hydrochloric acid. Excess sodium hydroxide alone is commonly used to separate aluminium from iron, titanium, magnesium, calcium and manganese[3]; DCTA enhances this separation.

Reagents

All the reagents used were of AnalaR grade, except DCTA and hexamine (GPR).

0.08 M DCTA. Dissolve a suspension of 14 g of DCTA by dropwise addition of 5 *N* sodium hydroxide and dilute to 500 ml.

Buffer solution pH 5.5. Dissolve 200 g of hexamine in water, add 40 ml of concentrated hydrochloric acid and dilute to 1 l.

0.025 M $ZnCl_2$. Dissolve 32.69 g of granulated zinc in hydrochloric acid, neutralize with ammonia solution (methyl red) and dilute to 1 l (0.5 *M*). Dilute this solution (1 : 20) as required.

Procedure

Weigh 0.200 g of a finely ground sample into a 50-ml silver crucible. Add 2.5 g of sodium hydroxide pellets, cover the crucible and heat at 650–750° for 10 min. Allow to cool; add 25 ml of water and allow to stand overnight. Extract with hot water, rinsing finally with a few drops of 1 : 1 hydrochloric acid. Through a long-stemmed polythene funnel, transfer into a 250-ml volumetric flask containing 100 ml of hot 2 *N* hydrochloric acid. Cool and dilute to 250 ml. Pipet a 50-ml aliquot into a 250-ml polypropylene beaker. Add 60 ml of 5% sodium hydroxide. Immediately add 10.00 ml of 0.08 *M* DCTA and a little paper pulp, and heat on a steam bath for 1 h. Allow to cool slightly and filter through a pulp pad into a 650-ml conical beaker. Wash the residue with cold 2% sodium hydroxide (6 × 6 ml). Add to the filtrate a few drops of bromocresol green indicator, and acidify with 1:1 hydrochloric acid; adjust to blue by adding drops of 5 *N* sodium hydroxide. Add 25 ml of buffer (pH 5.5) and 5 drops of 0.1% xylenol orange, and titrate the excess of DCTA with 0.025 *M* zinc chloride to the colour change from orange to purple. Repeat the procedure using reagents only to determine the blank.

Results and discussion

Results obtained for solutions containing proportions of various elements appropriate to soil clay fusates are given in Table I. Typical results for the recovery of aluminium added to soil clay samples and standard rock samples are shown in Table II. Standard rock samples were analysed with the results given in Table III.

A difficulty associated with the separation of aluminium using sodium hydroxide alone is the co-precipitation of aluminium with magnesium. This difficulty is

TABLE I

DETERMINATION OF ALUMINIUM IN SYNTHETIC SOLUTIONS

Elements present (mg)						*Al added*	*Al found*	*Difference*	*Error*
Si	*Mg*	*Ca*	*Fe*	*Ti*	*Mn*	*(mg Al_2O_3)*	*(mg Al_2O_3)*	*(mg Al_2O_3)*	*(%)*
	2					11.88	11.87	−0.01	−0.1
		2				11.88	11.87	−0.01	−0.1
			4			11.88	11.82	−0.06	−0.5
				0.6		11.88	11.92	+0.04	+0.3
					0.7	11.88	11.98	+0.10	+0.8
	2	2	4	0.6	0.7	11.88	11.88	0.00	0.0
20						9.87	9.86	−0.01	−0.1
20	2	2	4	0.6	1	9.87	9.92	+0.05	+0.5

TABLE II

RECOVERY OF ALUMINIUM ADDED TO CLAY AND ROCK SAMPLES

Sample no.		*Al found (mg Al_2O_3)*	*Al added (mg Al_2O_3)*	*Total Al recovered (mg Al_2O_3)*	*Difference (mg Al_2O_3)*	*Error (%)*
Clay samples	696	8.62	3.76	12.39	+0.01	+0.1
	X	10.19	3.76	13.96	+0.01	+0.1
	98	10.06	4.76	14.76	−0.06	−0.4
Rock samples	G 1	5.64	4.76	10.38	−0.02	−0.2
	W 1	5.99	4.76	10.74	+0.01	+0.3

TABLE III

DETERMINATION OF ALUMINIUM IN STANDARD CLAY AND ROCK SAMPLES

Sample no.		*Proposed method*		*Accepted value*	*Other values*
U. S. Bureau of Standards	97	38.0	38.1	38.8[a]	38.3[c]
	98	25.1	24.9	25.5[a]	25.2[c]
U. S. Geological Society	G 1	14.1	13.9	14.27[b]	13.9–14.95[d]
	W 1	15.1	14.9	15.03[b]	14.8–15.25[d]

[a] Certified values. [b] Arithmetic mean of preferred values[5]. [c] Given by SHAPIRO AND BRANNOCK[4]. [d] Given by FLEISCHER AND STEVENS[5].

overcome by the use of DCTA which preferentially complexes the aluminium. When the DCTA is added before the sodium hydroxide, precipitation of iron and manganese is incomplete. In the presence of much Mg ($>$ 1 mg) the DCTA must be added immediately after the sodium hydroxide, because ageing of the magnesium hydroxide precipitate and concomitant adsorption of aluminium is rapid and irreversible. An excess of 5 ml of 0.08 *M* DCTA gives full recovery of aluminium.

Under the conditions of the determination DCTA decomposes slightly, but this is allowed for in the blank determination. Polypropylene vessels were used for the digestion, because results with glass were less consistent. Pulp filtration was chosen for speed. (A batch of six samples can be filtered and washed in 25 min.) A Perspex filter disc, fitted centrally with a solid stem which projected loosely into the stem of a funnel, was more stable than the normal filter disc for preparing the pulp pad.

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Nonaqueous titration of halosilanes with tetrabromophenolphthalein ethyl ester as indicator

Chloro- and bromosilanes are hydrolyzed and alcoholyzed readily and quantitatively. The few exceptions result from steric hindrance or the solubility of the halosilane. The hydrogen halide formed is easily determined by titration with standard base. There are many mentions in the literature of this type of method for determining the hydrolyzable halide content of silanes. Most often, however, the reports are not of an analytical nature and details are not included as to solvents, sample handling, or indicators. In reports including some details of the base titration method, accuracy and precision data have not been presented. Perhaps this is due to lack of suitable standards.

For quality control purposes a nonaqueous method was developed for determining alcoholyzable halides in silanes and siloxanes. A balance of speed of analysis and acceptable accuracy and precision was achieved using common reagents. This method involves alcoholyzing a chloro- or bromosilane in isopropanol and titrating it with standard alcoholic potassium hydroxide to a tetrabromophenolphthalein ethyl ester end-point. This method is also suitable for the micro-determination of chlorosilanes[1]. An iodosilane, discussed below, was analyzed by a back-titration technique in an aqueous–alcoholic solvent. The first ten halosilane standards in Table I were solicited during the past 3 years from research chemists who had prepared them for other studies requiring high purity materials. The bromo- and iodosilane were purified especially for this work.

Tetrabromophenolphthalein ethyl ester (bromophthalein magenta E) indicator was used by Davis and Hetzer[2] in the nonaqueous titration of diphenylphosphate with sodium methoxide and with guanidine derivatives. The color change of this indicator (yellow to blue) is very sharp and is coincident with the potentiometric end-point in a variety of organic solvents, including isopropanol.

Isopropanol is a good over-all solvent for halosilanes, high molecular weight siloxanes containing silicon–halogen groups, and the hydrogen halides formed by alcoholysis. Hydrogen chloride, for example, is soluble to about 0.2 g/ml of isopropanol[3].

Reagents

0.15 *N* Potassium hydroxide in No. 3-A denatured ethanol was standardized against potassium biiodate[4] (G. Frederick Smith Chemical Co.) using phenol red.

Isopropanol, technical grade.

Tetrabromophenolphthalein ethyl ester (Eastman Kodak DPI) 0.5% in methanol–toluene. A fresh indicator solution was prepared every 2–3 months.

The halosilanes in Table I were carefully distilled in 90-cm, glass-helices packed, thermostatted columns of 45–60 theoretical plates until the impurities were estimated to be less than 0.08% by gas chromatography. Exceptions were dichlorodi-isopropoxysilane which may have disproportionated somewhat in the hot injection port of the gas chromatograph, and bromomethyldiphenylsilane and iodotrimethylsilane which hydrolyzed too easily in atmospheric moisture to be sampled at the 99.9% level by a microsyringe. Halosilanes with boiling points above 200° were distilled under reduced pressure. The iodotrimethylsilane was distilled in the absence of light. The halosilanes were analyzed within two days of their purification; iodotrimethylsilane was analyzed within 3 h but even by then had developed a light orange-brown tint.

Procedures

For chlorosilanes with boiling points above 150°: Add 150 ml of isopropanol and 5 drops of indicator solution to a 500-ml Erlenmeyer flask. When necessary, neutralize with a drop or two of 0.01 *N* potassium hydroxide or 0.01 *N* hydrochloric acid. Weigh 6–7 meq. of the silane from a screw-cap dropping-bottle and carefully transfer to the solvent. Stopper the flask and quickly recap the dropping-bottle. Swirl the solution for a few sec and, with the aid of a magnetic stirrer, titrate with standard alcoholic potassium hydroxide to the deep blue end-point. The buret was fitted to the flask through a hole in a rubber stopper. A very small slit down the side of the stopper broke the seal with the flask, but did not cause significant loss of hydrogen halides.

For chlorosilanes with boiling points below 150° and for bromosilanes: The manner of sampling volatile halosilanes was essentially that of SIGGIA[5]. The glass ampoules were in the form of a horseshoe with a 0.5-in. diameter bulb and a long capillary on opposite ends. The bulb was gently flamed and then lowered into a dry ice–isopropanol bath at the same time that the capillary was immersed into the silane. After approximately 12–14 meq. of the chlorosilane or 6–7 meq. of the bromosilane had been drawn into the ampoule, the capillary was lifted above the silane surface. The bulb remained in the cold bath until the last traces of silane drained from the capillary. The capillary end was then touched gently with soft paper to remove adhering silane and sealed with a Bunsen flame. The ampoules were reweighed after standing 15 min at room temperature. The titration was performed as above except that the magnetic stirring bar was dropped into the titration solution so as to break the ampoule. The ampoules were completely crushed just before the end-point.

Warning. Silanes containing silicon–hydrogen groups may not be sampled with soft-glass ampoules. Hydrogen gas is evolved and causes spurting of the silane from the capillary tip. A borosilicate glass ampoule was partially filled with trichlorosilane, but a blue-white flash, caused either by hydrogen gas and/or the trichlorosilane, resulted while attempting to seal the capillary tip with a Bunsen flame.

For iodosilanes: To a solution of 100 ml of water, neutralized to phenol red, and 100 ml of 0.15 *N* potassium hydroxide in ethanol, add an ampoule containing about 6–7 meq. of the iodosilane as described above. Stir for more than 5 min. Back-titrate with standard hydrochloric acid to the phenol red end-point.

Results and discussion

The exact purities of the Table I standards, although unknown, were estimated to be greater than 99.92%. Also unknown was whether or not the minute quantities of impurities contained alcoholyzable halides. It is reasonable, however, to assign a high accuracy and precision to this simple strong acid–strong base titration. The average halogen recoveries for 10 of the first 11 standards in Table I were within two standard deviations of theory; the other was within three standard deviations of theory. These standard deviations in terms of parts per thousand ranged from 0.7 for dichloro(2-carbomethoxyethyl)methylsilane to 2.9 for the volatile dichlorodimethylsilane, and to a better-than-expected 0.6 for the iodotrimethylsilane by the back-titration technique. As would be expected, however, the accuracy of halogen recovery for this last silane was not as good as for those previous.

TABLE I

RESULTS OF HALOGEN DETERMINATIONS IN HALOSILANES

Halosilane	*% Halogen*		*Number of determinations*
	Theory	*Found*[a]	
Silicon tetrachloride[b]	83.47	83.41 ± 0.19	5
Dichlorodimethylsilane[b]	54.94	54.85 ± 0.16	5
Hexachlorodisilane[b]	79.11	78.92 ± 0.15	5
Dichlorodiisopropoxysilane	32.65	32.62 ± 0.03	8[c]
Dichlorodiphenylsilane	28.00	27.96 ± 0.02	10
1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane	21.66	21.57 ± 0.05	10
Trichloro(3-chloropropyl)silane	50.17[d]	50.10 ± 0.05	11[e]
Dichloro(2-cyanoethyl)methylsilane	42.18	42.21 ± 0.03	10
Dichloro(2-carbomethoxyethyl)methylsilane	35.26	35.26 ± 0.02	10
Chloromethylphenylsilane	22.63	22.54 ± 0.03	9[f]
Bromomethyldiphenylsilane[b]	28.83	28.80 ± 0.04	5
Iodotrimethylsilane[b,g]	63.42	63.21 ± 0.04	5

[a] Average and standard deviation.
[b] Sampled and weighed in glass ampoules.
[c] Total available sample.
[d] Does not include, of course, chloride attached to carbon.
[e] Includes a 49.95% chloride determination; see discussion.
[f] Excludes a 22.44% chloride determination; see discussion.
[g] Reacted with aqueous–alcoholic base and back-titrated with standard acid.

Two chloride assays, footnoted in Table I, seemed out of line with their respective averages. Whether or not these assays were included in the averages was determined by the Q-test of DEAN AND DIXON[6].

As a general rule chlorosilanes with boiling points above 150° may be transferred to the titration flask while open to the air. This rule is limited, of course, by the hydrolyzability of specific halosilanes with atmospheric moisture. For example, although hexachlorodisilane and dichlorodiisopropoxysilane boil only 11° apart, 146° and 157° respectively, the hexachlorodisilane cannot be sampled except by sealed ampoule, whereas the dichlorodiisopropoxysilane can be sampled quantitatively in the open by acting quickly. Bromo- and iodosilanes, whatever the boiling points, hydrolyze rapidly with atmospheric moisture and may only be sampled by means of ampoules.

Iodosilanes have been determined, following reaction with excess ethanolic base, by back-titration with standard acid[7]. This method precludes the formation of ethyl iodide. An analysis of an iodosilane was also included in this paper since it was probably of a higher purity than was necessary for the above reference. Iodosilane assays by the direct nonaqueous method of this paper were not quantitative. When aqueous *tert.*-butanol was substituted for both the ethanol (tetrabutyl-phosphonium hydroxide as base) and the isopropanol solvent, quantitative results were approached. Too much time, however, was required to reach a stable end-point.

Hydrogen gas was not detected by mass spectrometry during titrations of chloromethylphenylsilane and hexachlorodisilane. Undetected quantities of hydrogen may possibly have evolved from the reactions between silicon–hydrogen or disilane linkages and alcohol or moisture during the addition of base. The role of this base would have been catalytic, however, and no net loss of titer would have resulted.

Potassium halides were precipitated during the chloro- and bromosilane titrations but in no way obscured the end-points or lessened the accuracy of the method. Addition of a few ml of water following the titrations cleared the solutions, even in the cases of silicon tetrachloride and hexachlorodisilane. Halide precipitates were eliminated by titration of halosilanes with tetrabutylammonium hydroxide. Under comparable conditions, however, the yellow to blue end-point of this base was not as sharp as when using the potassium hydroxide titrant.

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Spot test for formanilide and benzoin

It has been reported[1] that fused benzoin may act above its melting point (137°) as a hydrogen-donor for appropriate organic hydrogen-acceptors which are thus split off. This effect, which may be termed pyrohydrogenolysis or pyrohydrogenic cleavage, is due to the transformation of benzoin into benzil (1), followed or accompanied by the hydrogen-fixing (2). The addition of (1) and (2) leads to the net reaction (3):

$$C_6H_5CH(OH)COC_6H_5 \rightarrow C_6H_5COCOC_6H_5 + 2\ H^0 \qquad (1)$$

$$XY + 2\ H^\circ \rightarrow XH + YH \qquad (2)$$

$$C_6H_5CH(OH)COC_6H_5 + XY \rightarrow XH + YH + C_6H_5COCOC_6H_5 \qquad (3)$$

In many cases the above sequence of reactions is achieved only pyrolyticallyand does not occur in the wet way. Pyrohydrogenolyses leading to volatile cleavage products were utilized in organic spot test analysis[2] for the detection of aliphatic sulfonic acid (formation of sulfurous acid), aliphatic-bound halogens (formation of hydrogen halides), aliphatic-bound $-NO_2$ groups (formation of nitrous acid), compounds containing a $N-NO_2$ group (formation of nitrous acid) and aliphatic thiols (formation of hydrogen sulfide).

We have attempted to establish other pyrohydrogenolyses which may possibly find analytical applications. From pertinent experiments it was observed that a mixture of formanilide (m.p. 49°; b.p. 271°) and benzoin, when heated to a temperature of 150–170°, splits off aniline, which can be detected by the color reaction with sodium 1,2-naphthoquinone-4-sulfonate (Ehrlich reagent)[3]. When solid formanilide is heated alone or dissolved in an inert high-boiling solvent at the above temperature no aniline is split off. Therefore the following redox reaction may be assumed:

$$HCONHC_6H_5 + C_6H_5CH(OH)COC_6H_5 \rightarrow CH_2O + NH_2C_6H_5 + C_6H_5COCOC_6H_5 \qquad (4)$$

Acetanilide and probably other anilides of carboxylic acids are not altered when treated with fused benzoin. The behavior of formanilide is therefore characteristic for this compound and a specific test for it could be developed (Procedure I).

It is remarkable that contrary to expectation, a great excess of benzoin diminishes the sensitivity of the test, probably because benzoin and benzil, due to their C=O groups, condense with the aniline formed to give Schiff bases, so that less aniline is free to evaporate. Another explanation may be that benzoin in its tautomeric and more acidic "reduction" form, $C_6H_5C(OH)=C(OH)C_6H_5$, ties the liberated aniline as a rather heat-stable aniline salt. Furthermore it may be mentioned that it was not possible to detect the formaldehyde formed in (4) with a filter paper moistened with Nessler's reagent (blackening is a positive response); the reason may be that the formaldehyde and aniline vapors in contact with the moistened paper combine to give the pertinent Schiff base. In the latter the formaldehyde is masked, whereas the aniline component reacts with the Ehrlich reagent. This assumption was confirmed by the behavior of suitable mixtures of aniline and formaldehyde.

The pyrolytic reaction (4), when realized with excess of formanilide, permits the detection of benzoin (Procedure II). This test is more sensitive than that for formanilide, as the above-mentioned loss of aniline does not occur.

Procedure I (Detection of formanilide)

In a micro test tube a drop of the test solution is evaporated to dryness and a minimum amount of solid benzoin is added. The tube is then immersed in a glycerol bath preheated to 150–170° and covered with a piece of filter paper moistened with 1% Ehrlich reagent. The appearance of a violet fleck (on the yellow background) indicates a positive response.

Limit of identification: 50 μg formanilide.

Procedure II (Detection of benzoin)

In a micro test tube a drop of the test solution is evaporated to dryness and an excess of solid formanilide is added. The tube is then immersed in a preheated glycerol bath (150–170°) and covered with filter paper moistened with a drop of 1% Ehrlich reagent. A positive response is indicated by the appearance of a violet fleck.

Limit of identification: 20 μg benzoin.

It is highly probable that the test described here for benzoin may also be applied to the detection of acyloins. This was borne out by the behavior of furoin, anisoin and pyridoin.

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The reduction of titanium(IV), vanadium(V), chromium(III), molybdenum(VI), tungsten(VI), uranium(VI) and iron(III) with sodium–lead alloy

Sodium–lead alloy is a potentially useful reductant for analytical purposes, although its use as a reducing agent for multivalent cations in solution has not been reported, apart from the observation that copper is displaced from a copper(II) sulphate solution[1]. The alloy has been used as a drying agent for solvents[2]. Examination of known standard oxidation–reduction potentials[3] shows that metallic sodium should bring about the following reductions: Ti(IV) → Ti(III); V(V) → V(II); Cr(III) → Cr(II); Fe(III) → Fe(II). Metallic lead is a weak reducing agent[4].

We have investigated the reduction of Ti(IV), V(V), Cr(III), Mo(VI), W(VI), U(VI), and Fe(III) by sodium–lead alloy in mineral acids (hydrochloric and sulphuric) and developed quantitative procedures for Ti, V, Mo, U and Fe.

Reagents

Sodium–lead alloy (10% Na) was supplied by British Drug Houses. Reagent-grade chemicals were used throughout unless specified otherwise. Solutions of V(V), Mo(VI), U(VI), and Fe(III) were prepared by dissolving sodium metavanadate, molybdic acid, uranium trioxide, and iron(III) ammonium sulphate respectively in the appropriate concentration of hydrochloric or sulphuric acid. Titanium(IV) solutions were prepared from $Ti_2(SO_4)_3$ solution (15%, w/v) by oxidation with the minimum amount of hydrogen peroxide (100 vol.), removal of any excess of peroxide by boiling, and final adjustment of acidity by the addition of concentrated hydrochloric or sulphuric acid. All these solutions were standardised by established titrimetric procedures. Standard tungsten(VI) solution was made from A.R. sodium tungstate.

General reduction procedure

The apparatus consisted of two 250-ml conical flasks. One of these, the "reduction flask", had a side-arm filled with glass wool near the bottom, which was connected (by way of a stopcock) to the "titration flask". An aliquot of the sample solution was placed in the reduction flask, the sodium–lead alloy added, and a two-holed stopper inserted. A stream of nitrogen was passed into the flask, and the solution was heated to 95–100° for the required time, the flask being shaken intermittently; with the Ti(IV) solution, the reduction proceeded readily without heat. The reduced solution was run off through the stopcock and outlet tube into the titration flask, which contained an excess of iron(III) ammonium sulphate (10%) in 0.1 *M* sulphuric acid (except for Fe and U solutions). The reduction flask, the lead metal, and any unreacted sodium–lead alloy were washed several times with distilled water, and the washings run into the titration flask; the flow of nitrogen was maintained during this washing.

The reduced solutions were allowed to cool to room temperature, the indicator, etc. added, and then the solutions were titrated with standard oxidant (potassium dichromate, potassium permanganate, or ceric sulphate). In the case of the reduced uranium solution, the final titration was preceded by the passage of a brisk current of air through the solution to oxidise any U(III) to U(IV).

A blank determination was carried out in every instance, but this never amounted to more than 0.1 ml.

Quantitative reduction procedures

Preliminary experiments involving adjustments in the experimental parameters of acidity, metal ion concentration, amount of sodium–lead alloy, and the time and temperature of reduction, led to the following conditions:

(*a*) *For Ti(IV)* (1) 10 ml 2.5 *M* H_2SO_4 containing 0.03 g Ti(IV), 5 g Na–Pb alloy, 5 min reduction, no heating. (2) 10 ml 2.5 *M* H_2SO_4 containing 0.03 g Ti(IV), 3 g Na–Pb alloy, heating for 3 min at 95–100°.

(*b*) *For V(V)* 10 ml 2.5 *M* H_2SO_4 containing 0.05 g V(V), 5 g Na–Pb alloy, heating for 4 min at 95–100°.

(*c*) *For Mo(VI)* 10 ml 8 *M* HCl containing 0.03 g Mo(VI), 2 g Na–Pb alloy, heating for 3 min at 95–100°.

(*d*) *For U(VI)* 10 ml 6 *M* HCl containing 0.11 g U(VI), 2 g Na–Pb alloy, heating for 3 min at 95–100°.

(*e*) *For Fe(III)* 10 ml 2.5 *M* H_2SO_4 containing 0.07 g Fe(III), 3 g Na–Pb alloy, heating for 2.5 min at 95–100°.

Results and discussion

Reaction between sodium–lead alloy and solutions of Ti(IV), V(V), Cr(III), Mo(VI), W(VI), U(VI), and Fe(III) in hydrochloric acid (2.0–11.2 *M*) and sulphuric acid (1.0–5.5 *M*), with and without the application of heat, showed the formation respectively of Ti(III), V(II), Mo(III) (molybdenum blue was formed when solutions of Mo(VI) in 2 *M* HCl or *M* H_2SO_4 were reduced at room temperature), W(III), U(III) and (IV) and Fe(II). Thus the reducing action of the alloy was similar to that of zinc amalgam[5]. At acid concentrations lower than those quoted, Ti(IV), Cr(III), U(VI), and Fe(III) were precipitated as hydroxides; V(V), Mo(VI), and W(VI) were not studied at these lower acidities.

TABLE I

Element	*Weight taken (mg)*	*Weight found (mg)*
Ti, method 1	26.7	26.4; 26.5; 26.4
	53.4[a]	53.1; 53.2; 53.3
Ti, method 2	26.7	26.4; 26.7; 26.5
	53.4[a]	53.1; 53.2; 53.3
V	49.9	49.6; 49.8; 49.6
	99.8[a]	99.3; 99.4; 99.5
Mo	32.0	31.8; 31.9; 31.9
	64.0[a]	63.7; 63.3; 63.6
U	113.0	113.0; 112.6; 112.9
	226.0[a]	225.4; 225.0; 225.2
Fe	73.7	73.7; 73.5; 73.8
	147.4[a]	147.3; 147.0; 147.0

[a] In these experiments the recommended volumes of acid and amounts of sodium–lead alloy were doubled; the time of reduction remained unchanged.

The results of the quantitative reduction experiments are given in Table I.

Reduction of tungsten(VI) to tungsten(III) was not quantitative, however, even in concentrated hydrochloric acid with the addition of ammonium chloride. This agreed with LUKE's observation[6] that reduction by metallic lead in similar media was incomplete and required a final treatment involving the passage of the partially reduced solution through a lead reductor.

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BOOK REVIEWS

R. Strohecker und H. M. Henning, *Vitamin-Bestimmungen*, E. Merck AG., Darmstadt, Verlag Chemie GmbH, Weinheim/Bergstr., 1963, 365 S., preis Ganzl. DM 42.—.

Beim vorliegenden Buch handelt es sich um eine Neubearbeitung des vor einigen Jahren erschienenen Werkes *Vitamin-Analyse, Chemische Methoden.* Während in der damalige Ausgabe nur chemische und physikalisch-chemische Methoden angeführt waren, sind in der jetzigen, erweiterten Auflage auch mikrobiologische Methoden (zur Bestimmung der Vitamine der B-Gruppe) aufgenommen worden. Es dürfte sich bei diesem Werk wohl um das Beste handeln, das derzeit, ganz gleich in welcher Sprache, überhaupt an Literatur über Vitamin-Analysen, zu erhalten ist. Beim Durchlesen der einzelnen angeführten Methoden ist zu erkennen, dass es sich ausnahmslos um Verfahren handelt, die in den Merck'schen Laboratorien laufend angewandt werden, bzw. vor ihrer Aufnahme in das Buch überprüft wurden.

In einer ausführlichen Einführung werden die Vorteile bzw. Nachteile der einzelnen Methoden gegenüber gestellt und wertvolle Hinweise auf Fehlerquellen, Aufbereitung des Untersuchungsmaterials und kritische Beurteilung der Ergebnisse gegeben. Anschliessend werden in 15 Kapiteln ausführliche Arbeitsvorschriften für die Bestimmung aller Vitamine von A bis P gegeben, wobei jeweils für ein Vitamin mehrere Methoden *in extenso* angeführt werden. Dabei werden gleicherweise chemische und physikalisch-chemische Methoden berücksichtigt, neben den eingangs erwähnten mikrobiologischen Verfahren für die Vitamine der B-Gruppe. Äusserst wertvoll sind die bei jeder Vorschrift angeführten Hinweise auf mögliche Störfaktoren und deren Ausschaltung, sowie die Angaben über Empfindlichkeit und Spezifität der Methoden. Zusätzlich enhält jedes Kapitel nützliche Daten über die Aufarbeitung des Probenmaterials zur eigentlichen Bestimmung. Die Ausstattung des Buches ist ausgezeichnet, 42 Abbildungen und 8 Farbtafeln sind eine wertvolle Ergänzung. Ein ausführliches Sachverzeichnis erleichtert die Benützung.

Abschliessend kann gesagt werden, dass dieses Buch allen, die sich mit Vitamin-Bestimmungen, sei es in pharmazeutischen Präparaten, sei es in natürlichen Materialien, zu beschäftigen haben, bestens empfohlen werden kann.

W. Schöniger (Basel)

K. DOERFFEL, *Beurteilung von Analysenverfahren und Ergebnissen*, Springer-Verlag, Berlin–Göttingen–Heidelberg, 1962, 98 S., preis DM 14.80.

In dankenswerter Weise hat der Springer-Verlag die ursprünglich in der Zeitschrift für analytische Chemie (Band 185) erschienene Arbeit in Buchform auf den Markt gebracht und damit beigetragen, eine sehr fühlbare diesbezügliche Lücke in der deutschsprachigen Fachliteratur zu schliessen. Die Bedeutung der statistischen Bewertung von Analysenmethoden und Resultaten wurde in den letzten Jahren immer klarer erkannt und es muss wohl dem Mangel an einem kurzen, klaren und vor allem für den Analytiker, der zumeist keine mathematische Spezialausbildung genossen hat, erfassbaren Buch über die statistische Behandlung von Analysendaten zugeschrieben werden, dass die im deutschen Sprachraum erschienenden Publikationen vielfach unklare, uneinheitliche und oft auch einander widersprechende Aussagen in bezug auf statistische Beurteilungen enthalten. Das vorliegende Buch erscheint als Einführung in dieses durchaus nicht einfache Gebiet sehr gut geeignet, da sein Verfasser als Chemiker zu seinen Fachkollegen spricht und sie daher nicht von vornherein mit schwerem mathematischen Geschütz einschüchtert. Ein Buch dieses Umfanges wird selbstverständlich nicht jede der zahllosen Möglichkeiten erfassen können, die sich in der Praxis bei der Behandlung eines gegebenen Problemes ergeben. Für die wichtigsten und häufigsten Fälle wird der Analytiker zumindest einen Hinweis finden, wie die statistische Behandlung angepackt werden muss, um unrichtige Interpretationen zu vermeiden, die nur zu leicht mehr Schaden als Nutzen anrichten können. Die Einteilung des Buches ist klar und übersichtlich und man wird es, sobald man sich einmal durchgearbeitet hat, als ergiebige Informationsquelle schätzen lernen. Das ausführliche Literaturverzeichnis wird allen jenen, die sich mit diesem aktuellen Thema intensiver zu befassen wünschen, eine wertvolle Hilfe darstellen. Das Buch kann vom Studenten höherer Semester an jedem empfohlen werden, der in Praxis, Lehre oder Forschung mit der Bewertung von Analysen befasst ist.

H. MALISSA (Vienna)

G. CHARLOT, *L'Analyse Qualitative et les Réactions en Solution*, 5ème Ed., Masson et Cie, Paris, 1963, 442 pp., prix 65 F Broche; 75 F cartonne toile.

Six years have elapsed since the last edition of this well-know book appeared. In this latest revision, Professor CHARLOT has enlarged the text to cover reactions in the presence of a second solvent (that is, in addition to water), and separations by solvent extraction and by ion exchange. Values for equilibrium constants have been brought up-to-date and the number of exercises and worked examples has been increased. For many years, this book has been of value to analytical chemists, not only as a source of analytically useful reactions, but also for its lucid presentation of the theory of ionic equilibria. This new edition, enhanced by careful revision and the reputation of its predecessors, must continue to provide a valuable service to analytical chemistry.

W. I. STEPHEN (Birmingham)

L. S. BIRKS, *Electron Probe Microanalysis*, J. Wiley–Interscience Publishers, New York, 1963, ix + 253 pp., price 70 s.

This book provides an excellent account of a technique which has grown in importance at a very rate rapid in the last decade and which provides an interesting link between X-ray diffraction and electron microscopy. This connection is explained in the historical introduction and referred to in the final chapter which deals with future trends. Significantly, one of the features described in some detail is the possibility of developing low-cost equipment.

There are sections dealing with electron optics and X-ray crystallography in addition to those dealing more directly with specimen techniques and application of microanalysers.

This book can be recommended to specialists in the technique and to physicists and physical chemists generally. It is a most stimulating text and would be suitable post-graduate reading for physics, chemistry and metallurgy students.

J. R. MAJER (Birmingham)

Anal. Chim. Acta, 32 (1965) 196

ANNOUNCEMENTS

INTERNATIONAL SYMPOSIUM ON THERMAL ANALYSIS, APRIL 1965

A Symposium on Thermal Analysis will be held in London on 13th–14th April, 1965. The main Lecturers will be:

Prof. L. ERDEY (Technical University, Budapest), Prof. P. D. GARN (University of Akron), Dr. G. GUICHON (Ecole Polytechnique, Paris), Dr. M. HARMELIN (Laboratoire de Recherches Micro-Analytiques, Paris) and Prof. W. W. WENDLANDT (Texas Technological College).

Contributed papers are invited in all branches of the technique and application of thermal analysis. An exhibition displaying a wide range of thermal analysis equipment will be staged in conjunction with this Symposium.

This Symposium is organised by the Northern Polytechnic and further information may be obtained from Dr. W. GERRARD, Chemistry Department, Northern Polytechnic, Holloway Road, London, N. 7, England.

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2. INTERNATIONALES SYMPOSIUM "REINSTOFFE IN WISSENSCHAFT UND TECHNIK" – 28.9.–2.10. 1965 IN DRESDEN

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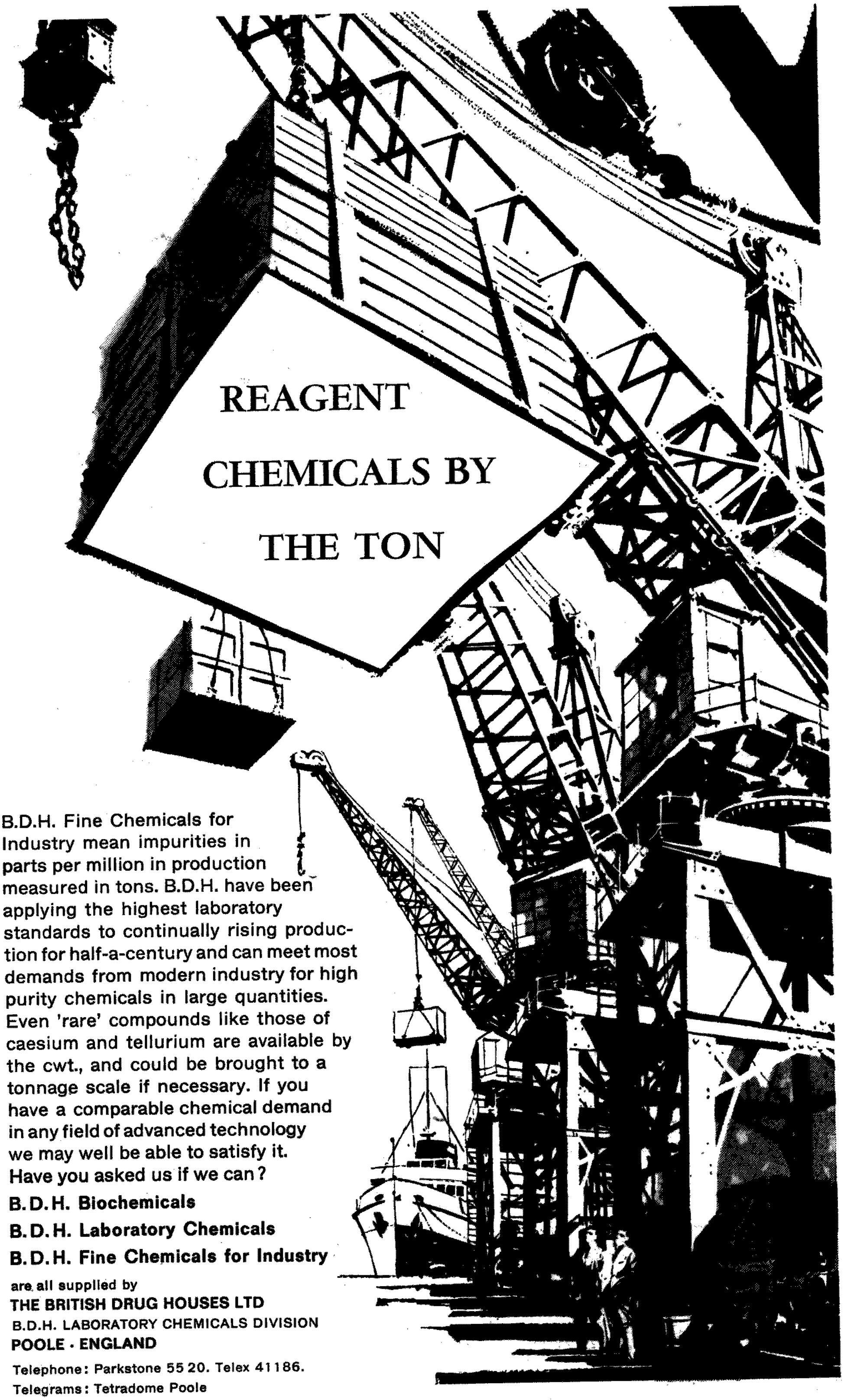

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