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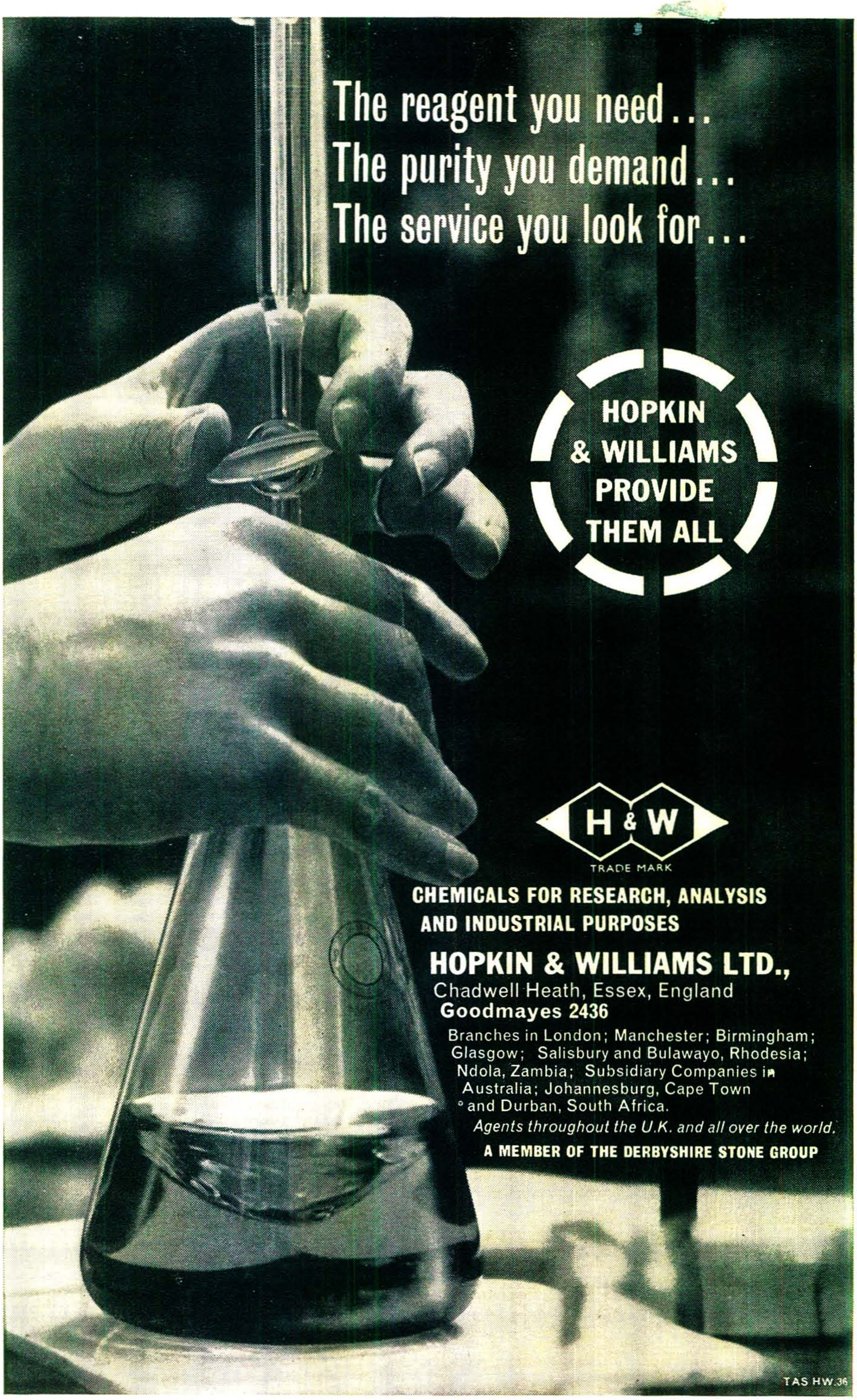
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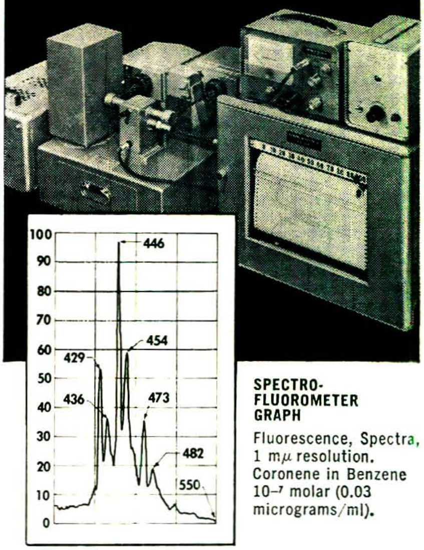

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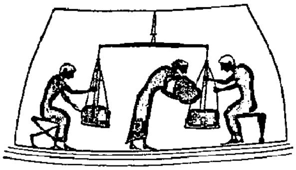

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OBITUARY

On 18 September 1965, the death occurred, in a motor car accident, of the prominent Russian analytical chemist and Corresponding Member of the U.S.S.R. Academy of Sciences

DMITRY IVANOVICH RYABCHIKOV

Professor Ryabchikov dedicated the 35 years of his research activity to investigations into the complex chemistry of the noble metals and of the rare earths. His work on the rare earths became the basis of methods for their separation and analysis. He paid particular attention to the applications of ion exchange and paper chromatography in analytical methods. As an author or coauthor he published more than 250 scientific papers and monographs. An outstanding organiser of research work, Professor Ryabchikov was one of the founders of the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences. He devoted much of his time to the young research chemists who studied under him.

A good memory will be kept for ever in the hearts of all who knew him.

Talanta, 1966, Vol. 13, pp. 333 to 339. Pergamon Press Ltd. Printed in Northern Ireland

ELECTROMETRIC INDICATORS IN THE AMPEROMETRIC TITRATION OF CATIONS AND ACIDS

WALENTYNA RUSKUL
Department of Inorganic Chemistry, University of Lodz, Poland

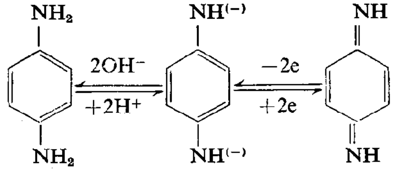
(*Received* 23 *April* 1965. *Accepted* 14 *October* 1965)

Summary—Amperometric titration is carried out at zero potential in the presence of hydroquinone and *p*-aminophenol as electrometric indicators. Solutions of sodium carbonate, sodium arsenite, sodium tetraborate and potassium cyanide have been used as reagents in neutralisation, precipitation and complex formation reactions for the determination of cations separately, the simultaneous determination of several cations in one sample and of acid and cations present simultaneously. After the equivalence point has been reached, hydroxyl ions appear in the solution as a result of salt hydrolysis and a considerable increase in the current voltage occurs. The indicator in alkaline solution induces the depolarisation of the electrode.

INTRODUCTION

THE technique of amperometric titration is based on the measurement of diffusion currents which arise at an electrode because of oxidation or reduction of substances at an applied potential depending on the change of concentration of the ion under examination. In some cases the titration can be performed with no externally applied e.m.f. at so-called zero potential. This procedure is admissible only in those cases where the e.m.f. of the cell (consisting of the solution under examination and a reference electrode) is sufficient for the reduction process to be completed, and when an electroactive substance is present. This method is, therefore, of restricted application. It can be applied neither to neutralisation reactions nor to precipitation reactions, where either an ion to be analysed or an ion precipitant do not undergo reduction at a cathode or oxidation at an anode.

This paper deals with the possibilities of applying an amperometric titration at zero potential to the determination of inactive substances and cations in neutralisation and precipitation reactions as well as to the formation of complex compounds by the introduction of small quantities of such substances as hydroquinone and *p*-aminophenol. These substances act as electrometric indicators. It was found that hydroquinone, pyrogallol, hydrogen peroxide and dimethylaniline can be used as electrometric indicators in neutralisation reactions for the determination of acids and bases by the amperometric method.[1] The amine and hydroxyl groups influence the facile oxidation of the benzene ring[2] particularly in an alkaline solution.



When oxidised to the quinone form, they become depolarisers of an electrode, causing an increase in the current voltage.

The indicator reacts with the hydrolysis product of the reagent. Their concentration does not depend on the concentration of an ion to be titrated and there is no need

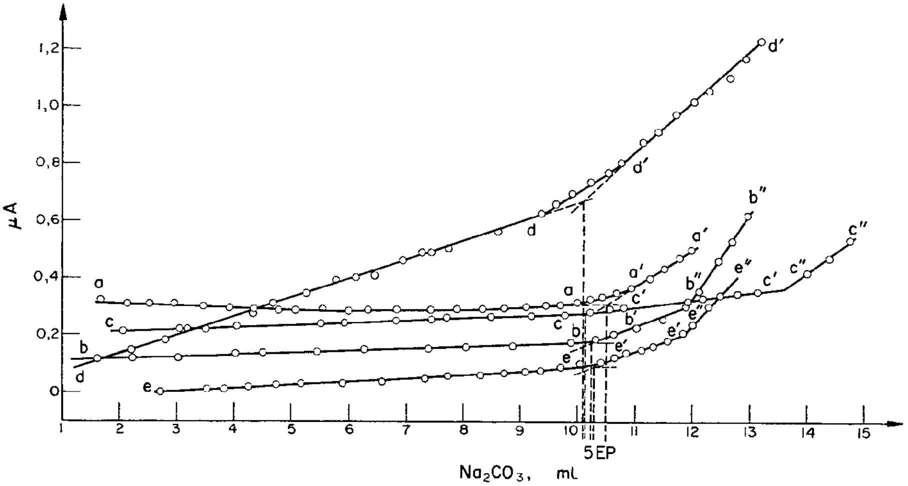


FIG. 1.—Curves for the amperometric titration of Ba^{2+}, Cd^{2+} and Zn^{2+} ions with a solution of sodium carbonate in aqueous alcohol in the presence of an electrometric indicator: (a) 0·1005N Ba^{2+}, *p*-aminophenol. (b) 0·0099N Cd^{2+}, *p*-aminophenol, (c) 0·01N Ba^{2+}, *p*-aminophenol, (d) 0·01N Ba^{2+}, hydroquinone, (e) 0·0099N Zn^{2+}, *p*-aminophenol.

to select them for the respective reactions as in classical amperometry.[4–10] Only minute quantities of these indicators (1–2 drops of a 0·001M solution) need be used for each determination.

Salts which readily undergo hydrolysis were used as precipitants, *e.g.*, sodium carbonate, sodium arsenite, sodium tetraborate and potassium cyanide.

In the course of precipitation the standard electrode is polarised and any change in diffusion current cannot be observed with the subsequent addition of a titrant.

TABLE I.—RESULTS OF AMPEROMETRIC TITRATIONS

Amount to be determined, *mg*	Number of determinations	Determined average $(\bar{x} \mp st)$, *mg*
Cd^{2+} 72·55	10	72·57 ± 0·04
Cu^{2+} 46·54	10	46·56 ± 0·06
Ba^{2+} 6·90	9	6·80 ± 0·09
Ni^{2+} 2·82	9	2·84 ± 0·05
Zn^{2+} 3·27	10	3·25 ± 0·05
Cd^{2+} 56·00	10	56·03 ± 0·07
Ba^{2+} 69·02		69·05 ± 0·10
Zn^{2+} 3·20	9	3·24 ± 0·07
Ba^{2+} 6·90		6·80 ± 0·12
Ni^{2+} 2·82	10	2·81 ± 0·03
Zn^{2+} 3·27		3·28 ± 0·04
Ag^{+} 106·90	9	107·00 ± 0·19
Cd^{2+} 56·00		56·19 ± 0·21
HCl 37·65	9	37·59 ± 0·08
Cd^{2+} 56·00		56·12 ± 0·17
HCl 3·77	10	3·78 ± 0·05
Cd^{2+} 5·60		5·62 ± 0·04
Ni^{2+} 2·82	10	2·79 ± 0·04
HCl 3·77		3·73 ± 0·05

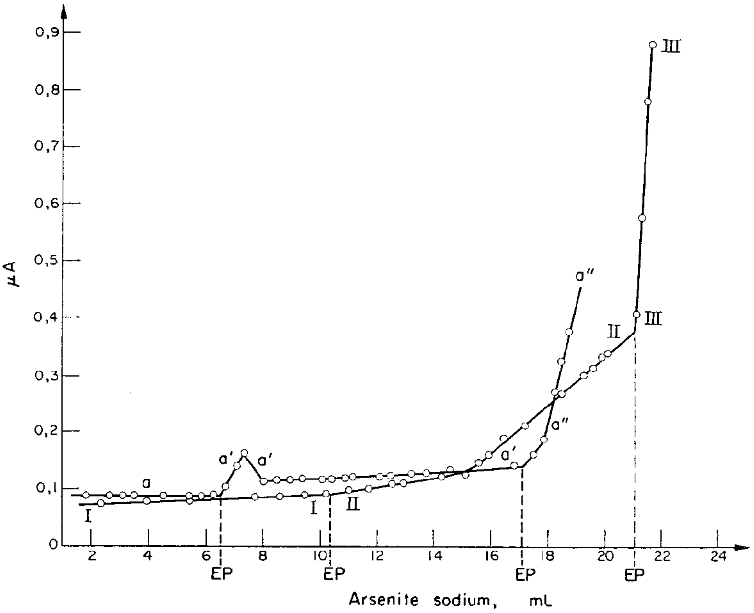


FIG. 2.—Simultaneous titration of Ag^+ and Cd^{2+} ions, nitric acid and Cd^{2+} ions with a solution of sodium arsenite in aqueous alcohol in the presence of *p*-aminophenol as indicator: (a) HNO_3, (a′) 0·01N Cd^{2+}, (a″) sodium arsenite solution; (I) 0·099N Ag^+, (II) 0·996N Cd^{2+}, (III) excess sodium arsenite solution.

TABLE II.—RESULTS OF AMPEROMETRIC TITRATIONS OF CATIONS WITH POTASSIUM CYANIDE SOLUTION

Amount to be determined, *mg*	Number of determinations	Number of bound CN^- groups	Determined average ($\bar{x} \pm st$), *mg*
Ni^{2+} 28·19	10	4	28·21 ± 0·08
Ni^{2+} 2·82	10	4	2·81 ± 0·05
Cd^{2+} 72·55	9	3	71·20 ± 0·22
Zn^{2+} 33·31	10	2	33·33 ± 0·09
Cu^{2+} 46·22*	9	4	46·08 ± 0·18
Cu^{2+} 4·62	10	4	4·63 ± 0·63

* In the determination of Cu^{2+} the ratio $Cu^{2+}:CN^-$ is 1:8. Therefore, the number of ml of potassium cyanide solution to be used should be doubled according to the reaction: $2Cu(CN)_2 \rightarrow 2CuCN + (CN)_2$.

The increase in the current voltage can be noticed only after the precipitation is completed.

Amperometric titration at zero potential of respective cations with a solution of potassium cyanide causes the formation of complex compounds of varying stability. Compounds with an increasing number of cyanide groups (Figs. 4 and 5) are formed with the same central ion. The transformation of one compound into another is marked by a change in current voltage. This can be seen from the graph as the intersection of the horizontal and inclined or of inclined and vertical sectors of the curve.

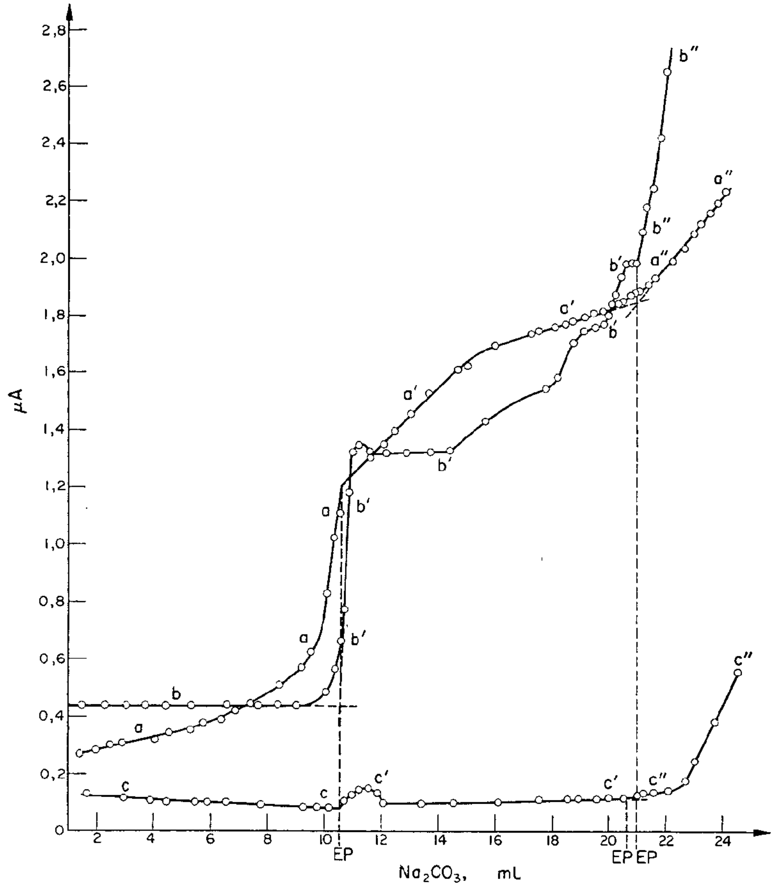


FIG. 3.—Curves for the simultaneous amperometric titration of Cd^{2+} and hydrochloric acid with a solution of sodium carbonate in aqueous alcohol: (a) 0·1031N HCl, (a′) 0·0996N Cd^{2+}, (a″) excess sodium carbonate solution; hydroquinone. (b) 0·01N Cl, (b′) 0·01N Cd^{2+}, (b″) sodium carbonate solution; hydroquinone. (c) 0·1N HCl, (c′)0·1N Cd^{2+}, (c″) excess sodium carbonate solution; *p*-aminophenol.

The horizontal sector of the curves determines a more stable complex compound than the inclined one.

When the cyanide ion does not form any stable complex with the cation, it undergoes hydrolysis, giving an hydroxyl ion and inducing an increase in the current voltage. This coincides in the graph with the inclined or even vertical sector of the curve.

EXPERIMENTAL

In this study of the determination of cations in precipitation at zero potential and with the use of electrometric indicators, oxygen has not been removed from the samples.

The titrations were carried out with the following cell:

$$Pt \mid Hg \mid Hg_2(NO_3)_2 \parallel KNO_3 \parallel \text{the solution} \mid Pt.$$

The solution was stirred, but not deoxygenated.

The concentration of salts of Ag^+, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} was determined by means of electrolysis,[11] and of barium chloride with sodium rhodizonate.[3]

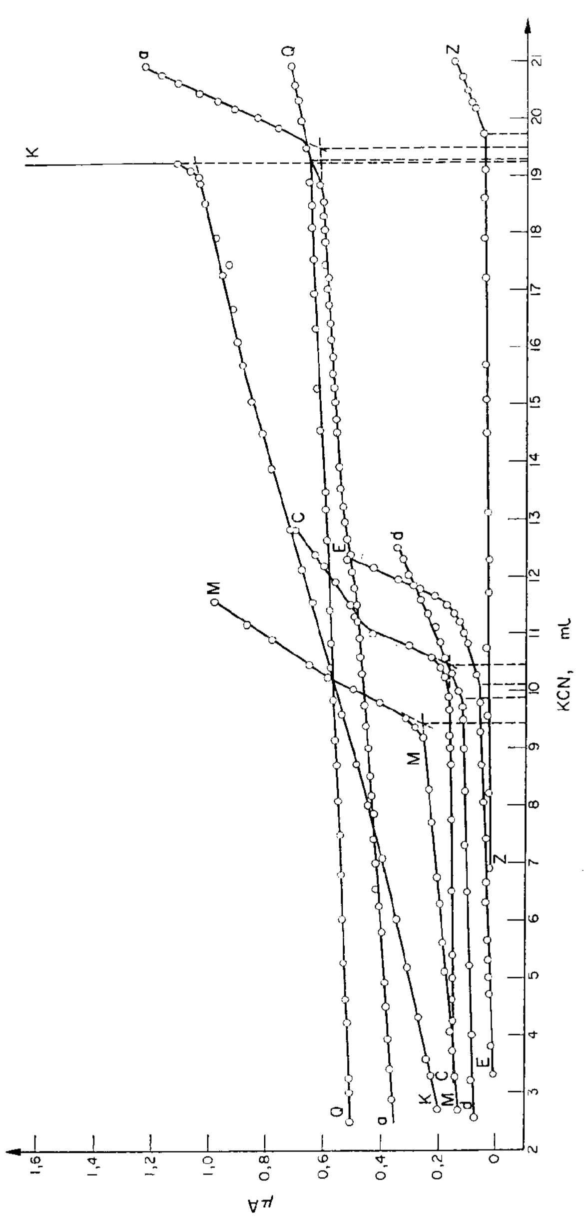


Fig. 4.—Curves for the amperometric titration of Ni^{2+}, Zn^{2+} and Cd^{2+} ions with potassium cyanide solution in the presence of *p*-aminophenol as indicator: (a) 0·1*N* Ni^{2+}, (C) 0·1*N* Zn^{2+}, (E) 0·1*N* Co^{2+}, (K) 0·1*N* Cd^{2+}, (M) 0·1*N*, Cr^{3+}, (d) 0·01*N* Cr^{3+}, (z) 0·01*N* Ni^{2+}, (Q) 0·01*N* Cd^{2+}

RESULTS AND DISCUSSION

Solutions containing the ions Ba^{2+}, Ag^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} in the concentration range 0·1–0·01*N* have been titrated with sodium carbonate, sodium arsenite and sodium tetraborate.

On a typical titration curve (Fig. 1) the horizontal part of the curve corresponds to precipitation and the sloping part to an excess of reagent. In some cases (*e.g.*, barium carbonate) ethyl alcohol must be added to reduce the absorption of ions on the precipitate; this also has the effect of reducing the solubility of the precipitate and increasing the sensitivity of the method.

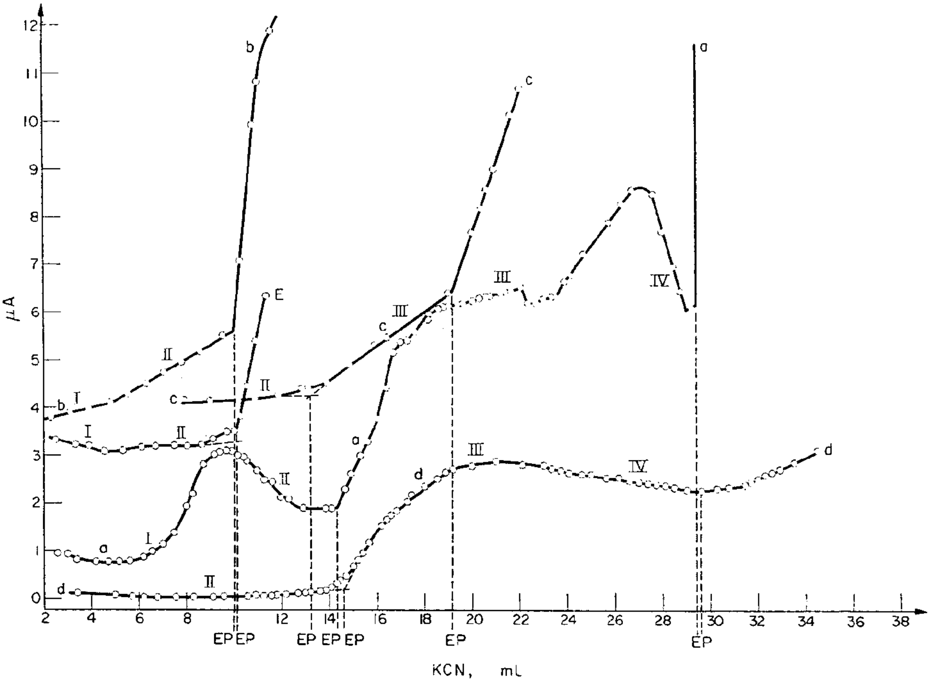


FIG. 5.—Curves for the amperometric titration of Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} ions with potassium cyanide solution in the presence of hydroquinone as indicator: (a) 0·0727*N* Cu^{2+}, (b) 0·0998*N* Zn^{2+}, (c) 0·1291*N* Cd^{2+}, (E) 0·0960*N* Ni^{2+}, (D) 0·0072*N* Cu^{2+}.

If the difference in solubilities of precipitates are sufficiently great, then several cations can be titrated (Fig. 2), the extreme case being that of an acid and a cation (Fig. 3). Complexometric titrations with potassium cyanide may be followed by measuring the hydroxyl concentration from the hydrolysis of unbound cyanide ions. Fig. 4 shows the formation of a stable $Ni(CN)_4^{2-}$ complex and that the last cyanide group in $Cd(CN)_4^{2-}$ is more loosely bound.

The results of determinations and their precision and accuracy at various concentrations are given in Tables I and II. The standard deviation was calculated statistically, applying the fiducial limits according to R.A. Fisher at the level of probability 0·05.

Résumé—On effectue des dosages ampérométriques à potentiel nul en présence d'hydroquinone et de *p*-aminophénol comme indicateurs électrométriques. On a utilisé des solutions de carbonate de sodium, arsénite de sodium, tétraborate de sodium et cyanure de potassium dans les réactions de neutralisation, précipitation et formation de complexes pour le dosage individuel des cations, le dosage simultané de plusieurs cations dans un seul échantillon, et le dosage d'acide et de cations présents simultanément. Lorsqu'on a atteint le point équivalent, des ions hydroxyle apparaissent dans la solution par suite de l'hydrolyse du sel et il se produit unaccroissement considérable du voltage du courant. L'indicateur en solution alcaline provoque la dépolarisation de l'éctrode.

Zusammenfassung—Es werden amperometrische Titrationen bei Nullpotential in Gegenwart von Hydrochinon und *p*-Aminophenol als elektrometrischen Indikatoren ausgeführt. Lösungen von Natriumcarbonat, Natriumarsenit, Natriumtetraborat und Kaliumcyanid wurden als Reagentien bei Neutralisations-, Fällungs- und Komplexbildungsreaktionen zur Bestimmung einzelner Kationen, zur gleichzeitigen Bestimmung mehrerer Kationen in einer Probe und zur gleichzeitigen Bestimmung von Säure und Kationen eingesetzt. Nach Erreichen des Äquivalenzpunktes erscheinen in der Lösung infolge Hydrolyse der Salze Hydroxylionen und die elektrische Leistung steigt beträchtlich an. Der Indikator bewirkt in alkalischer Lösung Depolarisation der Elektrode.

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DETERMINATION OF POTASSIUM BY TITRIMETRY

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Summary—Epp's method is modified by the addition of solid calcium hydroxide to the sample solution. This simplified the procedure, increased the rapidity and lessened the sources of error. With samples containing various ions except ammonium ion, potassium (conc. of KCl 0·25 to 1·8 × $10^{-2}M$) was determined within 0·4% of error, by means of corrections for the existence of a large quantity of sodium chloride and for the solubility of potassium tetraphenylborate.

SCHALL[1] developed a titrimetric procedure for the determination of potassium based on the precipitation of potassium with an excess of sodium tetraphenylborate, followed by filtration and the back-titration of the filtrate with cetyltrimethylammonium bromide using Bromophenol Blue as an indicator. Epps and Burden[2] recommended Clayton Yellow instead of Bromophenol Blue as the indicator.

Sodium tetraphenylborate is stable in an alkaline medium, but not in an acidic medium, so the precipitate should be formed in an alkaline medium; however, the precipitate is so fine that it is difficult to filter. The procedure is improved by adding solid calcium hydroxide, which makes the solution alkaline without changing the volume and coarsens the precipitate so that it can be easily filtered. Further, the alkalinity allows Clayton Yellow to be used. Potassium in a neutral or slightly acidic solution and in sea water has been successfully determined by this procedure.

EXPERIMENTAL

Reagents

Sodium tetraphenylborate solution. Dissolve 3·4 g of sodium tetraphenylborate (Kalibor, Dojindo & Co. Ltd.) in 50 ml of 0·10*N* sodium hydroxide solution and dilute to 500 ml with water to give a 2 × $10^{-2}M$ solution of sodium tetraphenylborate in $10^{-2}M$ sodium hydroxide. The solution is stable for 3 days.

Quaternary ammonium chloride solution. Dissolve 1·8 g of reagent grade Zeph-Cl (Zephiramine = tetradecyl dimethylbenzylammonium chloride, Dojindo & Co. Ltd.) and make up to 500 ml with water to give a 1 × $10^{-2}M$ solution. The reagent adheres to the surfaces of a burette and other glassware, which should be cleaned with fuming nitric acid.

Standard potassium chloride solution. Dissolve 0·7456 g of well-dried reagent-grade potassium chloride and dilute to 1 l. with water to give a 1·000 × $10^{-2}M$ solution.

Clayton Yellow solution. A 0·02% aqueous solution is used.

Standardisation of reagents

Sodium tetraphenylborate and Zeph-Cl solutions were standardised relative to the potassium solution. The sodium tetraphenylborate solution was standardised before use each time an accurate determination was made because it decomposes slowly.

Recommended procedure

Place 5 ml of sample solution containing between 1·25 × 10^{-5} and 9·0 × 10^{-5} mole of potassium into a 10-ml test-tube with a stopper, add sufficient solid calcium hydroxide to ensure that a few mg remain undissolved. Add 5 ml of sodium tetraphenylborate solution, shake and allow to stand for 5 min, then filter. Transfer 5 ml of the filtrate and 2 drops of the indicator solution to a 50-ml beaker and immediately titrate the solution slowly with the Zeph-Cl solution. If the temperature of the solution is low, warm the solution about 30° in order to obtain a sharp colour change of the indicator. It helps to exclude carbon dioxide from the solutions.

TABLE I.—DETERMINATION OF POTASSIUM IN AN ACIDIC MEDIUM*

Taken, *mg*	Found, *mg*	Recovery, %	Error, %
3·666	3·650	99·6	0·4
3·212	3·214	100·0	0·0
1·990	1·990	100·0	0·0
0·9951	0·9914	99·7	0·3
0·7961	0·7957	100·0	0·0
0·3981	0·4059	102·0	2·0

* 0·01*M* HCl

A positive error results from the solubility of potassium tetraphenylborate, which under the conditions of the procedure is $2{\cdot}8 \times 10^{-5}$ mole/l.[4-6] This salt is also titrated by the Zeph-Cl. (The precipitate must, of course, be removed from the solution.) If the calculation is carried out on a molar basis, 0·014 should be subtracted from the volume of Zeph-Cl required. Further corrections may be needed if a large quantity of sodium chloride is present (Table IV).

Typical results are shown in Table I.

RESULTS AND DISCUSSION

Effect of calcium hydroxide

Solutions which contain no other ions but potassium can be titrated directly with the Zeph-Cl solution, because the sodium hydroxide in the sodium tetraphenylborate solutions gives the filtrate a sufficiently high alkalinity. In such a case, the addition of calcium hydroxide is unneccessary but the precipitate of potassium tetraphenylborate is so fine that perfect separation can be attained only by the combined methods of centrifugation and filtration; the addition of calcium hydroxide makes centrifuging unnecessary. The reagent has the same coagulative ability as aluminium nitrate and chromium(III) chloride.

TABLE II.—DETERMINATION OF POTASSIUM BY CENTRIFUGATION AND CALCIUM HYDROXIDE METHODS

		Centrifugation		$Ca(OH)_2$	
Taken, *mg*	Conc., $M \times 10^{-2}$	Found, *mg*	Recovery, %	Found, *mg*	Recovery, %
1·955	1·000	1·953	99·9	1·955	100·0
0·9775	0·5000	0·9767	99·9	0·9785	100·1
0·4888	0·2500	0·4884	99·9	0·4903	100·3
0·3910	0·2000	0·3926	100·4	0·3937	100·7

The results obtained by centrifugation and the addition of calcium hydroxide are shown in Table II.

Basicity of the solution

The working range of pH for the end-point of Clayton Yellow was determined experimentally. When the solution was acidic or slightly basic, the colour change at the end-point was not observed. To obtain an exact end-point the pH of the solution

TABLE III.—EFFECT OF pH

a	pH	4·7	9·2	10·2	10·8	11·2	11·7	12·0
	Zeph-Cl, *ml*	no change	no change	4·745	4·720	4·705	4·705	4·707
b	$Ca(OH)_2$ added, *mg*		0	10		20	30	
	pH			11·4		~11·8		
	Zeph-Cl, *ml*		4·350	4·344		4·346	4·350	

must be kept above 11·2 (see Table III). Table III shows that this is readily achieved by adding calcium hydroxide.

Effect of acidity

It is well known that in an acidic medium the precipitate of potassium tetraphenylborate is coarse and can easily be filtered, whereas TPB ion is unstable and decomposes into benzene, phenylboric acid and diphenylboric acid.[3] The rate of decomposition was investigated (Fig. 1). To the acidified potassium solution ($0{\cdot}25 \sim 1{\cdot}8 \times 10^{-2}$ mole in 0·05*M* hydrochloric acid) an excess of sodium tetraphenylborate was added and the solution was allowed to stand for a given time. The solution was then filtered, calcium hydroxide was added and the solution was titrated with Zeph-Cl immediately. It is clear that 5% of TPB ion decomposes in 40 min and what is worse, the sharpness of the colour change of the indicator is lost with the progress of decomposition. For these reasons, it is desirable to keep the solution containing sodium tetraphenylbotate alkaline all the time.

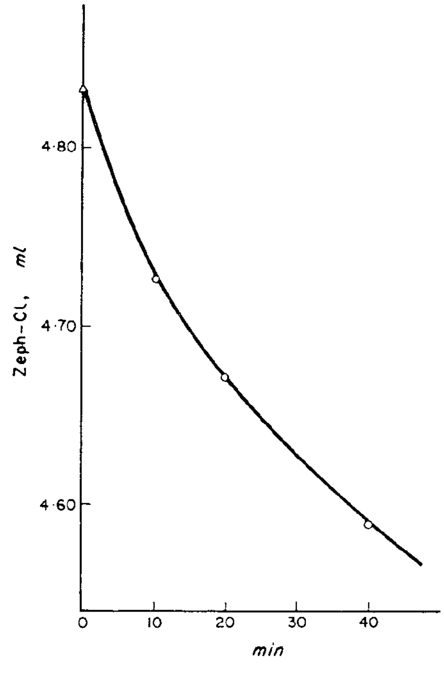

FIG. 1.—Decomposition of TPB ion on standing
(Δ = calculated value)

Effect of diverse ions

The effect of the ions which are present in sea water was examined. Among these ions, magnesium ion reduces the alkalinity of the solution by reacting with calcium hydroxide to form magnesium hydroxide, so a larger quantity of calcium hydroxide was used when the effect of magnesium ion was investigated. If this adjustment to the procedure is made, no significant effect is observed, provided that the concentration of these ions is not too high (Table IV). A large quantity of sodium chloride and sodium sulphate has a slight effect. From the fact that the effect of sodium sulphate (0·45*M*) is about twice that of sodium chloride (0·46*M*), it may be concluded that the interference is due to the sodium ion. Fluoride and perchlorate ions have an appreciable effect, but sea water does not contain these ions in concentrations which cause serious interference.

TABLE IV.—EFFECT OF DIVERSE IONS

Salt	Recovery of potassium, %	Salt	Recovery of potassium, %
$NaHCO_3$	100·1	H_3BO_3	100·0
NaBr	100·4		
NaF	99·1	$Sr(NO_3)_2$	100·1
NaI	99·5		
$NaNO_3$	100·2	$CaSO_4$	99·5
$NaC_2H_3O_2$	99·9		
$NaClO_4$	99·0	$MgSO_4$	100·5
Na_2SO_4	100·1		
Na_2SO_4 (0·45*M*)	102·1		
NaCl (0·46*M*)	101·4		

Conc. of salt: $1{\cdot}0 \times 10M^{-2}$
Conc. of KCl: $1{\cdot}000 \times 10M^{-2}$

Sea water

Sea water contains a large quantity of magnesium ion, so that a preliminary experiment is necessary to find out how much calcium hydroxide must be added. Fig. 2 shows that 30 mg of it in 5 ml of sea water is suitable.

Artificial sea water was prepared according to the method of Fleming.[7] The recovery of potassium from this solution was 101·5%. This result is satisfactory,

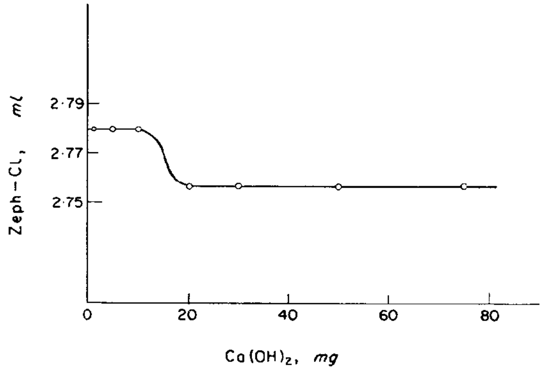

FIG. 2.—Effect of the amount of $Ca(OH)_2$ on titration of sea water.

provided that the effect of the sodium ion (0·46*M* NaCl) is taken into consideration (Table IV). Because the composition of sea water does not vary widely and moreover the effect of sodium ion is relatively small, it may be estimated that the effect of sodium ion on the determination of potassium is equal for any sea water. Consequently, potassium in sea water may accurately be determined if a constant correction for the sodium interference is made. The recovery of potassium from sea water was investigated and the results are shown in Table V.

TABLE V.—RECOVERY OF ADDED POTASSIUM FROM SEA WATER

Sea water, *ml*	Potassium added, *mg*	Present, *mg*	Found corr., *mg*	Difference, *mg*
5	—	1·845	—	—
5	0·131	1·976	1·974	0·002
5	0·262	2·107	2·100	0·007
5	0·393	2·238	2·225	0·013
5	0·524	2·369	2·352	0·017

Errors

Because an error in the final titre, X (*i.e.*, ΔX) is assumed to be inevitable it is useful to investigate the behaviour of the relative error in potassium concentration, $\Delta C/C$, for some expected ΔX.

Fig. 3 shows that as the concentration of potassium decreases to nearly zero, the error increases steeply. Therefore, under a given experimental condition, an accurately determinable lower limit of the concentration exists. On the other hand, in a concentrated solution ($C \simeq 2 \times 10^{-2}M$), the relative error is small, but there is new trouble, *i.e.*, the incomplete precipitation of potassium tetraphenylborate. This trouble can, however, easily be avoided by diluting previously the original potassium solution. In this method, a potassium concentration ranging from 0·25 to $1{\cdot}8 \times 10^{-2}M$ was determined within an error of 0·4%.

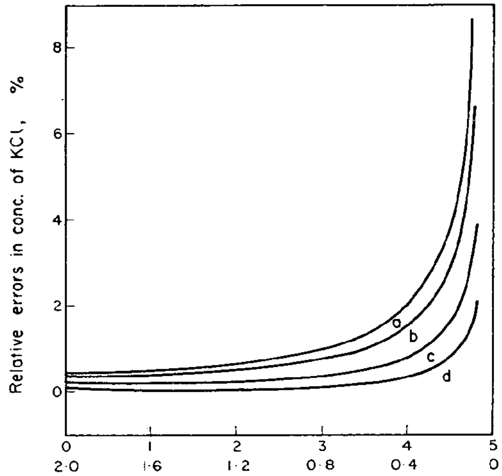

FIG. 3.—Effect of experimental error

(abscissa:— upper: Zeph-Cl, ml; lower: KCl, $M \times 10^{-2}$)
values of ΔX a 0·020 ml. c 0·008 ml.
b 0·015 d 0·004

Acknowledgement—The author wishes to express his gratitude to Professor Kyoji Tôei for his guidance throughout the course of this work.

Zusammenfassung—Die Methode von Epp wurde durch Zugabe von festem Calciumhydroxyd zur Probelösung modifiziert. Dies vereinfacht und beschleunigt das Verfahren und vermindert die Fehlerquellen. Mit Proben, die verschiedene Ionen außer Ammonium enthielten, ließ sich Kalium (KCl-Konzentration 0,25–1,8 . 10^{-2}) mit 0,4% Fehler bestimmen, wobei Korrekturen für die Anwesenheit großer Mengen Natriumchlorid sowie für die Löslichkeit von Kaliumtetraphenyloborat angebracht wurden.

Résumé—La méthode d'Epp a été modifiée par addition d'hydroxyde de calcium solide à la prise d'essai. Ceci simplifie la technique, accroît la rapidité et réduit les sources d'erreur. Dans les prises d'essai contenant divers ions à l'exception de l'ion ammonium, on a dosé le potassium (conc. en KCl de 0,25 à 1,8 × $10^{-2}M$) à 0,4% près, en introduisant des corrections tenant compte de la présence d'une forte quantité de chlorure de sodium et de la solubilité du tétraphénylborate de potassium.

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SPECTROPHOTOMETRIC DETERMINATION OF CERIUM WITH SULPHANILIC ACID

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Summary—In the presence of other rare earths, cerium(IV) can be determined spectrophotometrically by its reaction with sulphanilic acid with which it produces a red colour. Solutions containing 28-210 ppm of cerium absorb at 495 mμ according to Beer's law. Other rare earths, except neodymium, and many common ions do not interfere. Strong oxidising agents and neodymium in greater than fifty times the concentration of cerium interfere with this method. The precision depends on the control of pH and time. Cerium alloys have been analysed by this method and the results are compared with those obtained by another spectrophotometric method.

INTRODUCTION

A NUMBER of methods have been proposed for the determination of cerium. In a gravimetric method, Vickery[24] suggested reprecipitation and ignition of cerium to CeO_2. A few well-known methods have employed the reaction

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

as their basis. One of these methods used a potentiometric end-point to obtain a high accuracy.[6,26]

Lingane and Kennedy[12] described an excellent coulometric method in which electrogenerated titanium(III) was used to reduce cerium(IV) to cerium(III); however, electrogenerated silver(II) gave ill-defined potential inflections with slow reaction rates near the end-point.[5] Hexacyanoferrate(III) has been used to titrate cerium(III) in 4*M* potassium carbonate solution to amperometric[11] and to potentiometric[7] end-points. EDTA titration[14] has also been proposed, but only as a group titrant for the entire rare earth family.

Colichman[4] studied the non-aqueous polarography of cerium and other inorganic materials using molten ammonium formate. A fluorometric method[9] for cerium and other rare earths has also been suggested.

Spectrophotometric methods have utilised the yellow colour of cerium(IV) for its determination at 350 mμ[17] and 320 mμ.[13] However, when cerium was oxidised with persulphate, the excess persulphate interfered with that method at the latter wavelength. In another method,[23] cerium was determined by measuring the absorbance of a cerium(III)-potassium carbonate complex at 304 mμ. A better method appeared to be that of Gordon and Feibush,[8] in which cerium was determined by adding an excess of iron(II) to cerium(IV), then developing a colour with *o*-phenanthroline.

Although cerium, like the other members of the rare earth family, exists in the tervalent state, it is the only rare earth which can exist in aqueous solution in the

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quadrivalent state. In an acidic solution, cerium is a strong oxidising agent, a characteristic which differentiates it from the other members of the rare earth family. Sarma[18] used certain reducing agents to identify cerium(IV) in the presence of other rare earths. In his studies, sulphanilic acid, originally used by Montignie,[15] was found to be fairly specific for cerium. It gave a red colouration with more than 6 ppm of cerium. Because the reaction between cerium and sulphanilic acid appeared to be free from interferences of other rare eaths, the present authors studied this reaction as a spectrophotometric method for the determination of cerium in the presence of other rare earths.

EXPERIMENTAL

Apparatus

Spectrophotometers. Beckman Models DB and DU.
Recorder. Beckman Model 93500.
pH Meter. Beckman Expanded Scale Model 76.

Reagents

Sulphanilic acid solution. Ten g of reagent grade *p*-aminobenzenesulphonic acid (Matheson, Coleman and Bell, East Rutherford, New Jersey, U.S.A.) were dissolved in water and diluted to 1 litre.

Standard 0·1*M cerium(IV) solution.* Prepared from analytical reagent grade ammonium hexanitratocerate(IV) (G. F. Smith Chemical Company, Columbus, Ohio, U.S.A.) using the method of Smith and Fly.[19]

Rare Earths. Interferences of other rare earths were studied using 99·9% pure Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3 and Y_2O_3 (American Potash and Chemical Corporation, West Chicago, Illinois, U.S.A.). The oxides were dissolved in 6*M* sulphuric acid, then diluted to 0·1*M* with water.

TTA. Eleven g of 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Eastman Organic Chemicals, Rochester, New York, U.S.A.) were dissolved and diluted to 100 ml with xylene.

Oxalic acid. 0·05*M* and saturated solutions.

2% *Silver nitrate solution*

20% *Ammonium persulphate solution*

All other reagents were of reagent grade.

Procedure

Preparation of calibration curve. Five aliquots, 0·2, 0·5, 1·0, 1·5 and 2·0 ml, of the standard cerium(IV) solution, containing 2·8, 7·0, 14·0, 21·0 and 28·0 mg of cerium, respectively, were pipetted into separate 100-ml volumetric flasks. When the aliquot was less than 2 ml, (2 − x) ml of 1*M* sulphuric acid were added, where x was the number of ml of standard cerium(IV) solution taken. Twenty ml of sulphanilic acid solution were added to each flask and the mixtures were diluted to volume with water. Using water as a reference and a wavelength of 495 mμ, the percentage transmittance was measured at exactly 3 min after mixing. The pH of the solutions were then measured.

Preparation of samples. The sample size was so selected that when it was dissolved to a total volume of 100 ml, each aliquot of 10 ml, taken for analysis, gave 10 mg of cerium. The alloys were weighed to the nearest mg, transferred to a 400-ml beaker and 75 ml of water were added. Concentrated hydrochloric acid was added in 5-ml portions until the sample was completely dissolved. The solution was heated to boiling, cooled and filtered through Whatman No. 1 paper. Any residue was ignored. The filtrate was transferred to a 100-ml volumetric flask and diluted to volume.

A 10-ml aliquot was pipetted into a 50-ml glass centrifuge tube and 5 ml of saturated oxalic acid solution were added. The sample was digested in a water bath for 3 hr and allowed to stand overnight.

The supernatant liquid was removed by centrifugation and decantation. The oxalate precipitate was washed first with 5 ml of 0·05*M* oxalic acid solution and then with 5 ml of water by centrifugation and decantation. Because the control of pH was critical in this method, 2 ml of 1*M* sulphuric acid were added to the oxalate precipitate with a pipette. This was followed by 5 ml of 20% ammonium persulphate solution and 2 drops of 2% silver nitrate solution. The mixture was heated in boiling water until the precipitate had dissolved and the cerium had been oxidised to the quadrivalent state. Heating was continued for an additional 15 min to destroy any excess persulphate.

The solution was cooled to room temperature and transferred to a 100-ml volumetric flask containing 20 ml of sulphanilic acid solution. After diluting to volume with water, the percentage transmittance was measured at exactly 3 min after mixing, using a wavelength of 495 mμ and water as a reference.

After measurement of the percentage transmittance, the pH of the solution was measured. Because the colour formation was pH dependent, the percentage transmittance had to be corrected whenever the pH of the solution differed from that of the standard solutions used in preparation of the calibration curve. This correction was introduced using the equation $\%T_{std} = \%T_{sample} - 0{\cdot}18(\Delta pH)$, where ΔpH was the difference between the two pH expressed in multiples of 0·01 pH unit. After calculating the absorbance of the solution, the amount of cerium in the sample was determined using this absorbance and the calibration curve obtained previously.

With samples containing no interfering agents or coloured ions, the sulphanilic acid method should be applicable to the determination of cerium without the oxalate precipitation.

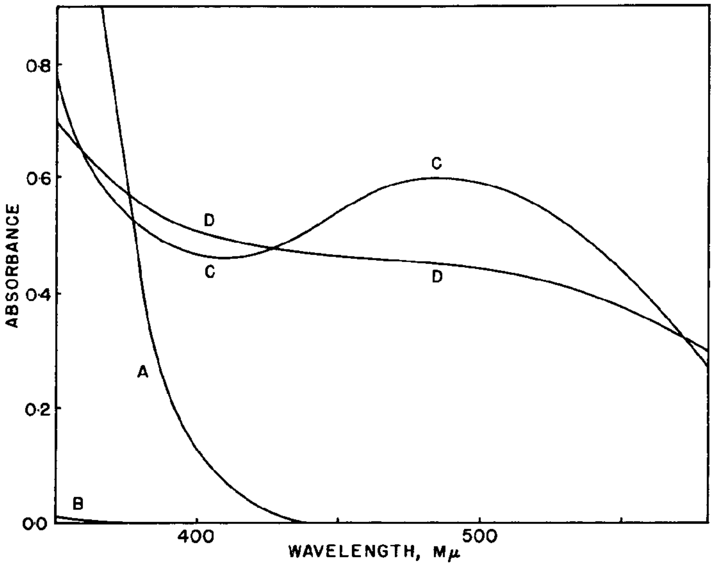

FIG. 1.—Absorption spectra of cerium(IV), sulphanilic acid and the reaction products of cerium(IV) with sulphanilic acid (reference water):

(A) 1 ml of 0·1*M* cerium(IV) in 1*M* sulphuric acid diluted to 100 ml.
(B) 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml.
(C) 1 ml of 0·1*M* cerium(IV) in 1*M* sulphuric acid and 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml; 3 min after mixing
(D) 1 ml of 0·1*M* cerium(IV) in 1*M* sulphuric acid and 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml; 30 min after mixing.

RESULTS AND DISCUSSION

Cerium (IV) reacted with sulphanilic acid producing a red colour. The products gave a broad absorption maximum near 500 mμ (Fig. 1). Because the interference from other rare earths was at a minimum, the wavelength of 495 mμ was chosen for measurements. At this wavelength, maximum absorption occurred when 3 or more mole of sulphanilic acid were added to 1 mole of cerium (Fig. 2). An excess of sulphanilic acid did not adversely affect the determination.

Attempts to isolate and identify the products by paper chromatography or by extraction into common organic solvents were unsuccessful. Treatment of the sulphanilic acid solution with other strong oxidising agents under the same experimental conditions produced red solutions, all of which absorbed between 350 and 600 mμ (Fig. 3). Therefore, strong oxidants interfered with this method (Figs. 1 and 3).

To determine the optimum concentration range for this method of determination,

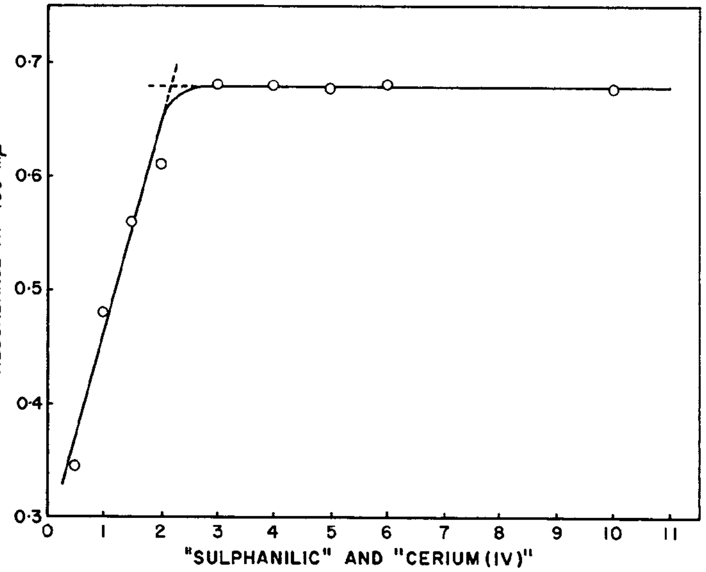

FIG. 2.—Determination of the optimal ratio of sulphanilic acid to cerium(IV) for maximal absorption (reference water).

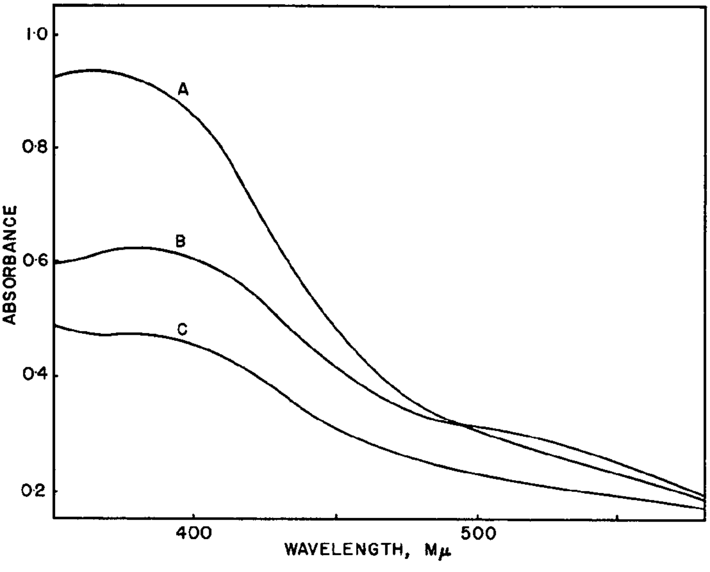

FIG. 3.—Absorption spectra of the reaction products of sulphanilic acid with some strong oxidants (reference water):

(A) 1 ml of 0·1*M* potassium bromate and 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml.

(B) 1 ml of 0·1*M* potassium metaperiodate and 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml.

(C) 1 ml of 0·1*M* potassium persulphate and 20 ml of 0·052*M* sulphanilic acid diluted to 100 ml.

percentage absorptances (100-%T) were plotted against the logarithms of the cerium concentration (Fig. 4). The region of greatest slope of this curve gave an optimum concentration range from 28 to 210 ppm of cerium.[2] Within this range, absorption followed Beer's law.

Because the molecular species was unknown, the molar absorptivity of the absorbing species could not be calculated. However, the sensitivity of the method was determined by calculating the molar absorptivity of cerium. Within the concentration range where Beer's law was followed, the molar absorptivity with respect to cerium was 6,310.

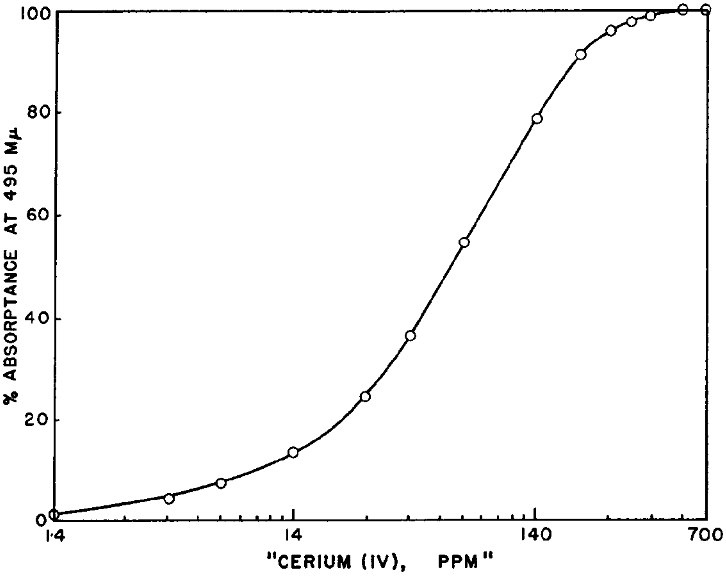

FIG. 4.—Optimal concentration range of cerium(IV) for its determination by the sulphanilic acid method (reference water).

Effect of pH

The intensity of the colour developed was dependent on the pH. Below pH 1, the colour development was incomplete. Although the solutions complied with Beer's law at these pH, the method lacked sensitivity. The colour intensity increased at higher pH. However, above pH 2·3, cerium began to precipitate. To increase the sensitivity of the method, without precipitating cerium, it was desirable to work slightly below a pH of 2·3. Because no true buffer system operated in that pH region, the pH was controlled by diluting each sample to 2 ml with 1*M* sulphuric acid, then adding 20·0 ml of sulphanilic acid solution in each case. Solutions treated in this manner had a pH of approximately 1·7 and produced a satisfactory colour without precipitating cerium.

The percentage transmittance of these coloured solutions decreased linearly with pH. Within the optimum concentration range various concentrations of cerium gave straight lines whose slopes were nearly equal. Therefore, within this concentration range, the observed percentage transmittance at a certain pH could be related to the percentage transmittance at another pH by the equation $\%T_A = \%T_B - 0{\cdot}18\ (\Delta pH)$, where ΔpH is the difference between the two pH expressed in multiples of 0·01 pH unit and —0·18 was the slope of the percentage transmittance *vs.* pH plot. This equation was investigated within pH 0·5 to 1·80.

Effect of temperature

The percentage transmittance of solutions containing 140 ppm of cerium increased linearly with temperature over a range of 20 to 40° and had a temperature coefficient of 0·66 percentage transmittance/°C. This was equivalent to an error of 2·8% of cerium/degree change in temperature.

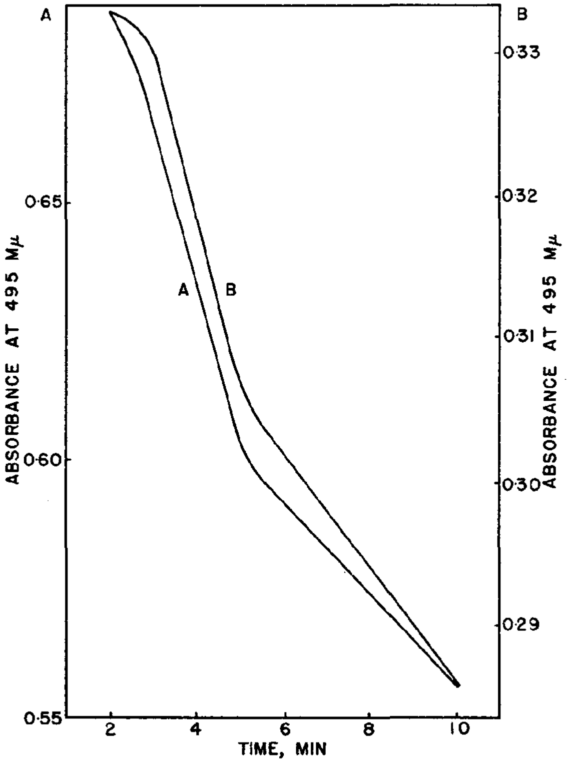

FIG. 5.—Stability of the reaction products of cerium(IV) and sulphanilic acid within the optimal concentration range (reference water):

(A) 1 ml of 0·1M cerium(IV) in 1M sulphuric acid, 1 ml of 1M sulphuric acid and 20 ml of 0·052M sulphanilic acid diluted to 100 ml.

(B) 0·5 ml of 0·1M cerium(IV) in 1M sulphuric acid, 1·5 ml of 1M sulphuric acid and 20 ml of 0·052M sulphanilic acid diluted to 100 ml.

Colour stability

The stability of the colour was studied at two cerium concentrations (Fig. 5). The red colour, which was most intense just after mixing, began to fade rapidly from bright red to dull red-brown in about 30 min (Fig. 1). The rate of fading increased with increasing cerium concentration. After an apparent induction period of 1–2 min since mixing, there was a marked decrease in the absorbance of the solution up to

5 min. A second mechanism became dominant after this period of time. The rate of fading during the second mechanism was less than that in the first mechanism. Because the absorbing species were unknown, the mechanism of the fading could not be explained.

The instability of the colour is a disadvantage of this method. However, there are spectrophotometric methods which are used in spite of the colour instability, *e.g.*, in the determination of chlorine by *o*-tolidine[3] the colour comparison is made 5 min after developing the colour. Another well-known example of colour instability is the determination of iron by the thiocyanate method.[16,27]

In the determination of cerium by sulphanilic acid the colour instability reduces the sensitivity. However, this method can still be used to determine 28–210 ppm of cerium (Fig. 4) in aqueous solution with good precision and accuracy (Table I). If the percentage transmittances are measured exactly at the end of 3 min after developing the colour and compared with those of standard cerium solutions, the error in the determination of cerium is less than 1 % (Table I). On the other hand, if the percentage transmittances are measured at any moment within a period of 7–10 min after developing the colour, the maximum error that can occur is about 5 % (Fig. 5). An error of 5 % in spectrophotometric methods of determination is not uncommon.

TABLE I.—ANALYSIS OF COMPOSITE SAMPLES WITH KNOWN AMOUNTS OF CERIUM AND OTHER METALS.

Sample	Cerium, μg		
	Taken	Found*	Error, %
A†	56·1	55·8 ± 0·38	0·95
B‡	56·1	55·9 ± 0·25	0·62
C¶	56·1	55·8 ± 0·38	0·95

* Average of three determinations.

† Simulated misch metal: 50% of Ce, 25% of La, 15% of Nd, 5% of Fe and 5% mixture of Pr, Eu, Gd and Er.

‡ Simulated flint: 70% of sample A and 30% of Fe.

¶ Simulated aircraft alloy: 6% of sample A and 94% of Mg.

Effect of interfering ions

The most important alloys of cerium, such as misch metal, flint and magnesium-base rare earth alloys, contain the other rare earths, iron and magnesium. In addition, they may also contain lesser amounts of aluminium, calcium, silicon or zinc.[10] In this investigation, the interference studies were limited only to the most probable constituents of these alloys.

Absorption studies with rare earth sulphate solutions agreed with those of Stewart and Kato;[22] only neodymium(III) absorbed at 495 mμ. However, the absorbance was so small that neodymium could be present in concentrations up to fifty times the concentration of cerium without causing an interference. Neodymium should not interfere with this method, because the concentration of cerium in the commonly encountered samples is much higher than that of neodymium. Also, many metals like aluminium, calcium, magnesium and zinc do not interfere with this method. Elements which give rise to coloured ions, such as manganese, chromium, copper, cobalt and nickel, must, however, be removed. Iron need not be removed if its amount is about the same as that of cerium. If the amount of iron is five times that of cerium, the sulphanilic acid method will give 10% too high cerium, unless the iron in the sample solution is reduced in concentration. In most cerium alloys, the iron content is about equal to or less than that of cerium.

Strong oxidants, like bismuthate, bromate, dichromate, periodate, permanganate, persulphate and lead dioxide, oxidise sulphanilic acid and thus interfere with this method of cerium determination (Fig. 3). Iron(III), tin(IV) and the other rare earths do not develop any colour with sulphanilic acid.

Removal of interfering ions

Smith and Moore[21] used 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) in xylene to extract selectively milligram amounts of cerium from fission products. Cerium formed a xylene-soluble complex with TTA, after being oxidised to the quadrivalent state by a dichromate-bromate solution. The cerium was stripped back into the aqueous phase with nitric acid.

Using their technique, a double extraction was found to yield an approximately quantitative separation of cerium from a sample of known cerium content. Cerium could be successfully extracted from a 1:1 mixture of chromium(III) and cerium(III); a 1:1 mixture of manganese(II) and cerium(III) could not, however, be separated because manganese was oxidised to permanganate, which in turn reacted with the extractant.

Controlled potential electrolysis with platinum electrodes was studied for removing the manganese interference. In a sulphuric acid solution at pH 2, manganese was precipitated as manganese dioxide at potentials more negative than —0·28 V *vs.* S.C.E. At potentials more negative than approximately —1 V *vs.* S.C.E. some permanganate was also formed. At lower pH both permanganate and manganese dioxide were formed at potentials more negative than —0·32 V *vs.* S.C.E.

Smith, Frank and Kott[20] quantitatively oxidised cerium(III) in strongly acidic media using a single compartment electrolysis cell. In the present investigation, cerium(III) in sulphuric acid solutions below pH 1 was oxidised at potentials more negative than —0·25 V *vs.* S.C.E. Between pH 1 and 2, oxidation was incomplete, while above pH 2, no oxidation took place. Because the difference between their oxidation potentials was small, a separation of cerium and manganese by controlled potential electrolysis did not appear feasible under these conditions.

Oxalate precipitation[25] has been generally accepted as one of the most effective means of separating the rare earths from other constituents in solution. Nearly all methods of rare earth analysis begin with this procedure. The oxalate precipitation appears to be a suitable adjunct to cerium determination by the sulphanilic acid method, because other rare earths do not interfere with this method. However, the oxalate separation required a long digestion period for complete separation. Prolonged digestion at elevated temperatures and the addition of alcohol[1] appeared to have little effect in reducing the digestion period.

Cerium oxidation

When hydrochloric or sulphuric acid was used to dissolve the samples, cerium existed in the tervalent state in solution. Furthermore, the oxalate ion used for precipitation would reduce cerium(IV) and cause precipitation as cerium(III) oxalate. Simultaneous dissolution of the oxalate precipitate and oxidation of cerium(III) were accomplished with ammonium persulphate using a modification of the Willard and Young[26] method.

Analytical results

Analysed samples of misch metal and flint were not available. Therefore, solutions containing known amounts of cerium, simulating the composition of these materials, were prepared and analysed by the sulphanilic acid method. The average of three determinations and the standard deviation of the mean are shown in Table I.

Magnesium-base cerium alloys were obtained from The Dow Chemical Company. These alloys were previously analysed by Dow using the following procedure:

> The samples were dissolved in hydrochloric acid and the rare earths were precipitated initially as sebacates and then as oxalates. The oxalates were ignited and weighed as oxides. The oxides were treated twice with perchloric acid and dried. Finally, the residue was dissolved in perchloric acid and cerium was determined by ultraviolet photometry at 245 mμ.

Three alloys were analysed by the sulphanilic acid method. The first of these alloys contained 0·70% of neodymium, 1·85% of cerium, 0·23% of praseodymium, 0·82% of lanthanum and 0·52% of zirconium by Dow's analysis. Based on three determinations, 1·88 ± 0·008% of cerium was found by the sulphanilic acid method. In the other two alloys, this method gave 0·054 and 0·063% of cerium. According to Dow, the second alloy contained 2·43% of neodymium, 0·33% of praseodymium, 0·06% of cerium, 0·07% of lanthanum and 0·46% of zirconium, and the third alloy contained 3·49% of neodymium, 0·47% of praseodymium, 0·07% of cerium, 0·09% of lanthanum and 0·56% of zirconium.

Acknowledgement—The authors thank the Dow Chemical Company, Midland, Michigan, U.S.A., for supplying the analysed alloys.

Résumé—On peut doser spectrophotométriquement le cérium(IV) en présence d'autres terres rares au moyen de sa réaction avec l'acide sulfanilique, avec lequel il développe une coloration rouge. La loi de Beer est respectée à 495 mμ pour des solutions contenant 28–210 p.p.m. de cérium. Les autres terres rares, à l'exception du néodyme, et de nombreux ions communs n'interfèrent pas. Les agents oxydants forts et le néodyme à des concentrations supérieures à cinquante fois celle du cérium interfèrent dans cette méthode. La précision dépend du contrôle du pH et du temps. Par cette méthode, on a analysé des alliages de cérium et l'on compare les résultats à ceux obtenus par une autre méthode spectrophotométrique.

Zusammenfassung—Cer(IV) kann in Gegenwart anderer seltener Erden spektralphotometrisch durch seine Rotfärbung mit Sulfanilsäure bestimmt werden. Die Absorption von Lösungen mit 28–210 ppm Cer bei 495 mμ folgt dem Beerschen Gesetz. Andere seltene Erden außer Neodym und viele häufig vorkommende Ionen stören nicht. Starke Oxydationsmittel und Neodym in mehr als fünfzigfachem Überschuß stören bei dieser Methode. Die Genauigkeit hängt von der pH-Einstellung und der Zeit ab. Mit dieser Methode wurden Cerlegierungen analysiert und die Ergebnisse mit einer anderen spektralphotometrischen Arbeitsvorschrift verglichen.

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DIRECT POTENTIOMETRIC TITRATION OF CHLORITE IN PRESENCE OF CHLORATE, CHLORINE DIOXIDE AND CHLORIDE

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Summary—A direct potentiometric titration of chlorite in the presence of chlorate, chlorine dioxide and chloride is described. Chlorite is determined in 0·01–0·0005*M* sodium chlorite at pH 2·0–3·5 using hypochlorite solution. The course of the reaction is followed potentiometrically using saturated calomel and platinum electrodes; the end-point is indicated by a potential jump of about 230 mV. Under these conditions no reaction takes place with chlorate, chlorine dioxide or chloride. Previously, the determination of chlorite in such mixtures was only possible by difference from several oxidimetric titrations.

INTRODUCTION

THE determination of oxy-chlorine compounds is often difficult because of their similar chemical properties and redox potentials. Under similar conditions, almost identical oxidation and reduction reactions are likely to occur. Determinations by redox titrations are possible if the pH conditions are exactly maintained and parallel determinations have to be performed very quickly. Results obtained by difference from several determinations are not very accurate because of the accumulation of errors. A direct method for the determination of chlorite in the presence of other oxy-chlorine compounds is so far unknown.

The oldest method for the determination of chlorite, as described by Bray,[1] is still used with some modifications, classical as well as instrumental.[2–4,6] Some modifications, *e.g.*, using arsenious oxide or *o*-toluidine or corrections in iodometric titration, as proposed by Lenzi and Rapson,[5] are limited to part of the analysis, *viz.* the determination of chlorine dioxide and chlorine in mixtures thereof.

In admixture with chlorate, chlorine and chlorine dioxide the following titrations need to be performed in order to determine chlorite:

(1) Chlorine is titrated with arsenite at pH 7–8.

(2) By iodometric titration of another aliquot of the solution at pH 7 chlorine is reduced to chloride and chlorine dioxide to chlorite.

(3) The solution from (2) is acidified with 2*N* sulphuric acid and again titrated iodometrically. Chlorite originally present in solution and that produced from the chlorine dioxide in the course of titration (2) is now reduced to chloride. The chlorite content is given by the equation:

$$\text{Titre (3)} - 4[\text{Titre (2)} - \text{Titre (1)}].$$

Our work on the decomposition of sodium chlorite with acids and/or chlorine[7] lead us to the following observations:

1. The rate of chlorite decomposition with acids depends on the concentration of hydrogen as well as of chloride ions.
2. The duration of the chlorite decomposition for concentrations ⩽0·1*M* varies between a few minutes and several hours, depending on the nature and concentration of the acid used (Fig. 1).

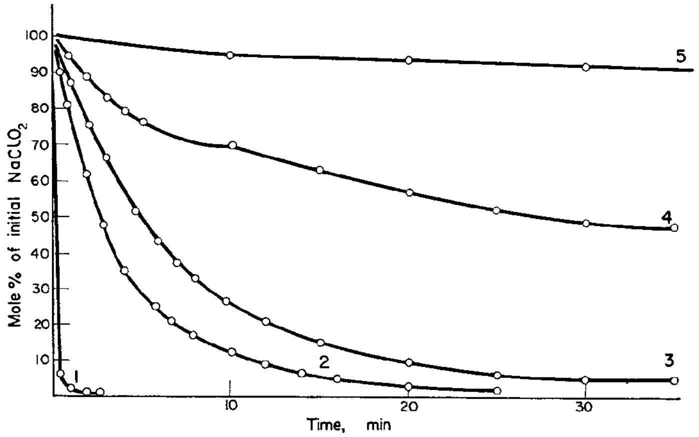

Fig. 1.—Decomposition curves of 0·1112*M* sodium chlorite solution at various concentrations of hydrochloric acid:
1. 5*M*, 2. 2·5*M*, 3. 1·25*M*, 4. 0·3*M*, and 5. 0·1*M*.

3. No chlorine may be detected in the presence of undecomposed chlorite in acidic solution by classical titrimetric or potentiometric determinations.
4. The reaction of chlorine with chlorite in solution at pH 3·5 is instantaneous, with quantitive oxidation of chlorite to chlorine dioxide (Fig. 2).

The above observations made it possible to develop a direct method for the determination of chlorite by potentiometric titration with chlorine (hypochlorite) solution in the presence of chlorine dioxide, chlorate and chloride.

EXPERIMENTAL

Reagents

Sodium chlorite. Sodium chlorite at least 99·7 % was used to prepare a 0·01*M* solution. Standardise by iodometric titration.

0·04*M* *Sodium Hypochlorite.* Prepare by absorbing commercial chlorine in c.p. sodium hydroxide solution to saturation. Remove residual chlorine with air. Standardise by titration against pure chlorite before each set of measurements.

Procedure

Acidify the sample, containing less than 0·01*M* sodium chlorite, with 0·1*M* hydrochloric acid. (In hydrochloric acid concentrations greater than 0·001*M* the hydrolysis of chlorine is completely reversed.) Titrate potentiometrically with sodium hypochlorite solution using saturated calomel and compact platinum electrodes. Mix the solutions with a magnetic stirrer. Stable readings are obtained within a few seconds of the addition of hypochlorite solution. The potentiometric titration curves obtained are well shaped. A potential jump occurs at about 830 mV and attains a value of about 1100 mV. Ensure that the chlorite and hydrochloric acid concentrations do not exceed 0·01*M* nor the pH 3·5.

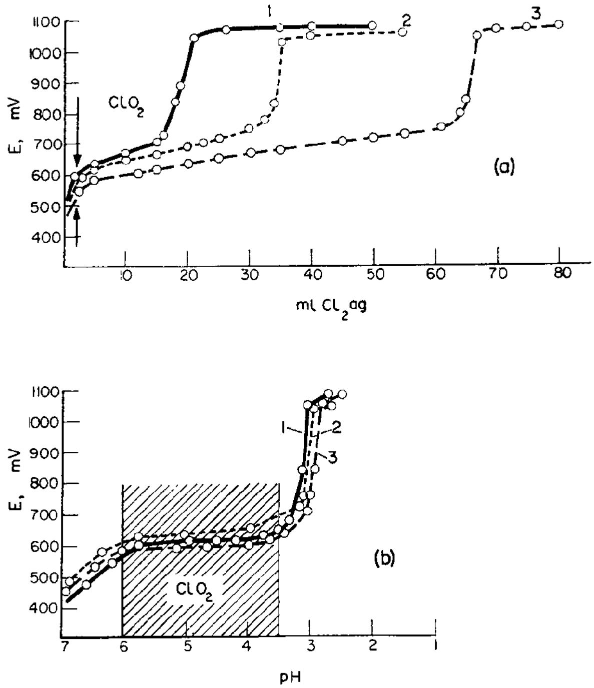

Fig. 2.—Titration curves for different concentrations of sodium chlorite with chlorine solution:

(a) The rise of redox potential accompanying the decomposition of sodium chlorite on addition of chlorine solution.

(b) pH changes corresponding to the redox potential changes during titration with chlorine solution.

Table I.—Iodometric titration of chlorite

Iodometric determination of chlorite alone, *mmole/litre*	Iodometric determination of chlorite* (by difference) in admixture with ClO_3^-, ClO_2 and Cl^-,† *mmole/litre*	Relative deviation of results, %
10·800	11·624	+7·61
8·644	8·232	−4·77
6·484	7·032	+8·45
4·320	5·011	−15·99
2·062	2·174	+5·42
1·624	1·873	+15·53
0·540	0·532	−1·52
0·111	0·094	−15·31

* Same concentrations as in column one of table.

† The solution contains 10 mmole/litre of each of ClO_3^-, ClO_2 and Cl^-.

Table II.—Potentiometric titration of chlorite (same solutions as in Table I with chlorate, *etc.*, present) with hypochlorite at various pH

pH 3·5		2·4		1·9		1·4	
mmole/litre	%	mmole/litre	%	mmole/litre	%	mmole/litre	%
10·842	+0·39	10·800	+0·02	10·784	−0·15	10·793	−0·06
8·701	+0·67	8·631	−0·13	8·624	−0·23	8·640	−0·05
6·513	+0·44	6·479	−0·08	6·451	−0·51	6·441	−0·67
4·385	+1·51	4·322	+0·04	4·339	+0·49	4·328	+0·19
2·078	+0·77	2·072	+0·48	2·055	−0·33	2·070	+0·37
1·620	−0·03	1·625	+0·08	1·615	−0·50	1·620	+0·24
0·553	+2·37	0·537	−0·57	0·550	+1·87	0·541	+0·11
0·112	+0·90	0·114	−0·54	0·112	+0·80	0·111	−0·55

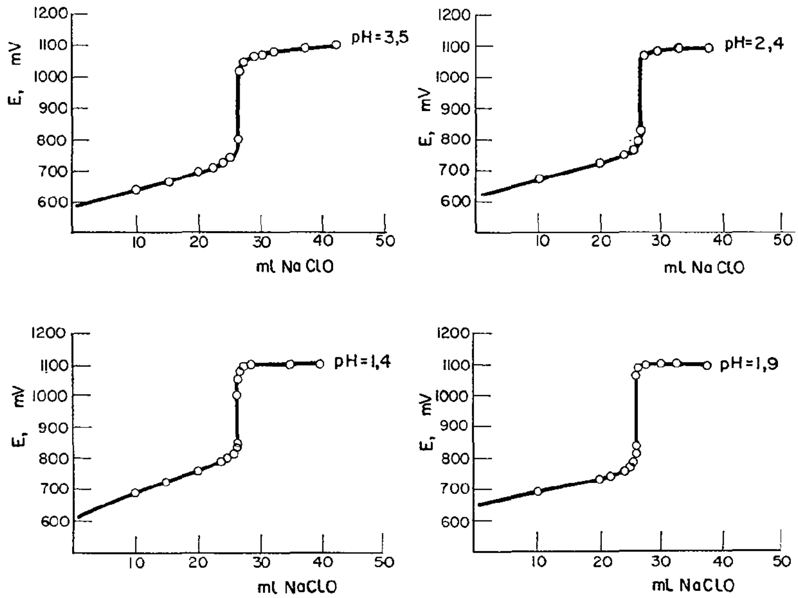

Fig. 3.—Titration curves of chlorite with hypochlorite at various pH.

At low concentrations chlorite decomposition is very slow in comparison with the very fast reaction with chlorine or hypochlorite, and its progress during the time of performing the titration is negligible. Reproducible results, in agreement with those obtained by iodometric titration, are obtained only by titration in a hydrochloric acid medium. If other strong acids[7] such as sulphuric or perchloric are used, then high results are obtained; this is possibly because of the low solubility of chlorine in these acids.

If it is desired to determine chlorite in an initially alkaline solution, when hypochlorite and chlorite can co-exist, hypochlorite should be determined before acidification by a suitable procedure, *e.g.*, by titration with arsenite solution.

RESULTS AND DISCUSSION

By comparison of the results obtained in titrating chlorite solution iodometrically and potentiometrically with hypochlorite solution (Tables I and II) the following reactions may be established for the potentiometric titration:

$$2ClO_2^- + ClO^- + H^+ + Cl^- \rightarrow 2ClO_2 + 2Cl^- + OH^- \qquad (1)$$

or

$$ClO_2^- + 0{\cdot}5Cl_2 \rightarrow ClO_2 + Cl^- \qquad (2)$$

The described method of chlorite determination is simple, rapid and precise and it may, therefore, prove useful in kinetic and technological investigations. Some results of the determination of chlorite during decomposition with hydrochloric acid are given in Figs. 3 and 4. The corresponding titration results are given in Table II.

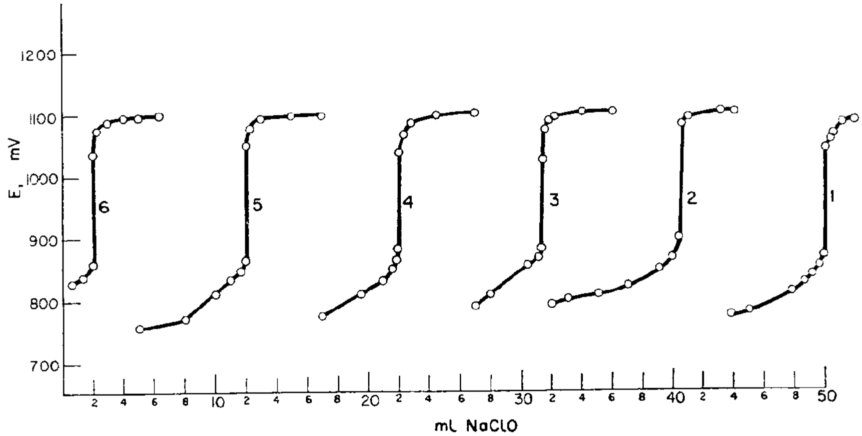

FIG. 4.—Titration curves of chlorite with hypochlorite solution in the presence of $0{\cdot}01M$ chlorine dioxide, chlorate and chloride:

1. Titration of undecomposed chlorite in $0{\cdot}05M$ hydrochloric acid.
2. Titration of chlorite partially decomposed with hydrochloric acid after 10 min.
3. As 2, after 30 min.
4. As 2, after 60 min.
5. As 2, after 105 min.
6. As 2, after 165 min.

Zusammenfassung—Eine direkte potentiometrische Titration von Chlorit in Gegenwart von Chlorat, Chlordioxyd und Chlorid wird beschrieben. In 0,01–0,0005 M Natriumchlorit wird Chlorit bei pH 2,0–3,5 mit Hypochloritlösung bestimmt. Der Reaktionsverlauf wird potentiometrisch mit gesättigten Kalomel—und Platinelektroden verfolgt; den Endpunkt zeigt ein Potentialsprung von etwa 230 mV an. Unter diesen Bedingungen reagieren Chlorat, Chlordioxyd und Chlorid nicht. Bisher ließ sich Chlorit in solchen Mischungen nur aus der Differenz mehrerer oxydimetrischer Titrationen bestimmen.

Résumé—On décrit un dosage potentiométrique direct du chlorite en présence de chlorate, bioxyde de chlore et chlorure. On dose le chlorite dans le chlorite de sodium 0,01–0,0005 M à pH 2,0–3,5 en utilisant une solution d'hypochlorite. La marche de la réaction est suivie potentiométriquement avec des électrodes de calomel saturé et de platine; le point de fin de titrage est indiqué par un saut de potentiel d'environ 230 mV. Dans ces conditions, il n'y a pas de réaction avec le chlorate, le bioxyde de chlore ou le chlorure. Auparavant, le dosage du chlorite dans de tels mélanges n'était possible que par différence, à partir de plusieurs titrages oxydimétriques.

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FLUOROMETRIC TITRATION OF CALCIUM, MAGNESIUM AND IRON USING CALCEIN BLUE AS INDICATOR

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Summary—Calcium, magnesium and iron can be determined by successive fluorometric titration without separation. Calcium is titrated directly with EGTA at a pH $\geqslant 13$; magnesium is determined by a substitution reaction with copper-EDTA complex at a pH of about 11; and iron is titrated directly with EDTA in the presence of hydrogen peroxide at a pH of 10·5, after destroying its triethanolamine complex. Calcein Blue serves as an indicator in all of the titrations and as a fluorescent standard. The end-points are sharp and the accuracy is good for various proportions of the metal ions. The method is simple, reproducible and inexpensive. Standard solutions of ions, limestone, cement and serum samples have been analysed by the proposed method.

INTRODUCTION

CALCIUM, magnesium and iron are associated in nature, *e.g.*, in limestone, salt water and blood. Their analysis by gravimetric methods has been time consuming. These components, when present in a mixture, have to be separated from each other by ion exchange, precipitation, extraction or other means, or their influence may be excluded by masking agents, in order to determine only one or two of them. Various indicators and chelating agents are used in titrimetric methods of determining these elements at varying pH. However, although not very selective, their use in chelometry has offered much promise.

Schwarzenbach, Biedermann and Bangerter[1] determined calcium in water using ammonium purpureate and the sodium salt of EDTA. They observed the titration to be unaffected by the presence of magnesium. Cheng and Bray[2] devised a method of determining calcium in the presence of magnesium by direct titration with EDTA using Murexide as the indicator for calcium. The method was not satisfactory because of the fading of the Murexide indicator. A stepwise, visual EDTA titration of calcium and magnesium was developed by Lott and Cheng[3] with either Calcon or Zinchrome R as the calcium indicator at pH 13. Magnesium was subsequently titrated with EDTA at pH 10·5 with another indicator, Eriochrome Black T.

Malmstadt and Hadjiioannou[4] determined calcium and magnesium by photometric titration with EDTA using Eriochrome Black T for total calcium and magnesium and using Calcon for calcium alone. Methods for the determination of calcium in the presence of magnesium using ethyleneglycol-bis(aminoethyl)ether-tetraacetic acid, EGTA, as titrant and Zinc-Zincon as visual indicator were developed by Ringbom, Pensar and Wänninen[5] at pH 10·25 and by Sadek, Schmid and Reilley[6] at pH 9·5. Schmid and Reilley[7] used the same system but applied a potentiometric method. Flaschka and Ganchoff[8] found this Zinc-Zincon system to be sensitive to changes in ammonia concentration and impractical. They determined calcium by a photometric titration with EGTA using Murexide as indicator at pH 10. Magnesium was titrated with EDTA using Eriochrome Black T as indicator. Burg and Conaghan[9] developed a stepwise method for the titration of calcium using EGTA and Zinc-Zincon and titrated the magnesium with EDTA using Eriochrome Black T. However, they found this end-point not satisfactory so they determined the sum of the calcium and magnesium in a second aliquot. Lindstrom and Diehl[10] used Calmagite for the determination of total calcium and magnesium. Flaschka and Sawyer[11] determined calcium and magnesium in submicrogram quantities, using Calmagite as an indicator. Using Chelaplex III solution as titrant, Jaeschke[12] determined the components of limestone in separate solutions using the following indicators: Murexide for calcium, Eriochrome Blue Black R for magnesium and sulphosalicyclic acid for iron. Onishi[13] determined iron spectrophotometrically in aluminium alloy using EDTA in the presence of hydrogen peroxide. Ringbom, Siitonen and Saxen[14] studied the reaction of iron(III)-EDTA and hydrogen peroxide spectrophotometrically at 450 mμ. Wilkins[15] oxidised iron with hydrogen peroxide and after eluting it from an ion-exchange column, he added an excess of EDTA which was back-titrated with standard copper using PAN as an indicator.

Although these metal ions occur naturally in mixtures, there has been no method by which all three ions can be determined in the same solution and with the same indicator. The fluorometric detection of end-point has not been employed. This paper attempts to describe a method of determination of these ions, either singly or in mixtures, without the need of separation and by using the fluorometer or the ultraviolet lamp.

The system developed is based on the differences in the conditional stability constants[16,17] of the metal chelates formed with the indicator, the titrants or the masking agents.

Eriochrome Black T was not used in these experiments because it is not fluorescent and because Přibil and Kopanica[18] stated that its indicator action was destroyed by the iron(III)-triethanolamine complex in an ammoniacal medium. Moreover, the author's unpublished results on the effects of environment on different Calcein-type indicators showed that Calcein Blue was the best indicator for this system. It is most fluorescent at high pH. It, also, was found to be stable. Therefore, Calcein Blue was used as a fluorescent standard in this experiment. Its indicator action is not affected by the iron(III)-triethanolamine complex at high pH.

The method is based on the following proposed mechanisms. Calcium reacts with Calcein Blue indicator (β-methylumbelliferonemethyleneiminodiacetic acid), first prepared by Wilkins,[19] forming a rather strong metal-indicator complex, calcium-Calcein Blue. It has a brilliant blue fluorescence, which is lost on addition of EGTA [ethyleneglycol-bis(aminoethyl)ether-*N*,*N*,*N*′,*N*′-tetra-acetic acid]. Calcium can be titrated with EGTA in the presence of magnesium because the logarithm of the stability constant of calcium-EGTA is much higher than that of magnesium-EGTA, the values[16] being:

$$\log K_{\mathrm{Ca-EGTA}} = 11{\cdot}0; \ \log K_{\mathrm{Mg-EGTA}} = 5{\cdot}2; \ \Delta\log K = 5{\cdot}8.$$

The conditional stability constant of calcium-EGTA, in equimolar solutions (0·001*M*) of calcium and magnesium when acid dissociation of EGTA can be ignored, and taking the concentration of magnesium into account, is:

$$\log K'_{\text{Ca-EGTA}} = \Delta\log K + pM_{\text{Mg}} = 5{\cdot}8 + 3 = 8{\cdot}8.$$

At pH 13, log $\alpha_{\text{EGTA(H)}}$ will be zero.[16] The excess hydroxyl ions present will mask the magnesium so that it will not be involved in side reactions and will remain in solution. The value of the log $K'_{\text{Ca-EGTA}}$ will thus be further increased. Because this value is great, there will be an abrupt decrease in pCa and a good end-point is obtained so that it is possible to detect the end-point by photometric titration or by the use of an ultraviolet lamp. The titration curve for calcium is shown in Fig. 1a.

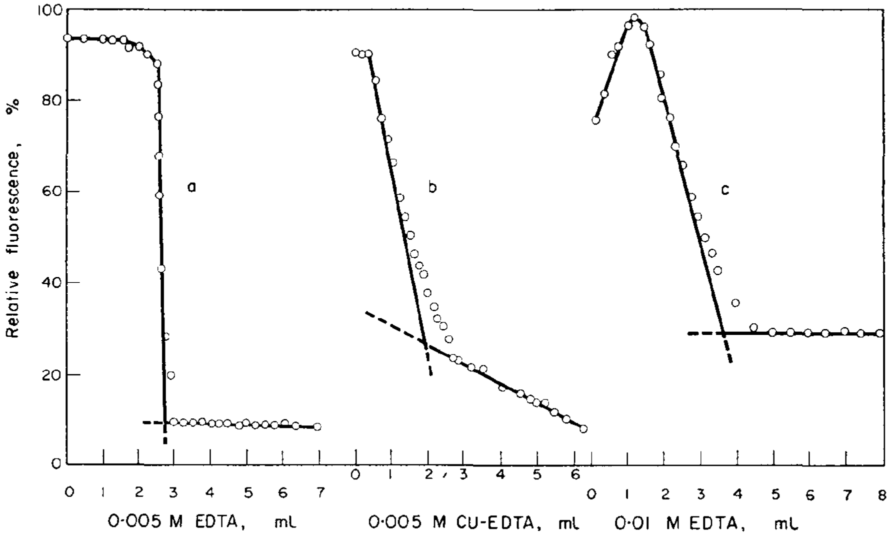

Fig. 1.—A representative plot of the fluorometric titration of calcium, magnesium and iron in the same aliquot using Calcein Blue as indicator.

The mixture contains:
a. 2·06 × 10^{-3} g of $CaCl_2{\cdot}2H_2O$,
b. 2·06 × 10^{-3} g of $MgCl_2{\cdot}6H_2O$,
c. 2·05 × 10^{-3} g of Fe.

A known excess of EGTA is added and the pH is adjusted to about 11. The magnesium is demasked from the excess hydroxyl ions, then reacts with the Calcein Blue indicator. A rather weak fluorescent blue complex is formed. A direct titration of the magnesium-CB complex with EDTA is possible and was found by the author to be stable. However, a copper-EDTA reagent is preferred if iron, too, is to be determined because a sharper end-point is obtained. The end-point is again the disappearance of fluorescence as the magnesium in the magnesium-indicator complex is preferentially chelated by EDTA. The overall reaction is given by:

$$\text{mEGTA} + \text{nMg} + \text{nCu-EDTA} \rightarrow \text{nMg-EDTA} + \text{nCu-EGTA} + (\text{m} - \text{n})\text{EGTA}.$$

The titration curve for the magnesium is shown in Fig. 1b.

Following the ideas introduced by Kinnunen and Merikanto[20] who first introduced the principle of demasking of metals in chelometry, and of Schwarzenbach,[17] the author found that iron which was masked with triethanolamine can be demasked with formaldehyde. The amount used, however, has to be controlled to avoid interference with the action of hydrogen peroxide, which will subsequently be added. The iron which is now free is oxidised to the tervalent state with hydrogen peroxide. The pH is about 10·5. Iron is then titrated with EDTA in the presence of hydrogen peroxide to form a 1:1:1 complex,[5] and the end-point is again the disappearance of the fluorescence of the iron calcein Blue complex:

$$\mathrm{Fe(III)} + \mathrm{CB} \rightarrow \mathrm{Fe(III)—CB}$$

$$\mathrm{Fe(III)—CB} + \mathrm{EDTA} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)—EDTA—H_2O_2} + \mathrm{CB}.$$

The titration curve is shown in Fig. 1c.

The end-point is therefore the same for each determination in the sequence, but the sharpness decreases in the order calcium, iron, magnesium.

EXPERIMENTAL

Reagents

All chemicals used were of the highest purity. Deionised water was used to prepare the solutions.

Standard EDTA solutions. A stock solution of 1*M* sodium ethylenediaminetetra-acetic acid (Fisher Scientific Co.) was prepared by dissolving 111·6771 g of the salt and diluting to 3 l. Aliquot portions of this solution were taken to prepare 0·001*M*, 0·005*M* and 0·01*M* solutions. These solutions were standardised by the method of Diehl and Smith.[21]

Standard EGTA solutions. A solution which contained 11·4131 g of ethyleneglycol-bis(aminoethyl)ether-tetra-acetic acid (G. F. Smith Chemical Co.) was mixed with 12 ml of 6*M* sodium hydroxide. The solution was neutralised with 3*M* hydrochloric acid. This was diluted to 3 l; the solution was 0·01*M*. Aliquot portions of this solution were taken to prepare 0·001*M* and 0·005*M* solutions. The EGTA solutions were standardised in the same manner as the EDTA solutions.

Standard copper solutions. A stock solution of copper was prepared by dissolving 12·7074 g of copper filings in 25 ml of 1 + 1 nitric acid. This was diluted to 2 l. Aliquots of this solution were taken to prepare more dilute solutions. The solutions were standardised iodometrically.[21]

Standard calcium solutions. Two solutions were prepared: (1) 3·0018 g of pure calcium carbonate were dissolved in a little dilute hydrochloric acid and the salt solution was made up to 3 l. This stock solution contained *Ca.* 1·00 mg of $CaCO_3$/1·00 ml. Aliquots were taken from this solution to prepare *eg.*, more dilute solutions, 0·100 mg of calcium carbonate/ml. (2)0·1027 g of pure $CaCl_2{\cdot}2H_2O$ (Baker Chemical Co.) was dissolved and the solution diluted to 100 ml using deionised water.

Standard magnesium solutions. Two solutions were prepared:

(1) 0·7359 g of Grignard-grade magnesium metal turnings (Fisher Laboratory Chemical) was dissolved in 12 ml of 6*M* hydrochloric acid and diluted to 3 l. Ten ml of this stock solution were pipetted into a 500-ml volumetric flask and diluted to the mark with deionised water. This solution contained 5·306 μg of magnesium/ml.

(2) 1·0290 g of $MgCl_2{\cdot}6H_2O$ (Merck and Co., Inc.) was dissolved and the solution diluted to 1 l.

Standard iron solution. 1·0253 g of electrolytic iron (Fisher Scientific Co.) was dissolved in 10 ml of 6*M* hydrochloric acid and diluted to 1 l.

Standard copper-EDTA. Equal volumes of 0·0106*M* EDTA and 0·0100*M* copper solutions were mixed to form a 0·005*M* solution.

Calcein Blue indicator, 0·02%. 0·2054 g of Calcein Blue (G. F. Smith Chemical Co.) was dissolved in 30 drops of 1*M* potassium hydroxide and 250 ml of deionised water. This was diluted to 1 l. and placed in a polyethylene bottle and kept in a refrigerator.

Ammoniacal buffer. This solution was prepared by dissolving 67·5 g of ammonium chloride in 570 ml of concentrated aqueous ammonia. This was diluted to 1 l. with deionised water and kept in a polyethylene bottle.

Fluorescent standards for electrophotofluorometer. A blank to read zero % relative fluorescence was prepared by taking 10·0 ml of deionised water and adding 5 drops of 0·2*M* potassium hydroxide. Solutions to read up to 100% fluorescence were prepared by taking 6 ml of deionised water and 4 ml of 0·02% Calcein Blue indicator or 8 ml of deionised water and 2 ml of 0·02% Calcein Blue. To these solutions 5 drops of either 0·2*M* potassium hydroxide or 1·0*M* hydrochloric acid were added. These fluorescent standards when stoppered can stand for months at room temperature without appreciable change in fluorescence.

Apparatus

Fluorescence. Readings were made with a Coleman electrophotofluorometer Model 12 C equipped with a galvanometer Model 22 and Corning filters Cs-5-60 and Cs-3-67. An ultraviolet titration box, as described by Diehl,[22] was used in some titrations. Beakers, cuvettes, as well as 13 × 17 × 300-mm combustion tube, Pyrex, glass No. 7740 with one end closed, were used as titration vessels. The mixtures were stirred by either pure nitrogen or shaken mechanically.

pH. A Beckman Model G pH meter with a fibre-type calomel and Type E glass electrodes were used. Microburettes and 5- and 10-ml capacity burettes were used.

Sample preparation

Preparation of limestone sample. The limestone sample was dissolved in the same manner as the procedure adopted by Diehl and Ellingboe.[23] 0·3010 g of the argillaceous limestone was dissolved in two portions of 20 ml of 6*M* hydrochloric acid and evaporated to dryness. The residue was redissolved in 5 ml of 1 + 9 hydrochloric acid, filtered and diluted to 250 ml with deionised water. Five- and 10-ml aliquots of this solution were taken for analysis.

Preparation of cement sample. 0·3009 g of the cement sample was dissolved in 20 ml of 6*M* hydrochloric acid and heated to dryness. The residue was taken up with 5 ml of 1 + 9 hydrochloric acid, filtered and diluted to 250 ml with deionised water. Five-ml aliquots were used in the analysis.

Preparation of versatol serum sample. Five ml of deionised water were added to each vial of serum and allowed to stand for 30 min with little shaking. One and 2-ml aliquots were used in the analysis.

Recommended procedure

Calcium. Pipette a 1- to 6-ml aliquot of the sample, containing calcium alone or together with magnesium and iron, into the titration vessel. Mask the iron, and any aluminum or manganese which may be present, with 0·5 ml of 20% triethanolamine. Add 1 ml of 0·02% Calcein Blue indicator. Adjust the pH to 13 or greater with 2*M* potassium hydroxide. Usually 1·0 ml of the base is needed. Stir the mixture and titrate with 0·001*M* or 0·005*M* EGTA, adding enough titrant until 100% past the end-point. Read the % relative fluorescence at the same intervals of time with small increments of the titrant.

If a direct titration with an ultraviolet lamp is used, take the end-point as that volume which will produce a sudden decrease or disappearance of the intensely bright blue fluorescence of the indicator.

TABLE I.—FLUOROMETRIC ANALYSIS OF CALCIUM, MAGNESIUM AND IRON WITH CALCEIN BLUE INDICATOR

Calcium			Magnesium			Iron		
Present, × *10⁻⁴g*	Found, × *10⁻⁴g*	Error, %	Present, × *10⁻⁴g*	Found, × *10⁻⁴g*	Error, %	Present, × *10⁻⁴g*	Found, × *10⁻⁴g*	Error, %
$CaCl_2 \cdot 2H_2O$								
10·27	10·28	0·10						
20·54	20·54	0						
51·35	51·25	0·19						
$CaCO_3$								
0·10	0·10	0						
25·80	26·40	0·23						
$MgCl_2 \cdot 6H_2O$			20·58	20·61	0·15			
Fe						20·50	20·48	0·10
1:1 Ca:Mg								
20·54	20·56	0·09	20·58	20·67	0·44			
1:25 Ca:Mg								
0·10	0·10	0	2·65	2·60	1·89			
1:1 Mg:Fe			20·58	20·40	0·87	20·50	20·66	0·78
1:1:1 Ca:Mg:Fe								
20·54	20·56	0·09	20·58	20·63	0·24	20·50	20·66	0·78
1:1:100 Ca:Mg:Fe								
0·10	0·10	0	0·11	0·11	0	10·25	10·33	0·78
1:1:200 Ca:Mg:Fe								
0·10	0·10	0	0·11	0·11	0	20·51	20·39	0·59

TABLE II.—FLUOROMETRIC ANALYSIS OF STANDARD SAMPLES WITH CALCEIN BLUE INDICATOR

Sample aliquot	Present, %*CaO*	Found, %*CaO*	Deviation, %	Present, %*MgO*	Found, %*Mgo*	Deviation, %	Present, %Fe_2O_3	Found, %Fe_2O_3	Deviation, %
				Fluorometric end-point					
Limestone, NBS No. la									
5 ml	41·32	41·39	0·07	2·19	2·19	0	1·63	1·64	0·01
10 ml		41·39	0·07		2·18	0·01		1·63	0
Cement No. 2, T. Smith									
5 ml	61·76	61·70	0·06	3·84	3·85	0·01	2·72	2·71	0·01
				Visual end-point					
Limestone, NBS No. la									
5 ml	41·32	41·39	0·07	2·19	2·24	0·05	1·63	1·65	0·02
10 ml		41·39	0·07		2·19	0		1·63	0
	Ca, mg/100			Mg, mg/100			Fe, mcg/100		
				Fluorometric end-point					
Serum									
Lab-Trol									
1 ml	10·3	10·3	0	3·3	3·3	0	122	123	1
2 ml	20·6	20·6	0	6·6	6·6	0	244	244	0
Versatol									
1 ml	10·5	10·5	0						
2 ml	21·0	21·0	0						
Versatol-A									
1 ml	6·9	7·0	0·1						
2 ml	13·8	13·8	0						
Versatol-A Alternate									
1 ml	12·4	12·4	0						
2 ml	24·8	24·8	0						
				Visual end-point					
Serum									
Versatol									
1 ml	10·5	10·5	0						
Versatol-A									
1 ml	6·9	6·8	0·1						
Versatol-A Alternate									
1 ml	12·4	12·4	0						

It is best to observe the change of fluorescence from the top of the solution in a dark room.

Magnesium. After titrating the calcium to 100% beyond the end-point, add 2 ml more of 0·005*M* EGTA and about 0·1 ml of 1*M* hydrochloric acid to the solution containing the magnesium. Introduce 1 ml of 0·02% Calcein Blue, 2 ml of the ammoniacal buffer and 1·0 ml of 0·1*M* potassium chloride. The pH should be about 11. The magnesium should be titrated with standard 0·005*M* copper-EDTA to 100% past the end-point.

Iron. To the solution, from the titation of calcium and magnesium, containing iron, add the following reagents in order: 0·1 ml of 37% formaldehyde, 0·5 ml of 30% hydrogen peroxide, 2 ml of 0·02% Calcein Blue and 1 ml of ethyl alcohol. The pH should be about 10·5. Titrate the iron with 0·001*M*, 0·005*M* or 0·01*M* EDTA. It is best to stopper the titration vessel during the determination of iron.

RESULTS AND DISCUSSION

The *Recommended Procedure* can be adopted for the analysis of either of the three ions when alone or in mixtures. In the same aliquot of a mixture, the calcium is determined first, followed by the titration of magnesium and then iron.

The galvanometer sensitivity and the fluorescent standards used for standardising the electrophotofluorometer may be varied as the case may be. All readings were steady and were taken after the same interval of shaking, stirring, settings, *etc.* The complete analysis of all three ions took less than 2 hr.

Table I gives the results of analysis of standard solutions of calcium, magnesium and iron, in varying ratios, in the same aliquot of sample. Table II gives the results of analysis of standard samples using the electrophotofluorometer and the ultraviolet lamp.

CONCLUSION

The stepwise fluorometric titration of calcium, magnesium and iron in the same aliquot is possible with the use of the same indicator. Calcein Blue provides a very appropriate indicator for this purpose because it fluoresces at high pH, is stable as a fluorescent standard and does not have residual fluorescence. An exchange ligand mechanism with the ions, without varying the pH to a great extent, makes this method devoid of many side reactions. The results are accurate. The method provides a means of determining iron in highly alkaline solutions.

The analysis of standard samples proves the feasibility of this method.

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Zusammenfassung—Calcium, Magnesium und Eisen können nacheinander ohne Trennung durch fluorometrische Titration bestimmt werden. Calcium wird direkt mit EGTA bei pH $\geqslant$ 13 titriert; Magnesium wird durch Substitutionsreaktion mit dem Kupfer-EDTA-Komplex bei pH $\approx$ 11 bestimmt und Eisen wird nach Zerstörung seines Triäthanolaminkomplexes direkt mit EDTA in Gegenwart von Wasserstoffperoxyd bei pH 10,5 titriert. Calceinblau dient bei allen Titrationen als Indikator und als Fluoreszenzstandard. Die Endpunkte sind scharf und die Genauigkeit ist bei verschiedenen Verhältnissen der Metallionen gut. Die Methode ist einfach, reproduzierbar und billig. Mit der vorgeschlagenen Methode wurden Standardlösungen der Ionen, Kalkstein, Zement und Serumproben analysiert.

Résumé—On peut doser le calcium, le magnésium et le fer par titrages fluorométriques successifs sans séparation. Le calcium est dose directement au moyen d'EGTA à un pH $\geqslant$ 13; le magnésium est dosé par une réaction de substitution aves le complexe cuivre-EDTA à un pH d'environ 11; et le fer est dosé directement à l'EDTA en présence d'eau oxygénée à pH 10,5, aprés destruction de son complexe avec la triéthanolamine. On utilise le Bleu Calcéine comme indicateur dans tous les dosages, et comme étalon de fluorescence. Les points de fin de dosage sont nets et la précision est bonne pour diverses proportions des ions métalliques. La méthode est simple, reproductible et peu coûteuse. Par la méthode proposée, on a analysé des solutions étalons d'ions et des échantillons de calcaire, ciment et sérum.

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A HIGH-TEMPERATURE INERT GAS FUSION APPARATUS

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Summary—A high-temperature inert gas fusion apparatus capable of operating at crucible temperatures as high as 3100° is described. While this apparatus has been used primarily for the determination of oxygen in pyrolytic carbon-coated uranium carbide particles, its usefulness is not limited to this type of material. It can be generally applied to the determination of oxygen and nitrogen in metals, alloys and other materials amenable to analysis by vacuum-fusion techniques. Analytical results obtained on steel and uranium carbide samples are presented. The apparatus, in its present form, has been in daily use for nearly 2 years. Down time during this period has been negligible. A total of 20 samples can be run in duplicate in an 8-hr shift.

INTRODUCTION

THE development of pyrolytic carbon-coated microspheres of uranium dicarbide and thorium dicarbide as fuel for high temperature gas-cooled nuclear reactors has created a need for an analytical method for the determination of oxygen in these materials.

These pyrolytic carbon coatings have made the vacuum-fusion techniques used at General Atomic and elsewhere[1,2] ineffective for the determination of oxygen in uranium carbide. A high temperature inert gas fusion apparatus, designed and built at General Atomic, has proved to be useful in the analysis of these pyrolytic carbon-coated materials. In this apparatus, the samples are heated in a graphite crucible to temperatures up to 3100°, using induction heating. A 25 kW, 450 kc induction unit is used in conjunction with a current concentrator to reach these high temperatures in an uninsulated graphite crucible. The furnace and concentrator used are similar to those described by Smith *et al.*[3] These authors determined oxygen manometrically after oxidising the evolved carbon monoxide to carbon dioxide. Nitrogen is not determined by their procedure.

Previous work at this laboratory[4] had shown that impurities in helium could be quantitatively collected in a liquid nitrogen-cooled trap before analysis by gas chromatography. The use of a gas chromatograph to measure the gases evolved from the sample makes it possible to determine nitrogen in those materials having nitrides which decompose to release nitrogen on being heated to high temperatures.

EXPERIMENTAL

The samples are heated in a graphite crucible. Oxygen contained in the sample is rapidly released as carbon monoxide, while nitrogen is evolving as elemental nitrogen. A stream of purified helium sweeps these gases from the furnace tube into a silica gel-packed cold trap held at liquid-nitrogen temperatures. The contents of this cold trap are subsequently analysed on a gas chromatograph using a 30–60 mesh Type 5A molecular sieve as the column packing material. Separate peaks for nitrogen and carbon monoxide are obtained. The integrated areas of these peaks are used to calculate the oxygen and nitrogen contents of the sample.

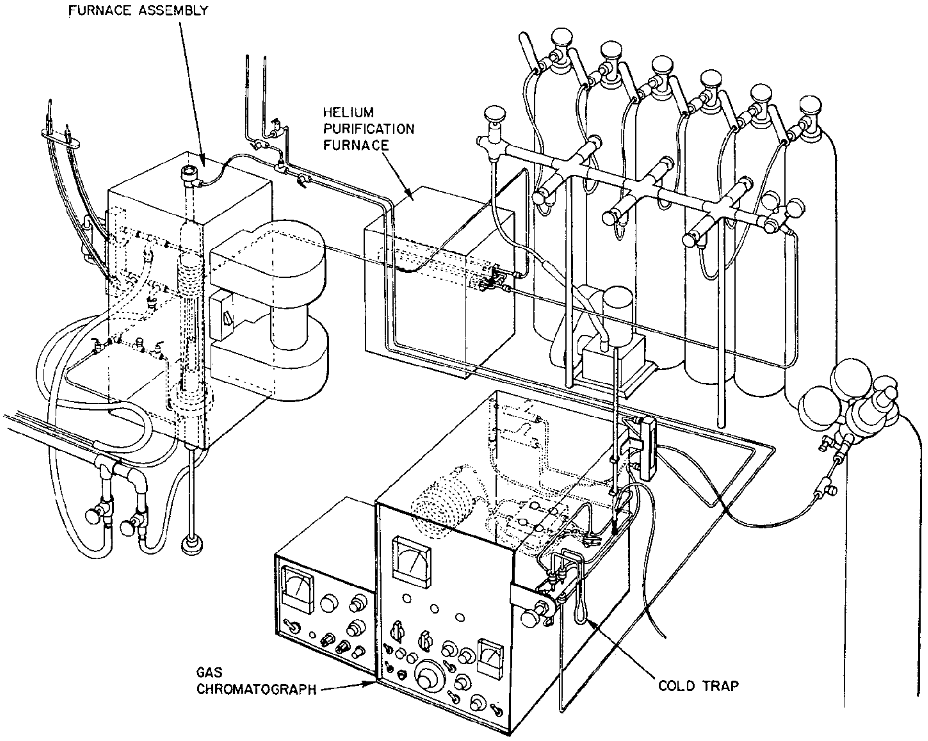

Fig. 1—Inert gas fusion apparatus.

Apparatus

Fig. 1 is a drawing of the entire apparatus except for the induction unit. The apparatus can be conveniently divided into three sections: the helium purification section, the furnace section and the gas chromatograph.

Helium purification. A bank of gas cylinders on a manifold provides the helium supply used to purge the furnace tube and sweep the carbon monoxide and nitrogen evolved from the sample into the cold trap. This gas must be of high purity because about 1000 ml of it passes through the cold trap during the collection step, and even small amounts of oxygen or nitrogen will lead to excessive blanks. Oxygen in the purge gas is converted to carbon monoxide on contact with the hot graphite crucible and, thus, directly interferes with the determination of oxygen in the sample.

Helium from the manifold is passed through hot zirconium chips, then through hot titanium chips. The metal chips are packed into carbon steel lined, Type 304 stainless steel tubes of 1 in. diameter. These chips are held at 900° in a glow-bar furnace. Gas lines from the helium manifold to the induction furnace are made of ¼ in. i.d. stainless steel tubing. From the induction furnace through the chromatograph, ⅛ in. i.d. stainless steel tubing is used.

When new helium cylinders are attached to the manifold, the manifold is evacuated with amechanical vacuum pump up to the valve on the gas cylinders. A pressure regulator at the end of the manifold is used to control the helium flow.

A separate tank of helium supplies the carrier gas for the chromatograph. The purity requirements for the chromatograph carrier gas are not as stringent as for the furnace purge gas because the carrier gas does not pass through the cold trap when the trap is at liquid nitrogen temperatures. The impurities in the carrier gas are not concentrated in the trap as are the impurities in the furnace purge gas.

Furnace section. Fig. 2 is a cutaway drawing of the furnace tube and current concentrator showing the graphite crucible in place. The current concentrator is made of OFHC copper. The centre portion of the current concentrator is water cooled. This part of the concentrator is 1⅛ in.

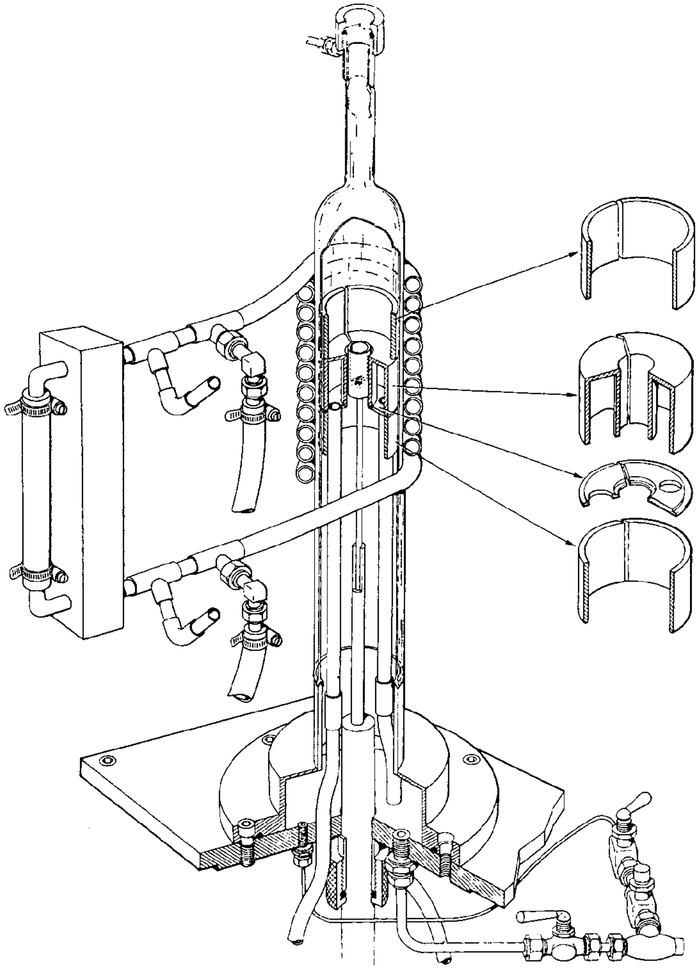

FIG. 2—Cutaway view of furnace section showing details of current concentrator.

high with an o.d. of $1\frac{3}{4}$ in. and has a $\frac{5}{8}$ in. diameter centre hole to accommodate the crucible. Copper fins $\frac{1}{8}$ in. thick, 1 in. high and $1\frac{3}{4}$ in. o.d. are brazed to the top and bottom of the water cooled section of the concentrator. A $\frac{1}{16}$ in. slot runs the full length of the concentrator to avoid circumferential electrical continuity. The slot is cut with a 45° angle at the outer edge of the concentrator to avoid heating the furnace tube opposite the slot due to radiation from the crucible. The concentrator is supported on the copper tubing used to bring in the cooling water supply. Separate cooling water supplies are provided for the furnace coil and the power leads from the induction unit. Cooling water for the coil flows through the fittings nearest the furnace tube in Fig. 2. The water-cooled cables from the induction unit are attached to the outer fittings. The two copper tees in each line are connected by a solid copper plug. A short piece of rubber tubing in the cooling water line for the induction unit cables eliminates electrical continuity in the cable cooling water line.

In early work with this system, corona discharges formed within the furnace tube. At high power settings arcing occurred between the current concentrator and the induction coils. Prolonged arcing produced holes in the furnace tube. However, electrical isolation of the furnace assembly has eliminated the formation of corona discharges and arcing. This was accomplished by using a piece of Teflon tubing inserted in the incoming helium line to isolate the furnace from the helium purification system. Also, a short piece of Pyrex tubing loosely packed with glass wool was inserted in the line between the furnace tube and the chromatograph. This electrically isolated the furnace tube from the chromatograph and acted as a filter to remove any particulate matter in the gas stream coming from the furnace tube. Short pieces of heavy-walled rubber tubing in the water lines to the current concentrator isolate that portion of the furnace assembly.

The induction unit used is a Tocotron Model 4EG251 manufactured by the Ohio Crankshaft Company. This is a thyratron controlled unit capable of producing 25 kW of power at 450 kc.

The furnace tube is made of 2 in. o.d. Pyrex tubing and tapers to ¾ in. o.d. at the top. A 2 in. diameter Kovar glass-to-metal seal at the bottom of the furnace tube is brazed to a brass base. A ¾ in. Kovar seal is used at the top of the furnace tube. A Swagelok fitting with a large knurled nut was brazed to the Kovar seal. A sight glass is held in place in the knurled nut by an O-ring, which also serves as a gas-tight seal. A hole was drilled into the side of this fitting below the nut and a Swagelok connector for ⅛ in. tubing brazed into place. Stainless steel tubing leads from this point to the chromatograph cold trap.

The brass base of the furnace tube is bolted to a brass base plate. An O-ring provides a gas-tight seal.

Helium sweep gas and cooling water for the current concentrator are brought to the furnace tube through fittings in the base plate. Crucibles are inserted and removed through a centre hole in the base plate. The crucibles are supported on a graphite rod ⅛ in. in diameter by 4 in. long. The support rod fits into a hole drilled into the end of a molybdenum rod. The molybdenum rod is inserted into a ¾ in. diameter polished stainless steel rod which extends through the base plate, where another Swagelok fitting with an O-ring serves as a gas-tight seal.

The crucible must be centred in the hole in the current concentrator. For this reason, the support rod assembly must be vertical and have no lateral movement.

The crucible is machined from ½ in. diameter spectrographic electrode rods (Ultra Carbon Corporation Grade UF-4-S). This crucible is 1¼ in. high with a 0·045 in. wall thickness. The bottom of the crucible has a thickness of ¼ in. A ⅛ in. diameter hole is drilled ⅛ in. into the bottom to accept the support rod.

Many different graphite crucibles were tested in this apparatus. Most failed by cracking well before 3000° was reached. The crucible described above has proved to be the most satisfactory, from the standpoint of thermal stability, of those that were tested.

Temperature measurements are made with an optical pyrometer through a quartz window at the top of the furnace tube. Temperatures are corrected for absorption by this window.

Gas-chromatograph. A Loenco Model 15 B chromatograph is used in this apparatus. A Harrison Laboratory Model 865 B power supply provides direct current for the thermal conductivity detectors. The output from the instrument is recorded on a 1-mV Wheelco recorder.

The external sample valve is equipped with a trap made of ¼ in. diameter stainless steel tubing filled with 60-mesh silica gel. A soap-bubble flow meter is used to measure the flow in the two legs of this split stream, carrier gas system.

Gas contents are measured by integration of the areas under the nitrogen and carbon monoxide peaks. The recorder is equipped with a Disk integrator.

Operating procedure

The helium purification furnace is operated continuously at 900°. The chromatograph also operates continuously, thus ensuring temperature stability. For this work a carrier gas flow rate of 80 ml/min has been used for the chromatograph.

The furnace and crucible are outgassed using a fast purge (10 litre of helium/min) and the following heating cycle: 15 min with no heating; 5 min with the crucible heated to 2800° and the furnace cooling fans off; and finally, 15 min at 2800° with the furnace cooling fans on.

After outgassing, the helium flow rate is reduced to 200 ml/min and the valves are positioned to carry the helium stream through the cold trap. From the cold trap the helium stream flows through a rotometer-type flowmeter to the atmosphere. The cold trap is cooled in a dewar of liquid nitrogen. After 5 min the induction furnace is turned off and the cold trap is removed from the dewar of liquid nitrogen. The sample is injected into the chromatograph by pushing the sample valve to the "in" position and immediately immersing the cold trap in a dewar of hot water. The system blank is determined from the areas under the carbon monoxide and nitrogen peaks.

Blanks obtained by simulating the sample loading step, *i.e.*, opening the cap, inserting the funnel, *etc.*, are the same as those obtained without going through the simulated sample loading. During sample loading the fast purge is on. A helium flow of 10 litre/min is sweeping up around the crucible and out of the top of the furnace tube. If the helium purge is run at the normal flow rate (200 ml/min) during loading, the blank obtained is considerably higher than that obtained without the simulated sample loading. The temperature cycling and gas collection times are identical for blank and sample.

Samples are placed in the crucible by removing the furnace cap and pouring the sample through a long stemmed funnel. The fast purge is turned on during the loading step. After the sample is loaded, the cap is replaced and the crucible is heated to 700° for 1 min while the fast purge remains on. With the heat still on, the valves are adjusted to give a 200 ml/min flow through the cold trap. The dewar of liquid nitrogen is placed on the cold trap and the induction unit turned up to give the crucible temperature desired. The time required to raise the crucible temperature from 700° to operating temperature is only a few seconds. A 5-min collection time is used. The analysis is carried out in the same manner as for the blank.

When this apparatus is used for the analysis of metal samples, or when metal baths or fluxes are used, a graphite lid is placed on the crucible. The lid serves to greatly reduce the problem of metal vapour fogging the sight glass in the furnace cap. The lid is machined to fit the crucible loosely and has a ½ in. long stem on the top. A pair of long tweezers is used to place the lid on the crucible in the furnace tube. *The power to the induction coil must be off when handling the crucible lid.* After outgassing, the lid is not removed from the furnace tube. When loading a sample, the lid is removed from the crucible and set on the current concentrator. After the sample is loaded, the lid is replaced.

Calibration

The gas chromatograph is calibrated by using standard gas mixtures containing known amounts of nitrogen and carbon monoxide in helium. A 1-ml sample loop is placed on the sample valve in place of the cold trap. A sample of a standard gas mixture is taken by purging the sample loop with the gas mixture. This sample is then analysed on the chromatograph using the same instrumental conditions, filament current, column temperature and carrier gas flow rate used for the analysis of sample and blank. The sensitivities are calculated in terms of integrator units/ml of carbon monoxide and of nitrogen. These sensitivities are then used to calculate the volume of these two gases released from a sample.

RESULTS AND DISCUSSION

Oxygen

Table I presents data obtained for oxygen on National Bureau of Standards steel samples using this inert gas fusion apparatus. Also presented are results obtained by vacuum-fusion analysis.

With the exception of N.B.S.-160a steel, the coefficient of variation is well below 10% for all cases by both methods. The high manganese and silicon content of N.B.S.-160a steel may cause gettering problems in the analysis of this material. However, gettering would be expected to be more serious in vacuum fusion than in inert gas fusion; here the vacuum-fusion result is higher than that obtained by inert gas fusion.

No bath or flux was used for the vacuum-fusion analyses. A 10-min extraction period with a crucible temperature of 1600° was used for vacuum fusion.

The inert gas fusion results were obtained using a small amount of tin flux (0·16 g of tin in the form of tin capsules) and a crucible temperature of 2200°. The crucible was covered with the graphite lid.

Table II presents some data on the analysis of uncoated uranium dicarbide by inert gas fusion and by vacuum fusion. Use of a platinum bath in the inert gas fusion apparatus did not give oxygen results different from those obtained with no bath.

Inert-gas fusion blanks on the steel analyses reported in Table I varied from less than 2 μg to 7·9 μg, but variation between blanks for any one set was less than 1 μg. Blank corrections were, in all cases, less than 2·5%. For uranium dicarbide, the inert-gas fusion blanks vary from about 3 to 10 μg of oxygen with a variation between initial and final blanks of about 3 to 5 μg.

Nitrogen

Table III presents the results obtained for nitrogen on three N.B.S. steel samples. There is quite good agreement between the inert gas and vacuum fusion results except for the N.B.S.-160a sample. The inert gas fusion results agree quite well with the N.B.S. values.

Table I.—Determination of oxygen in steel samples

Sample	Composition	Inert gas fusion			Vacuum fusion		
		Average* oxygen %	Standard deviation	Coefficient of variation, %	Average* oxygen, %	Standard deviation	Coefficient of variation, %
N.B.S.-55e	Ingot iron, 0·035% of Mn	0·061	0·0033	5·4	0·069	0·0028	4·1
N.B.S.-72f	Cr-Mo steel (SAE-4130), 0·5% of Mn, 0·26% of Si	0·017	0·0009	5·5	0·016	0·0009	5·6
N.B.S.-160a	19-Cr, 14-Ni, 3-Mo steel, ‘ 1·6% of Mn, 0·6% of Si	0·016	0·0022	13·8	0·019	0·0026	13·7

* All averages are based on five determinations.

Table II.—Determination of oxygen and nitrogen in uncoated uranium dicarbide

Method	Number of determinations	Oxygen			Nitrogen			Operating conditions
		Average oxygen, %	Standard deviation	Coefficient of variation, %	Average nitrogen, %	Standard deviation	Coefficient of variation, %	
Inert gas fusion	10	0·061	0·0017	2·8	0·042	0·0032	7·6	Crucible temperature 2650°; no bath or flux
Vacuum fusion	5	0·075	0·0034	4·5	0·046	0·012	26·1	Crucible temperature 1900°; platinum bath
Inert gas fusion	2	0·062	—	—	0·033	—	—	Crucible temperature 2650°; platinum bath

TABLE III.—DETERMINATION OF NITROGEN IN STEEL SAMPLES

			Inert gas fusion			Vacuum fusion		
Sample	Composition	N.B.S. nitrogen value, %	Average* nitrogen, %	Standard deviation	Coefficient of variation, %	Average* nitrogen, %	Standard deviation	Coefficient of variation, %
N.B.S.-55e	Ingot iron, 0·035% of Mn	0·004	0·0032	0·0006	19	0·0045	0·0009	20
N.B.S.-72f	Cr-Mo Steel (SAE-4130) 0·5% of Mn, 0·26% of Si	0·009	0·010	0·00034	3·4	0·0081	0·0015	19
N.B.S.-160a	19-Cr 14-Ni, 3-Mo Steel,	0·051	0·047	0·0054	11·5	0·035	0·0036	10

* All averages are based on five determinations.

In the case of uranium dicarbide, nitrogen results obtained by either inert gas fusion or vacuum fusion are unreliable. While the results presented in Table II for nitrogen in uranium dicarbide show good agreement between the two methods, the results are quite low. Twenty-seven samples of uranium dicarbide analysed at General Atomic by inert gas fusion were also analysed by another laboratory using the Dumas method. The inert gas fusion result for each of the 27 samples was lower than those obtained using the Dumas method. If we assume the Dumas results to be correct, the inert gas fusion results were low by from 12% to 80% with an average error of −42%.

Nitrogen blanks on the inert gas fusion apparatus ranged from 7 to 15 μg of nitrogen in the steel analyses. Initial and final blanks varied by 2 to 3 μg. For uranium dicarbide, nitrogen blanks were much higher, ranging from 10 to 40 μg of nitrogen. Blanks varied by 10 to 20 μg between the start and finish of a series of analyses.

Pyrolytic carbon-coated uranium dicarbide

The above apparatus has been used primarily for the determination of oxygen in pyrolytic carbon-coated uranium dicarbide particles. Smith *et al.*,[3] found that a temperature of 2500° was sufficient to rupture the coatings of the particles used in the work described in that paper. Since that work pyrolytic carbon-coatings have been developed that require much higher temperatures to rupture. Smith *et al.*,[5] report that some coatings require temperatures in excess of 2900°. They have described a sample-handling device which permits the particles to be crushed in the inert atmosphere of the furnace before analysis.

In experiments at General Atomic, we have been able to rupture the coatings on nearly all samples by heating at 3100° for 10–20 sec and finishing the run at 2700°. For those samples of coated particles that cannot be analysed in this manner, crushing by some means such as that described by Smith *et al.*[5] will be necessary.

Zusammenfassung—Es wird eine Apparatur zur Inertgasschmelze bei hohenTemperaturen beschrieben, mit der man bei Tiegeltemperaturen von 3100° arbeiten kann. Während diese Apparatur primär zur Sauerstoffbestimmung in pyrolytisch mit Kohlenstoff überzogenen Urancarbidteilchen diente, ist ihr Nutzen nicht auf diesen Stofftyp beschränkt. Sie kann allgemein auf Sauerstoff- und Stickstoffbestimmung in Metallen, Legierungen und anderem Material angewandt werden, das der Analyse durch Vakuumschmelze zugänglich ist. Analysenergebnisse von Stahlund Urancarbidproben werden vorgelegt. Die Apparatur war in ihrer gegenwärtigen Form nahezu 2 Jahre in täglichem Gebrauch. Die Ausfallzeit in diesem Zeitraum war geringfügig. Insgesamt 20 Proben können in einer 8-Stunden-Schicht mit Duplikat analysiert werden.

Résumé—On décrit un appareil de fusion à haute température sous gaz inerte, capable d'opérer à des températures de creuset pouvant atteindre 3100°. Bien que cet appareil ait été essentiellement utilisé pour le dosage de l'oxygène dans des particules pyrolytiques de carbure d'uranium recouvertes de carbone, son intérêt n'est pas limité à ce type de substance. On peut l'appliquer en général au dosage de l'oxygène et de l'azote dans les métaux, les alliages et d'autres matériaux susceptibles d'être analysés par les techniques de fusion sous vide. On présente des résultats analytiques obtenus avec des échantillons d'acier et de carbure d'uranium. L'appareil, dans sa forme actuelle, a été utilisé quotidiennement pendant près de deux ans. Les temps d'arrêt durant cette période ont été négligeables. On peut, en 8 h, traiter en double un total de 20 échantillons.

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DETERMINATION OF CERTAIN TRACE IMPURITIES IN URANIUM CONCENTRATES BY ACTIVATION ANALYSIS

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Summary—A method is presented for the simultaneous determination of chromium, iron, cobalt and zinc in samples of uranium concentrates, oxides and metallic uranium by neutron-activation analysis. The method involves adequate decontamination of gross fission product activities by adsorption on silica gel, removal of uranium by solvent extraction, separation of most carrier-free rare-earth activities by coprecipitation with aluminium chloride, and, finally, fractional separation of the elements concerned by ion-exchange chromatography. The method can assay ppm of such elements in limited quantities of samples by scintillation γ-ray spectrometric analysis with a reproducibility of 10–15%.

INTRODUCTION

REACTOR-GRADE uranium samples are initially analysed for foreign impurities by microanalytical methods, which are, generally, based on flame photometry or emission spectroscopy. The use of neutron-activation analysis as a possible method for the determination of trace elements in uranium samples or concentrates suffers from substantial limitations because of the increasingly high level of fission-product activities accumulated in irradiated targets. In all cases, elaborate methods of chemical separations are required for the decontamination of the radionuclides concerned.[1] Nevertheless, uranium is readily assayed in a variety of cases through one of the fission products formed in irradiated samples.[2] This method has been used to evaluate the power of and extent of burn up in irradiated fuel.[3] Quite recently, Ward and Foreman,[4] determined some of the rare earths separated from samples of irradiated fuel elements using ion-exchange chromatography.

In the present paper, neutron-activation analysis is applied to the determination of certain metallic impurities in samples of uranium concentrates, oxides and in metallic uranium foils of different purity. It was initially planned to study the possible determination of the elements having atomic numbers from $Z = 24$ to 30 in the samples investigated. However, because of the comparatively short half-lives of the radioisotopes ^{56}Mn, ^{65}Ni and ^{64}Cu, the determination of manganese, nickel and copper by the scheme proposed is limited while that of chromium, iron, cobalt and zinc is carried out. In Table I, a concise summary is given of some useful nuclear data of the elements concerned and for a number of important radioisotopes produced by fission which may interfere in the measurements carried out.

TABLE I.—NUCLEAR DATA

At. No.	Element	Abund.,* %	Cross-section,* σ	Isotope formed	Half-life	Fission yield, %	Main gamma,† *MeV*
24	Chromium	4·13	15·9	^{51}Cr	27·8d		0·321
25	Manganese	100	13·3	^{56}Mn	2·58h		0·85, 1·81
26	Iron	0·33	1·01	^{59}Fe	45·0d		1·10, 1·29
27	Cobalt	100	20·0	^{60}Co	5·27a		1·17, 1·33
28	Nickel	1·08	1·52	^{65}Ni	2·56h		0·37, 1·12, 1·49
29	Copper	69·09	4·51	^{64}Cu	12·8h		1·34
30	Zinc	48·89	0·47	^{65}Zn	245d		1·12
38	Strontium	82·56	0·005	^{89}Sr	50·4d	4·8	—
				^{90}Sr	28·0a	5·8	—
39	Yttrium	100	1·26	^{90}Y	64·5h		1·73
				^{91}Y	58·0d	5·8	1·19
40	Zirconium	17·40	0·076	^{95}Zr	65·0d	6·4	0·76, 0·72
41	Niobium			^{95}Nb	35·0d		0·77
44	Ruthenium	31·61	1·44	^{103}Ru	40·0d	2·9	0·498
				^{106}Ru	1·0a	0·38	—
52	Tellurium	31·79	0·015	^{129m}Te	33·0d	1·0	0·11
53	Iodine			^{131}I	8·05d	2·9	0·361, 0·637
55	Caesium			^{137}Cs	30·0a	6·0	0·662
56	Barium			^{140}Ba	12·8d	6·4	0·54, 0·162 (oths)
57	Lanthanum	99·91	8·20	^{140}La	40·2h		0·49, 0·33 (oths)
58	Cerium	88·48	0·31	^{141}Ce	32·5d	5·8	0·145
				^{144}Ce	284d	5·6	0·031, 0·131
59	Praseodymium			^{144}Pr	17·5m		0·695, 2·18, 1·48
60	Neodymium	17·22	1·8	^{147}Nd	11·1d	2·6	0·533, 0·322 (oths)

* The values tabulated are for the stable nuclides producing the corresponding radioisotopes by (n, γ) reactions.

† Other energy levels corresponding to gamma rays of less predominance are not included.

EXPERIMENTAL

Chemicals and pile irradiations

Uranium samples analysed. (i) Two representative uranium concentrates, each containing about 75% of U_3O_8 calculated on a dry basis; both are from Spain and provided by the "Junta de Energia Nuclear" in Madrid; SP1 and SP2; (ii) two uranium trioxide samples, one from "Aktiebolaget Atomenergi", Sweden, sample H632, and the other is from B.D.H. (A.R.) purity; and (iii) a sample of metallic uranium foil from USSR, 0·16 mm thick.

Standards, carriers, scavengers and in general all chemicals used are of A.R. purity.

Adsorbents. B.D.H. silica gel (50–100 mesh) for chromatography is used. It is digested twice with $5M$ nitric acid, washed repeatedly with water and finally activated for 24 hr at 150° directly before use. The anion exchanger used is the strongly basic quaternary amine polystyrene divinyl benzene (Dowex 1 × 8, 100–200 mesh) which is freed from particles of smaller size and activated as described elsewhere.[5]

Pile irradiations. Irradiations are carried out in the UAR R-1 2MW Research Reactor at Inchass for 48 hr with a neutron flux of $1{\cdot}3 \times 10^{13}$ n.cm^{-2}.sec^{-1}. Duplicate samples (each about 100 mg) are separately wrapped in thin aluminium foil and irradiated under identical conditions as the standards of the elements to be determined. The chemical treatment, however, is not allowed to begin before cooling the irradiated targets 4 to 5 weeks.

Processing of irradiated targets

The method developed for the separation of the radionuclides concerned from irradiated uranium and the successive decontamination steps from gross foreign activities formed by fission is represented in Fig. 1. In a suitably shielded (5 cm of lead) and well ventilated fume hood, separate duplicates of irradiated samples are dissolved in 10–15 ml of $8M$ nitric acid. Known aliquots of chromium, cobalt, iron and zinc standard carrier solutions are subsequently added and the solution carefully boiled to allow for the removal of radioactive volatile fission products.

For the separation of main fission product activities, the solution is made $0{\cdot}04M$ in nitric acid and allowed to pass through a column (about 8 mm) containing 20 g of freshly activated silica gel at a flow rate of about 0·5 ml/min. The charged column is then washed with about 40 ml of dilute nitric acid solution. Both effluants and collected washings are evaporated to a small bulk and the solution transferred to a continuous extractor of the Kutscher-Steudel type for removing uranium by ether extraction in the presence of nitric acid and with aluminium nitrate as a salting agent.[6]

The aqueous layer, after being freed from uranium, is treated successively with concentrated hydrochloric acid and evaporated to expel all fumes of nitric acid. The bulk of concentrated chlorides is cooled to 0° and is subjected to the prolonged action of dry gaseous hydrogen chloride for the quantitative separation of aluminium chloride with most of the rare earth carrier-free activities. The precipitated chlorides are separated and washed with ice cold concentrated hydrochloric acid. The collected filtrates and washings, being 11–12M in hydrochloric acid, are allowed to pass through a column (10 mm) containing 20 g of activated resin (in its chloride form) previously equilibrated with concentrated hydrochloric acid, at a flow rate of 0·3 ml/min. The charged column is subsequently eluted with hydrochloric acid or hydrochloric/hydrofluoric acid mixtures of different concentrations and the successive eluates collected separately. The elements concerned in the respective fractions (chromium in the 12M hydrochloric acid fraction, cobalt in the 4M hydrochloric acid fraction, iron from the 2M hydrochloric/3M hydrofluoric acid fraction and zinc in the 0·02M hydrochloric acid fraction) are then subjected to a limited number of further decontamination steps This ensures removal of remaining foreign activities before the precipitation of each element in a form suitable for measurements of activity.[5]

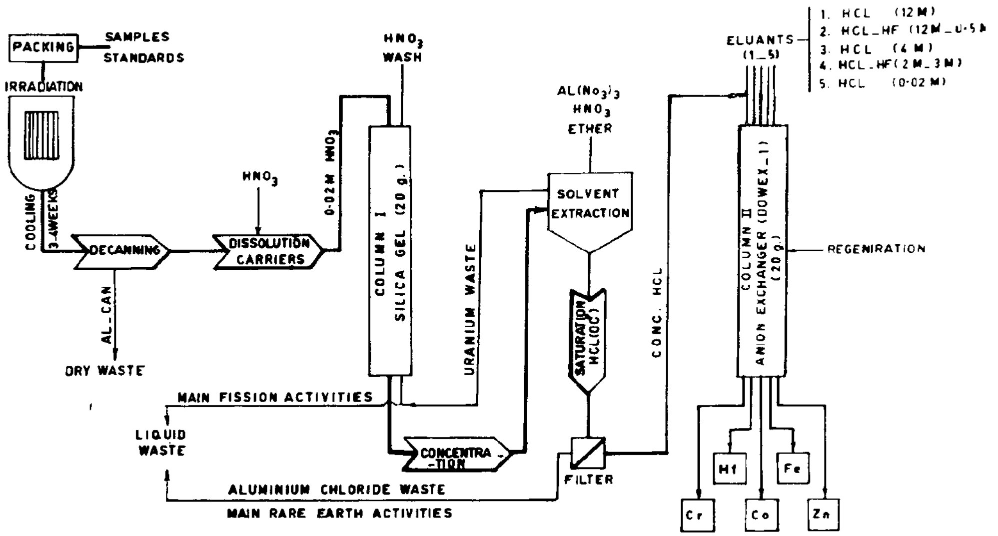

FIG. 1.—Separation of certain trace impurities from irradiated uranium — flow sheet.

Charged silica is finally washed with two column volumes of concentrated nitric acid. Washings, together with the organic uranium extracts, aluminium chloride separated by crystallisation as well as the liquids resulting from regeneration of used resin, and in general all radioactive residues and washings are allowed to pass to the highly radioactive waste.

Chemical separations

The following procedures are recommended and used for the separation of radionuclides concerned in high radiochemical purity from the eluant fractions collected after the ion exchange separations carried out.

Chromium ($Z = 24$). Chromium(III) is eluted from the resin in the 12M hydrochloric acid fraction. It is separated from other cations eluted in this fraction by careful oxidation to chromate with 30% hydrogen peroxide at pH 5·5. After removing excess hydrogen peroxide, the solution is acidified with concentrated hydrochloric acid and passed through a second column of the anion exchanger (Dowex 1), to affect the adsorption of chromium(VI). Most of the remaining cationic contaminants are removed by successive washings with concentrated hydrochloric acid and water.

Chromium is then reduced and eluted from the column before being reoxidised to alkali chromate.[7] Further decontamination is carried out by the addition of ferric chloride carrier and the removal of ferric hydroxide before the separation of chromium as barium chromate in an acetic acid medium.

Iron ($Z = 26$). The collected fraction of $2M$ hydrochloric/$3M$ hydrofluoric acid eluant is concentrated and treated with concentrated aqueous ammonia and ammonium sulphide solutions. The precipitate is dissolved in concentrated hydrochloric acid and boiled to expel hydrogen sulphide before the addition of tin and antimony carriers. The sulphides of these elements are readily separable with hydrogen sulphide and discarded. To the filtrate, saturated tartaric acid is added and iron sulphide precipitated with ammonium sulphide solution. The purified precipitate is dissolved in concentrated hydrochloric acid and iron is oxidised with few drops of concentrated nitric acid. It is then extracted with diethyl ether and freed from non-extractable ions before being washed down the organic layer. The last traces of ether are removed, iron separated as ferric hydroxide, dried and ignited to ferric oxide.[8]

Cobalt ($Z = 27$). The $4M$ hydrochloric acid eluant (about 75 ml) contains mainly cobalt and a limited number of foreign ions. It is readily separable therefrom as described by Meinke.[9] Both iron and copper carriers are added and subsequently separated as copper sulphide and ferric hydroxide, respectively, with most foreign activities. Cobalt is then separated from the collected filtrates by extraction with diethyl ether in the presence of saturated ammonium thiocyanate solution at pH 5·5. It is washed back from the organic layer with $6M$ aqueous ammonia, the solution acidified and the process repeated. Finally, cobalt is precipitated as cobalt(II) sulphide.

Zinc ($Z = 30$). From the $0{\cdot}02M$ hydrochloric acid eluant fraction, zinc is separated as $ZnHg(CNS)_4$.[10] Saturated oxalic acid solution (1 ml) is added and the medium made $1M$ in nitric acid, cooled and zinc precipitated with mercury(II)chloride-potassium thiocyanate reagent. The precipitate is dissolved in $6M$ nitric acid, boiled and zinc is further precipitated before being dissolved to remove mercury as mercury(II) sulphide with excess hydrogen sulphide. Bismuth carrier is then added to the filtrate and bismuth sulphide separated. Finally, the precipitation of $ZnHg(CNS)_4$ is repeated and the precipitate washed and dried.

In all cases, the samples separated and the corresponding standards have the same chemical form and the activity is measured in each under identical geometry. Gamma-ray spectrometric determinations are carried out with a 100-channel pulse height analyser of the Sunvic PHA-3 type with a printing out facility and a sodium iodide (thallium activated) crystal (1·5″ × 1″). Energy calibration was performed with sources of well known gamma-ray lines.

RESULTS AND DISCUSSION

Experimental approach

The elements with atomic numbers from $Z = 24$ (chromium) to $Z = 30$ (zinc) produce neutron-induced radioactive species which are not formed by uranium fission nor as decay products therefrom. The determination of these elements in uranium by neutron-activation analysis necessitates, therefore, proper decontamination from the fission products formed in irradiated targets. The use of silica gel as a suitable inorganic exchanger for the removal of most carrier-free foreign activities formed by fission is now recommended because of its high radiation and temperature resistance, its chemical stability within a wide range of pH, and the comparatively rapid sorption and elution properties without any operational difficulties. Under a variety of conditions, ^{95}Zr, ^{95}Nb as well as ^{90}Sr, ^{137}Cs, ^{140}Ba, ^{103}Ru, ^{106}Ru and ^{144}Ce are separable on silica gel from solutions of irradiated uranium samples.[11] Under our experimental conditions, gross decontamination from most fission products took place and neither any of the elements concerned nor uranium proved to be appreciably adsorbed. However, specific details about the radioisotopes separated are not included.

In addition, removal of uranium is readily achieved by the ether extraction in the presence of aluminium nitrate; the distribution coefficients of uranium and related actinide complexes (mainly Np and Pu) are high compared with those of most other elements under these conditions.[12] Also, the subsequent separation of aluminium chloride together with a number of the tervalent rare earth chlorides in concentrated hydrochloric acid,[13] gives good decontamination from most remaining foreign activities.

Nevertheless, further decontamination is carried out by the fractional separation of the elements concerned with ion-exchange chromatography. The scheme used has been previously applied in a similar investigation[5] and the order of decreased hydrochloric acid concentrations or the hydrochloric/hydrofluoric acid mixed eluants used, favours the possibility of sharp and successive separation of chromium, cobalt, iron and zinc because of obvious differences in their distribution coefficients under such conditions (*cf.* Fig. 2).[14]

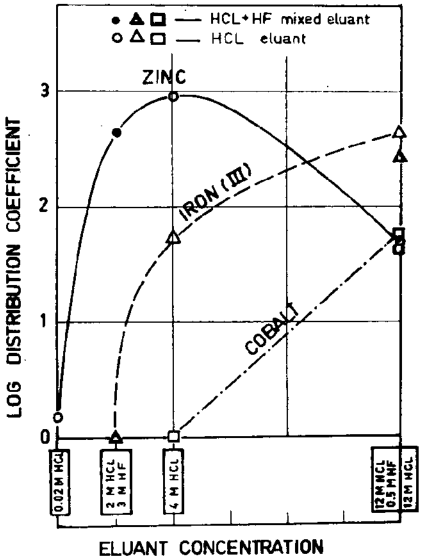

FIG. 2.—Change in the distribution coefficients of cobalt, iron and zinc ions on Dowex 1 with different HCl and HCl/HF eluant concentrations.

RESULTS

The results of the determinations carried out are summarised in Table II. Iron, zinc and chromium are common impurities in the uranium concentrates analysed, while cobalt is present only in concentrations not exceeding 0·0010%. The analytical figures are based on the scintillation gamma-ray spectrometric analysis of the characteristic photopeaks corresponding to the high energy gamma-ray lines of ^{51}Cr, ^{59}Fe, ^{60}Co and ^{65}Zn. The radiochemical purity in all cases was checked (not less than 99%) by the identity of the spectrum shape from separated samples and reference standards. Within the accuracy of the measurements carried out, the results obtained, in general did not differ from those based on the whole gamma-ray spectrum consideration, or in particular, from those based on the 1·10-MeV and 1·17-MeV photopeak areas of ^{59}Fe and ^{60}Co, respectively, thus giving further evidence on the radiochemical purity of the samples assayed. Chromium, however, being not adsorbed on the anionite used from 12*M* hydrochloric acid, was found to contain foreign activities which necessitated further purification on a second ion-exchange column. This is of particular importance because of the comparatively low maximum energy of the rays emitted from ^{51}Cr (E_{max} 0·321 MeV).

Precision

In the early stages of the present work, the successive operations carried out influenced the chemical yield of separated samples which affected the reproducibility of the data obtained. This source of error was brought to a minimum by careful operational conditions leading in most cases to not less than 50% recovery of added carriers. Other errors encountered in the activity measurements are of the normal statistical nature, while errors due to neutron flux inhomogeneity are of the expected order of magnitude. (Standards were wrapped in the same sort of aluminium sheets used for the samples and were irradiated surrounded by the samples. The results in Table II suggest that self-absorption is not serious under the condition of these experiments.) In most cases, however, duplicate determinations are obtainable within 10–15% reproducibility; and a further check on some of these results was made by chemical and emission spectrographic analysis of the uranium concentrate SP2 for both iron and zinc, respectively.

TABLE II.—DETERMINATION OF CERTAIN METALLIC IMPURITIES IN URANIUM BY NEUTRON-ACTIVATION ANALYSIS

Sample	Weight, *mg*	Elements determined, *ppm*			
		chromium	iron	cobalt	zinc
U-Concentrate SP1	109·5	239·5	7621	6·3	252
	144·1	389·5	9700	5·2	271
	85·0	—	11094	6·8	350
		314·5	9471	6·1	291 mean
U-Concentrate SP2	289·1	—	4384	3·8	251
	474·8	12·6	6804	2·2	254
	524·9	6·1	3107	1·8	304
		9·4	4765	2·6	267 mean
			4775*		200†
UO_3-H632	68·2	40·6	66	2·0	94
	120·3	39·2	61	1·2	101
		39·9	63	1·6	97 mean
			54·6*	<3·0†	
UO_3-B.D.H. (A.R.)	110·2	14·0	—	2·5	5·2
	181·0	16·0	b.d.‡	2·3	3·2
		15·0	b.d.‡	2·4	4·2 mean
U-foil	52·6	71·6	1·3	0·8	3·3
	78·0	78·1	4·0	0·2	3·2
		74·8	2·6	0·5	3·3 mean

* The data reported are obtained from the determination of iron by the 2,2′-dipyridyl chelating complex method.

† The analysis carried out by emission spectrographic technique.

‡ b.d. represents concentrations beyond detection under the specified conditions.

CONCLUSION

In the light of all the above considerations, the conventional technique of neutron-activation analysis can be generally applied for the determination of elements producing neutron-induced radioisotopes not formed by uranium fission in the samples analysed. In one of the uranium concentrates analysed (SP1), hafnium (Z = 72) has been identified in the 12*M* hydrochloric-0·5*M* hydrofluoric acid eluant fraction through the 42·5d ^{181}Hf activity (E_{max} 0·133, 0·346 and 0·482 MeV). Hafnium represents one of the elements having a high atomic number and can be determined by the scheme worked out. However, the possibility of assaying other elements formed through uranium fission by the same technique is not totally excluded.

Acknowledgement—We thank Mr. H. Fouad and Mr. T. Z. Bishay for their helpful aid.

Zusammenfassung—Eine Methode zur gleichzeitigen Bestimmung von Chrom, Eisen, Kobalt und Zink in Proben von Urankonzentraten, Oxyden und metallischem Uran durch Neutronenaktivierungsanalyse wird beschrieben. Dabei wird der Hauptteil an Spaltproduktaktivitäten durch Adsorption an Silicagel beseitigt, Uran durch Lösungsmittelextraktion entfernt, die meisten trägerfreien Aktivitäten von seltenen Erden durch Mitfällung mit Aluminiumchlorid abgetrennt und schließlich die gewünschten Elemente durch Ionenaustauschchromatographie in Fraktionen zerlegt. Mit der Methode können ppm-Konzentrationen solcher Elemente in begrenzten Probemengen durch Szintillations-γ-Spektrometrie bestimmt werden. Die Reproduzierbarkeit beträgt dabei 10–15%.

Résumé—On présente une méthode de dosage simultané du chrome, du fer, du cobalt et du zinc dans des échantillons de concentrats d'uranium, d'oxydes et d'uranium métallique par analyse par activation de neutrons La méthode comprend une décontamination appropriée des activités du produit de fission brut par adsorption sur gel de silice, l'élimination de l'uranium par extraction au moyen de solvant, la séparation de la majeure partie des activités des terres rares exemptes d'entraîneur par coprécipitation au chlorure d'aluminium et, finalement, la séparation fractionnée des éléments concernés par chromatographie d'échange d'ions. On peut utiliser la méthode pour doser des p.p.m. de tels éléments dans des quantités limitées d'échantillon par analyse spectrométrique par scintillation de rayons γ aves une reproductibilité de 10–15%.

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A COMPARISON OF NEUTRON-ACTIVATION ANALYSIS AND HOT EXTRACTION ANALYSIS OF THE OXYGEN CONTENT OF STEEL

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Summary—A system developed for the fast neutron-activation analysis of the oxygen content of metals has been tested comparatively with the conventional vacuum fusion and carrier-gas fusion techniques. The results of these tests indicate that neutron-activation analysis is much faster (the total analysis takes only 2 min or less), and more reliable than vacuum fusion and carrier-gas fusion methods because all oxygen present is analysed. Samples can be much larger than the 0·2–3 g commonly used for the fusion methods. Furthermore, the analysis is non-destructive—the same samples can be re-analysed as often as desired. The fast neutron-analysis system includes a 14-MeV neutron generator producing 10^{11} neutrons/sec, a dual-tube pneumatic transfer system, a 5 × 5 inch NaI(Tl)crystal, a single-channel analyser, two scalers, and timers and switch-gear. A sample, in a polyethylene bottle, and a Lucite reference are irradiated simultaneously, after which the sample is returned to a detector for counting the ^{16}N gammas from the $^{16}O(n,p)^{16}N$ reaction. The reference is then counted in a second detector; the ratio of the sample counts to the reference counts is proportional to the oxygen content of the sample. Samples with oxygen contents from 0·002 to 0·1 % of oxygen have been analysed by neutron activation, then cut in several pieces for hot extraction analysis of the total sample.

INTRODUCTION

THE DEMAND for rapid and reliable oxygen determinations of steel has greatly increased in recent years. Rapid oxygen determinations are needed for both process and production control purposes and for quality control. The accurate determination of oxygen in steel is essential because oxygen-containing compounds, precipitated during solidification, have significant effects on the properties of some steels.

The conventional hot extraction techniques, vacuum fusion or carrier-gas fusion techniques, are not completely satisfactory, with the possible exception of some new and promising approaches such as the Baltzer-Bendix rapid vacuum fusion analyser and the Leco or RCI rapid inert gas, gas-chromatographic oxygen analysers.

In connection with oxygen analysis, there are three requirements in which the analytical chemists are mainly interested. The technique must be accurate, fast and reasonably inexpensive.

Based on these requirements, the various analytical techniques used for the determination of oxygen in steel were compared and evaluated (Table I). The neutron-activation technique, based on the $^{16}O(n, p)^{16}N$ reaction, offered an excellent approach

TABLE I.—COMPARISON OF ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF OXYGEN IN STEEL

	Unit size	Time of analysis*-10-g sample, *min*	Factor affecting results
Hot Extraction Techniques			
Vacuum fusion (regular)	1–4 g	35–45	Extraction recovery Standardisation
Rapid vacuum fusion (Baltzers)	1–3 g	12–15	
Rapid inert-gas fusion			
New Leco, RCI, *etc.*	1–3 g	14–18	
D.C. arc extraction + Spec.	0·5–1·5 g	60–90	
Direct Techniques			
Vacuum spectroscopy	1–2 mg	—	Spectrographic conditions Standardisation
Spec. in controlled atm.	1–3 mg	—	
Neutron activation	7–50 g	1·5–2	

*Including rebuilding time, *etc.*

for a very rapid determination of oxygen in reasonably large steel samples. However, previous activation studies[1–6] involved lower sensitivities and/or inadequate automation compared to the requirements of modern analytical and quality control laboratories in the steel industry.

Activation analysis is now rapidly branching out from the laboratory into production process control applications and the system described here was developed specifically for rapid, routine analyses of the oxygen content of steel.

On these grounds, a co-operative programme was initiated between the Kaman Aircraft Corporation's Nuclear Division at Colorado Springs, Colorado, and the Jones and Laughlin Steel Corporation's Research Division at Pittsburgh, Pennsylvania, to develop a new system and to establish optimum conditions for the analysis of approximately 10-g, or larger, steel samples by neutron-activation analysis. A large number of samples were analysed by neutron activation, by conventional vacuum fusion analysis, and by the new Leco carrier gas fusion oxygen analyser.

Mylar standards with known oxygen contents are used for calibration. The system gives approximately 2200 counts/mg of oxygen at 10^{11} neutrons/sec output.

SYSTEM DESCRIPTION

A block diagram of the system is shown in Fig. 1. The neutron source is a Kaman A-1001 Cockroft-Walton type accelerator (Fig. 2) operating at 200 kV accelerating voltage and up to 2 mA beam current. The ^{3}H(d, n)^{4}He reaction is used to obtain 1–2 × 10^{11} neutrons/sec at an energy of 14·2 MeV. This machine is stable enough so that irradiations can be made by turning the ion source on and off, which eliminates any neutron background during counting.

The transfer system is designed for bottles ("rabbits") up to 0·5 inch in diameter. The standard polyethylene bottle is shown in Fig. 3 with the typical steel pin sample, 0·25 inch in diameter by 1·5 inches long. The rabbit is loaded into the transfer system at the console and blown to the irradiate position along with a Lucite reference in the second tube. A 40 psi air line is used for the transfer. Fig. 4 shows the irradiation station with the neutron generator moved back (at left) for clarity. The samples are irradiated parallel to the plane of the target (perpendicular to the deuteron beam). Both sample and reference are rotated on their own axes during irradiation to eliminate "hot spots." Recent work has been done with a "double rotator" (Fig. 5) which rotates sample and reference around an axis parallel to the deuteron beam as well as on their own axes. After irradiation the sample is blown to the counting station (Fig. 6) and the reference stops at a storage port outside the lead shield. The stopping block at centre contains a light source at the centre, two photocell position detectors (bottom photocell removed from its port) and two air-driven stop pins

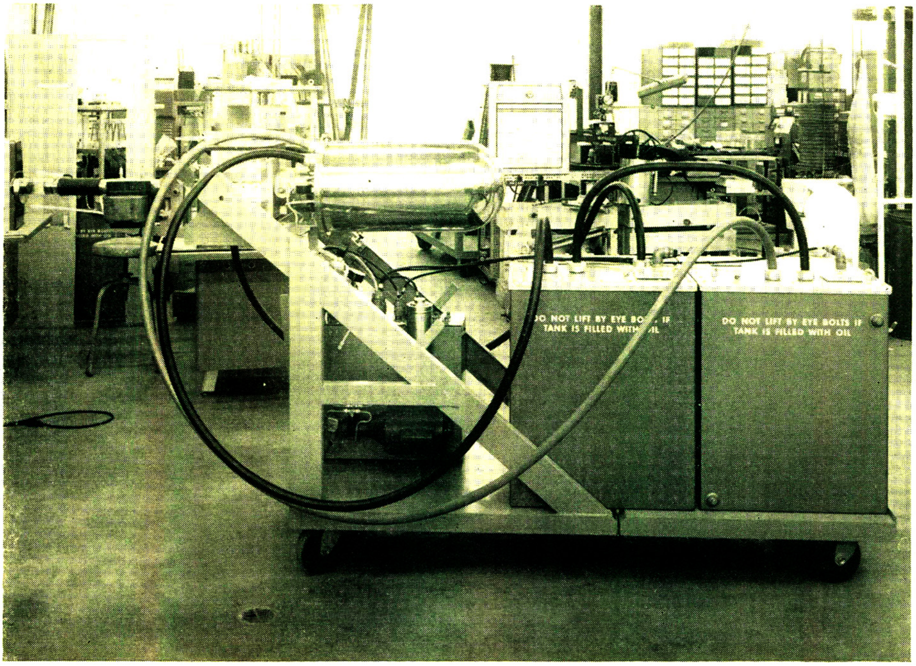

FIG. 2.—Kaman A-1001 neutron generator

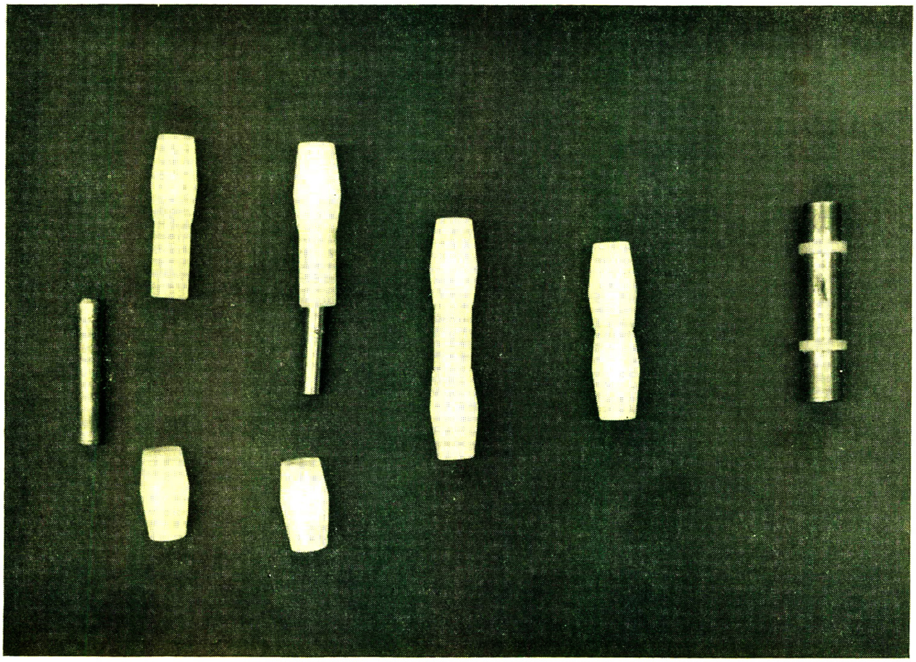

FIG. 3.—Carrier bottles and steel pin samples

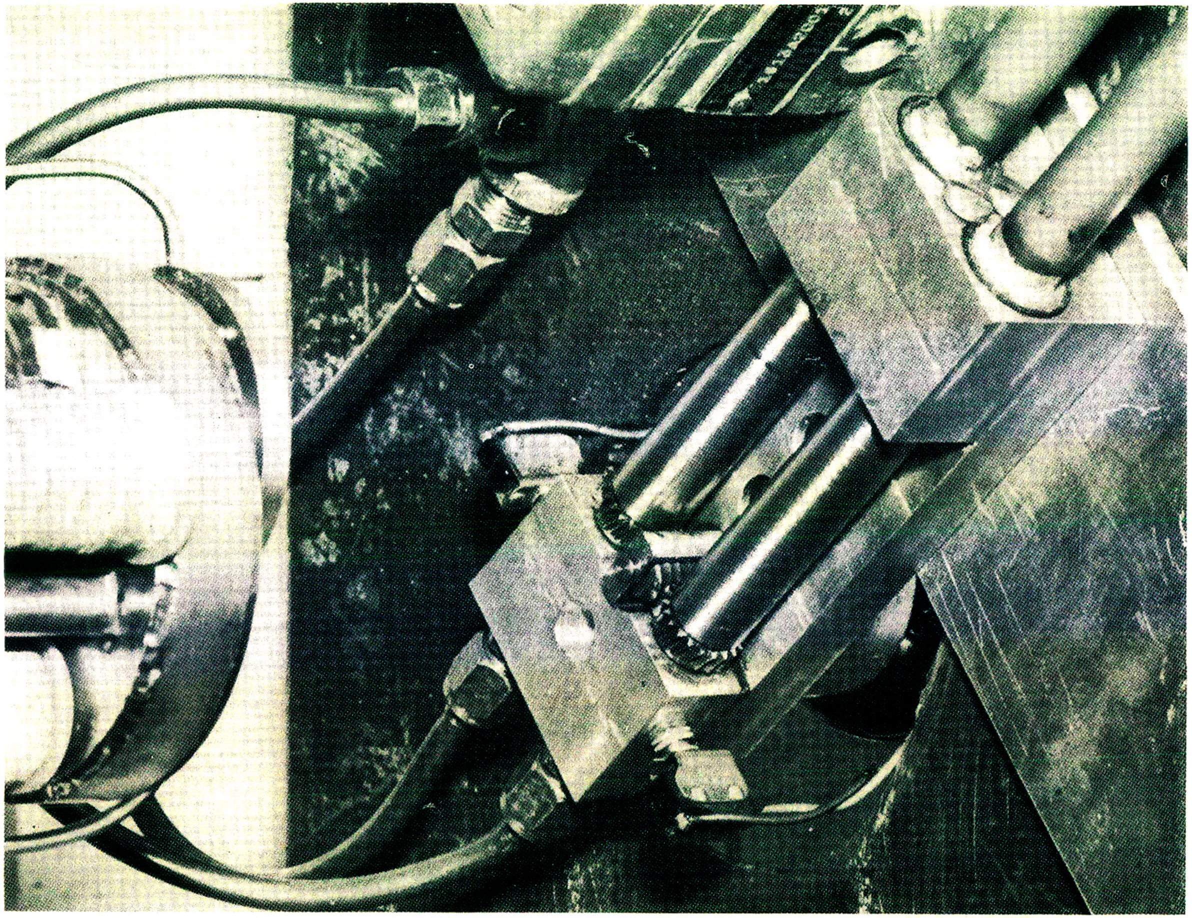

FIG. 4.—Irradiation station: single-axis rotator

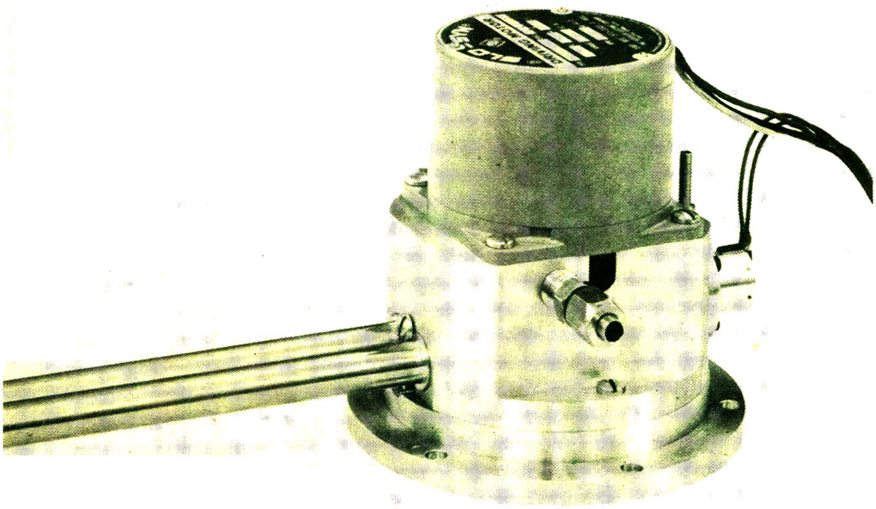

FIG. 5.—Double-axis rotator

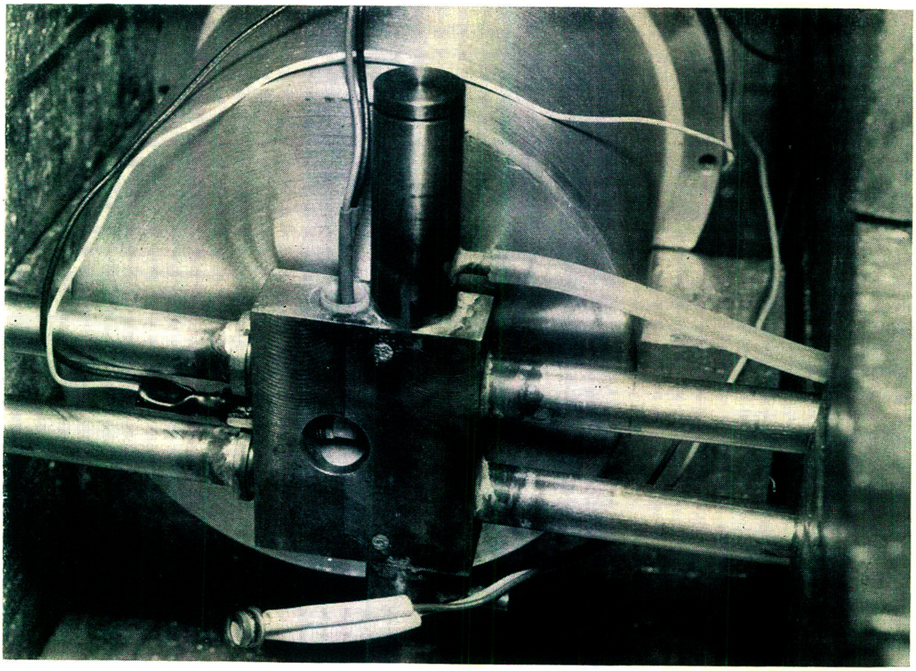

FIG. 6.—Counting station

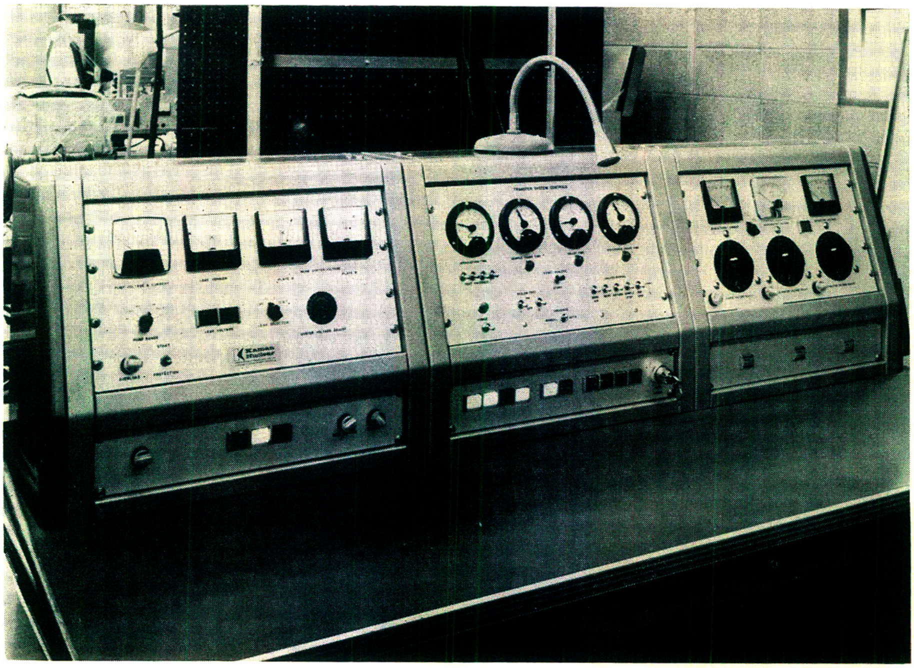

FIG. 7.—Oxygen analyser console

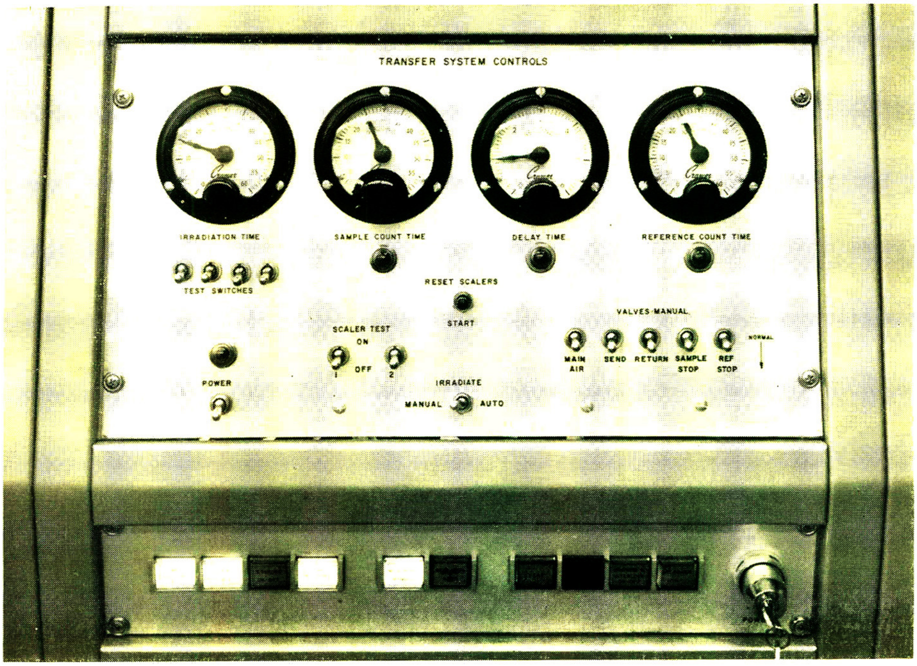

FIG. 8.—Transfer system controls

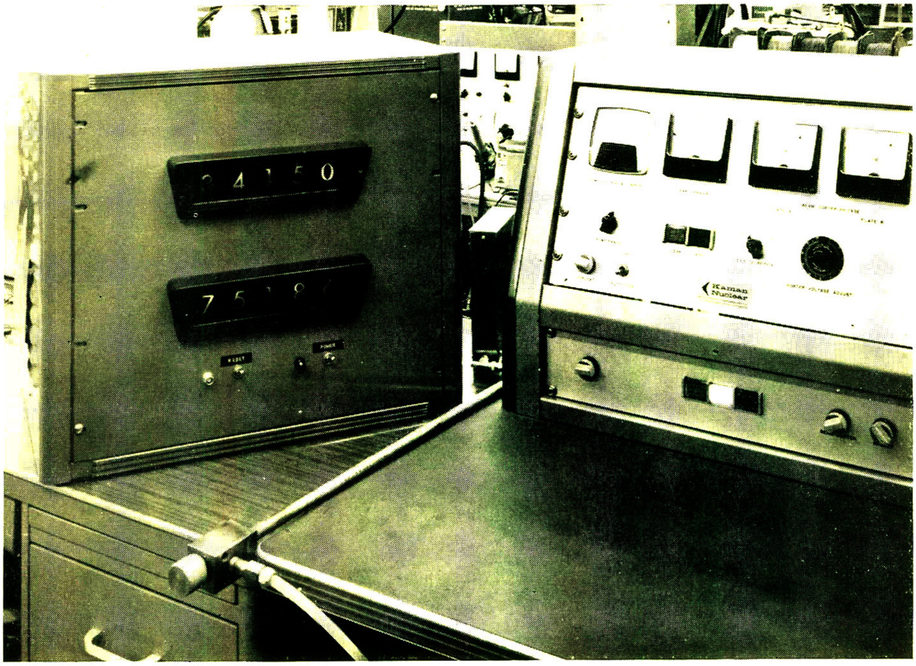

FIG. 9.—Scalers and loading port

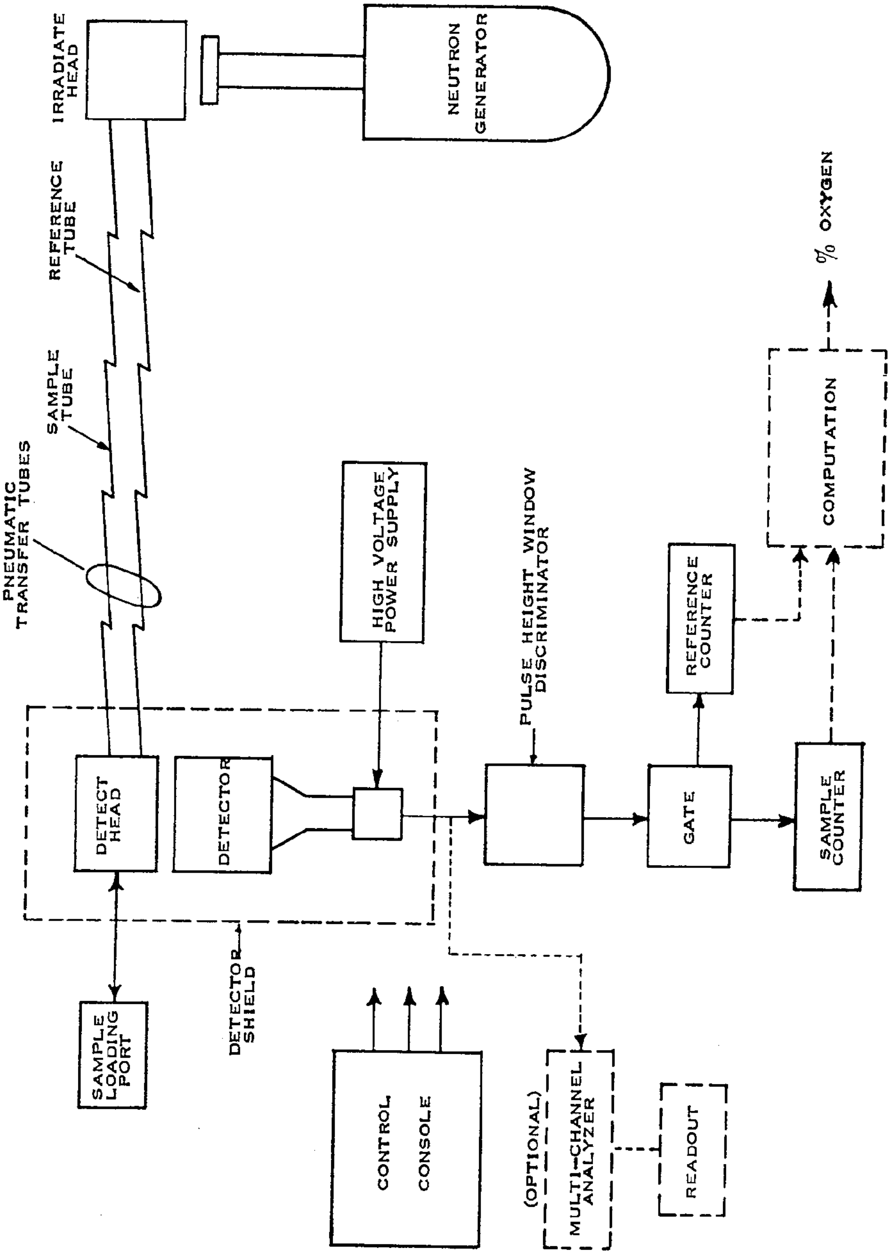

FIG. 1.—Block diagram of oxygen analyser.

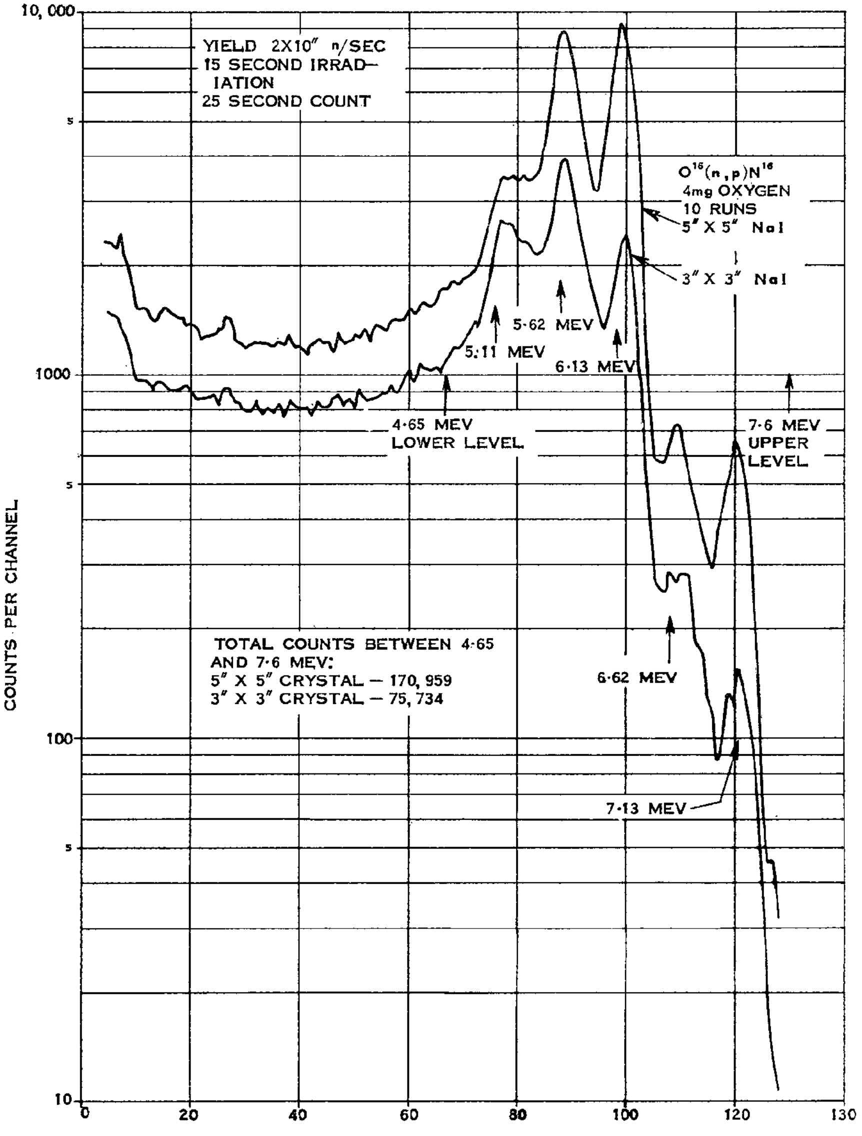

Fig. 10.—Comparison of gamma-ray spectra of ^{16}N with 5 × 5 inch and 3 × 3 inch NaI crystals

(brass cylinders at top and bottom). The 5 × 5 inch NaI(Tl) crystal is shown behind the stopping block and a 4-inch lead shield surrounds the assembly. The sample is counted for 25 sec, then returned to the loading port. At the same time the reference is blown into the counter for a 25-sec count. In order to avoid lost time between runs, the sample can be removed from the bottle and replaced by a new sample while the reference is being counted. The mildly radioactive sample needs to be handled for only a few seconds, so the radiation dose is negligible. In fact, even a box full of irradiated samples gives a reading of only a few mrem/hr, which decays to a negligible level in a few hours.

The control console for the entire system is shown in Fig. 7. The centre panel, shown in Fig. 8, is the transfer and counting system control. Fig. 9 shows the scaler readouts and loading port.

The Lucite reference was chosen as a flux monitor to minimise errors from space and time variations of the neutron flux. Time variations are eliminated by counting a reference whose activity builds up and decays at the same rate as the sample—ideally the same isotope, although other techniques are possible. Space variations are eliminated by placing the sample and reference in the same physical volume during irradiation. Ideally, the sample and reference would be intimately mixed, but double rotation with a period ($\sim$1 sec) that is short compared to the ^{16}N half life (7·35 sec) accomplishes the same purpose. Other methods of flux monitoring (neutron counter feeding scaler or count ratemeter, counting cooling water activity, activating a foil near the sample, or counting the iron peak of the sample) fail to account for either the space or time variation of the neutron flux during irradiation.

Successive counting of sample and reference, rather than simultaneous counting in two separate counters, was chosen to minimise the effects of drifts in the electronics. The present system can operate for months at a time without recalibration of the single-channel window because slow drifts affect the sample and reference counts equally. Separate counters would require frequent checks, because their drifts might be in opposite directions.

The single-channel analyser was chosen to reduce the effect of dead time. If the total count is $\sim$100,000 in 25 sec, a multi-channel analyser might have as high as 50% dead time loss at the start of the count. A single-channel system with a dead time of 2 μsec or less is needed to keep the loss below 2% at the start of the count.

The 5 × 5 inch crystal was chosen to increase efficiency and to suppress the second escape peak from the 6·13-MeV gammas. Fig. 10 shows the spectrum of ^{16}N gamma rays taken with 5 × 5 inch and 3 × 3 inch crystals. The 5 × 5 inch crystal is more than twice as efficient as the usual 3 × 3 inch crystal. Furthermore, the second escape peak at 5·11 MeV is suppressed, thus allowing a cleaner separation of the nitrogen gammas from the sum peaks of ^{56}Mn (3·94 MeV) and ^{24}Na (4·12 MeV). Fig. 11 shows the ^{16}N spectrum with the ^{56}Mn and ^{24}Na spectra, all taken with the 5-inch crystal. The analyser is set to accept gammas from 4·65 to 7·6 MeV. Any lower setting could allow part of the sum peak to be counted. This effect is recognised when a steel sample is run several times in succession, because the ^{16}N decays between runs, but the ^{56}Mn does not.

Neutron shielding is an annoying, but necessary, part of the activation system. For 10^{11} neutrons/sec output, a shield of 5–7 feet of concrete is necessary on all sides of the neutron generator. The ceiling may be 1–2 feet thinner if the area above is unoccupied, but air-scattering (skyshine) prevents a further reduction. Personnel access is provided by a shielded labyrinth or a motorised shield door.

INTERFERENCES

The energy of the ^{16}N gammas is high enough so that most interferences are eliminated. However, a few special kinds of interference still occur. The most serious interference arises from ^{19}F(n, α)^{16}N, because the same isotope is produced. Thus, if fluorine is suspected, a separate check must be made with the ^{19}F(n, p)^{19}O reaction. Interference from sum peaks from ^{27}Al(n, α)^{24}Na and ^{56}Fe(n, p)^{56}Mn has been mentioned above. A few light elements have isotopes which emit high energy betas which may penetrate into the crystal. Reactions leading to these isotopes, the radiations and their energies in MeV, and the fraction of disintegrations giving the radiations are listed in Table II. Trace elements which activate to the listed isotopes are not very serious, because many of the betas lose enough energy to be below 4·65 MeV when they enter the crystal. However, major constituents can be serious interferences. For example, a bottle containing 1 g of boron and a few mg of oxygen was activated to look at the ^{11}B(n, p)^{11}Be reaction (half life 13·6 sec, cross section $\sim$3 mbarn). The ^{11}Be completely obscured the ^{16}N in terms of count rate and measured half life. Thus, a reasonable amount of care is required in analysing oxygen even though the interferences are relatively rare, and advanced techniques such as spectrum-stripping are seldom necessary.

STANDARDISATION

Before the measurements of the oxygen contents of the steel samples, the instrument is regularly standardised. The standardisation includes running a background (once a day), the standards for calibration (only once for a given sample size), a small piece of Mylar as a secondary standard (once an hour), and the empty bottle (once an hour to check for changes in the blank value). Subsequently, the steel samples in the bottles are analysed. The oxygen content is calculated from

$$\text{Percentage oxygen (by weight)} = \frac{1}{CM}\left(\frac{S-b}{R} - B\right) \qquad (1)$$

where C = a calibration factor which includes geometry and counter sensitivities,
M = the sample mass (g),
S = the count on the sample,
b = the background,
R = the count on the Lucite reference (background in comparison to total counts is negligible and therefore ignored),
and B = the ratio of counts for the empty bottle to reference counts.

Calibration is performed with the aid of five artificial standards, 1·5 inches long, which are made

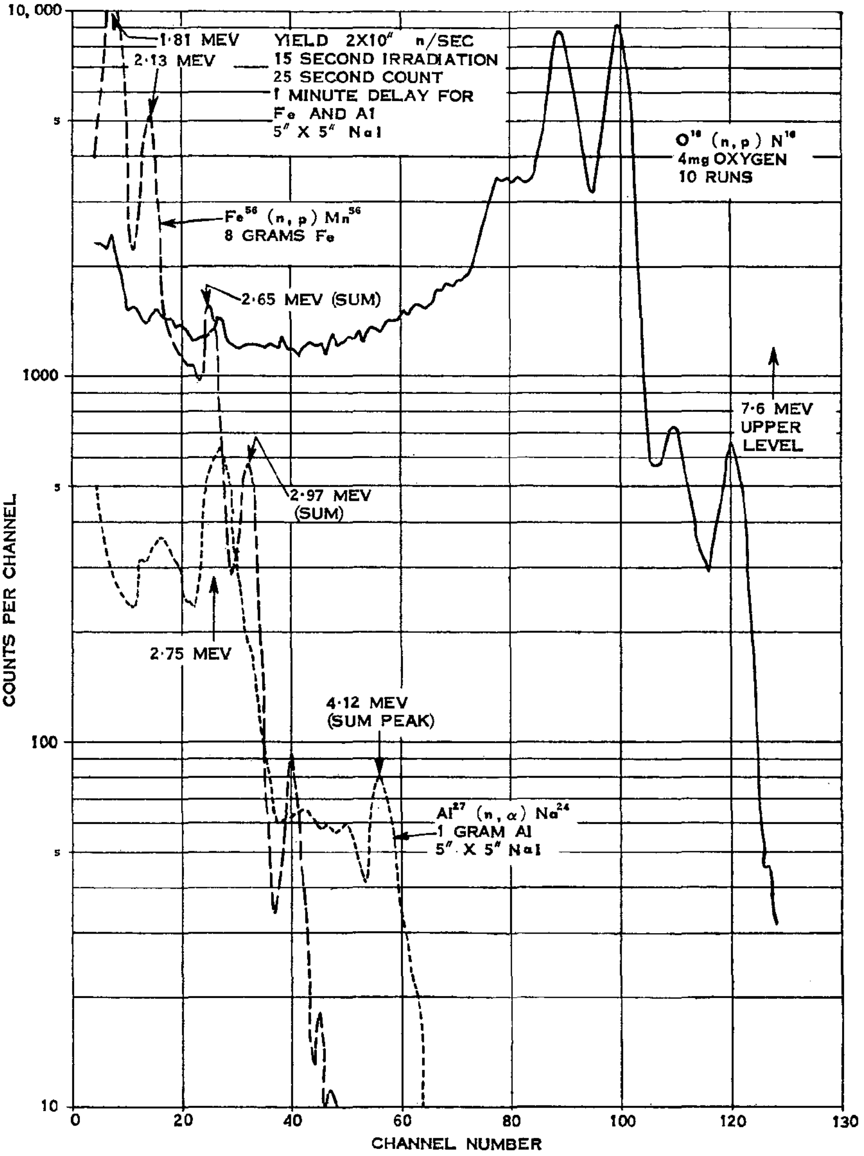

Fig. 11.—Gamma-ray spectra from irradiation of oxygen, iron and aluminium with fast neutrons.

TABLE II.—NUCLEAR REACTIONS*

Reaction	Half life, *sec*	Radiations, *MeV*
$^{16}\mathrm{O}(n, p)^{16}\mathrm{N}$	7·35	γ 6·13 (73%), 7·12 (5%); β 4·3 (68%), 10·4 (26%)
Direct interference:		
$^{19}\mathrm{F}(n, \alpha)^{16}\mathrm{N}$	7·35	Same
Indirect interference:		
$^{11}\mathrm{B}(n, \alpha)^{8}\mathrm{Li}$	0·84	β 13·0, 6·0
$^{11}\mathrm{B}(n, p)^{11}\mathrm{Be}$	13·6	γ 2·12 (32%), 6·8 (4%), 4·6–8·0; β 11·5 (61%), 9·3 (29%)
$^{12}\mathrm{C}(n, p)^{12}\mathrm{B}$	0·019	γ 4·4; β 13·4 (97%), 9·0 (1%)
$^{15}\mathrm{N}(n, p)^{15}\mathrm{C}$ or $^{18}\mathrm{O}(n, \alpha)^{15}\mathrm{C}$	2·3	γ 5·3 (32%); β 4·51 (68%), 9·81 (32%)

Range of 10-MeV beta in aluminium: ~5000 mg/cm² or 1·85 cm

of 1/4 inch discs of iron (1/16 inch thick) alternating with 1/4 inch discs of Mylar which are 0, 1/4, 1/2, 1 or 2 mils thick, respectively, for the five standards. The discs are stacked, one by one, into a sample bottle which is then heat-sealed to prevent relative motion of the discs during use. The steel discs are punched from a sheet of C-1095 alloy which contains 0·005% of oxygen. The artificial standards can be made in any size, shape and oxygen content; they can be used many times and in different laboratories, if desired; and they provide an absolute calibration which does not depend on subsequent chemical analyses of the samples. The range of oxygen covered by these standards is 1·4–25 mg of oxygen, which corresponds to 0·014–0·25% of oxygen in 10-g steel samples. The oxygen content of Mylar (polyethylene terphthalate) is taken as 33·2% by weight from the formula $(C_{10}H_8O_4)_n$. The standards are run several times and the ratio $(S - b)/R$ is plotted (Fig. 12) *vs.* the oxygen added as Mylar. The slope of the line is then the calibration factor, C, and the negative x-intercept is the oxygen content of the bottle and steel discs with no oxygen added. The calibration is absolute and does not depend on the subsequent chemical analyses of steel samples. The calibration curve was run several times and found to be linear within 1%. The value of C is about 0·333. Experiments with changes in beam size and neutron-generator position showed a range of 0·270 to 0·350 for C with the single rotator, although C could be held to within 1% as long as operating conditions were not changed. The double rotator reduced the variation in C to ±3% for changes in the generator position (~0·5 inch in any direction).

Typical values of the numbers in equation (1) for a 10-g steel sample containing 0·01% of oxygen are:

$$R = 60{,}000,\ S = 3050,\ b = 50,\ B = 0{\cdot}0167,\ C = 0{\cdot}333, \text{ and } M = 10.$$

Thus

$$\text{Percentage oxygen} = \frac{1}{0{\cdot}333 \times 10}\left(\frac{3050 - 50}{60{,}000} - 0{\cdot}0167\right)$$

$$= \frac{1}{3{\cdot}33}(0{\cdot}05 - 0{\cdot}0167) = \frac{0{\cdot}0333}{3{\cdot}33} = 0{\cdot}01\%.$$

The bottle weighs about 2 g and contains about 0·5 mg of oxygen in the polyethylene. Air is removed by drilling holes in the bottle so that the activated air is blown out and through the counter before the bottle arrives. This blank value (0·5 mg of oxygen) corresponds to about 0·005% of oxygen in the steel sample, so the lower limit of detection is set by the blank rather than by statistical limitations. Measurements on a 10-g sample can be made down to 0·001%, but the reproducibility is only about ±30% for a single run. To improve the precision several runs are required, or else the blank value must be reduced. For machined samples with controlled dimensions, the carrier bottle can be replaced by thin polyethylene rings or a small cap on one end, which reduces the blank to ~0·1 mg of oxygen. However, the standard pin samples are quite variable in diameter, cross-sectional shape, and straightness. Thus, the bottle is necessary unless the cost and time needed for machining can be tolerated.

Background from natural radioactivity is not a problem, because the induced background in the bottle (~1000 counts) is much larger than natural background (~50 counts) for the 5 × 5 inch crystal shielded by 4 inches of lead. Care must be exercised to keep the neutron generator off (or well shielded) during counting and the reference must be 5 feet or more away from the detector when counting the sample.

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* John F. Stehn, *Table of Radioactive Nuclides* in *Nucleonics*, 1960, **18**, 186.

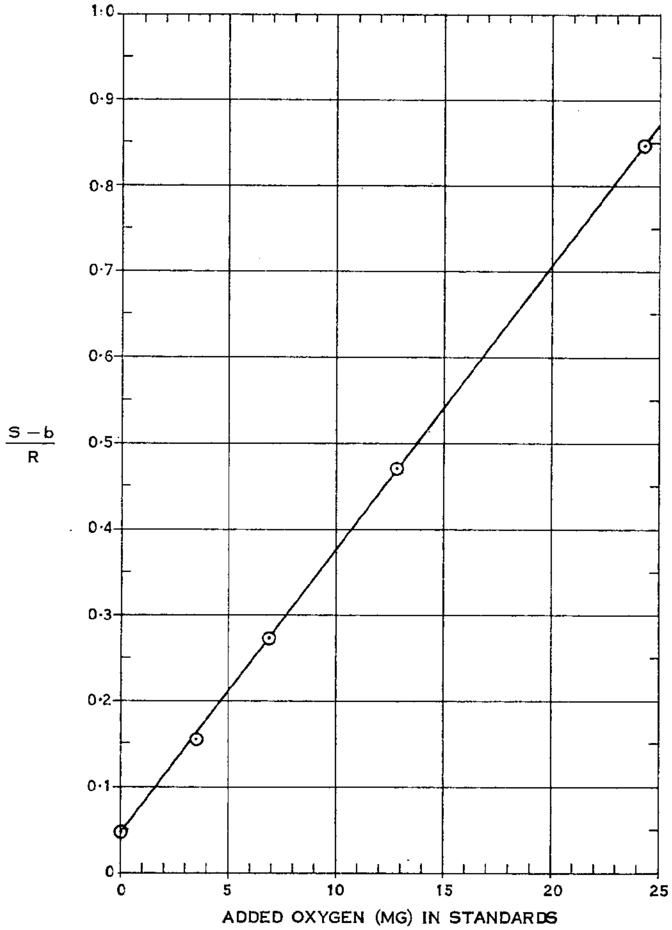

FIG. 12.—Calibration of oxygen analyser.

COMPARISON WITH HOT EXTRACTION ANALYSIS

After the calibration of the system with Mylar standards was completed, steel samples with a wide range of oxygen contents were used to test the reliability of this instrument. When necessary, surface oxides were removed by filing, then the samples were cleaned with ether and weighed. More then 1000 samples have been analysed and all were run in duplicate or triplicate to obtain reproducibility data. Finally, 220 selected samples covering oxygen levels from 0·002 to 0·1 % of oxygen were cut in three or more pieces to permit analysis of the same samples by vacuum fusion or carrier-gas fusion analysis at Jones and Laughlin Steel Corporation Research. In this work the percentage of oxygen was calculated from the total weight of oxygen and from the weight of the pin sample. The comparison of the results obtained on the same samples (Fig. 13) showed that the correlation between neutron activation and vacuum fusion results was generally good, especially because the activation system is calibrated on an absolute basis and thus does not use the fusion results

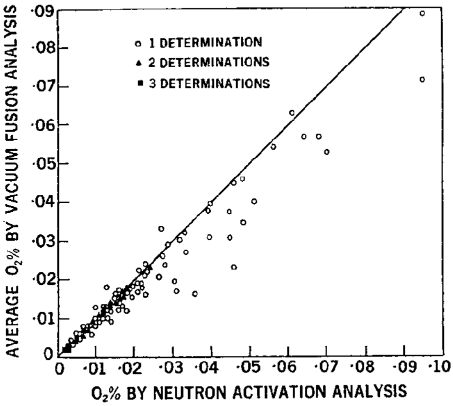

FIG. 13.—Comparison of activation and vacuum fusion results for oxygen contents of steel pin samples.

for calibration. The difference between neutron activation and vacuum fusion results in 65% of the determinations was 0·001% of oxygen or less at the 0·002 to 0·07% level of oxygen. In general, the reproducibility (95% confidence limit) of the activation results is much better than the comparison with fusion results—typically ±2% for high oxygen samples (>0·1%) where statistics are not limiting and ±15% in the 0·005% range of oxygen.

The correlation between neutron-activation analysis and inert-gas fusion analysis (using the new Leco carrier-gas fusion oxygen analyser) is shown in Fig. 14. The agreement of activation with carrier-gas fusion is somewhat better than with vacuum fusion, partly because the samples for inert gas fusion were run later in the programme. Thus, both the activation technique and the sample preparation technique were improved by the time the samples for inert gas fusion were taken.

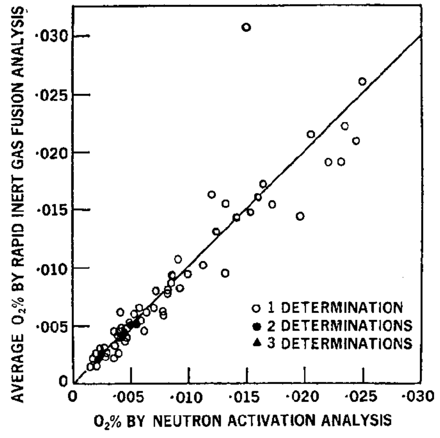

FIG. 14.—Comparison of activation and inert gas fusion (Leco) results for oxygen content of steel pin samples.

HETEROGENEITY EFFECTS

For reliable chemical or spectroscopic analyses and particularly for the determination of oxygen, the elements should be uniformly distributed throughout the samples. Thus, when the sample is homogeneous, both the analytical chemist and the metallurgist are satisfied with the results. Unfortunately, samples taken from liquid steel usually are substantially heterogeneous. The various sampling techniques seldom produce samples with oxygen uniformly distributed.

Past sampling studies and evaluations have shown that the oxygen distribution is significantly less uniform in molten steel samples than in finished steels. Bomb samples and pin samples obtained even with refined techniques are still far from being satisfactory. Often 2- to 6-fold differences were observed on adjacent 2- to 3-g portions of 1·5 inch long pin samples.

A thorough study of the effect of sample size on the oxygen content demonstrated that from molten steel, approximately 10-g or larger samples give the best results. Typical oxygen variations in pin samples taken from liquid steels are shown in Table III. This study of the variation in oxygen content *vs.* sample size showed that the average variation was 9 to 1 for 0·5-g samples, 5 to 1 for 1-g samples and 2 to 1 for 3-g samples. Thus, samples larger than the 0·5- to 3-g samples which are typically used for fusion analysis are required. Neutron activation can use samples of 100 g or more, although the problem of drawing or taking good samples larger than the 7- to 10-g pin samples used in this study has not been satisfactorily solved. The large variations in the oxygen contents of the pin samples are caused by the formation of oxide inclusions in the pins. The oxygen from oxide inclusions is often not recovered by hot extraction techniques[7–11] and this could be the main reason for the deviations seen in Fig. 13 and also to a certain extent in Fig. 14.

TABLE III.—TYPICAL OXYGEN VARIATIONS IN PIN SAMPLES TAKEN FROM LIQUID STEELS
(Oxygen range 0·01–0·05%)

Sample size, *g*	Variations = (min.:max.)			Average variation
	1:15	1:3	1:7	
0·5	1:6	1:5	1:4	1:9·1
	1:9	1:18	1:5	
	1:7	1:4	1:2	
1·0	1:4	1:9	1:6	1:5·1
	1:5	1:6	1:3	
	1:2	1:1·4	1:2·5	
3·0	1:5	1:1·5	1:1·9	1:2
	1:1·5	none	1:2·2	

These results are for nominal 9-g samples which were cut in 3 to 15 pieces for fusion analysis.

The variation in oxygen content also affects the activation measurements, because the measurements are made with the sample centered on the beam and perpendicular to the beam axis. Thus, the ends of the sample receive less radiation than the centre. A flux traverse (Fig. 15) taken in the bottle showed that the flux at the ends was only about 60% of the flux at the centre. A small variation of oxygen along the steel pin would introduce only a small error because the rotation tends to average out the variation; however, extreme variations (such as a concentrated oxide inclusion) could

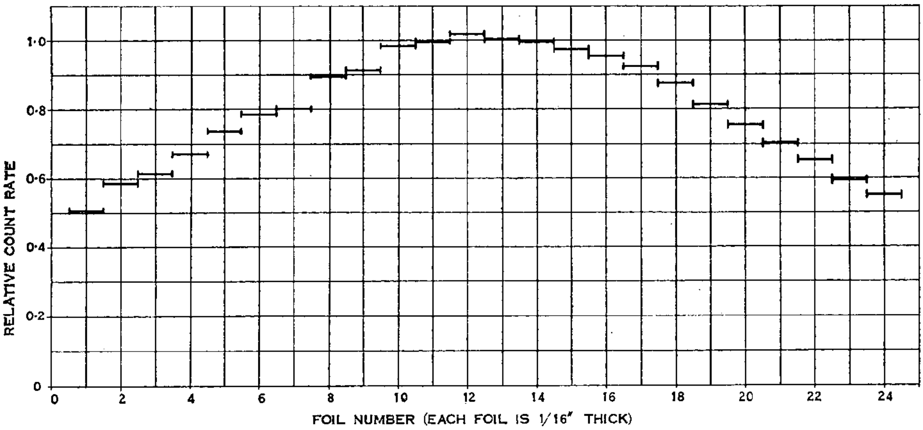

FIG. 15.—Flux traverse in standard sample bottle.

introduce substantial error. Inhomogeneity was also found in measurements made on NBS Standard 1040, although 1044 and 1045 were homogeneous within the precision of the measurement. These standards are supplied as 1-inch diameter cylinders, so 1/4 inch samples were cut from the centre and edge of each standard. Activation results for these samples are given in Table IV.

TABLE IV.—ACTIVATION ANALYSIS OF NBS 1040 SERIES STANDARDS

Standard number	Portion sampled	Activation result, $\%O_2$	Nominal value, $\%O_2$
1040	Centre	0·0271	0·018
1040	Edge	0·0132	0·018
1044	Centre	0·0090	0·009
1044	Edge	0·0089	0·009
1045	Centre	0·0076	0·007
1045	Edge	0·0071	0·007

RELIABILITY AND ERROR ANALYSIS

The total system has been rebuilt several times over a period of 11 months as weaknesses in components and design appeared. System reliability (or availability) has increased from 30% to 90% of the time during this "shakedown" period. Approximately 3000 samples have been analysed from many sources—all have included two runs to prove the reproducibility of the results.

About once per month, a series of 10–15 runs is made on a sample with 20–30 mg of oxygen, so that both sample and reference have 40,000–60,000 counts, thus reducing statistical uncertainty to ~0·8%. Timer variations introduce about 0·7% uncertainty. The standard deviation for several runs is calculated from

$$\sigma(x) = \frac{100}{x}\sqrt{\frac{\sum_{1}^{n}(x_i - \bar{x})^2}{n - 1}}$$

where $\sigma(x)$ = the percentage standard deviation,
x = the variable,
and n = the number of runs.

Values of σ have been obtained from 1·0 to 1·9%. Thus, system uncertainties are mostly in the counting statistics and timer errors. An electronic timer has been constructed to minimise timing uncertainty, so the system will be limited only by counting statistics.

CONCLUSIONS

The reproducibility of the neutron-activation technique measured at the 95% confidence limit is $\pm 10\%$ based on a single count and $\pm 7\%$ based on the average of two counts for low oxygen steels (30–300 ppm). On steels with homogeneous oxygen contents, such as NBS standards and finished steel products, the reproducibility has been significantly better. For high oxygen content samples for which statistical variation is low ($<1\%$), the reproducibility is $\pm 2\%$.

The correlation between neutron activation and vacuum fusion results is generally good. The difference between neutron activation and vacuum fusion results in 65% of all the determinations is 0·001% of oxygen or less.

There is a tendency towards a slight bias between the vacuum fusion and neutron-activation results, the neutron-activation results being higher. The bias was found to be greatest on samples heavily killed with aluminium and, in approximately 20% of the aluminium-killed samples, the difference was greater than 20%.

The correlation between neutron-activation analysis and inert gas fusion analysis with the new Leco oxygen analyser is somewhat better, the bias being less. This is in good agreement with the often reported low oxygen recoveries on aluminium-killed steels by routine-type vacuum fusion techniques.[7–11]

The results of this study indicate that the neutron-activation technique is at least as reliable as the conventional techniques used for the routine determination of oxygen in steels. In neutron-activation analysis, large, 7- to 50-g samples can be analysed accurately in half the time needed for the smaller, 1- to 3-g samples in the other rapid techniques. A significant advantage of the neutron-activation analysis is that it is a direct non-destructive technique. The problems and sources of error present in hot extraction techniques, *i.e.*, incomplete decomposition of stable oxides, mechanical ejection or creeping of oxides, the gettering effect, *etc.*, which lead to poor, usually low oxygen results with hot extraction techniques, are eliminated. Moreover, the sample can be run several times, if necessary.

The neutron-activation analysis is not inexpensive, because the initial costs are high—$35,000 or more for the analyser, plus $10,000 minimum for the necessary shielding. However, the actual operation of the neutron-activation oxygen analyser is less expensive for the same reliability of results than the operation of the other oxygen analysers.

This evaluation in its entirety has shown that neutron-activation is a practical approach for the rapid, routine determination of oxygen in steel, especially when larger samples (such as required from molten steels because of their non-uniform oxygen distribution) are to be analysed.

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Zusammenfassung—Eine Einrichtung zur Aktivierungsanalyse des Sauerstoffgehaltes von Metallen mit schnellen Neutronen wurde im Vergleich zu den herkömmlichen Arbeitsweisen der Vakuumschmelze und Trägergasschmelze geprüft. Die Ergebnisse zeigen, daß die Neutronenaktivierungsanalyse viel schneller geht (die ganze Analyse dauert 2 Minuten oder weniger) und zuverlässiger ist als die Vakuum- und Trägergasschmelzmethoden, da aller anwesende Sauerstoff erfaßt wird. Die Proben können viel größer sein als die 0,2–3 g, die bei den Schmelzmethoden gewöhnlich verwendet werden. Ferner ist die Analyse zerstörungsfrei-dieselben Proben können beliebig oft nacheinander analysiert werden. Die Apparatur zur Analyse mit schnellen Neutronen enthält einen 14 MeV-Neutronengenerator, der 10^{11} Neutronen pro sec liefert, ein pneumatisches Transportsystem mit zwei Röhren, einen 5 × 5-Zoll-NaJ(Tl)-Kristall, einen Einkanalanalysator, zwei Zähler, Zeitgeber und ein Schaltgerät. Eine Probe in einer Polyäthylenflasche und eine Blindprobe aus Lucite (Acrylharz) werden gleichzeitig bestrahlt, dann wird die Probe vor einen Detektor gebracht, der die ^{16}N-Gammaquanten von der Reaktion $^{16}O(n, p)^{16}N$ zählt. Die Blindprobe wird vor einem zweiten Detektor vermessen; das Verhältnis der Impulse von Probe zu Blindprobe ist dem Sauerstoffgehalt der Probe proportional. Proben mit Sauerstoffgehalten von 0,002–0,1 % wurden durch Neutronenaktivierung analysiert und dann in Stücke zerlegt, um die ganze Probe durch Heißextraktion zu analysieren.

Résumé—Un système élaboré pour la détermination de la teneur en oxygène des métaux par analyse par activation de neutrons rapides a été essayé en comparaison avec les techniques usuelles de fusion sous vide et de fusion avec gaz porteur. Les résultats de ces essais montrent que l'analyse par activation de neutrons est beaucoup plus rapide (l'analyse complète nécessite seulement 2 mn ou moins encore) et plus exacte que la fusion sous vide et al fusion avec gaz porteur, car tout l'oxygène présent est analysé. Les échantillons peuvent être beaucoup plus importants que les 0,2–3 g utilisés habituellement pour les méthodes de fusion. En outre, l'analyse n'est pas destructive, les mêmes échantillons peuvent être analysés à nouveau aussi souvent qu'on désire. Le système d'analyse par activation de neutrons rapides comprend un générateur de neutrons 14 MeV produisant 10^{11} neutrons/sec, un système de transfert pneumatique à double tube, un cristal de NaI(Tl) de 5 × 5 pouces, un analyseur à canal unique, deux échelles de comptage, et des "timers" et un système de commutation. Un échantillon en flacon de polyéthylène et une référence en Lucite sont irradiés simultanément, après quoi l'échantillon est renvoyé à un détecteur pour le comptage des $\gamma^{16}N$ de la réaction $^{16}O(n, p)^{16}N$. La référence est alors soumise au comptage dans un autre détecteur; le rapport des comptages de l'échantillon et de la référence est proportionnel à la teneur en oxygène de l'échantillon. Les échantillons à teneur en oxygène comprise entre 0,002 et 0,1 % ont été analysés par activation de neutrons, puis coupés en plusieurs morceaux pour analyse par extraction à chaud de l'échantillon total.

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PRECISE TITRIMETRIC DETERMINATION OF URANIUM IN HIGH-PURITY URANIUM COMPOUNDS

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Summary—A procedure has been developed for the very precise determination of uranium in high-purity uranium compounds. Uranium(VI) is reduced in a strong hydrochloric acid solution with aluminium in the presence of cadmium ions to uranium(III). It is oxidised to uranium(IV) in the presence of excess orthophosphoric acid and then quantitatively oxidised to uranium(VI) with potassium dichromate using a potentiometric end-point detection. The coefficient of variation based on 20 analyses is $\mp 0{\cdot}003\,\%$.

INTRODUCTION

FOR preparation of uranium standards, the uranium has to be determined in uranium metal and compounds such as U_3O_8 with a very high precision (at least $\pm 0{\cdot}01\,\%$). It is also very desirable that the method should be simple and easily followed in other laboratories.

A few such methods have been described which approximately meet these demands. In most cases, uranium(VI) is reduced to a mixture of uranium(III) and uranium(IV) and then quantitatively converted to uranium(IV) and finally oxidised to uranium(VI) with potassium dichromate. The instability of uranium(IV) in solution complicates the procedure because of the spontaneous oxidation of detectable quantities to uranium(VI) and this affects the results appreciably. Voss and Green[1] used a Jones reductor followed by oxidation with potassium dichromate; a nitrogen atmosphere was used throughout to prevent unwanted oxidation. Two end-points, corresponding to the oxidation of uranium(III) to uranium(IV) and of uranium(IV) to uranium(VI), were determined potentiometrically. The uranium content was calculated from the difference between the end-points. Vita, Trivisonno and Walker[2] modified this method; after potentiometric determination of the first end-point [uranium(III)-uranium(IV)], they added an excess of potassium dichromate and then determined the excess of chromium(VI) ions colorimetrically. Lerner and Rodden[3] used an electrolytic reduction of uranium and took advantage of the spontaneous oxidation of uranium(III) by hydrogen ions to uranium(IV) while simultaneously controlling the potential and adding an excess of potassium dichromate when this reached the uranium(III)-uranium(IV) end-point. The excess dichromate was determined by titration with iron(II).

According to Volkov[4] solid uranium(IV) phosphate is stable. It is also shown here that uranous ions are stable in solution in the presence of a corresponding amount of orthophosphoric acid. Uranous phosphates, however, are soluble only in concentrated acids and to convert uranium(VI) to uranium(IV) strong hydrochloric acid must be used; the oxygen-containing acids interfere with the reduction. The use of aluminium metal in the presence of cadmium for reduction, as described by Davies,[5]

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proved to be very suitable under these conditions. On this basis the following procedure was developed:

1 Uranium(VI) is reduced to uranium(III) in concentrated hydrochloric acid with aluminium metal in the presence of cadmium ions.

2 Uranium(III) is oxidised spontaneously in the presence of orthophosphoric acid by hydrogen ions, producing a stable uranium(IV) solution.

3 In order to prevent the precipitation of uranium(IV) phosphate, phosphate ion is complexed by ferric ion and the sample diluted to a hydrochloric acid concentration of less than 2*N*. Solid potassium dichromate is added immediately to oxidise the major fraction of the uranium(IV) and the remainder is finally titrated with a dilute potassium dichromate solution using a potentiometric end-point detection.

EXPERIMENTAL

Equipment

pH Meter. "Radiometer" type PHM 22r equipped with platinum electrode type P 101 and saturated calomel electrode type K 100.

Stirrer. Magnetic stirrer with magnetic stirring bar covered with inert plastic.

Microburette. "Metrohm" piston burette, model E 298 or normal microburette graduated to 0·02 ml with a long end to dip into the titrating solution.

Splash head. Special glass splash head (see Fig. 1) for 1000-ml conical flasks with normal socket joint NS 29/32.

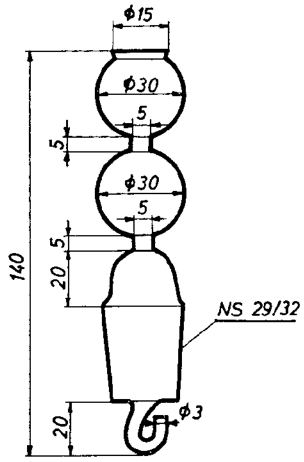

FIG. 1.—Splash head.

Reagents

Use only analytical-grade materials and redistilled water.

Hydrochloric acid (*sp. gr.* 1·19)

Nitric acid (*sp. gr.* 1·40).

Orthophosphoric acid (*sp. gr.* 1·71).

Hydrochloric acid solution, 1*M*.

Cadmium chloride solution, 50%. Dissolve 50 g of $CdCl_2 . H_2O$ in about 50 ml of water and dilute with water to 100 ml.

Ferric chloride solution, 25%. Dissolve 1 kg of $FeCl_3 . 6H_2O$ in about 2 l. of water and dilute with water to 4 l.

Aluminium wire. BDH "Analar", ϕ 0·7 mm.

Potassium dichromate. U.S. National Bureau of Standards, oxidimetric standard No. 136 b. Effective oxidising power 99·98%.

Potassium dichromate solution, 0·05*N*. Dry solid $K_2Cr_2O_7$ NBS Standard for 1 hr at 110°, weigh 2·45160 g (weight corrected to vacuum) to ±0·01 mg, dissolve in about 500 ml of water and dilute with water to 1000 ml at 20°. Mix carefully.

Preparation of samples

Preparation of U_3O_8 *samples.* Heat the sample for 1 hr at 850–880° and allow to cool to room temperature in a desiccator. Place 5·8 to 5·9 g in a stoppered weighing bottle and weigh with an accuracy of ±0·01 mg. Transfer the sample carefully to a 1000-ml Erlenmeyer flask with a standard taper neck, using 20–30 ml of distilled water for washing out the weighing bottle; Add 20 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric acid and stopper the flask with a special splash head (Fig. 1).

Warm the flask on a steam bath and swirl occasionally until the sample dissolves. Next transfer to a hot plate, boil without removing the splash head and evaporate until the formation of the first traces of a solid phase. Next remove the flask from the hot plate for a short time in order to allow the condensate in the splash head to be sucked back into the flask. Evaporate once more to remove nitrate but do not allow the solution to go to dryness. Repeat the evaporation twice more, adding 20 ml of concentrated hydrochloric acid each time through the splash head.

After the third evaporation, remove the flask from the hot plate and dip into cold water, adding simultaneously 30 ml of concentrated hydrochloric acid to the splash head. This flushes the splash head and is also sucked into the flask as a strong spray which washes down the walls of the flask.

Preparation of uranium metal samples. Etch about 5 g of uranium metal in 8*M* nitric acid until the oxide layer is completely removed, wash with distilled water followed by acetone and dry first in air and then for 10 min in a desiccator. Weigh the sample to an accuracy of 0·01 mg, transfer to a 1000-ml Erlenmeyer flask, add 40 ml of 6*M* hydrochloric acid and close with the splash head. Dissolve with occasional agitation. Warm slightly and add 0·5 ml of concentrated nitric acid through the splash head to ensure solution of the small black residue which is often observed. Evaporate three times with hydrochloric acid as described for U_3O_8.

Preparation of UO_2 *or* UO_3 *samples.* UO_2 or UO_3 samples can be weighed without previous treatment. The dissolution of UO_2 samples is the same as for U_3O_8 with the difference that 2 ml of concentrated nitric acid instead of 1 ml are added. UO_3 can be dissolved without the addition of nitric acid and evaporated only once.

Procedure

Weigh, with an accuracy of ±0·01 mg, an amount of solid potassium dichromate corresponding to 12 to 15 mg less than the theoretical quantity needed for the oxidation.

To the sample dissolved in 30 ml of concentrated hydrochloric acid add 1 ml of 50% cadmium chloride solution and 0·75 g of aluminium wire cut into 5-cm pieces. Put the flask closed by the splash head on a steam bath until the solution turns deep red. Wash the splash head with a few ml of 1*M* hydrochloric acid and warm until complete solution of the aluminium wire. Remove the flask from the steam bath, add 15 ml of concentrated orthophosphoric acid through the splash head and boil the solution on a hot plate for 1 min. Again wash out the splash head with a few ml of 1*M* hydrochloric acid and cool the solution to room temperature by dipping the flask into cold water. The solution is now deep green. Remove the splash head, add 100 ml of 25% ferric chloride solution, dilute with 100 ml of 1*M* hydrochloric acid and mix well. Immediately add the previously weighed solid dichromate, stir until it completely dissolves and transfer the clear solution to an 800-ml beaker. The volume should now be about 250 ml. Dip the platinum and calomel electrodes and the tip of the burrette into the liquid and introduce the magnetic stirrer. Titrate with 0·05*N* potassium dichromate using strong stirring. Near the end-point, add the titrant in 0·02-ml aliquots.

Titrate the blank at the same time.

Calculate the uranium content from the total amount of dichromate used, after subtracting the blank and correcting the value for the oxidation power of the dichromate.

Reduce all weighings to vacuum.

Optimum conditions for procedure

Use of splash head. All operations in the flask should be carried out with the splash head (Fig. 1) fitted. This is especially important in all manipulations involving evolution of gases: the dissolution of samples, reduction and oxidation of uranium(III) to uranium(IV) after the addition of phosphoric acid. If the analysis is carried out in open vessels, there is a loss of uranium, which can amount to a few hundreths of a per cent of the total uranium.

Amount of cadmium chloride. The uranium sample ought to be dissolved before the reduction in a small amount of concentrated hydrochloric acid (normally 5 g of the uranium in 20 ml of hydrochloric acid), because the concentration of hydrochloric acid after dilution, *i.e.*, before oxidation with potassium dichromate, cannot be higher than 2*N*. In such a concentrated uranium solution the reduction of uranium(VI) to uranium(IV) with aluminium metal alone does not proceed completely, even when using a large excess of aluminium. In the presence of cadmium ion the reduction goes very quickly, uranium(VI) is reduced to uranium(III) (deep red colour of solution) and the consumption of aluminium metal is not much higher than the theoretically calculated amount (0·113 g of Al/1 g of U). During the reaction the formation of a black precipitate of metallic cadmium is observed on the surface of aluminium. The precipitate is dissolved very rapidly in the solution. This observation suggests the following mechanism of reduction as the most probable:

$$3Cd^{2+} + 2Al^{\circ} \rightarrow 3Cd^{\circ} + 2Al^{3+}$$

$$Cd^{\circ} + U^{6+} \rightarrow Cd^{2+} + U^{4+}$$

$$Cd^{\circ} + 2U^{4+} \rightarrow Cd^{2+} + 2U^{3+}$$

One ml of 50% cadmium chloride sloution was found experimentally to bring about the reduction in 3–5 min. With insufficient cadmium chloride, the reduction is too slow, while with too large an amount, cadmium sponge is formed. This sponge dissolves with difficulty and its remainder can later reduce potassium dichromate to give an error in the determination.

Amount of aluminium metal. Aluminium in the form of wire was found to be most convenient. The optimum quantity is that which gives a stable deep red colour to the uranium solution in a few minutes. An excess is undesirable because of slow dissolution of the metal in the absence of unreduced uranium.

Amount of orthophosphoric acid. Although only a small quantity of phosphoric acid is needed to cause the immediate and quantitative oxidation of uranium(III) to uranium(IV) by hydrogen ions, a distinct excess is necessary to keep uranium(IV) stable. On the other hand, too large an excess can cause an undesirable diminution of the potential difference at the end-point. The quantity given above ensures stability of the uranium(IV) ions for about 1 hr and has no significant influence on the titration. By boiling the solution after the addition of phosphoric acid, the titration proceeds in a better manner.

Amount of ferric chloride. Ferric chloride in large excess entirely prevents the precipitation of uranous phosphate in the diluted hydrochloric acid solution. A minimum amount, however, is desirable to keep any blank correction as small as possible, and the quantity chosen allows only a small amount of gelatinous precipitate to form which readily dissolves during the oxidation with solid potassium dichromate. To prevent entirely the formation of the precipitate, at least twice the recommended quantity of ferric chloride would be required.

Titration. There is about 150 mV potential difference at the end-point on the addition of 0·02 ml of 0·05*N* potassium dichromate. The stabilisation of the potential in the region of the end-point, however, is slow and one should allow about 1 min between additions of the titrant and the reading of the potential change.

DISCUSSION AND RESULTS

It was found that the stability of uranous phosphate in solution depends on the concentration of phosphoric acid. In a 5*M* solution (15 ml of H_3PO_4 added to the sample), the rate of spontaneous oxidation of uranium(IV) to uranium(VI) is 0·0015% of total uranium content per hour. This effect can be explained by the influence of phosphoric acid concentration of the relative values of the formal potential uranium(IV) to uranium(VI).[6] The addition of an excess of ferric chloride to the solution increases its oxidation rate almost 50 times. For this reason dilution of the sample must be followed immediately by the oxidation with with solid dichromate.

The reaction:

$$U(IV) + 2\ Fe(III) \rightleftharpoons U(VI) + 2\ Fe(II)$$

proceeds very slowly to the right in a strong phosphoric acid medium, and is even reversed in very high acid concentrations.[7] When the solution is dilute, however, as in the last stage of the titration, the rate of the direct reaction is rapid and a considerable amount of the remaining uranium(IV) is oxidised by iron(III). Because the amount of ferrous ion produced is equivalent to the uranium(IV) oxidised, the consumption of dichromate is unaffected. The presence of ferrous ion is necessary to obtain a large potential difference at the end-point.

Applicability of procedure

The method is proposed for the very accurate determination of uranium in pure preparations such as uranium standards and similar samples, which do not contain interfering impurities in significant quantities. The elements which could cause interference are those which are reduced and oxidised under the same conditions as uranium (copper, vanadium, titanium, iron, molybdenum, tin, *etc.*). If their total concentrations in the sample exceeds 20 ppm, then corresponding amounts should be added to the blank. The presence of phosphates and perchlorates makes the reduction to uranium(III) or even quantitative reduction to uranium(IV) impossible. Sulphates significantly slow the reduction and can give difficulty soluble precipitates with uranium(IV). Nitrates must be removed before the reduction because their presence would cause an increased consumption of aluminium and also could give involatile reduction products which would later reduce dichromate.

Precision and accuracy

Under normal analytical precautions, the method has a precision better than ±0·01 %. The coefficient of variation calculated from 20 determinations was ±0·003 %. Table I shows two series of the determination of uranium in U_3O_8 in which series 2 was carried out by an analyst who used the method for the first time. The tri-uranium octoxide was prepared from very pure UO_2 by heating to 850°. The total content of impurities did not exceed 20 ppm.

TABLE I.—ANALYSIS OF U_3O_8 SAMPLES

	U_3O_8, %	
	First series	Second series
	99·994	100·004
	99·995	99·994
	99·998	99·999
	99·998	99·992
	100·002	100·000
	99·996	100 001
Average	99·997	99·998

U_3O_8- Standard 950a from the National Bureau of Standards was analysed in order to test the accuracy of the method. The certified value of 99·94 ± 0·02 % is to be compared with the average of results by this method (Table II) of 99·946 %.

TABLE II.—ANALYSIS OF U_3O_8

	N.B.S. Standard sample No. 950a U_3O_8, %
	99·945
	99·946
	99·945
	99·948
	99·945
	99·947
Average	99·946

Acknowledgements—The author wishes to thank Dr. G. B. Cook and Dr. L. Kosta for the suggestion of the theme of this work and fruitful discussions.

Zusammenfassung—Es wurde die hochprezise Uranbestimmungsmethode in reinen Uranpraeparaten bearbeitet. Uran(III) wird in einer stark sauren Salzsaeureloesung mit Aluminium-Metall in Gegenwart der Kadmium-ionen bis Uran(III) reduziert. Uran(III) wird in Gegenwart eines Orto-Phosphorsaeureueberschusses mit Wasserstoffion bis Uran(IV) oxidiert. Quantitative Oxidation bis Uran(VI) wird mit Kaliumdichromat bei potentiometrischer Endpunktbestimmung durchgefuehrt. Variationskoeffizient berechnet auf Grund zwanzig Analysen betraegt ±0,003%.

Résumé—On a élaboré une méthode très précise de dosage d'uranium dans les composés d'uranium de très haute pureté. On réduit l'uranium (VI) dans une solution forte à l'acide chlorhydrique par l'aluminium metallique en présence d'ions de cadmium vers l'uranium(III). Après l'oxidation vers l'uranium(IV) en présence d'un excès de l'acide ortophosphorique on oxidise quantitativement l'uranium(IV) vers l'uranium (VI) par le dichromate de potassium en trouvant la fin d'oxidation par le mode potentiometrique. Le coefficient de variation calculé d'après 20 dosages comporte ±0,003%.

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MICRODETERMINATION OF OXYGEN, CARBON AND WATER IN INORGANIC MATERIALS USING A CARRIER-GAS TECHNIQUE

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Summary—A description is given of the accurate determination of small quantities of oxygen, carbon and water in inorganic compounds. Oxygen and carbon are determined by a conductimetric technique and water by a coulometric technique. The limits of detection of the different methods are: 0·1 μg of oxygen, 0·1 μg of carbon and 0·03 μg of water. This is accomplished by taking special care to obtain a low blank and by using stable instruments. A suggestion is made for the simultaneous determination of water and hydrogen.

INTRODUCTION

THE carrier-gas technique has been used frequently for the determination of oxygen, carbon and water in inorganic materials.[1,2,7,12] Since the introduction of commercial instruments, this technique has become very popular.

In the work described in this paper both oxygen and carbon are converted to carbon dioxide which is determined by a conductimetric method.[3,4,6,8–10] Water is absorbed in a thin layer of phosphorus pentoxide and electrolysed to hydrogen and oxygen. The apparatus used for this determination is the so-called phosphorus pentoxide cell.[13]

Special care has been taken to obtain a high sensitivity. This is necessary for an accurate determination in small samples and for the determination of very small quantities in large samples. To obtain this high sensitivity it is in the first place necessary that in the oxygen determination the concentration of carbon and oxygen compounds in the carrier gas should be very low; in the case of carbon determination, the concentration of carbon compounds in the carrier gas should also be very low; again, in the water determination the carrier gas should be very dry. This has been achieved by thoroughly purifying the carrier gas and by using a gas-tight apparatus. Moreover, the conductimetric carbon dioxide determination must be very sensitive and stable. This has been accomplished by using two identical absorption cells of the construction described by Still *et al.*[7] (placed in a thermostat) for temperature compensation, by equalising the evaporation of water from the cells and by using a highly sensitive measuring bridge (and recorder), fed by a stabilised voltage source. The limit of detection of carbon and oxygen attained is 0·1 μg. A further requirement is that the furnace tubes and crucibles or boats do not give off carbon dioxide during heating.

The carrier gas used for the determination of oxygen is very pure argon, containing less than 0·1 ppm of carbon compounds, water and oxygen. The graphite crucible used for this analysis is placed inside a water-cooled silica tube and is preheated at 2200° by means of a 6-kW high-frequency generator. By suitable matching of coil and crucible the power input is sufficient to obtain this temperature using an unshielded crucible, thus avoiding the use of graphite powder insulation.

The carrier gas used for the determination of carbon is very pure oxygen containing less than 0·1 ppm of carbon compounds. Heating tube and crucibles are manufactured from silica, recrystallised alumina or gas-tight ceramic material. Samples of non-conducting material are burned in a platinum-wire resistance furnace; a 500-W high frequency generator is used for metals requiring a high temperature for burning.

The type of phosphorus pentoxide cell used is the "Beckman electrolytic hygrometer". Its efficiency was found to be 100%. Purified argon was also used as a carrier gas. The limit of detection of water attained is 0·03 μg. The flow rate of the carrier gas is in all cases about 6 litre/hr. Each determination can be carried out in about 10–20 min. It is possible to obtain more detailed information by temperature programming.

For a determination of oxygen the blank is 0·2 μg, for carbon and water <0·1 μg. The blank of a determination of carbon carried out in a high-frequency furnace cannot be made as low as that, and is determined by burning iron, which has a low carbon content.

EXPERIMENTAL

Oxygen determination

The apparatus (Fig. 1) consists of the following elements:

1. Argon gas of high purity from a cylinder, connected by means of a glass to copper seal to a Pyrex glass purification train (2 to 5).

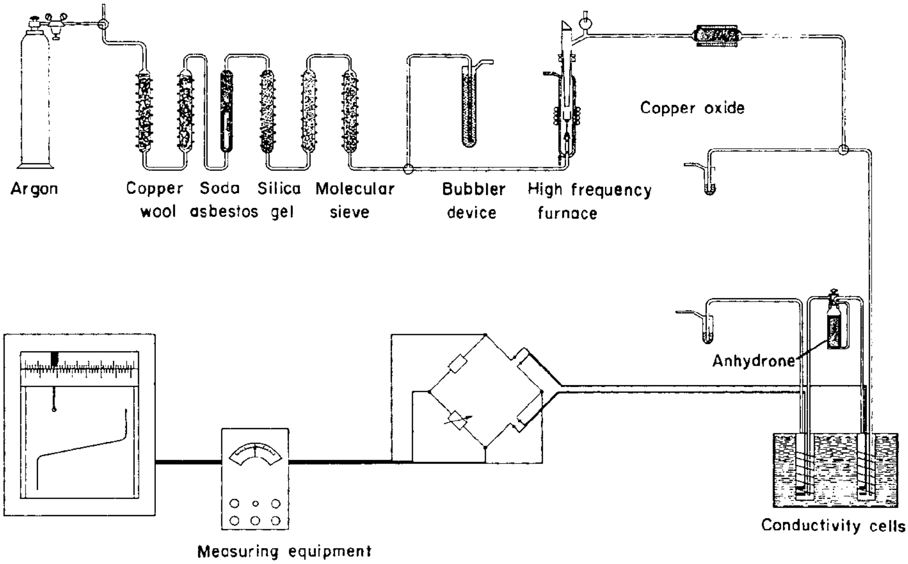

FIG. 1.—Apparatus for determination of oxygen.

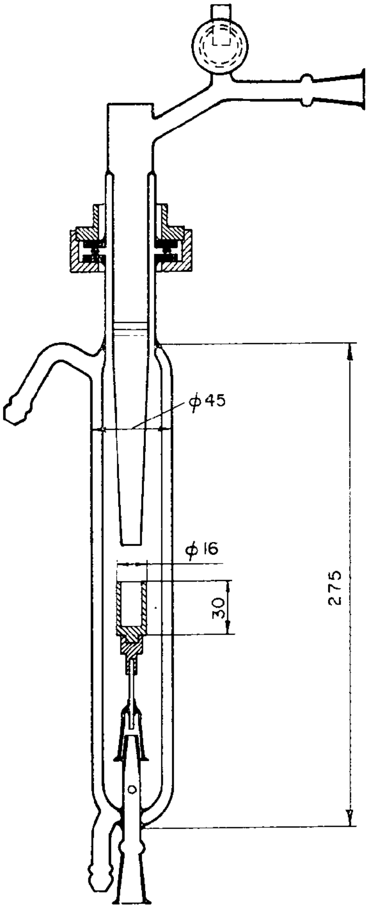

Fig. 2.—Silica tube with graphite crucible (size in mm).

2. Two columns of copper wool (the first part of the first column is oxidised) at 400°, oxidising traces of hydrogen and carbon compounds and eliminating oxygen.
3. A column of soda asbestos (8–14 mesh) at room temperature, eliminating acid gases, *e.g.*, carbon dioxide.
4. A column of silica gel (8–14 mesh) at room temperature (regenerated at 300°).
5. Two columns of molecular sieve 5A at room temperature (regenerated at 300°).
   The last three columns serve to eliminate water.
6. A bubbler device filled with silicone oil Dow Corning 705 Fluid to give a constant gas pressure.
7. A water-cooled silica tube connected to the purification train by means of a ground glass joint greased with Apiezon N or L and containing a graphite crucible (content about 2·5 ml) mounted on a tungsten rod (Fig. 2). The crucible, surrounded by a high-frequency coil on the outside of the water-cooled tube, is heated by means of a 6-kW high-frequency generator (Philips PH 1006/13). To obtain a large range of temperatures the power of the generator is regulated by a variable transformer (0–380 V, 15·6 kVA). By using a 12-kW generator a temperature as

high as 2600° can be reached. A prism on top of the silica tube enables the operator to measure the temperature of the crucible by means of an optical pyrometer.

8. A Teflon stopcock to introduce samples (maximum size: diameter 7 mm, length 13 mm) into the crucible without interrupting the gas flow. In this two-way stopcock fits a massive Teflon plug which has a hole 8 mm in diameter and 15 mm deep. The sample is placed in the hole and is introduced into the crucible by turning the stopcock through 180° (Fig. 2).
9. A Pyrex glass tube filled with granulated activated copper oxide, held at 400°, in which carbon monoxide is converted to carbon dioxide. A plug of silica wool at the entrance of the tube serves to trap traces of evaporated materials.
10. Two conductivity cells placed in series, filled with 0·025*M* caustic soda giving a conductivity of about 10,000 μmho, and separated by a small column of magnesium perchlorate (anhydrone) to equalise water loss in both cells. The cells, placed in a water thermostat at 20° (temperature constancy 0·1°), form two adjacent arms of a Wheatstone bridge which is part of the conductivity measuring system (Philips PT 1200, Direct Reading Measuring Bridge for strain gauges); the other arms of the bridge are a 100-Ω precision resistor and a four-decade resistance box, the latter being placed in the circuit in such a way that the conductivity of the first cell (measuring cell) is read on the dials of the resistance box.
11. A recording millivoltmeter (Philips PR 2210A/21 or PR 2400A/02) is connected to the conductivity measuring system.

Calibration. Calibration of the measuring cell is performed by reducing nickel oxide, sintered at 1200° in air. The nickel content was determined and was found to have the theoretical value within the experimental error (0·2% rel.). The nickel oxide samples (about 1 mg) are weighed on an ultramicro balance (Mettler UM 7).

The maximum amount of carbon dioxide which can be absorbed by the cell without loss of linearity is equivalent to about 2000 μg of oxygen. The following data are representative of the calibration reproducibility. 100·0 μg of oxygen correspond to 83·5, 83·3, 83·7, 83·2, 82·7 and 83·4 μmho.

Samples. Whenever possible a lump of the material to be analysed is used; powders are wrapped in a weighed piece of metal foil, *e.g.*, iron, tin, copper or platinum; if necessary the foil is reduced by hydrogen. The oxygen content of the metal foil is determined separately.

Outgassing and blank. In the first place the graphite crucible is heated at a low temperature to remove large quantities of gases (the heating tube not yet being connected to the copper oxide column). After a while the temperature is raised to 2200°. After outgassing at 2200° for 1 hr the copper oxide column and the cells are connected to the gas stream.

The conductivity of the measuring cell is registered on the recorder as a function of time. A determination is started when the rate of decrease of the conductivity has become sufficiently small.

According to the nature of the sample either the graphite crucible as such or a metal bath in the crucible is used. Metal baths are used, *e.g.*, in the analysis of high melting metals and compounds.[5] For a working temperature of 1500° outgassing for about 4 hr of the crucible at 2200° is needed to reach a blank value of 0·2 μg of oxygen during 10 min, for 2000° about 8 hr at 2200° is needed, for 2200° about 20 hr. The time of outgassing can be reduced by using a temperature of 2600°.

Instead of waiting till the blank is as low as given above, one can evaluate the blank graphically on the recorder chart. The procedure chosen depends on the amount of oxygen in the sample and the sensitivity needed. After the blank has reached the required value the metal bath (if necessary) is prepared by introducing pieces of the metal (total weight 5–10 g) into the crucible *via* the Teflon sampling stopcock, followed by heating at the working temperature until the blank has become low enough. After this the sample can be introduced and its oxygen content measured (Fig. 3).

Carbon determination

The apparatus (Fig. 4) consists of the following elements:

1. Oxygen gas of high purity from a cylinder, connected by means of a glass to copper seal to a Pyrex glass purification train (2 to 4).
2. A column of granulated activated copper oxide at 400°, oxidising traces of carbon compounds.
3. A column of soda asbestos (8–14 mesh) at room temperature, eliminating acid gases, *e.g.*, carbon dioxide.
4. A column of Anhydrone to eliminate water.
5. A bubbler device filled with silicone oil to give a constant gas pressure.

6a. A platinum wire resistance furnace, the temperature of which is regulated by means of a thermostat using the platinum wire as a sensing element. The maximum temperature of the furnace is 1400°. Up to 1100° a silica tube is used in which a tube of recrystallised alumina serves to protect the

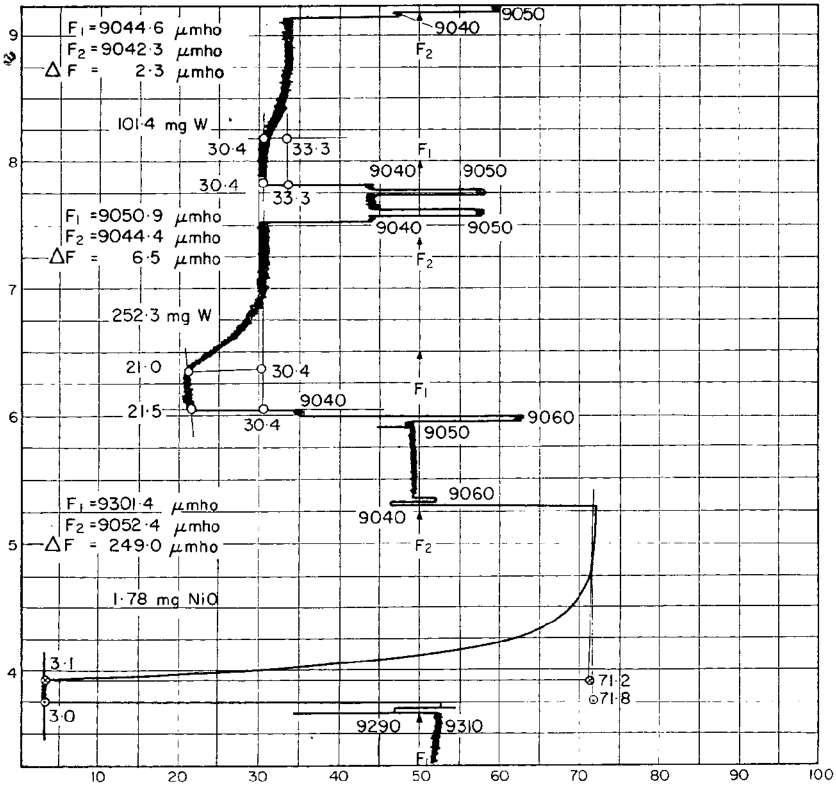

FIG. 3.—Determination of oxygen in tungsten filaments and calibration with nickel oxide. In this figure are illustrated the calibration of the conductivity cell by means of nickel oxide (1·78 mg) and two determinations of oxygen in tungsten filaments (252·3 mg and 101·4 mg). During a calibration or a determination the conductivity of the cell is recorded for controlling the process. The distance between two horizontal lines corresponds to 225 sec. Before and after a calibration or a determination the conductivity of the cell is determined by balancing the measuring bridge (F_1 and F_2). The gas flow rate was 6 litre/hr.

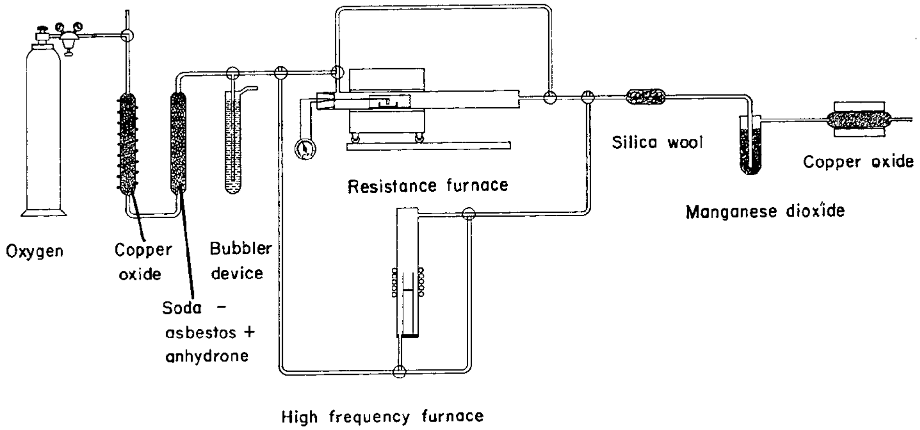

FIG. 4.—Apparatus for determination of carbon.

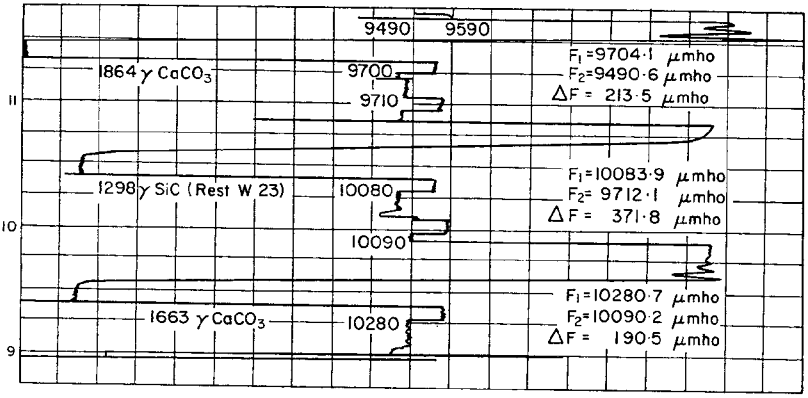

FIG. 5.—Determination of carbon in silicon carbide and calibration with calcium carbonate ($\gamma = \mu g$). In this figure are illustrated two calibrations of the conductivity cell by means of calcium carbonate (primary standard) (1·663 mg and 1·864 mg) and the determination of carbon in silicon carbide (powdered crystals) (1·298 mg). During a calibration or a determination the conductivity of the cell is recorded for controlling the process. The distance between two horizontal lines corresponds to 225 sec. Before and after a calibration or a determination the conductivity of the cell is determined by balancing the measuring bridge (F$_1$ and F$_2$). The gas flow rate was 6 litre/hr.

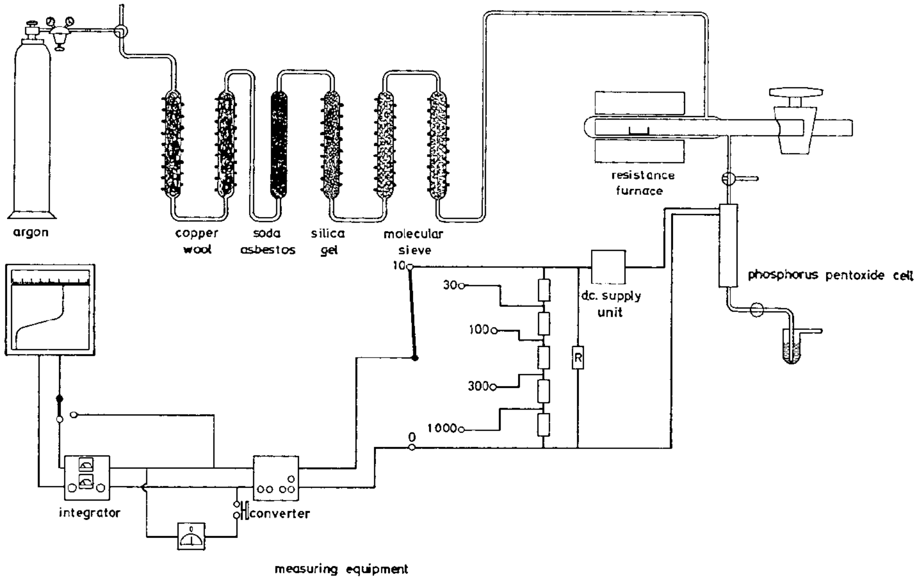

FIG. 6.—Apparatus for determination of water.

silica. Up to 1400° a gas-tight ceramic tube is used. To the ends of this tube Pyrex glass parts have been fused and the whole is connected to the gas train by means of a ground glass joint greased with Apiezon N or L. A bypass enables the operator to introduce samples into the tube without interrupting the gas flow.

6b. A 500-W high-frequency generator instead of 6a for burning metals (Philips PH 1095).

7. A plug of silica wool to filter the gas stream.
8. A column of active manganese dioxide to oxidise and absorb any sulphur dioxide.
9. A column of granulated activated copper oxide at 400°, to oxidise traces of carbon compounds.
10. Two conductivity cells and measuring equipment as described in the section on the determination of oxygen (Fig. 1).

The furnace tube is about twice as long as the furnace and the latter can be moved along the tube. In this way a sample can be introduced into the cold part of the tube, after which the furnace is brought around this part. This is done to ensure that carbon dioxide entering when the sample is introduced does not disturb the determination.

Calibration. Calibration of the measuring cell is performed by heating analytical-reagent grade calcium carbonate (preheated at 500°) at 1000°. The calcium carbonate samples (about 1 mg) are weighed on an ultramicro balance. The following data are representative of the calibration reproducibility. 100·0 μg of carbon correspond to 84·8, 84·6, 84·9, 84·8, 84·8 and 84·4 μmho.

Samples. Samples are burned in either a silica boat or a recrystallised alumina boat with or without accelerator.[8] Several materials need an accelerator for complete oxidation, *e.g.*, silicon carbide powder is oxidised at a temperature of 1050° using lead borate (a melt of 2 g.m.w. of PbO + 1 g.m.w. of B_2O_3), according to Wiebke and Braun.[11] Silica boats are preheated at 1100°, alumina boats at 1700° (in oxygen in a silicon carbide furnace). Metal turnings are used for burning in the high-frequency furnace.

Outgassing and blank. The furnace tube is heated at the working temperature in a stream of oxygen. The outgassing is complete when the rate of decrease of the conductivity has become less than a value corresponding to 0·1 μg of carbon in 10 min. Usually this is the case after a few hours. After this the sample can be introduced and its carbon content measured (Fig. 5).

In case the 500-W high-frequency generator is used for burning metals and alloys, calibration is performed by burning 1 g of a standard sample, *e.g.*, U.S. Bureau of Standards sample 55c (0·010% of carbon). The following data are representative of the calibration reproducibility. 100·0 μg of carbon correspond to 89·3, 89·7, 89·5, 88·8, 89·6 and 89·0 μmho.

The ceramic crucibles are preheated for several hours at 1200° immediately before use (Kantal furnace). The blank is determined by burning a 1-g sample of pure iron turnings having a low and known carbon content.

Water determination

The apparatus (Fig. 6) consists of the following elements:

1 to 5. As used in the section on determination of oxygen.

6. A silica tube for heating samples connected to the purification train by means of a ground glass joint greased with Apiezon N or L. The tube is heated by a small resistance furnace, the temperature of which is regulated as described in the section on determination of carbon (6a).
7. A phosphorus pentoxide cell as described by Keidel for water determination (Beckman electrolytic hygrometer cell, cat. no. 76285), connected to glass tubing by means of a glass-metal joint and built in a Pyrex glass tube for gas-tightness (Fig. 7). The coulometric water determination is performed in the following way. The electrolytic current through the cell is transformed into a voltage proportional to this current (using precision resistors); the voltage is amplified by a mV/mA converter (Philips PR 9603), the output of which is fed into an integrator (Philips 110·832/01). A miniature recorder (Philips PR 2400A/02) registers either the voltage (water content of the gas stream) or the integrated voltage (total amount of water).

Control of cell calibration. The efficiency of the system is determined by heating 100–1000 μg of analytical-reagent grade nickel sulphate heptahydrate (stored above a saturated solution of nickel sulphate) to 150°. The nickel content of the samples was determined and was found to have the theoretical value within the experimental error (0·2% rel.). The samples were weighed on an ultramicro balance. Using a rate of gas flow of 6 litre/hr and the amount of sample given, the cell efficiency was found to be 100% within 1%.

Samples. The material to be analysed was placed in a small platinum boat, preheated at 1000°, or in a recrystallised alumina boat, preheated at 1700°.

Outgassing and blank. The furnace is heated to a temperature which is somewhat higher than the working temperature, until the water content of the gas has again fallen to 0·1 ppm (flow rate 6 litre/hr).

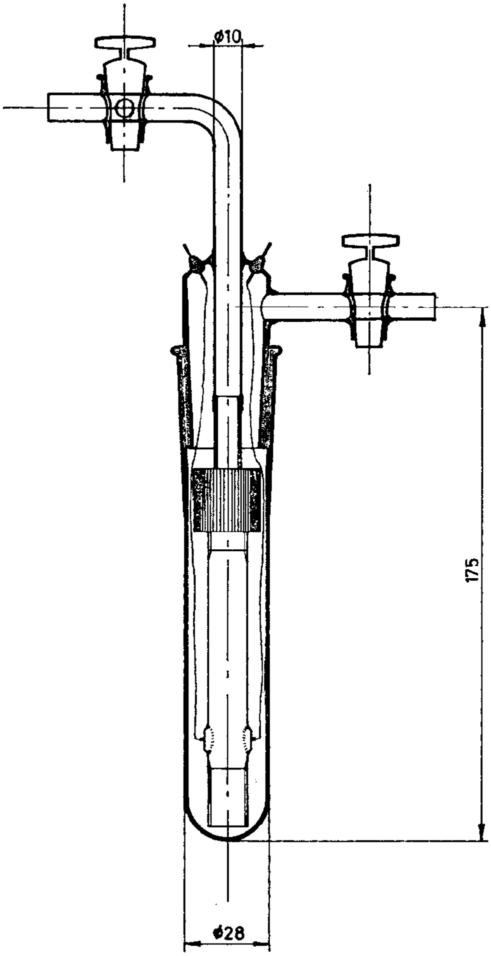

FIG. 7.—Phosphorus pentoxide cell in Pyrex glass tube.

After this the sample can be introduced and its water content measured (Fig. 8). After regeneration of the purification train it takes about 4 days of continuous flow before a level of 0·1 ppm of water content is reached.

Determination of hydrogen in samples can be carried out by placing a column of granulated activated copper oxide at 400° behind the phosphorus pentoxide cell, followed by a second cell in the water determination line and measuring the water in the first cell and the sum of hydrogen and water in the second cell.

A second possibility for the determination of hydrogen is to place the phosphorus pentoxide cell in the oxygen determination line between elements 9 and 10.

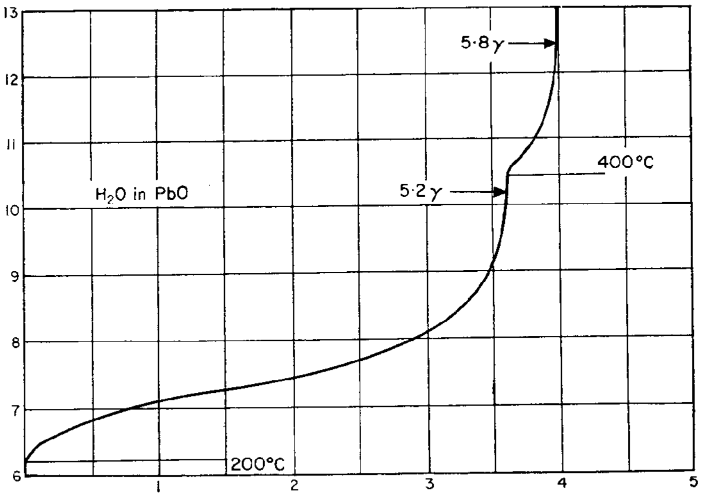

Fig. 8.—Determination of water in lead oxide ($\gamma = \mu g$). In this figure is illustrated the determination of water in lead oxide. In this particular experiment the full scale sensitivity is 0·00725 mg of water. At 200° 0·0052 mg of water is liberated, at 400° another 0·0006 mg of water is found. The distance between two horizontal lines corresponds to 600 sec. The gas flow rate was 6 litre/hr.

RESULTS

In Tables I, II and III a number of examples are given, respectively, of oxygen, carbon and water determinations in different materials.

Table I.—Oxygen determination*

(Before the oxygen in a sample is determined it is verified that the corresponding oxide is reduced quantitatively.)

Sample		Weight, *mg*	Bath	Temperature, °*C*	Oxygen content, %
MnSb	crystal	100	tin	1500	0·20–0·20–0·20–0·21
W	powder	50	iron	1750	1·3–1·4
FeN	powder	20	iron	1750	2·03–2·04
Mo	powder	1	iron	1750	0·27–0·27
Ti	powder	1	platinum	2000	20·6–20·7
Ti	wire	500	platinum	2000	0·18–0·18
B_2O_3	crystal	0·5	platinum	2000	69·1–69·2
ZnO	powder	1	platinum	2000	19·6–20·1
NbSn	powder	10	platinum	2000	3·1–2·9
NbZr	rod	150	platinum	2000	0·18–0·18–0·20
KCl	crystal	100	—	1500	0·0034–0·0035
Sn	foil	100	—	1500	0·020–0·020–0·021
In	rod	500	tin	1500	0·022–0·022–0·024
GaAs	crystal	500	tin	1500	0·0001–0·0002–0·0002
GaP	crystal	200	tin	1500	0·0005–0·0005
cathode	nickel tube	500	—	1750	0·002–0·003
Mo	rod	500	iron	1750	0·0029–0·0031
Fe	rod	500	—	1750	0·010–0·010
W	filaments	100–250	iron	1750	0·0035–0·0040
GeAlIn	alloy	200	platinum	2000	0·0005–0·0007
V	foil	200	platinum	2000	0·071–0·072
Pt	foil	100	—	2000	0·021–0·022
Nb	wire	150	platinum	2000	0·024–0·025

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* Our sincere thanks are due to Mr. A. v.d. Aalst for carrying out the experiments.

TABLE II.—CARBON DETERMINATION*

Sample	Weight, *mg*	Boat	Accelerator	Temperature, °*C*	Carbon content, %
SiC crystal (powder)	1	alumina	2PbO + $1B_2O_3$ 30 mg[11]	1050	30·0–30·0–30·0
Steel NBS11d (0·202% C)	50	ceramic	Fe 1000 mg	(HF)	0·210
Steel NBS10d (0·419% C)	30	ceramic	Fe 1000 mg	(HF)	0·415
Steel NBS 8g (0·069% C)	100	ceramic	Fe 1000 mg	(HF)	0·068
P powder	100	silica		1000	0·0001–0·0002–0·0003
GaP crystal	100	alumina	2PbO + $1B_2O_3$ 300 mg	1050	0·0008–0·0009
Mo sheet	1000	ceramic	—	(HF)	0·0017–0·0018
Fe	1000	ceramic	—	(HF)	0·0010–0·0011
PbO	500	silica	—	1000	0·060–0·060
ZnS	500	silica	—	1000	0·0097–0·0099
W-filaments	500	silica	—	1000	ranging from 0·0010–0·0020

* Our sincere thanks are due to Mr. F. de Groot and Mr. A. de Ridder for carrying out the experiments.

TABLE III.—WATER DETERMINATION

Sample	Weight, *mg*	Boat	Temperature, °*C*	Water content, %
$NiSO_4{\cdot}7H_2O$ crystal	0·5	platinum	150	44·3–44·7
PbO crystal	20	alumina	950	0·13–0·15
Silicone grease	40	silica	200	0·06–0·07
Silicone grease	40	silica	200	0·011–0·010
$CsCoJ_4$ crystal	2	platinum	400	0·05–0·03
NaJ clear crystal	200	platinum	700	0·0001
NaJ cloudy crystal	200	platinum	700	0·0004

TABLE IV.—INFORMATION ABOUT TEMPERATURES AND BATHS USED IN THE ANALYSIS OF METALS AND OTHER INORGANIC MATERIALS

Metals	Oxides	Bath	Temperature, °*C*	Other materials	Bath	Temperature, °*C*
Ag	—	—	1500	CaF_2	—	1500
As	As_2O_3	Sn	1500	KCl	—	1500
Cu	CuO	—	1500	GaAs	Sn	1500
Ga	Ga_2O_3	Sn	1500	GaP	Sn	1500
Ge	GeO_2	Sn	1500	Li_3N	Sn	1500
In	In_2O_3	Sn	1500	MnSb	Sn	1500
Mn	Mn_3O_4	Sn	1500	FeN	Fe	1750
Pb	PbO	Sn	1500	AlN	Pt	2000
Sb	Sb_2O_3	Sn	1500	BN	Pt	2000
Si	SiO_2	Cu or Sn	1500	Be_3N_2	Pt	2150
Sn	SnO_2	—	1500	GeAlIn	Pt	2000
Co	—	—	1750	NbZr	Pt	2000
Fe	Fe_2O_3	—	1750	WZr	Pt	2000
Mo	MoO_3	Fe	1750			
Ni	NiO	—	1750			
W	WO_3	Fe	1750			
Al	Al_2O_3	Pt	2000			
B	B_2O_3	Pt	2000			
Be	BeO	Pt	2150			
Cd	CdO	Pt	2000			
Mg	MgO	Pt	2150			
Nb	Nb_2O_5	Pt	2000			
Pt	—	—	2000			
Ru	RuO_2	Pt	2000			
Ta	Ta_2O_5	Pt	2000			
Ti	TiO_2	Pt	2000			
V	V_2O_5	Pt	2000			
Zn	ZnO	Pt	2000			
Zr	ZrO_2	Pt	2000			

Zusammenfassung—Die genaue Bestimmung kleiner Mengen Sauerstoff, Kohlenstoff und Wasser in anorganischen Substanzen wird beschrieben. Sauerstoff und Kohlenstoff werden konduktometrisch, Wasser coulometrisch bestimmt. Die Nachweisgrenzen der Methoden sind 0·1 μg Sauerstoff, 0·1 μg Kohlenstoff und 0·03 μg Wasser. Dies wird erreicht durch besondere Sorgfalt beim herstellen eines möglichst niedrigen Blindwerts und durch stabile Anzeigeinstrumente. Für die gleichzeitige Bestimmung von Wasser und Wasserstoff wird ein Vorschlag gemacht.

Résumé—On décrit le dosage précis de petites quantités d'oxygène, carbone et eau dans les composés inorganiques. On dose l'oxygène et le carbone par une technique conductimétrique et l'eau par une technique coulométrique. Les limites de détection selon les différentes méthodes sont: 0,1 μg pour l'oxygène, 0,1 μg pour le carbone et 0,03 μg pour l'eau. Ceci est réalisé en prenant un soin spécial pour l'obtention d'un témoin faible et en utilisant des instruments stables. On présente une suggestion pour le dosage simultané de l'eau et de l'hydrogène.

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TALANTA REVIEW*

SEPARATION OF TRANSPLUTONIUM ELEMENTS

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Summary—A critical review of the group separation of tervalent lanthanides and actinides and of the separation of individual transplutonium elements is presented. The theoretical principles involved are also discussed.

Transplutonium elements, TP, can be generally produced by two methods: (a) by irradiation of uranium or plutonium by neutrons in a nuclear reactor or in thermonuclear explosion, (b) by irradiation of uranium, plutonium or lighter TP by accelerated ions of helium, carbon, oxygen, neon, *etc.* In all these nuclear reactions fission products are formed in great yield as well as the TP. The separation of TP from the majority of the fission products, with the exception of the lanthanides, can be easily achieved using common chemical methods. However, the separation of TP from lanthanides and the separation of adjacent TP is a more complicated task. Because TP are predominantly tripositive in solution, oxidation and reduction cycles are of limited utility as are most conventional chemical separations individual TP have a great resemblance. Further, in many cases the TP are very short lived and are obtained in exceedingly low yield. For these reasons highly specific and rapid methods are necessary for their separation.

The aim of the present paper is to give a review of newer methods for separation of TP, especially ion exchange and solvent extraction. Older methods used for this purpose are described in detail in the excellent monographs of Seaborg and Katz.[34,71]

PRECIPITATION

Precipitation methods are generally used for separation of TP from the majority of fission products. After addition of lanthanum or cerium as carrier for TP ($\sim$0·1 mg/ml of solution) the tervalent actinides can be precipitated by hydrofluoric acid (the equilibrium concentration of hydrofluoric acid should be approximately 1–3M). Similarly TP can be coprecipitated with lanthanum oxalate at pH 0–2 (equilibrium concentration of oxalic acid should be 0·1M) or with bismuth phosphate in the presence of 0·1M perchloric acid.[34,71] If neptunium or plutonium is present it is advantageous to oxidise these elements using suitable oxidising agents (*e.g.*, dichromate, permanganate) before the precipitation of TP.

For isolation of greater amounts of americium from lanthanides and other TP can be used the oxidation of americium to the quinquevalent state [in a 30% solution of potassium carbonate Am(III) is slowly oxidised by 0·1M sodium

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

hypochlorite to Am(V), which is precipitated as $K_5AmO_2(CO_3)_3]$ or to the sexivalent state [Am(VI) is not precipitated by hydrofluoric acid].[34,71]

In the past the separation of TP from lanthanides has been achieved by precipitation with fluorosilicic acid in a nitric acid medium.[34,71] However, this method has now been replaced by more selective ion-exchange or solvent-extraction methods.

ION EXCHANGE

During the past fifteen years ion exchange has developed into the most powerful method for separation of TP from lanthanides as well as for separation of adjacent TP. Using this method it was possible to make the chemical identification of five new TP (berkelium, californium, einsteinium, fermium and mendelevium).

Cation-exchange resins

The separation of TP on cation-exchange resins involves two major steps: (a) sorption of the mixture of TP by resin from a solution, (b) selective desorption of individual elements by an appropriate eluting solution.

For the sorption of tervalent TP by a cation-exchange resin the reaction may be written:[70]

$$M^{3+} + 3NH_4R \rightleftharpoons MR_3 + 3NH_4^+ \tag{1}$$

where R is the resin anion.

From the equilibrium constant of this reaction*

$$K_{c.ex} = \frac{[MR_3][NH_4]^3}{[M][NH_4R]^3} = \varphi_0 \frac{[NH_4]^3}{[NH_4R]^3} \tag{2}$$

it follows, that the distribution coefficient φ_0 decreases as the third power of the [ammonium] concentration. For instance, the value φ_0 (g.ml^{-1}) of americium and curium between cation exchanger Amberlite IR-120 and aqueous phase is equal to $1{\cdot}8 \times 10^5$ at ionic strength $\mu = 0{\cdot}2$ and $1{\cdot}0 \times 10^4$ at $\mu = 0{\cdot}5$.[93] For this reason, the transfer of the mixture of TP to the resin is best done in a solution of very low ionic strength.

The simplest type of desorption, *i.e.*, the displacement of TP by a sufficiently high concentration of a cation, such as hydrogen ion, is not applicable because of low differences in φ_0 of adjacent TP.† However, in the presence of a complexing agent H_vB which forms with TP neutral or negatively charged complexes of the type MB_n, the distribution ratio φ between cation exchanger and aqueous phase will be expressed by the following equation:

$$\varphi = \frac{[MR_3]}{[M] + [MB_n]} = \frac{\varphi_0}{1 + \beta_n[B]^n} \tag{3}$$

where β_n is the stability constant of complex MB_n. [B] is the equilibrium concentration of the anion of the complexing agent. From equation (3) it is evident that the amount of TP in the resin phase decreases with the increase of stability constant or concentration of the anion B.

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* For simplicity in this and following equations the charges will be omitted.

† From analogy with lanthanides it can be expected that the values φ_0 of TP will decrease with increase of atomic number Z.[86]

The separation factor, S^z_{z+1}, of two adjacent TP can be expressed as follows

$$S^z_{z+1} = \frac{\varphi_z}{\varphi_{z+1}} = \frac{\varphi_{0,z}(1 + \beta_{n,z+1}[B]^n)}{\varphi_{0,z+1}(1 + \beta_{n,z}[B]^n)} \tag{4}$$

As it can be seen from equation (4) the separation factor is determined to a first approximation by the ratio of the stability constants of the separated elements

$$\left(\frac{\varphi_{0,z}}{\varphi_{0,z+1}} \sim 1 \qquad \text{and} \qquad \beta_n[B]^n \gg 1\right).$$

By the elution of a mixture of TP the sorption and desorption processes are repeated many times. The volume of eluting agent, $\bar{v}$, which has passed through the resin bed, when the concentration of the element investigated in the eluate is a maximum, can be easily calculated from the equation[70]

$$\bar{v} = W \cdot \varphi + v_0 \tag{5}$$

where W is the weight of the ion exchanger in the column and v_0 = free column volume. From equation (5) it follows that the value $\bar{v}$ decreases with the decrease of φ, *i.e.*, with the increase of stability constant β_n [equation (3)]. Because the stability of complexes of tervalent TP and lanthanides with complexing agents in general increase with an increase of their atomic number Z (Table I), the heavier TP or lanthanides will be eluted from a cation-exchange column faster than the lighter.

Complexing agents for the separation of TP may be inorganic as well as organic acids and their salts. Street and Seaborg[16,85] have found that a group separation of the TP is possible by elution with 13·3*M* hydrochloric acid or with a 20% solution of ethanol saturated by gaseous hydrogen chloride. TP form more stable complexes than lanthanides and for this reason all tervalent TP are eluted from a column of Dowex-50 resin faster than the heaviest lanthanides. Analogously, the group separation of TP can be accomplished with a 1·8*M* solution of ammonium thiocyanate;[16,86] however, the separation is not so effective as in the case of hydrochloric acid. The difference between the stability constants of chloride or thiocyanate complexes of TP is not great enough to permit easy purification of a complex mixture. The complexing agent which received the earliest study for the separation of TP was citric acid (~0·2*M*), partly neutralised by ammonia.[8,71,88,89] Citric acid (H_3Cit) forms with americium in a slightly acid medium complexes of the type $M(H_2Cit)_3$, and in neutral or a slightly alkaline medium complexes of the type $M(Cit)_3^{3-}$.[23] Complexes of this type are formed also with lanthanides[77,90] and probably with heavier TP.

The elution position of each TP relative to gadolinium (gadolinium number) and separation factor between neighbouring TP are given in Table II. Because of the long time required for the elution of a given element (several hours or days) the citric acid was replaced by lactic acid,[8,10,43,69] glycolic acid[84] and especially α-hydroxyisobutyric acid (0·1–0·4*M*)[8,11,20,45,76] partly neutralised by ammonia. Complexing agents of this type form with TP complexes of the type MB_3.

From Table II, it is evident that TP are eluted simultaneously with the lanthanides (*e.g.*, americium with promethium, curium with samarium, *etc.*), which have to be separated by another method.

From the stability constants of lanthanides with various α-hydroxycarboxylic acids it follows that it is not to be expected that they will separate lanthanides or TP more effectively than α-hydroxyisobutyric acid. However, in organic-aqueous solutions (*e.g.*, dioxan-water, acetone-water, *etc.*) the ratio of stability constants of complexes of lanthanides (and consequently, the separation factor) increases.[92] It can also be expected that using organic-aqueous solutions of complexing agents the separation of TP will be more effective than in the case of aqueous solution.

TABLE I.—STABILITY CONSTANTS OF TRANSPLUTONIUM AND RARE EARTH ELEMENTS WITH VARIOUS COMPLEXING AGENTS

	HLact[a]	HBut[b]	H_2Tart[c]	H_2Oxal[d]	H_3X[e]		H_4Y[f]	H_4Z[g]	H_5T[h]
Element	$\log \beta_3$ $\mu = 0·5$	$\log \beta_3$ $\mu = 0·5$	$\log \beta_2$ $\mu = 0·1$	$\log \beta_3$ $\mu = 0·1$	$\log \beta_1$ $\mu = 0·1$	$\log \beta_2$ $\mu = 0·1$	$\log \beta_1$ $\mu = 0·1$	$\log \beta_1$ $\mu = 0·1$	$\log \beta_1$ $\mu = 0·1$
Am	5·70	6·1	6·78	11·8	10·7	19·71	16·91	18·21	23·2
Cm	5·75	6·2	6·84	12·1	11·0	20·13	17·10	18·35	23·3
Bk	(5·9)[i]	(6·6)[i]					(17·7)[i]		23·1
Cf	6·08	(6·9)[i]	6·8	12·5	11·3	21·0	17·9		22·6
Es	(6·25)[i]	(7·05)[i]							
Fm	6·36	(7·31)[i]	6·8						
	$\mu = 0·2$	$\mu = 0·2$	$\mu = 0·06$	$\mu = 0·1$	$\mu = 0·1$	$\mu = 0·1$	$\mu = 0·1$	$\mu = 0·1$	$\mu = 0·1$
La		5·00	6·02		10·47	17·84	15·5	16·26	19·48
Ce	5·32	5·39	6·32		10·70	18·68	15·98	16·76	20·5
Pr	5·13	5·77			10·88	19·06	16·40	17·31	21·07
Nd	5·37	6·16			11·11	19·54	16·61	17·68	21·60
Pm			6·8	11·8	~11	19·74	16·94	18·17	
Sm	5·77	6·44			11·33	20·43	17·14	18·38	22·34
Eu	5·83	6·62	6·79	12·1		20·42	17·34	18·51	22·39
Gd	5·98	6·79			11·43	20·78	17·38	18·77	22·46
Tb	6·09	7·08	7·06				17·81	19·50	22·71
Dy	6·14	7·34			11·61	21·01	18·30	19·69	22·82
Ho	6·47	7·59					18·74		22·78
Er	6·70	7·71					18·98	20·68	22·74
Tm	6·75	7·94	7·53				19·32	20·96	
Yb	6·93	8·20			12·08	21·13	19·51	21·12	
Lu	7·16	8·39		12·8[j]			19·83	21·51	

[a] Lactic acid, see refs. 15 and 18.
[b] α-Hydroxyisobutyric acid, see refs. 15 and 82.
[c] Tartaric acid, see refs. 40, 41, 79–82.
[d] Oxalic acid, see refs. 72, 79, 80 and 82.
[e] Nitrilotriacetic acid, see refs. 1, 6, 37, 79–82.
[f] Ethylenediaminetetra-acetic acid, see refs. 6, 79–82.
[g] 1,2-Diaminocyclohexanetetra-acetic acid, see refs. 6, 79 and 80.
[h] Diethylenetriaminepenta-acetic acid, see refs. 46 and 57.
[i] Estimated from ion-exchange data.
[j] $\mu = 1·0$.

For the separation of americium and curium tartaric acid can be used;[24] this agent is not suitable for separation of heavier TP (see Table I). The use of oxalic acid as an eluting agent is of limited value because of the low solubility of the oxalates of TP.

Theoretically, the highest separation factors can be expected when aminopolyacetic acids are used as eluting agents (see Table I). Fuger[19] used ethylenediaminetetra-acetic acid ($0·001M$, pH = 2·35, $\mu = 0·1$, 80°) for separation of americium (Gd. No. ~1·2), curium (Gd. No. ~1·1), berkelium (Gd. No. ~0·5) and californium (Gd. No. ~0·25). For a highly selective separation of californium from curium hydroxyethylenetriacetic

TABLE II.—GADOLINIUM NUMBERS AND SEPARATION FACTORS OF TRANSPLUTONIUM AND RARE EARTH ELEMENTS ON DOWEX-50 IN THE PRESENCE OF SOME COMPLEXING AGENTS

	H_3Cit[a]		HLact[b]		HGlyc[c]		HBut[d]			
	87°		90°		20°		87°		20°	
Element	Gd. No.	S.[e]	Gd. No.	S.	Gd. No.	S.	Gd. No.	S.	Gd. No.	S.
Am	1·80		2·27		1·45		5·0		6·3	
		1·20		1·21		1·25		1·45		1·4
Cm	1·50		1·87		1·16		3·45		4·55	
		1·63		1·54				2·22		2·7
Bk	0·92		1·21				1·63		1·68	
		1·42		1·58				2·25		2·0
Cf	0·65		0·77		0·543		0·76		0·86	
		1·2		1·24		1·20		1·54		1·46
Es	0·54		0·62		0·457		0·49		0·59	
		1·2		1·77				1·84		
Fm	0·45		0·35				0·264			
		1·18		1·3				1·4		
Md	0·38		0·27				0·189			
La			11·8		15·45		34·10			
				1·83		1·64		2·2		
Ce	4·0		6·47		7·93		16·7		15·5	
		1·69		1·73		2·2		1·6		
Pr	2·37		3·74		3·60		10·45			
		1·18		1·36		1·37		1·57		
Nd	2·0		2·74		2·63		6·6		10·45	
		1·09		1·33		1·83		1·61		2·0
Pm	1·83		2·06		1·44		4·10		5·00	
		1·38		1·32		1·33		1·82		1·57
Sm	1·32		1·56		1·08		2·25		3·18	
		1·19		1·28		1·08		1·6		2·06
Eu	1·12		1·22		1·00		1·40		1·54	
		1·12		1·22		1·00		1·4		1·54
Gd	1·00		1·00		1·00		1·00		1·00	
		1·37		1·73		1·08		2·2		1·57
Tb	0·73		0·572		0·93		0·49		0·64	
		1·40		1·56		1·04		1·88		1·84
Dy	0·52		0·366		0·89		0·26		0·346	
		1·37		1·38		1·23		1·62		1·95
Ho	0·38		0·266		0·725		0·16		0·177	
		1·58		1·52		1·28		1·23		
Er	0·24		0·175		0·566		0·13			
		1·60		1·47		1·4		1·30		
Tm	0·16		0·119		0·405		0·10		0·10	
		1·53		1·43		1·37		1·33		1·37
Yb	0·105		0·083		0·295		0·075		0·073	
		1·31		1·31		1·33		1·36		1·45
Lu	0·08		0·63		0·222		0·055		0·050	

[a] Citric acid, see refs, 8, 71, 88 and 89.
[b] Lactic acid, see refs, 8, 10 and 69.
[c] Glycolic acid, see refs, 84.
[d] α-Hydroxyisobutyric acid, see refs, 8, 11 and 76.
[e] Separation factor.

acid has been recommended.[19] Diethylenetriaminepenta-acetic acid was used for separation of gram amounts of promethium from americium[51] (the stability constant of the complex with promethium is ten-times higher than that with americium, Table I). A high separation factor for TP can also be expected using nitrilotriacetic acid or 1,2-diaminocyclohexanetetra-acetic acid (Table I). Some disadvantages of using aminopolyacetic acids lies in the low solubility of these acids in an acidic medium and in the slow establishment of the chemical equilibrium.

Anion-exchange resins

For the separation of TP on anion-exchange resins it is necessary to convert these elements into anionic complexes, which after sorption on the resin can be selectively eluted by a solution of suitable complexing agent. For the sorption of an anionic complex of type MB_n the following equation can be written:

$$MB_n + RB \rightleftharpoons RMB_n + B \tag{6}$$

The equilibrium constant of this reaction is

$$K_{a.ex.} = \frac{[RMB_n][B]}{[MB_n][RB]} = \frac{[RMB_n]}{\beta_n[M][B]^{n-1}[RB]} \tag{7}$$

The higher the stability constant β_n or equilibrium concentration of anion B, the greater the amount of anionic complex transferred into the resin phase. The elements which form, with the complexing agent used, the weakest complexes are eluted from the anion-exchange column faster than elements forming stronger complexes. For instance, $13M$ hydrochloric acid elutes americium and curium before berkelium and californium, which form more stable chloride complexes than lighter TP.[71] This effect has subsequently been found to be more pronounced in concentrated lithium chloride solution. Hulet, Gutmacher and Coops[30] found an excellent lanthanide-actinide separation as well as separation of TP (two member groups) using $10M$ lithium chloride acidified to $0{\cdot}1M$ in hydrochloric acid. Under these conditions lanthanides elute very quickly, and essentially as a group, while TP are retained by the resin (Table III).

Surls and Choppin[87] have studied the anion-exchange behaviour of the TP and lanthanides in thiocyanate solution. The less stable thiocyanate complexes of lanthanides can be easily separated from TP (Table III). This method was used for the separation of gram amounts of americium from large quantities of light rare earths using Dowex-1 and $5M$ ammonium thiocyanate.[13]

Very interesting results have been obtained in the anion-exchange resin–nitrate systems. Marcus and Nelson[42] have obtained an excellent separation of a complex mixture of light rare earths; these elements are eluted in order of decreasing atomic number Z, which is the same sequence shown on cation-exchange column elutions and the reverse of that with lithium chloride or ammonium thiocyanate anion exchange. The same order of elution can be expected from distribution ratios of TP in this system.[55] From Table III it can be seen that using nitrate it is impossible to separate TP from lanthanides; however, the separation factor for the americium-curium pair is relatively high (2·15). A still higher separation factor (3·25) for this pair can be obtained using nitric acid solution in methanol.[29]

The use of organic reagents for the separation of TP on an anion-exchange column has not been investigated.

TABLE III.—GADOLINIUM NUMBER AND SEPARATION FACTOR OF TRANSPLUTONIUM AND RARE EARTH ELEMENTS ON DOWEX-1 USING INORGANIC COMPLEXING AGENTS

Element	LiCl, $10M$[a] 87°		$LiNO_3$, $4·4M$[b]		NH_4CNS, $2M$[c] 20°	
	Gd. No.	S.	Gd. No.	S.	Gd. No.	S.
Am	7·7		4·5		7·2	
		0·82		2·15		1·16
Cm	9·1		2·1		6·2	
		1·08				0·67
Bk	8·4				9·2	
		0·35				0·87
Cf	24		1·8		10·5	
		0·64		1·0		1·1
Es	38		1·8		9·0	
		1·05		0·95		0·9
Fm	36		1·9		10·0	
La	0·50		12			
		0·69		1·71		
Ce	0·72		7		0·46	
		0·80		1·4		
Pr	0·90		5			
		0·98		1·66		
Nd	0·92		3			
				1·5		
Pm			2		0·77	
				1·33		
Sm	1·3		1·5			
		1·0		1·5		
Eu	1·3		1·0		1·0	
		1·3		1·0		1·0
Gd	1·0		1·0		1·0	
		0·86				1·0
Tb	1·16				1·0	
		0·91				0·88
Dy	1·27				0·88	
		1·02				1·0
Ho	1·24				0·88	
		0·95				
Er	1·30					
		0·93				
Tm	1·38				0·92	
		0·85				
Yb	1·62					
		0·98				
Lu	1·64		0·7		1·08	

[a] Ref. 30.

[b] Refs. 42 and 55.

[c] Ref. 87.

SOLVENT EXTRACTION

The only simple salt of TP extractable by organic solvents is $AmO_2(NO_3)_2$.[34] However, the complexes of TP as ion-association complexes or chelates can be readily extracted into a variety of solvents. Solvent extraction can be used not only for group separation of lanthanides-actinides but also for selective isolation of adjacent TP using extraction chromatography.

Extraction of ion-association complexes

One of the oldest reagents used for extractive isolation of TP is tributyl phosphate (TBP). The extraction of tervalent actinides and lanthanides from nitric acid can be described by the following equation:[28]

$$M^{3+} + 3NO_3^- + 3(TBP)_{org} \rightleftharpoons [M(NO_3)_3(TBP)_3]_{org} \tag{8}$$

where the subscript *org* denotes the organic phase.

The extraction constant K_{ex} can be expressed as follows

$$K_{ex} = \frac{[M(NO_3)_3(TBP)_3]_{org}}{[M][NO_3]^3[TBP]^3_{org}} \tag{9}$$

From equation (9) it is evident that for reaching the maximum of extractibility of the element investigated it is necessary to use a high concentration of nitrate ions in the aqueous phase (or chloride ions if the metal is extracted as $[MCl_3(TBP)_3]$) and a high concentration of TBP in the organic phase.

Peppard and coworkers[58] concluded that the logarithm of the extraction constant K_{ex} was an increasing linear function of atomic number Z of the lighter rare earths using 100% TBP and 15·6*M* nitric acid. The separation factor between adjacent lanthanides was reported as 1·9. Gray and Thompson,[25] Best *et al.*[5] and recently Brandštetr *et al.*[9] compared the data on lanthanides with their measurements on several TP (Fig. 1). From Fig. 1 it is evident that higher separation factors can be obtained using extraction from hydrochloric acid (12*M*) than from nitric acid (13·1*M*). The great difference between distribution ratios of americium (q = 0·073) and of californium (q = 0·91) in 12*M* hydrochloric acid was used for the separation of these elements by a multiple extraction scheme with scrubbing (batch counter-current method).[32]

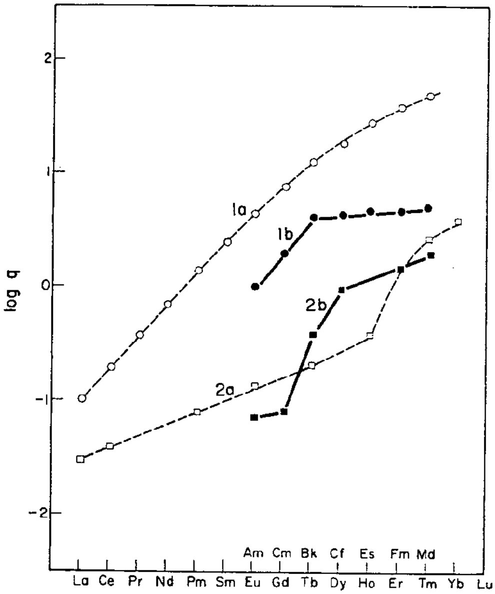

FIG. 1.—Distribution ratio of tervalent actinides and lanthanides between 100% TBP and 13·1*M* HNO_3 (1a-lanthanides, 1b-actinides) and between 100% TBP and 12·0*M* HCl (2a-lanthanides, 2b-actinides).

Isaac and coworkers[33] have found that the distribution ratio of tervalent actinides and lanthanides using extraction by TBP in a mixture of polyphenols as the inert diluent from fused lithium nitrate-potassium nitrate eutectic (150°) are higher by a factor of 10^2–10^3 as compared with concentrated aqueous nitrate solution. The high separation factor for americium-curium (3·2) suggests a possible application to the separation of these two elements.

The extraction by a 5% solution of TBP in decane allows a high degree of purification of plutonium from americium and curium.[91] By extraction from 1·33*M* nitric acid-2·5*M* magnesium nitrate the separation factor becomes 10^4.

Recently, the systematic investigation of the extraction of americium and curium by a number of neutral organophosphoric compounds has been made by Gureev and coworkers.[26] From their results it follows that the introduction of a positive group in the extractant, *e.g.*, alkyl radical elongation, should intensify the extractibility. However, when a radical is highly elongated the steric factors acquire more importance, hence there is an extractibility maximum at a certain carbon radical chain-length. The highest extraction is observed at $R = -C_9H_{19}$. The introduction of a negative group (*e.g.*, aromatic group) in the extractant sharply reduce the extractibility. The number of C—O—P bonds greatly influences the extractibility. The extraction of americium and curium is considerably lowered with the increase of the oxygen bonds, *i.e.*, in the order

$$R_3PO > ROR_2PO > (RO)_2RPO > (RO)_3PO.$$

Table IV shows the extraction constants of americium and curium extrapolated to zero ionic strength.

For the separation of adjacent lanthanides and tervalent TP the extraction chromatography (reversed-phase partition chromatography) can be used. In this method the extractant is adsorbed on a column bed of inert hydrophobic particles. The solvent

TABLE IV.—EXTRACTION CONSTANTS OF AMERICIUM AND CURIUM WITH NEUTRAL ORGANOPHOSPHORIC COMPOUNDS

Reagent[a]	K_{ex}	
	Am	Cm
$(C_8H_{17}O)_3PO$	0·3	0·25
$(iC_8H_{17}O)_3PO$	0·2	0·2
$(iC_8H_{17}O)_2(C_6H_4CH_3)PO$	0·02	0·02
$(iC_8H_{17}O)(CH_3C_6H_4O)(CH_3)PO$	1·3	1·85
$(iC_4H_9O)_2(C_8H_{17})PO$	2·6	2·6
$(C_8H_{17}O)_2(CH_2Cl)PO$	4·2	2·8
$(iC_4H_9O)_2(C_9H_{19})PO$	5·4	5·4
$(iC_4H_9O)_2(C_{10}H_{21})PO$	2·7	2·7
$(iC_8H_{17}O)_2(C_6H_5)PO$	0·08	0·08
$(C_8H_{17})(CH_3)(C_8G_{17}O)PO$	1200	1200
$(C_4H_9)_2(C_4H_9O)PO$	1800	1100
$(C_4H_9)_2(C_8H_{17}O)PO$	2060	2200
$(C_4H_9)_2(iC_8H_{17}O)PO$	2500	2900
$(C_4H_9)(C_6H_5)(C_4H_9O)PO$	45	38
$(C_4H_9)(C_8H_{17})_2PO$	1600	1800
$(C_8H_{17})_2(C_8H_{17}O)PO$	580	506
$(C_8H_{17})_3PO$	3000	3000
$(iC_8H_{17})PO$	100	100

[a] Solvent-*n*-decane.

extraction processes—extracting and back-extracting—are carried out by a flowing aqueous solution through the bed. By this means the solute of concern is allowed to partition many times between the stationary organic phase and mobile aqueous phase. Elements having lower distribution ratio are eluted faster than those with higher distribution ratio [equation (5)].

Siekierski and Fidelis[74] obtained excellent separation of light rare earths with TBP sorbed on kieselguhr treated with dichlordimethylsilane as stationary phase and nitric acid as the mobile phase. A similar method has been used for isolation of heavy TP (Cf, Fm, Md);[9] however, the separation is not so effective as that using cation-exchange chromatography (in 12·3*M* hydrochloric acid the separation factor for the pair fermium-californium equals 1·45, and for mendelevium-fermium 1·4). Also, the separation factors of TP in systems which employ a mixture of tetrabutylhypophosphate-tetrabutylpyrophosphate-nitric or perchloric acid do not allow the effective separation of adjacent TP[21,44] (in 6·5*M* perchloric acid the separation factor for fermium-americium is 1·54).

For extractive isolation of tervalent actinides and lanthanides alkylamines can also be used. The separation factor of adjacent lanthanides using the primary amine primene JM—T ($H_2NCRR'R''$: $R + R' + R'' = 17\text{-}23$ carbon atoms) equals 1·4; however, reagents of this type do not allow the group separation of tervalent actinides-lanthanides.[57] Tertiary amines such as Alamine-336 (mixture of trioctyl- and tridecylamine),[50] tri-iso-octylamine,[49] *etc.*, were recommended for isolation of TP from lanthanides from highly concentrated chloride solutions. Extraction of tervalent TP can be described by the following reaction:

$$MCl_5^{2-} + 2H^+ + 2(R_3N)_{org} \rightleftharpoons [(R_3NH_2)_2MCl_5]_{org} \qquad (10)$$

As was mentioned above, TP form more stable chloride complexes than do lanthanides and for this reason they can be extracted more effectively than lanthanides. The group separation factor in the system 30% Alamine 336 in xylene-11*M* lithium chloride acidified with hydrochloric acid (0·02–0·2*M*) is higher than 100 (Fig. 2). This method has been used for separating weighable amounts of TP from lanthanides after long irradiation of 10 kg of ^{239}Pu.[53]

For isolation of curium from europium the extraction by a 0·2*M* solution of tridecylamine in xylene from 11·2*M* lithium chloride can be recommended (distribution ratio of curium and europium is equal 1·0 and 0·004, respectively; separation factor 250).[91]

Recently, Moore[47] proposed, for the extractive isolation of TP, a 30% solution of Aliquat 336-NCS (tricaprylmethyl-ammonium thiocyanate) in xylene. Values of the distribution ratios of individual TP and lanthanides are summarised in Fig. 2 (aqueous phase 6*M* ammonium thiocyanate). The composition of the extractable complex is probably $R_4NM(NCS)_4$. The group separation factor using the extraction from 0·5*M* sodium bicarbonate or 6*N* aluminium nitrate is much smaller than in the case of 6*M* ammonium thiocyanate.[52]

Extraction of chelates

Extraction of TP with chelating agents of the type HA can be expressed by the following equation:

$$M^{3+} + 3(HA)_{org} \rightleftharpoons (MA_3)_{org} + 3H^+ \qquad (11)$$

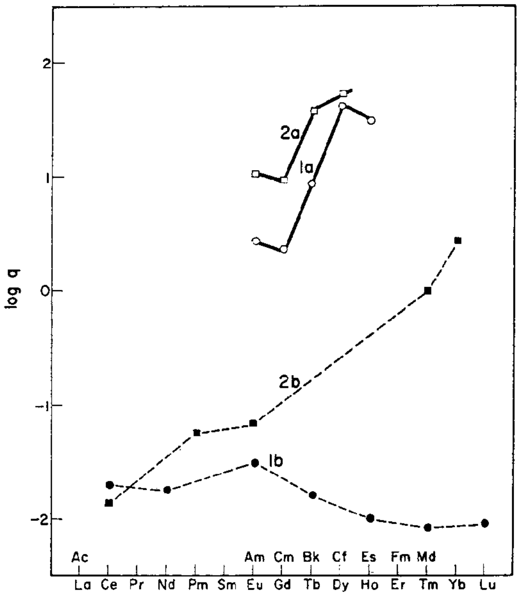

FIG. 2.—Distribution ratio of tervalent actinides and lanthanides in
1. 30% Alamine 336 in xylene-11*M* LiCl (1a-actinides, 1b-lanthanides),
2. 30% Aliquat 336-NCS in xylene-6*M* NH_4NCS (2a-actinides, 2b-lanthanides).

The equilibrium constant of the above reaction (extraction constant) is defined by

$$K_{ex} = \frac{[MA_N]_{org}[H]_N}{[M][HA]_{org}^N} = q\,\frac{[H]_N}{[HA]_{org}^N} \qquad (12)$$

where q is the distribution ratio of metal.

From the known value of the extraction constant it is possible to calculate the distribution of TP for every value of pH and $[HA]_{org}$, provided the metal ion in the aqueous phase is predominately uncomplexed. As can be seen from equation (12) the value of the distribution ratio q decreases with the increase of concentration of hydrogen ion (for extraction of TP in the form of ion-association complexes the reverse is often true).

Separation factors of adjacent TP can be easily calculated from the equilibrium constants according to the following equation

$$S_z^{z+1} = \frac{q_{z+1}}{q_z} = \frac{K_{ex,z+1}}{K_{ex,z}} \qquad (13)$$

In the presence of a masking agent H_vB, forming non-extractable complexes of type MB_n, the separation factor can be calculated as follows

$$S_z^{z+1} = \frac{K_{ex,z+1}(1 + \beta_{n,z}[B]^n)}{K_{ex,z}(1 + \beta_{n,z+1}[B]^n)} \qquad (14)$$

where $\beta_{n,z}$ and $\beta_{n,z+1}$ are the stability constants of the complexes M_zB_n and $M_{z+1}B_n$, respectively.

A widely used reagent for the extraction of TP is a β-diketone, the thenoyltrifluoracetone (HTTA). The values of extraction constants of TP and lanthanides using various organic solvents are summarised in Table V (organic phase 0·2–0·5M HTTA in solvert, aqueous phase ~0·1M $NaClO_4$).[68,78–82]

With toluene as the organic solvent the values of the extraction constants of TP are diminished;[27,39] however, with oxygen-containing solvents the values of the extraction constants are higher than in the case of toluene.[91]

HTTA has found its greatest application for separation of TP from uranium, neptunium, plutonium or fission products.[34,78]

Another chelating agent 5,7-dichloro-8-hydroxyquinoline can be used for separation of americium from europium (the separation factor is 10 if chloroform is used as solvent).[73]

Recently, the widespread use of dialkylphosphoric or dialkylphosphonic acids has been made for group separation of lanthanides and actinides as well as for separation of individual TP. Reagents of this type are present in organic solutions as dimers and the extraction of tervalent TP can be described by the following equation[60]

$$M^{3+} + 3(H_2A_2)_{org} \rightleftharpoons (M(HA_2)_3)_{org} + 3H^+ \tag{15}$$

with the extraction constant

$$K_{ex} = \frac{[M(HA_2)_3]_{org}[H]^3}{[M][H_2A_2]^3_{org}} = q\,\frac{H]^3}{[H_2A_2]^3_{org}} \tag{16}$$

Peppard and coworkers[60] using di-(2-ethylhexyl)phosphoric acid in toluene in their complete work, report a linear relationship between log K_{ex} and atomic number of lanthanides with a separation factor between adjacent lanthanides of approximately 2·5 [in the presence of mono-(2-ethylhexyl)phosphoric acid as contaminant the separation factors are decreased].

The values of extraction constants of TP and lanthanides with dibutylphosphoric acid (dibutyl ether-0·1M perchloric acid), di-(2-ethylhexyl)phosphoric acid (toluene-1M perchloric acid for lanthanides, toluene-1M hydrochloric acid for TP) and 2-ethylhexylphenylphosphoric acid-diethylbenzene-2M hydrochloric acid, are summarised in Table V. From the values of extraction constants of TP with dialkylphosphoric and dialkylphosphonic acids it is evident that reagents of this type have a marked advantage in that they can extract TP at much higher acidities than HTTA, thus avoiding many difficulties with hydrolysis. From the separation factors of TP with di-(2-ethylhexyl) phosphoric acid or 2-ethylhexylphenylphosphonic acid it is evident that these acids are more selective reagents for separation of TP than α-hydroxyisobutyric acid.

The extraction of TP by reagents of this type strongly depends on the nature of the solvent used. For instance, the extractibility of americium and californium by 2-ethylhexylphenylphosphonic acid in various solvents decreases in the following order:[54,55] heptane (2·55; 0·47), decane (2·22; 0·20), cyclohexane (2·18; 0·10), diethylbenzene (1·85; —0·15), carbon tetrachloride (1·8; —0·2), xylene (1·5; —0·54) and toluene (1·4; —0·65). In brackets are given the values of the logarithm of the extraction constants of californium and americium, respectively.

The extraction constants of lanthanides are much higher than those of TP. In the presence of the pentasodium salt of diethylenetriaminepenta-acetic acid (0·05M, pH ~ 3) and glycolic acid* (1M) as masking agents for TP (Table I) it is possible to separate

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* Glycolic acid can be successfully replaced by lactic acid, α-hydroxy-isobutyric acid, *etc.*[56]

TABLE V.—EXTRACTION CONSTANTS AND SEPARATION FACTORS OF TRANSPLUTONIUM AND RARE EARTH ELEMENTS WITH VARIOUS CHELATING AGENTS

	HTTA[a] (benzene)		HDBP[b] (dibutylether)		HDEHP[c] (toluene)		HEHϕP[d] (diethylbenzene)	
Element	log K_{ex}	S	log K_{ex}	S	log K_{ex}	S	log K_{ex}	S
Am	−7·48		1·9		−1·67		−0·1	
		1·48		1·0		1·74		1·25
Cm	−7·31		1·9		−1·43		0·0	
		2·5				10·8		32
Bk	(−6·9)[e]				−0·4		1·5	
		2·0				1·7		2·5
Cf	−6·6		3·5		−0·17		1·9	
		1·0		0·63				1·25
Es	(−6·6)[e]		3·3				2·0	
								2·5
Fm	−6·3				0·49		2·4	
						2·0		
Md					0·8			
La	−10·51		1·3		−2·24		−0·15	
		12		4		2·96		
Ce	−9·43		1·9		−1·77			
		9		1·2		2·05		
Pr	−8·48		2·0		−1·46			
						1·38		
Nd	−8·57				−1·32			
		3·3				2·19		
Pm	−8·05		2·4		−0·98			
		2·3		2		3·02		
Sm	−7·68		2·7		−0·50			
		1·05		2·5		1·91		
Eu	−7·66		3·1		−0·22		1·7	
		1·2		1·6		1·45		
Gd	−7·58		3·3		−0·06			
		1·2		6·3		4·9		
Tb	−7·51		4·1		0·63		2·5	
		3				2·09		
Dy	−7·03				0·95			
						1·95		
Ho	−7·25		4·9		1·24		3·3	
						2·24		
Er					1·59			
						2·5		
Tm	−6·96		5·9		1·99		4·0	
		1·7				3·1		
Yb	−6·72				2·48			
						1·86		
Lu	−6·47		6·8		2·75		4·9	

[a] Thenoyltrifluorocetone, refs. 68 and 78–82.

[b] Di-(*n*-butyl)phosphoric acid, ref. 17.

[c] Di-(2-ethylhexyl)phosphoric acid, refs. 22, 66 and 67.

[d] 2-Ethylhexylphenylphosphoric acid, ref. 52.

[e] Estimated from ref. 39.

lanthanides from TP using 0·1*M* 2-ethylhexylphenylphosphonic acid in diethylbenzene ($q_{La} = 26$, $q_{Ce} = 16$, $q_{Eu} = 9$, $q_{Tb} = 20$, $q_{Tm} = 170$ $q_{Am} = 0{\cdot}09$, $q_{Cm} = 0{\cdot}11$, $q_{Cf} = 1{\cdot}6$).[57]

For selective separation of quadrivalent berkelium from tervalent actinides and lanthanides the extraction by 0·1*M* di-(2-ethylhexyl)phosphoric acid in toluene from hydrochloric acid containing potassium bromate has been recommended.[61] A 1*M*

Solution of 2-ethylhexylphenylphosphonic acid in diethylbenzene was used for separation of lighter TP (Am, Cm) from heavy TP (Bk, Cf, Es, Fm) in a counter-current extraction column.[52]

Separation of individual TP can be achieved by extraction chromatography. Di-(2-ethylhexyl)phosphoric acid as stationary phase and 0·5*M* hydrochloric acid as mobile phase have been used for the separation of americium and curium ($\bar{v} = 2v_0$) from berkelium ($\bar{v} = 6v_0$) and from californium ($\bar{v} = 12v_0$).[38] An extraction column filled with a silica bed supporting 0·2*M* di-(2-ethylhexyl)phosphoric acid in heptane was used for isolation of sexivalent americium from curium (mobile phase 0·1*M* nitric acid) or quadrivalent berkelium from other tervalent TP (mobile phase 10*M* nitric acid).[31] Excellent separation of heavy TP has been obtained on a column containing 1·5*M* di-(2-ethylhexyl)phosphoric acid in toluene. Using 1·02*M* hydrochloric acid as mobile phase californium ($\bar{v} = 2{\cdot}7v_0$), can be separated from fermium ($\bar{v} = 4{\cdot}3v_0$) and from mendelevium ($\bar{v} = 10\text{–}12v_0$).[22] The lighter TP or lanthanides[7,66,75] are eluted faster than the heavier (the extraction constants of tervalent actinides and lanthanides, in general, increase with an increase of their atomic number, Table V).

A great advantage of extraction chromatography compared with ion-exchange chromatography lies in the fact that in the separated fraction of TP is not present an excess of organic complexing agent which has to be destroyed before subsequent chemical operations or before measurement of the radioactivity.

For group separation of lanthanides and tervalent actinides monoalkylphosphoric acids, which are highly polymerised, in common organic solvents can also be used.[62] For instance, a 0·48*M* solution of mono-(2-ethylhexyl)phosphoric acid in xylene predominantly extracts lanthanides from 10*M* lithium chloride acidified by 0·5*M* hydrochloric acid.[3] A 0·35*M* solution of this acid in toluene can be used for the isolation of promethium ($q = 1{\cdot}55$) from americium ($q = 0{\cdot}074$) when the aqueous phase is 14·1*M* hydrochloric acid.[63,65]

ELECTROPHORESIS

The difference between the mobilities in an electric field of tervalent cations of TP is not high enough to permit their separation. However, in the presence of complexing agents the total mobility $\bar{u}$ of TP can be expressed as follows:[14]

$$\bar{u} = \frac{u_M[M] + u_{MB}[MB]}{[M] + [MB]} = \frac{u_M + u_{MB}\beta_1[B]}{1 + \beta_1[B]} \tag{17}$$

where u_M is the mobility of the free cation M^{3+}
and u_{MB} is the mobility of the complex MB.

The separation factor of two adjacent TP can be calculated according to the following equation:

$$S_z^{z+1} = \frac{(u_{M_{z+1}} + u_{M_{z+1}B}\beta_{1,z+1}[B])\,(1 + \beta_z[B])}{(u_{M_z} + u_{M_zB}\beta_{1,z}[B])(1 + \beta_{1,z+1}[B])} \tag{18}$$

Comparing equation (18) with equation (4) it can be stated that the separations of TP by electrophoresis are not so effective as those by ion exchange using the same complexing reagent. However, a great advantage of electrophoresis lies in the possibility of very rapid separation of TP, even using continual methods. Knobloch deduced from theoretical considerations, and experimentally verified, that in the presence of aminopolyacetic acid it is possible to separate the lighter lanthanides in a matter of minutes.[35,36]

For rapid separation of americium and curium (8 min) nitrilotriacetic acid (0·002M, pH $\sim$3·6, 310 V/cm) was used as complexing agent. Under these conditions complexes of type $MB_2{}^{3-}$ are formed. Similarly, it is possible to separate californium from americium and curium.[37] The optimum concentration of the anion of the complexing agent can be found from the equation[35–37]

$$[B] = (\beta_{1,z}\beta_{1,z+1})^{1/2} \tag{19}$$

where $\beta_{1,z}$ and $\beta_{1,z+1}$ are the stability constants of complexes MB of adjacent TP.

Using complexing agents, which form with TP less stable complexes than aminopolyacetic acids, the separation of TP is much smaller.[12]

CONCLUSION

From the review of methods used for separation of TP it is evident that precipitation can be used for the separation of TP from a majority of fission products, but not the lanthanides. Ion exchange and solvent extraction are excellent methods not only for group separation of tervalent actinides and lanthanides but also for the selective isolation of adjacent TP. In some respects extraction chromatography using dialkylphosphoric and dialkylphosphonic acids as stationary phases has some advantage over ion-exchange chromatography. An attractive method for the rapid separation of TP seems to be electrophoresis.

Résumé—On présente une revue critique sur la séparation par groupes des lanthanides trivalents et des actinides et sur la séparation individuelle des éléments transplutoniens. On discute aussi des principes théoriques mis en jeu.

Zusammenfassung—Es wird eine kritische Übersicht über die Gruppentrennung dreiwertiger Lanthaniden und Actiniden sowie über die Trennung einzelner Transplutoniumelemente gegeben. Die zugrundeliegenden theoretischen Prinzipien werden ebenfalls diskutiert.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—VII*

CHELOMETRIC DETERMINATION OF INDIUM

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Summary—Optimum conditions have been found for the chelometric determination of indium by biamperometric titration with EDTA. Two stationary platinum electrodes (Pt-Pt) or two graphite electrodes (C-C) may be used to indicate the end-point of the titration. At pH 1-1·5 the determination is highly selective. The applied potential only influences the absolute value of the current; the accuracy of the determinations remains constant over a wide interval of applied potential. At a potential of 1·0-1·7 V the change of current during a titration with 0·05*M* EDTA solution is of the order of 10 μA. Analytical applications of the method are discussed.

In a previous paper in this series the universal nature of biamperometry for indication of chelometric or all complexometric titrations has been shown.[1] In the present paper are summarised the empirical results of a study of the biamperometric determination of indium by titration with EDTA. The course of the titration curves is of the same nature as those curves obtained for the titration of thorium with EDTA.[2] Up to the equivalence point there is no change of current, but then a minimum excess of EDTA causes an increase of current because of the electrode reaction of free EDTA (probably its anodic oxidation). An exact evaluation of the titration curves will be presented subsequently.

EXPERIMENTAL

Reagents

0·05*M* EDTA *solution*. Prepared by dissolving 37·5 g of the reagent (Chelaton 3, Lachema, Prague, Czechoslovakia) and diluting to 2000 ml. The titre of this solution (0·048*M*) was determined against standard lead nitrate solution using Xylenol Orange as indicator.

0·02*M Indium solution*. Prepared by dissolving 5·738 g of metallic indium (99·99%) in perchloric acid and diluting to 1000 ml.

Buffer solutions (pH range 1–4·5). Prepared from 1*M* solutions of trichloroacetic, monochloroacetic and acetic acids by neutralisation with aqueous ammonia under potentiometric control using a glass electrode.

All other solutions were prepared from analytical reagent grade chemicals.

Apparatus

For indication of the end-point identical apparatus was used to that described previously.[3] Two platinum plates (7 × 5 × 0·2 mm) or two graphite rods (99·99% C) impregnated with Ceresine† were

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* Part VI: *Talanta*, 1965, **12**, 671.

† Mixture of solid saturated hydrocarbons with higher m.p. than paraffin.

used as indicator electrodes. pH was measured with an electronic pH meter (Multoscop V, Lab. potřeby, Prague, Czechoslovakia) and a glass electrode. Titrations were carried out with an automatic burette (motor-driven hypodermic syringe) reading to ±0·005 ml.

Procedure

To a known amount of standard 0·02*M* indium solution were added 10 ml of buffer solution (or a chosen amount of 7·2*M* nitric acid.) When the selectivity was being studied, the appropriate solution of metal salt was added followed by dilution to about 100 ml. The resulting solution was titrated with 0·05*M* EDTA solution 3 min after inserting the electrodes and applying the potential. During titration the solution was stirred with a propellor (1500 rpm) at room temperature. After each addition of titrant the value of the current was read, stabilisation of the current being practically instantaneous. Quantitative evaluation of the titrations was carried out graphically. All results presented in this paper are an arithmetical mean of three determinations.

RESULTS AND DISCUSSION

Influence of pH

Indium forms a stable complex with EDTA (pK = 24·9). This fact enables its chelometric determination to be made even in a relatively acidic solution.

Figure 1 illustrates the course of the titration of indium in dilute nitric acid with an indicator system of two platinum electrodes. Satisfactory detection of the end-point with an error under 0·2% rel. is possible in 0·1*M* nitric acid and at pH 1·3–3·5. Above pH 3·5 the titration curves are deformed and stabilisation of the current takes much longer.

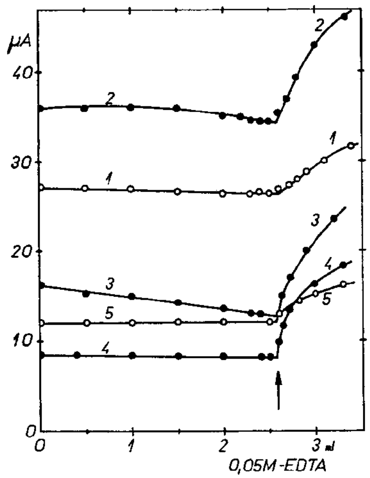

FIG. 1.—Influence of pH on titration of indium (Pt electrodes):
1. 0·35*M* HNO_3, 3. pH 1·35,
2. 0·11*M* HNO_3, 4. pH 1·95,
5. pH 3·2
[2·5 ml of 0·05*M* $In(ClO_4)_3$; HNO_3 or 10 ml of 1*M* buffer solution; applied potential: 1·5 V; total volume: 100 ml]

Similar results to those with platinum electrodes have been found with the use of two graphite electrodes. These latter electrodes are more convenient in a strongly acidic medium (see curves 1 and 2, Fig. 2), in which the current at the beginning of the titration is relatively smaller but the equivalence point is more pronounced. When using graphite electrodes for analysis there is no need to make a graphical extrapolation of the equivelence point.

Influence of applied potential

As in the chelometric titration of other metals the applied potential has practically no influence on the biamperometric titration of indium, which means that the accuracy of the determination is unaffected by the applied potential. At an applied potential <1 V the current changes are, however, smaller. By using a sufficiently sensitive indicator instrument (ammeter, galvanometer) the described technique can be successfully applied.[4] It is , of course, more convenient to use an applied potential >1 V.

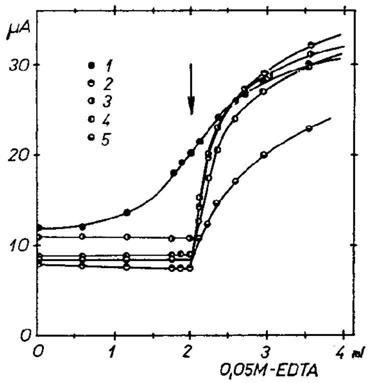

FIG. 2.—Influence of pH on titration of indium (C electrodes):
1. 0·35*M* HNO_3, 3. pH 1·5,
2. 0·075*M* HNO_3, 4. pH 3·4,
5. pH 4·8
[2 ml of 0·05*M* $In(ClO_4)_3$; HNO_3 or 10 ml of 1*M* buffer solution; applied potential: 1·3 V; total volume: 100 ml]

Influence of temperature

Fig. 3 shows titration curves obtained at different temperatures and illustrates the influence of temperature on the absolute value of the current (curves 2 and 3). Even under these conditions detection of the end-point is accurate enough, and the error is not greater than ±0·2% rel.

Passivation of electrodes

After repeated chelometric titrations of indium with platinum or graphite electrodes no accumulation of the reaction products occurs on the surface of the electrodes. Therefore, it is quite sufficient to wash the electrodes with water after each titration. When the electrodes are not in use they should be immersed in distilled water.

When the potential is applied and the solution intensively stirred, stabilisation of the current occurs after 3 min.

Accuracy and concentration range

Using the described procedure it is possible to determine 2·5–50 mg of indium with a mean error of 0·3% rel. The determination of lesser amounts of indium using more dilute EDTA solutions will be described in a further paper.

Selectivity

By the described biamperometric method it is possible to determine indium in a strongly acidic medium (0·1*M* nitric acid—about pH 3·5). Under these conditions several metals do not form complexes with EDTA or only weak complexes are formed.

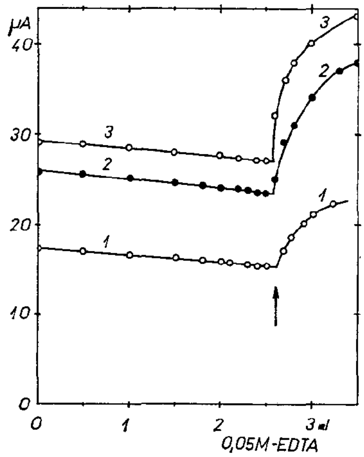

FIG. 3.—Influence of temperature on titration of indium:
1. 25°, 2. 50°, 3. 80°
[2·5 ml of 0·05*M* $In(ClO_4)_3$; pH 1·5; applied potential: 1·5 V; Pt electrodes; total volume : 100 ml]

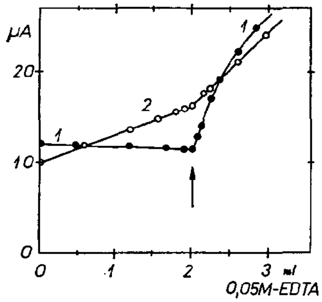

FIG. 4.—Influence of cobalt and nickel on titration of indium:
1. 250 mg of Co, 2. 177 mg of Ni
[2 ml of 0·05*M* $In(ClO_4)_3$; pH 1·5; applied potential: 1·5 V; C electrodes; total volume : 100 ml]

Thus, practically all bivalent metals (with the exception of copper) do not interfere with the determination of indium.

Experiments have shown that 6·9 mg of indium can be determined at pH 1–1·3 in the presence of an excess of Mg, Sr, Ba, Ca, Be, Ag, U, Al, Ti, Zn, Cd, Pb and Co, with a maximum error of 0·3% rel. More than 200 mg of nickel and 10 mg of cobalt interfere with the determination. Fig. 4 illustrates the influence of nickel and cobalt on the determination of indium (under identical conditions).

Small amounts of Fe(III), Bi, Ga, Th, Zr and rare earths also interfere with the determination of indium. Because the determination of indium can be carried out in the presence of fluoride ions it is possible to mask some metals (thorium and rare earths) with an excess of fluoride ions.

Practical applications

Practical utilisation of the described method has been verified by the determination of indium in solid solutions with antimony and zinc or cadmium. By means of repeated evaporations with hydrobromic acid antimony was separated. Zinc and cadmium, even when present in large concentrations, do not interfere with the described determination of indium.

Procedure. 0·5 g of the powdered alloy was dissolved with a mixture of 3 ml of sulphuric acid (1 + 9) and 5 ml of 40% hydrobromic acid in a porcelain basin placed on a sand bath. Subsequently, the solution was evaporated with 10 ml of hydrobromic acid and this operation repeated five times. The residue from these evaporations was then taken to dryness with 5 ml of hydrochloric acid (1 + 1) when the final residue should be white. This residue was dissolved in 5 ml of *ca.* 1*M* nitric acid and after dilution to 50 ml the indium determined by biamperometric titration with 0·05*M* EDTA solution at an applied potential of 1·5 V.

In Table I the results obtained by the above procedure (Method B) are compared with those from an EDTA titration of indium in an alkaline medium carried out after partial separation of zinc or cadmium using an ion-exchange technique (Method A).[5]

TABLE I

	Indium found,* %	
Alloy	Method A	Method B
Cd–Sb–In	1·00	1·03
Zn–Sb–In	0·65	0·64

* Average of 3 determinations.

Acknowledgment—The authors wish to express their thanks to the Institute of Solid State Physics, Czechoslovak Academy of Sciences, for kindly providing the samples of indium alloys.

Zusammenfassung—Die besten Arbeitsbedingungen zur chelometrischen Bestimmung von Indium durch biamperometrische Titration mit EDTA wurden ermittelt. Zwei feststehende Platinelektroden (Pt—Pt) oder zwei Graphitelektroden (C—C) können zur Anzeige des Titrationsendpunktes verwendet werden. Bei pH 1–1,5 ist die Bestimmung hochselektiv. Die angelegte Spannung beeinflußt nur den Absolutwert des Stromes; die Genauigkeit der Bestimmungen bleibt über einen weiten Bereich angelegter Spannungen konstant. Bei einer Spannung von 1,0–1,7 V liegen die Stromänderungen während einer Titration mit 0,05*M* EDTA-Lösung in der Größenordnung von 10 μA. Analytische Anwendungen der Methode werden diskutiert.

Résumé—On a trouvé les conditions optimales de dosage chélatométrique de l'indium par titrage biampérométrique à l'EDTA. On peut utiliser deux électrodes stationnaires en platine (Pt—Pt) ou deux électrodes en graphite (C—C) pour indiquer le point de fin de dosage. A pH 1–1,5, le dosage est hautement sélectif. Le potentiel appliqué n'influence que la valeur absolue de l'intensité du courant; la précision des dosages reste constante dans un large intervalle de potentiel appliqué. Pour un potentiel de 1,0–1,7 V, les variations d'intensité durant un dosage au moyen d'une solution d'EDTA 0,05*M* sont de l'ordre de 10 μA. On discute des applications analytiques de la méthode.

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DETERMINATION OF IRON, COPPER AND ALUMINIUM BY GAS-LIQUID CHROMATOGRAPHY

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Summary—Gas chromatography has been utilised in the analysis of two National Bureau of Standard alloys for quantitative determination of aluminium, iron and copper. In the analysis of N.B.S. 162a the relative mean errors were 3·13% for aluminium, 2·06% for iron and −1·72% for copper and for N.B.S. 164a the relative mean errors were −1·39%, −0·19% and −0·89% for aluminium, iron and copper, respectively. The procedure for analysis involves solution of the alloy, conversion of the metal ions to trifluoroacetylacetonates by solvent extraction and, finally, complete separation of the metal chelates and quantitative determination by gas chromatography using a column containing Gas Pack F coated with Tissuemat E, a polyethylene wax. Other metals present in the N.B.S. samples did not interfere with the determination of aluminium, iron and copper.

INTRODUCTION

FROM a previous study[1] it was concluded that gas chromatography could be used as a reliable and accurate detecting system for metal chelates in analytical procedures where quantitative conversion of samples to volatile, stable species could be accomplished. Recently, a solvent-extraction method was developed[2] which permits the simultaneous quantitative formation of the aluminium, iron and copper trifluoroacetylacetonates (tfa's) through the use of a trifluoroacetylacetone-chloroform extraction from an aqueous solution of the three metals. This was the first extraction procedure to include several metal tfa's applicable for quantitative gas chromatography.

From the standpoint of stability and volatility a gas chromatographic study using the tfa's of aluminium, iron and copper appeared to be promising. Aluminium tfa has been reported[1] to exhibit sufficient thermal stability and volatility. Injection-port studies[3] revealed that the copper chelate was thermally stable but the iron chelate left a residue in the injection port at a port temperature of 135°.

Previously, gas chromatographic conditions were found for the partial resolution of the iron and copper tfa's as well as their separation from aluminium tfa.[4]

This study was undertaken to establish gas chromatographic conditions for the complete separation of the aluminium, iron and copper tfa's, to investigate the thermal stability of the iron and copper complexes, to adapt the new extraction method for a procedure to include separation of the three metal chelates by gas chromatography and finally, to integrate these phases into an analytical scheme for determination of aluminium, iron and copper in alloys.

EXPERIMENTAL

Apparatus

The gas chromatograph used was an F & M model 500 with a thermal conductivity detector containing W-2 tungsten filaments. The injection port was modified by installing a borosilicate glass insert.[3] The peak areas were measured with a disc-chart integrator on the recorder. Helium was the carrier gas. Chelate solutions were injected with a 10-μl Hamilton syringe. A Thomas Capillary Melting Point Apparatus was employed for determination of melting points. Differential thermal analyses and thermal gravimetric analyses were run on a Dupont model 900 Differential Thermal Analyser. A dummy glass injection port apparatus[3] was used in studies to test chelate stability. Measurements of pH were taken on the Beckman Zeromatic pH Meter. Ultraviolet spectra were run on a Cary Recording Spectrophotometer model 14 and infrared spectra on a Perkin-Elmer Infracord.

Reagents

All chemicals were of reagent grade unless specified otherwise.

0·25M Trifluoroacetylacetone solution. 19·25 g of trifluoroacetylacetone (Peninsular Chem. Research, Inc., Gainesville, Florida, U.S.A.; the product was double distilled and the 106° fraction used) were diluted to 500 ml with alcohol-free chloroform. The solution was placed in a dark coloured vessel and stored in a refrigerator.

N.B.S. 162a solution.[2] Prepared by dissolving 2·5061 g of alloy in 18 ml of concentrated hydrochloric acid and 6 ml of concentrated nitric acid and heating to remove most of the nitric acid. The solution was diluted with about 100 ml of water, allowed to cool to room temperature, then filtered to remove the silica. The filtrate was diluted to the mark with water in a 250-ml volumetric flask with a ground-glass stopper. The pH was 1·4.

N.B.S. 164a solution.[2] A weight of 2·1169 g of alloy was treated with 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid until solution occurred, then most of the nitric acid was evaporated by heating. After the solution cooled to room temperature it was diluted to 500 ml with water in a volumetric flask with a ground-glass stopper. The pH was 0·6.

1M Sodium acetate solution

0·05M Ethylenediaminetetra-acetic acid disodium salt solution

Preparation of metal chelates

Metal chelates were prepared by solvent extraction. An aqueous solution of each metal was shaken with a chloroform solution containing twice the stoichiometric amount of the double distilled H(tfa). The pH of the aluminium solution was adjusted to about 4·5 with sodium acetate before extraction. The two phases were mixed for several minutes. The organic layer was isolated and evaporated to dryness. The residue was washed with generous portions of hexane, then recrystallised from hexane with the aid of heating. A vacuum desiccator was used for drying the metal chelates. The tris(1,1,1-trifluoro-2,4-pentandiono)aluminium(III) and iron(III) complexes melted at 120–1° and 114·5°, respectively. Bis(1,1,1-trifluoro-2,4-pentandiono) copper(II) melted at 197–8°. The uncorrected melting points of the iron and copper chelates were confirmed by differential thermal analysis. Infrared spectra of the iron and copper tfa's indicated that formation of a metal complex with H(tfa) had occurred. Ultraviolet spectra of these two chelates were in agreement with those given in the literature.[5] The carbon, hydrogen, fluorine and metal analyses of all three metal tfa's were in good agreement with calculated values.

Chelate mixture solutions

Calibration solution. 10, 30 and 40 mg amounts of the aluminium, iron and copper tfa's, respectively, were weighed in a 2·0-ml volumetric flask and diluted to volume with chloroform. Solution was achieved by mixing for 1 min. The contents were then placed in a 1-dram bottle equipped with an injection cap (described below) to prevent evaporation of chloroform.

Standard solution. 2 ml of the chloroform solution contained approximately 12, 35 and 35 mg of the aluminium, iron and copper chelates, respectively. After mixing for 1 min, the solution was stored in a 1-dram bottle with an injection cap. The composition of this solution is adjusted to the approximate concentration of chelates in the sample.

Materials

Injection cap. The plastic screw cap from a 1-dram bottle was modified by drilling a 1/32 in.–1/16 in. hole through the centre to permit entry of the needle from a 10-μl Hamilton syringe. The paper backing was replaced first by a 13 mm diam. silicone rubber injection port septum from an F & M 810 gas chromatograph, cut to one third thickness, followed by a thin Teflon disc cut from a Teflon sheet (E. I. DuPont de Nemours & Co., Inc., Wilmington, Delaware, U.S.A.)

Chromatographic columns. The coating of solid supports and packing of columns was carried out in the usual manner.[6] All columns were fabricated from borosilicate glass tubing.

Column A—This was 46 cm in length by 3 mm i.d. It was packed with 80–120 mesh Gas Pack F

(Matronic Instrument Co., Newark, Delaware, U.S.A.) which was coated 12% by weight with Tissuemat E (Fischer Scientific Co., Chicago, Illinois, U.S.A.). A total of 2·5953 g of packing was used. Conditioning the column for 72 hr at 120° in the instrument with the carrier gas flowing is recommended before use.

Column B—This was a 30-cm column with a 4 mm i.d. and contained 10% 710 Silicone oil (Dow Corning, Midland, Michigan, U.S.A.) on 60–80 mesh Chromosorb W (Applied Science Laboratories, Inc., State College, Pennsylvania, U.S.A.).

Column C—The dimensions of this column were 61 cm by 4 mm i.d. The packing consisted of 10% paraffin wax (Grade A, Type I, Esso Standard Oil Co., Bayonne, New Jersey, U.S.A.) on Gas Chrom Z (Applied Science Laboratories, Inc.).

Column D—This column was similar to Column B except that 10% Dow Corning High Vacuum Silicone Grease was used.

Column E—This column was similar to Column B except for using 10% Apiezon L (Apiezon Products Limited, England) as the substrate.

Column F—Column F was similar to Column C except that 10% Tissuemat E was substituted for the paraffin wax.

Column G—This was a 102 cm by 4 mm i.d. column coated 0·5% with Tissuemat E on glass beads (Applied Science Laboratories, Inc.).

Column H—Column H was similar to Column A except that 10% Alathon 7040 (F & M Scientific Corp., Avondale, Pennsylvania, U.S.A.) was used as the liquid phase.

Gas chromatographic conditions for alloy analyses

The following conditions were used for all gas chromatographic analyses except where noted.

Column A.
Carrier gas flow rate: 46 ml/min at a column temperature of 105°
Reference flow rate: 25 ml/min
Injection port temperature: 135°
Block heater temperature: 190°
Actual block temperature: 135°
Attenuator setting: IX
W-2 Tungsten detector filaments
Chart speed: 0·5 inch/min

Composition of N.B.S. Alloys

162a	164a (provisional certificate)
63·95% Ni	82·25% Cu
30·61% Cu	9·59% Al
2·19% Fe	4·05% Fe
1·60% Mn	3·72% Ni
0·93 % Si	0·22% Mn
0·50% Al	0·07% Zn
0·076% Co	0·04% Pb
0·042% Cr	0·04% Sn
0·005% Ti	

RESULTS AND DISCUSSION

Thermal stability of the metal chelates

Although the three metal tfa's have been included in other gas chromatographic studies,[3,4] additional information concerning their thermal stability was obtained from injection port studies and collection of eluted chelates.

Aluminium tfa was found to be stable under the full range of conditions used for investigation of its thermal stability. Lack of residue in the glass injector-port insert indicated that the chelate was completely vaporised at 135°. The melting point of the eluted chelate was the same as the pure starting material, so that no destructive interaction was taking place in the gas chromatograph.

Iron tfa exhibited good stability; only a trace of residue was detected in the glass insert when the injection-port temperature was 135°. Apparently the residue was not caused directly by thermal instability, but from incomplete vaporisation which was a function of residence time in the injection port, because iron tfa vaporised completely at 175°. Differential thermal analyses (D.T.A.) furnished further evidence for the thermal stability of the complex at 135°. The reason for the difference in evaluation of the stability or degree of vaporisation between an earlier report[3] and the above findings, stems from the degree of purity of the iron complex and possibly the concentration of solutions used. It was observed in the course of these studies that recently purified materials must be used. Recrystallisation of a two month old iron tfa preparation caused a significant reduction in the amount of residue remaining in the injection port insert and removal of a shallow endotherm which appeared in the thermogram from its D.T.A. For a true test of thermal stability it is recommended not only that pure compounds be used but that chelate solutions be about the same concentration as those used in analyses.

The eluted iron tfa melted at the same temperature as the material in the sample injected.

The quantitative data obtained for iron tfa at an injection port temperature of 135° (Table I) suggested that the amount of residue observed had no bearing on accuracy of determination.

Copper tfa was completely vaporised at injection port temperatures ranging from 135 to 175°. The D.T.A. implied that the complex is stable to at least 197–8°.

Collection of effluents of several injections of copper tfa revealed the presence of two differently coloured species. Besides the blue copper tfa material, a red solid band of higher volatility was obtained and verified as iron tfa. A thorough study proved that copper tfa reacted with the metal parts of the gas circuit to a slight degree forming iron tfa. This reaction was minimised by operating the detector block at 135°.

Separation of the metal tfa's

One of the important criteria on which the development of a quantitative analytical procedure depended was the separation of the iron and copper tfa's by gas chromatography. At the time this study was initiated a partial separation had been reported[4] using an SE-30 substrate which also made possible their complete separation from aluminium tfa. Therefore, a survey was undertaken to find a column which would resolve the complexes of aluminium, iron and copper efficiently and expediently and thus be useful for quantitative studies.

The first column tested (Column D) contained Silicone grease and provided the same degree of resolution as the SE-30 column. Using Column B with 710 Silicone oil permitted a somewhat better separation but the interesting point noted in this case was a reversal in the order of elution so that the iron tfa was eluted before copper tfa. This order of elution was maintained by all columns in the discussion to follow. The Apiezon L substrate (Column E) caused an improvement in the separation from the standpoint of difference in retention times but peaks were also broader. A complete separation was first obtained for the iron and copper tfa's with Column C which contained paraffin wax. Although this column showed promise for application to quantitative investigations, the liquid phase bled from the column at 95° causing erratic helium flow and its use was discontinued. Tissuemat E, a polyethylene wax

(Column F) was then tried. With this column a complete separation of the three metal chelates was achieved and the rate of bleeding was slower than with Column C even when used above 100°.

The next step in the column survey involved the screening of solid supports. Using Tissuemat E, various solid supports were evaluated with the goal of finding a column that could successfully separate all three metal tfa's in a single isothermal run. Analysis of chelate mixtures on Column F (Gas Chrom Z solid support) necessitated an increase in column temperature following elution of aluminium tfa to reduce the retention times for the iron and copper complexes due to their wide separation from the aluminium tfa peak. Using a glass bead support (Column G) chelate separations adequate for quantitative analysis were obtained only by making two runs at different column temperatures. The next support investigated, Gas Pack F (Column A), provided a marked improvement in the distribution of peak retention times enabling all three chelates to be separated with an isothermal analysis (Fig. 1).

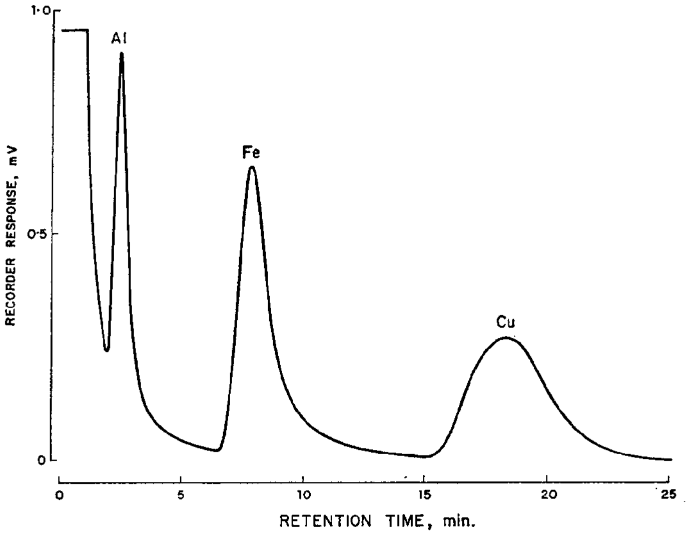

FIG. 1.—A complete separation of the aluminium, iron and copper tfa's by gas chromatography using an isothermal analysis (see *Gas Chromatographic Conditions for Alloy Analyses*).

Column A showed a tendency to bleed when the column temperature was 120° or higher during the first 2 or 3 days of use and before proceeding to the quantitative phase of this work a more stable polyethylene was briefly tried. Alathon 7040 (Column H), stable up to 240°, showed an improvement over Tissuemat E in rate of bleeding but retention data indicated that chelate solubility was too low. Therefore, Column A was chosen as the most suitable for use in the alloy analyses and the final conditions established for use in the quantitative determination of aluminium, iron and copper are listed in *Gas Chromatographic Conditions for Alloy Analyses.*

Development of Analytical Procedure

Modification of extraction procedure

The procedure of Scribner *et al.*[2] was modified mainly in the area of increasing chelate concentrations in the chloroform phase from extraction in order that volumes from a 10-μl syringe could be used for chromatographic analyses. This was easily done by employing a larger aliquot of the alloy stock solutions and a larger volume of a more highly concentrated H(tfa)-chloroform stock solution. The resulting increase in volume of extract also offered the advantage of reducing the percentage volume lost by evaporation of chloroform throughout the various phases of sample preparation for gas chromatography.

Although gas chromatographic conditions had been found for the complete separation of all three chelates, the percentage composition of the two alloys was such that no single volume of extract could be used for their simultaneous analysis regardless of the type of detector used unless the attenuation was changed during the course of the analysis.

Increasing the concentration of extracts presented a problem with respect to insolubility of copper tfa in chloroform. However, by removing a sufficient amount of copper from the extract with the disodium salt of EDTA before the concentration step, complete solution was achieved.[2] A gas chromatographic study to establish what effect the EDTA treatment has on the aluminium and iron tfa's showed that the former chelate was not removed while the effect on the latter depends on the degree to which copper is removed. When a solution of all three chelates in chloroform was treated with an aqueous solution containing a stoichiometric amount of the disodium salt with respect to copper, all the copper was removed (no chromatographic peak) along with 8% of the iron. In a second treatment of this solution (copper previously removed) with the same volume of the EDTA solution no iron was removed. The iron also remained completely complexed with tfa when only one half the stoichiometric amount of EDTA was used for the copper present. During analysis of the N.B.S 162a alloy up to 88% of the total copper was removed leaving about 15 mg, without affecting the determination of iron. Therefore, the important factor to be noted is that treatment with EDTA should not result in complete removal of copper when the concentrate is to be analysed for iron.

Preliminary investigation

Before a sample can be analysed, it is necessary to know the approximate percentage of aluminium, iron and copper present. When little or no information of this nature is available it is recommended that a trial extraction be made and that the extract be tested on the gas chromatograph. This investigation yields valuable information concerning procedural requirements for proper regulation of chelate concentration in extracts, the presence of interferences, adjustment of the pH of the alloy solution and when required, the conditions for the EDTA back-washing procedure.

The recommended procedure for the preliminary investigation is outlined as follows. The first step to be taken is the running of a calibration curve (refer to that section under *Quantitative Aspects*). Next, the sample stock solution is prepared. It is best to start with a solution of rather high concentration. Take an aliquot of the sample stock to be used for the trial run and determine the amount of 1*M* sodium acetate to give an equilibrium pH of 4·5. Run a trial extraction by the procedure given in the succeeding section or a modification thereof. The extract is examined by gas chromatography to determine if an adjustment in chelate concentration is necessary. To do this, find the volume (or volumes) of extract that produces a peak area for each metal chelate which falls within that portion of the linear range of its calibration curve representing areas large enough to make calculations reliable. For example, when the extract from N.B.S. 162a was injected, 50 μl produced peak areas of suitable magnitude for the aluminium and iron tfa's whereas 6 μl was needed for copper tfa. By comparing the area to volume ratios for chelates in the sample with those in the calibration solution for similar sized peaks, sample concentration can be adjusted. Concentrations and injected volumes of the calibration and sample solutions should be similar because area to microgram ratios for the iron and copper tfa's are concentration dependent.

Having made a trail analysis of the extract, this information can be used to prepare a standard solution with roughly the same chelate concentrations. This solution is prepared and run on the gas chromatograph before analysis each day to supply a corrected value for the intercept in the equation derived from the original calibration curve. Otherwise, intercept values were often found to change enough from day to day to affect the accuracy of analyses.

The test analysis of the extract also yields information concerning the presence of chromatographic peaks which might interfere in the analysis of aluminium, iron or copper. The trial extraction can also reveal the presence of an interfering component *via* precipitation of its tfa complex in the organic phase as was actually the case with nickel in the N.B.S. 162a sample when the equilibrium pH was somewhat higher than 4·5 using the extraction procedure similar to that detailed in the following section.

Another detail that can be learned from a preliminary investigation concerns the conditions for removal of copper before concentration of an extract. Test injections are used to establish whether concentration is necessary and preparation of the concentrate will reveal whether the solubility limit of copper tfa in chloroform has been exceeded. Information in sections entitled *Modification of extraction procedure* and *Procedure for alloy analyses*, may be used as a guide for choosing the EDTA treatment required to remove copper before concentration of the extract.

Procedure for alloy analysis

After the preliminary investigation has been made and the details of the sample preparation are worked out, the alloy analysis is attempted using the same alloy solution which was adjusted to the proper concentration. The data from the calibration curve is used again for the alloy analysis.

Preconditioning of column. When a chromatographic column has been idle for several hours (overnight) it will produce smaller peaks from the first sample injected once operation is resumed. Repetitive sample injections and chromatograms are required until duplicate peak areas are obtained. We find this type of column behaviour much more prominent for metal chelates than for purely organic materials. The fourth and subsequent injections give reproducible results. When the nature of the metal chelate sample is changed during the course of active use of the column for a day, the first injection of the new sample may produce a smaller peak and this result is rejected. A second injection of this new sample produces a reliable peak for quantitative work. This technique was applied in the determination of iron in the concentrated sample after having used the column for copper determination in the dilute sample.

Extraction of metal chelates. While the column was being preconditioned there was ample time to prepare the first of two samples for analysis by extraction as follows. Accurately measured volumes of 25·0 ml each of the alloy stock solution and the H(tfa) stock solution were pipetted into a 125-ml separatory funnel fitted with a Teflon stopcock and a rubber stopper protected by a thin sheet of

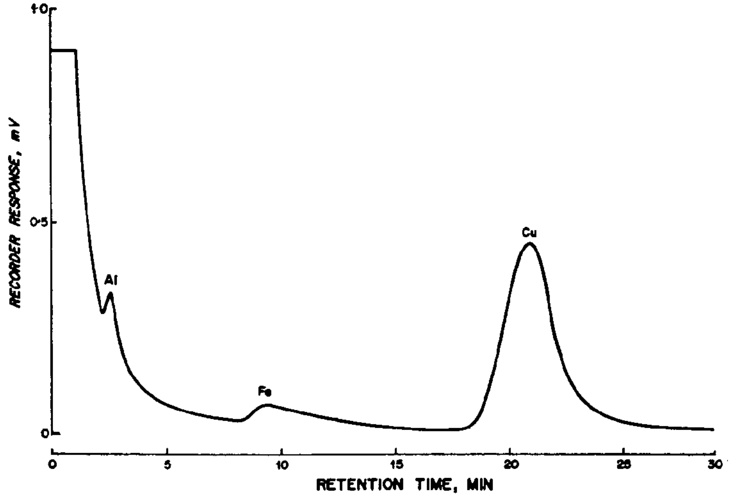

Fig. 2.—Analysis of N.B.S. 162a: A chromatogram representing the analysis of the chloroform extract for the determination of copper (see *Gas chromatographic conditions for alloy analyses*).

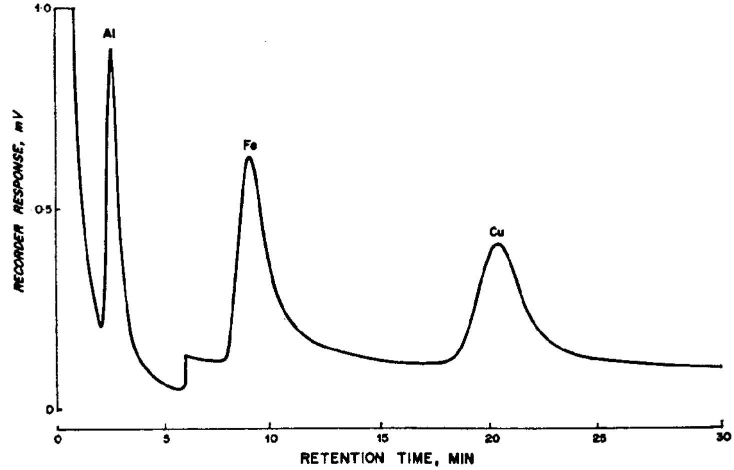

Fig. 3.—Analysis of N.B.S. 162a: A chromatogram representing the analysis of the concentrated chloroform extract for the determination of aluminium and iron (see *Gas chromatographic conditions for alloy analyses*). The copper tfa peak represents the amount remaining after EDTA treatment of the extract before concentration. The baseline was adjusted manually at 6 min to keep the chromatogram on scale.

polyethylene. The contents were mixed for 10 min, then 20·0 ml of 1*M* sodium acetate were added. This mixture was shaken for 10 min and allowed to stand for another 10 min.

Treatment of organic phase from extraction of N.B.S. 162a stock solution. Take 2–3 ml of the chloroform phase and place in a 1-dram bottle with an injection cap. This solution was saved for the gas chromatographic determination of copper (Fig. 2). The remainder of the extract was transferred to another 125-ml separatory funnel which contained about 20 ml of the EDTA stock solution. The mixture was shaken slowly for 10 sec and another 30 sec were allowed for phase separation. The organic phase was transferred to a small beaker. Then 16·0 ml of the solution were pipetted into another small beaker and evaporated to dryness by placing under a bell jar fitted with a packed drying

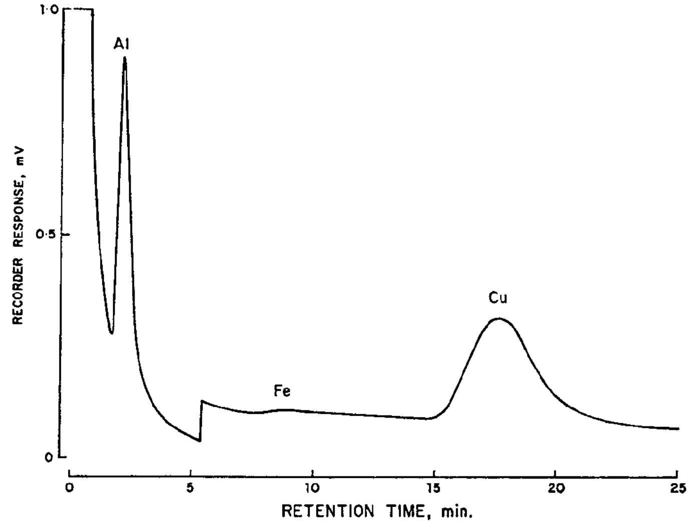

FIG. 4.—Analysis of N.B.S. 164a: A chromatogram representing the analysis of the chloroform extract for the determination of aluminium and copper (see *Gas chromatographic conditions for alloy analyses*). The baseline was adjusted manually at 6 min to keep the chromatogram on scale.

tube and applying suction with a water aspirator. Care should be exercised in adjusting the flow of dry air to prevent splattering of the solution and loss of the dried solid. Evaporation required about 2 hr. The residue was carefully placed in a 2·0-ml volumetric flask by means of a small spatula and chloroform rinses and the contents were diluted to the mark with the solvent. Solution was obtained by mixing for 1 min and the contents were stored in a 1-dram bottle with an injection cap. The concentrate was subsequently used for determination of iron and aluminium (Fig. 3).

Following column preconditioning, four replicate runs were made with the standard solution, whose chelate concentrations approximated that of the sample solutions used for analysis. At this time both the extract and the concentrate had been prepared and were ready to be analysed. Three injections of the extract were followed by four injections of the concentrate. The first run on the concentrate was used to ensure that the column had been preconditioned for iron tfa.

Treatment of organic phase from extraction of N.B.S. 164a *stock solution.* The procedure for preparation of the extract for analysis is the same as that used for N.B.S. 162a. The extract was used for the determination of aluminium and copper (Fig. 4). The EDTA treatment on the remainder of the extract was similar to that used for N.B.S. 162a. The mixing lasted 40 sec (for the higher copper content), then 20·0 ml of the organic phase were evaporated to dryness. The last three of four runs were made on the 2·0 ml concentrate for the determination of iron (Fig. 5).

Eight hr were required to obtain quantitative data for each alloy. This includes 5·5 hr for column preconditioning and running the standard. It does not include time for the calibration study or a preliminary investigation if the latter becomes necessary.

Quantitative Aspects

Calibration curve

The technique for injection of solutions is that described in reference 1, page 1220, with the following exception. Immediately upon emptying the syringe it was withdrawn from the injection port and the remaining solution removed from the hot needle by withdrawing the plunger to the original sample volume while the barrel was positioned vertically with the needle up. This residual volume was subtracted from the sum of the barrel and needle volumes to give the actual volume injected.

Specially fabricated injection caps were used to reduce the rate of evaporation of chloroform. In addition to their usefulness for storage of solutions, they were also

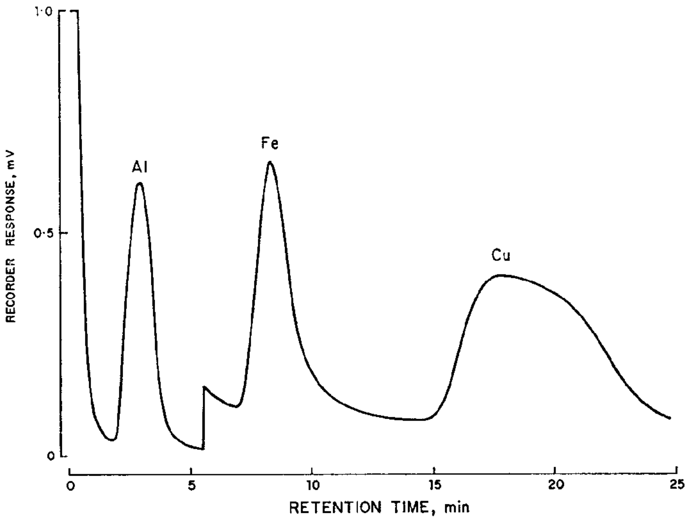

FIG. 5.—Analysis of N.B.S. 164a: A chromatogram representing the analysis of the concentrated chloroform extract for the determination of iron (see *Gas chromatographic conditions for alloy analyses*). The aluminium tfa peak is attenuated 8 X and the copper tfa peak represents the amount remaining after EDTA treatment of the extract before concentration. The baseline was adjusted manually at 6 min to keep the chromatogram on scale.

convenient for sampling because removal of the cap was not necessary for introduction of the syringe needle and the silicone rubber disc permitted a tight seal after removal.

The calibration study began with four injections of a chelate mixture to precondition the column. The calibration curve was composed of four points and four replicate runs were used to determine each point. Volumes of the calibration solution injected were chosen so that most of the data represented amounts of each chelate greater than the lower limit of detectability and smaller than that which produced overloading. The concentration of each chelate was adjusted so that each of the four volumes injected yielded peaks whose height fell within the 0·3–1·0 mV recorder range using a 1X attenuation.

Calculation of quantitative results

Peak areas were measured with a disc-chart integrator. A line was drawn across the base of the peak tangent to the curve. This was called the adjusted base line. The total area under the curve between the two points of tangency was determined. The true area of the curve was the difference between the total area and the area below the adjusted base line.

Using data from the test analyses on the extract (see *Preliminary investigation*) the optimum range of the three calibration curves was chosen for calculating quantitative results by comparing the peak area of the chelate in the sample to pertinent points on the curve representing nearly the same peak area for that chelate in the calibration solution. Two adjacent points on each curve were employed for computation of slopes when the area per microgram ratio varied significantly over the full range of the curve. Values of the slopes calculated in this manner were 111·7, 67·5 and 51·2 for the aluminium, iron and copper curves, respectively, used to compute results of the N.B.S. 162a analysis and 113·6, 72·9 and 42·1 for the curves used in the analysis of N.B.S. 164a. The difference in slopes for the two copper curves resulted from using different copper tfa concentrations in each of the calibration solutions to compensate for the percentage of copper in the alloys so that curves would cover an appropriate area–microgram range. The slope values were incorporated in the equation for calculating the amounts of each metal determined. A corrected intercept value for this equation was derived from a second equation composed of terms from the calibration study and the injection of the standard solution. The terms obtained from replicate runs of the standard solution were the average peak area for each metal, $\bar{A}_s$, and the average weight of metal in micrograms, $\bar{w}_s$. The corrected intercept, b_c, was calculated from $\bar{A}_s - \bar{w}_s m = b_c$, where m is the slope of a calibration curve. Thus, the equation used for calculation of quantitative results was $y = mx + b_c$, using y for peak area values and solving for x, the number of micrograms of metal found.

Results of alloy analyses

Three aliquots of each alloy stock solution were taken for analysis. The aliquots used for N.B.S. 162a analysis were run on separate days along with freshly prepared standard solutions and the calibration curve was run the day before the first analysis. Results of this analysis are summarised in Table I. The data tabulated were calculated from the equation $y = mx + b_c$, where b_c is the value for the corrected intercept. (Refer to *Calculation of quantitative results* for derivation of the equation.) A single standard solution and three aliquots of the N.B.S. 164a stock solution used for analysis were run on the same day. The calibration curve was run 5 days before the analysis. Table I also lists the results for the N.B.S. 164a analysis.

TABLE I.—N.B.S. ALLOY No. 162a

	Aluminium, %	Iron, %	Copper, %
Present	0·50	2·19	30·61
Found	0·52	2·24	30·08
Relative mean error	3·13	2·06	−1·72
Relative deviation	1·83	1·99	1·32

N.B.S. ALLOY No. 164a

	Aluminium, %	Iron, %	Copper, %
Present	9·59	4·05	82·25
Found	9·46	4·04	81·52
Relative mean error	−1·39	−0·19	−0·89
Relative deviation	1·08	0·84	2·55

The relative mean error and relative deviation data were calculated from the relative percentage error for each chromatographic run. A result was rejected when the suspected value differed from its nearest neighbour by 50% of the range for the series when composed of six or more values.[7]

Interferences

Chromatograms representing the analyses of alloys were similar to those from synthetic chelate solutions when compared from the standpoint of examination for the presence of interfering peaks or irregular baselines. Calculations show that very small amounts of the secondary metals were present in volumes of extracts and concentrates injected for the determination of aluminium, iron and copper. Of the secondary metals present in the two alloys, only the tfa's of manganese(III), chromium(III) and zinc(II) are known to produce gas chromatographic peaks and they were present in concentrations too small to be detected with the thermal conductivity detector.

CONCLUSION

An analytical procedure is given for the quantitative determination of aluminium, iron and copper in N.B.S. alloys which utilises a new extraction method for efficient conversion of the three metal ions to metal trifluoroacetylacetonates and gas chromatographic conditions which permit their complete separation.

Samples which are unknown or vary significantly in percentage composition from the N.B.S. alloys used in this study may also be analysed after a preliminary investigation to determine the proper adjustment of chelate concentrations in extracts.

Acknowledgement—The authors wish to thank D. R. Gere for helpful discussions concerning evaluation of quantitative data and K. J. Eisentraut for running samples on the Differential Thermal Analyser.

Zusammenfassung—In zwei Legierungen des National Bureau of Standards wurden Aluminium, Eisen und Kupfer gaschromatographisch bestimmt. Bei der Analyse von N.B.S. 162a waren die mittleren relativen Fehler 3,13% für Aluminium, 2,06% für Eisen und −1,72% für Kupfer; bei N.B.S. 164a waren die mittleren relativen Fehler −1,39%, −0,19% und −0,89%. In der Analysenvorschrift sind enthalten Lösen der Legierung, Überführung der Metallionen in Trifluoroacetylacetonate durch Lösungsmittelextraktion und zuletzt vollkommene Trennung der Metallchelate und ihre quantitative Bestimmung durch Gaschromatographie an einer Säule aus GasPack F, das mit dem Polyäthylenwachs Tissuemat E imprägniert ist. Die anderen Metalle in den N.B.S.-Proben störten bei der Bestimmung von Aluminium, Eisen und Kupfer nicht.

Résumé—On a utilisé la chromatographie en phase gazeuse pour le dosage de l'aluminium, du fer et du cuivre lors de l'analyse de deux alliages du "National Bureau of Standards". Dans l'analyse du N.B.S. 162a, les erreurs relatives moyennes ont été de 3,13% pour l'aluminium, 2,06% pour le fer et −1,72% pour le cuivre; pour le N.B.S. 164a, les erreurs relatives moyennes ont été de −1,39%, −0,19% et −0,89% pour l'aluminium, le fer et le cuivre, respectivement. La technique d'analyse comprend la mise en solution de l'alliage, la conversion des ions métalliques en trifluoroacétylacétonates par extraction au moyen de solvant et, finalement, la séparation complète des chélates métalliques et le dosage par chromatographie en phase gazeuse, en utilisant une colonne contenant du Gas Pack F recouvert de Tissuemat E, une cire de polyéthylène. Les autres métaux présents dans les échantillons du N.B.S. n'ont pas interféré dans le dosage de l'aluminium, du fer et du cuivre.

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SUBSTOICHIOMETRIC DETERMINATION OF MANGANESE BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A simple and rapid method for the substoichiometric determination of traces of manganese in various materials by neutron-activation analysis has been developed. After dissolution of the irradiated test sample, manganese(II) carrier is added and subsequently oxidised by peroxodisulphate to the heptavalent state. The permanganate thus formed is finally extracted into chloroform as tetraphenylarsonium permanganate using a substoichiometric amount of tetraphenylarsonium chloride. This single separation step isolates radiochemically pure manganese-56 in the analysis of a relatively simple material in which interfering elements (gold, rhenium, *etc.*) are absent. When this is not true, a preliminary separation of manganese from the irradiated sample, based on the extraction of manganese diethyldithiocarbamate into chloroform and followed by stripping of the manganese with dilute sulphuric acid, must be used. A simultaneously irradiated standard containing manganese must be treated in exactly the same way as a test sample. In the materials analysed by the new method 10^{-5} to $10^{-3}\%$ of manganese has been determined.

INTRODUCTION

DURING the last few years a number of procedures[3] for the substoichiometric determination of traces of various metals by neutron-activation analysis have been developed but, until recently, development of a procedure suitable for manganese seemed to be impossible. The reason was that the common chelating agents form with manganese much less stable chelates than with most other metals. Therefore, a separation procedure based on the use of chelating reagents would be unselective and the reproducibility of a substoichiometric separation would probably be poor.

TABLE I.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF MANGANESE[7]

Stable isotope	Natural abundance, %	Isotopic activation cross section, *barns*	Product on thermal neutron irradiation	Half-life, *hr*	Mode of decay and energy (*MeV*)
^{55}Mn	100	13·3	^{56}Mn	2·58	β^-: 2·86; 1·05; 0·75 γ : 0·85; 1·81; 2·12

On the other hand, the nuclear properties of maganese (see Table I) are suitable for a very sensitive determination of this element by neutron-activation analysis. Theoretically, amounts of 10^{-10} g of manganese can be determined using a thermal neutron flux of 10^{12} neutrons. cm^{-2}. sec^{-1}.

In the past year we have been concerned with the possibilities of using ion-association extraction systems for substoichiometric separation. From a theoretical consideration,[1] based on the extraction data of Bock and Beilstein,[4] it follows that the substoichiometric determination of several elements will probably be possible in this way. Also, the work of Alimarin and Perezhogin[2] on the substoichiometric determination of gold by neutron-activation analysis, published recently, further stimulated our efforts in this field. The substoichiometric determination of manganese by neutron-activation analysis using tetraphenylarsonium chloride has now been successfully completed.

EXPERIMENTAL

Apparatus

Scintillation counter. Well-type with NaI(Tl) crystal.
pH *meter.* phM-2, Radiometer, Copenhagen, Denmark.
Separatory funnels. 150-ml volume.

Reagents

Manganese(II) *Carrier solution.* $1 \cdot 8 \times 10^{-2} M$ aqueous solution of manganese(II) sulphate.

Labelled carrier solutions. Manganese(II) carrier solution labelled with carrier-free ^{54}Mn, and $0 \cdot 01 M$ potassium permanganate solution labelled with carrier-free ^{54}Mn.

Tetraphenylarsonium chloride solution. $2 \times 10^{-3} M$ aqueous solution of the reagent.

Chloroform. Twice distilled.

Irradiation

The samples of chalk, analytical-reagent grade calcium carbonate and analytical-reagent grade potassium hydroxide were sealed in polyethylene ampoules and irradiated in a nuclear reactor in a neutron flux of 10^{11} to 10^{12} neutrons . cm^{-2}. sec^{-1}. for 20 hr. Standard samples containing 100 and 60 μg of manganese(II) sulphate were prepared by evaporating to dryness in polythene ampoules 0·1 and 0·06 ml of manganese(II) carrier solution, and irradiated simultaneously.

Development of Method

Influence of pH

It has been found that the substoichiometric extraction of tetraphenylarsomium permanganate is practically independent of the pH of the extracted solution, except for very acid or very alkaline media when destruction of the reagent or reduction of the permanganate takes place. This fact is in good agreement with our theoretical considerations.[1] Henceforth, a pH of 8-9 was used for all substoichiometric extractions (see *Selectivity*).

Reproducibility

The reproducibility of the substoichiometric extraction has been investigated in a manner previously described;[3] to increasing amounts of labelled $0 \cdot 01 M$ potassium permanganate carrier solution, placed in a series of separatory funnels, 2·0 ml of tetraphenylarsonium chloride solution were added and the ion-association complex formed extracted with 5·0 ml of chloroform for 3 min. The activities of 3·0 ml of the organic extracts were measured and plotted *vs.* the amount of manganese present in the extracted solution. From Fig. 1 it can be seen that, after reaching the equivalence point, very good reproducibility of the substoichiometric extraction was obtained; also, the time of 3 min for reaching extraction equilibrium is confirmed as being satisfactory.

Selectivity

From the known values of distribution ratios[4] and extraction constants,[1] various anions, *e.g.*, perrhenate, molybdate, pertechnate, nitrate, perchlorate, thiocyanate, bichromate, *etc.*, will be simultaneously extracted with permanganate. For this reason sulphuric acid is the only convenient acid for the dissolution of test samples because the sulphate anion is practically not extracted with tetraphenylarsonium chloride. (If other acids must be used for dissolution of a test sample, a preliminary separation of manganese, as described below, must be carried out.) The interfering influence of molybdenum(VI) can be eliminated if the extraction is performed at a pH higher than 8; from this solution neither molybdenum(VI) nor chromium(VI) is extracted.[4-6] In the presence of chloride ions some metals (mercury, gold, iron, tin, palladium, *etc.*) the anionic chloro complexes of

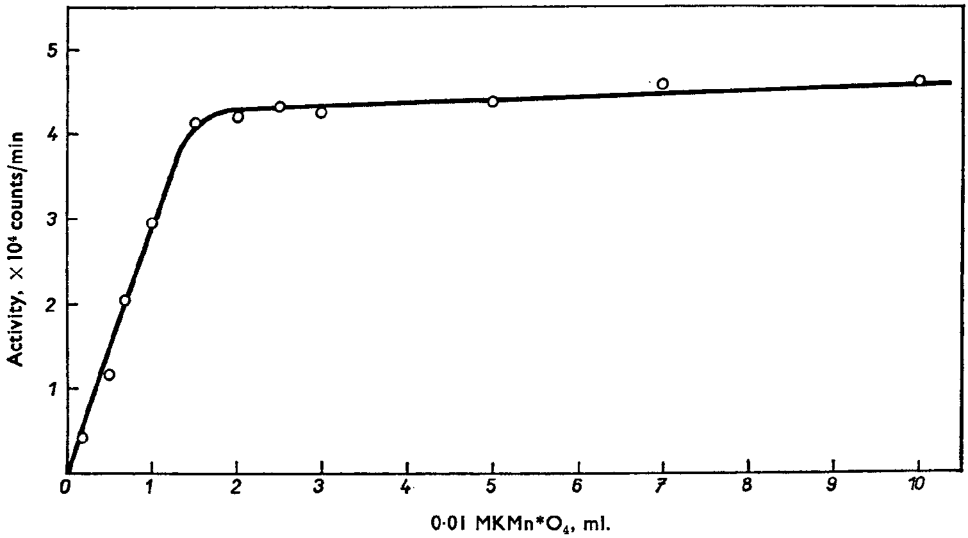

FIG. 1.—Reproducibility of the substoichiometric extraction into chloroform of manganese with tetraphenylarsonium chloride.

which are extractable with the tetraphenylarsonium cation, may also interfere. From our experiments it follows that the small amount of chloride ions present in the extracted solution as a result of using tetraphenylarsonium chloride can only give rise to interference from gold.[6] Large amounts of chloride ions must, of course, be avoided not only because other metals forming chloro-complexes would be extracted, but also because the dissociation of tetraphenylarsonium chloride itself would be decreased. If the latter does occur, then the reproducibility of the substoichiometric separation will be affected.

To avoid the above-mentioned interferences, a preliminary separation of manganese can be carried out as follows. The test sample is dissolved in the presence of manganese(II) carrier solution and the pH adjusted to about 8 with aqueous ammonia. An aqueous solution of sodium diethyldithiocarbamate is then added (in 5- to 10-fold excess) and the precipitate of manganese diethyldithiocarbamate[8] formed extracted with about 10 ml of chloroform. The manganese is then stripped from the separated organic phase by shaking with a 1- to 2-fold excess of zinc sulphate dissolved in 10^{-3} *M* to 10^{-2} *M* sulphuric acid until the organic phase is almost colourless. Subsequently, the separated aqueous phase is oxidised and extracted as described under *Procedure*.

When relatively simple materials were analysed it was found, from the decay measurements, that no interfering elements (gold, rhenium and technetium*) are present in detectable amounts and the preliminary separation step was, therefore, unnecessary.

Procedure

The irradiated samples of chalk or calcium carbonate were dissolved by boiling in 10 ml of 1*N* sulphuric acid; the irradiated sample of potassium hydroxide was dissolved in 10 ml of water.

To all dissolved test samples were added 0·60 ml of manganese(II) carrier solution, 2 drops of concentrated phosphoric acid, 50 ml of water, 1 ml of concentrated sulphuric acid, 1 ml of 1% silver nitrate solution and 1 g of ammonium peroxodisulphate. The solution was then heated to oxidise manganese(II) to the heptavalent state, excess of peroxodisulphate subsequently being destroyed by boiling. After cooling, the pH was adjusted to 8-9 with aqueous ammonia and the solution transferred to a separatory funnel, 2·00 ml of tetraphenylarsonium chloride solution and 5·00 ml of chloroform were added and the contents of the funnel shaken for 3 min. For measurement of the activity, 3·00 ml of the organic extract were evaporated to dryness in a glass counting jar and the residue dissolved in 2 ml of hot, concentrated hydrochloric acid. (When the activity of the organic extract is measured, a dark precipitate which appears on standing, affects the efficiency of counting during the decay measurements.)

* ^{99m}Tc can be expected as a result of the nuclear reaction $^{98}\text{Mo}(\text{n}, \gamma)^{99}\text{Mo} \xrightarrow[66\text{hr}]{\beta} {}^{99m}\text{Tc}$, if traces of molybdenum are present in a sample.

A simultaneously irradiated manganese standard-sample was dissolved in approximately 10^{-1} *M* sulphuric acid and diluted to 250 ml. A suitable aliquot of this solution was treated in exactly the same way as described above for the test sample.

The amount of manganese in the test sample (y) is calculated from the relationship[3]

$$y = y_s \frac{a}{a_s}$$

where y_s is the amount of manganese in the aliquot of the solution derived from the irradiated standard sample, and a and a_s are the activities obtained from the test sample and from the aliquot of solution derived from the irradiated standard sample, respectively.

RESULTS

Some results from the application of the method to the analysis of various materials are presented in Table II. Because of the single determination the analysis of the potassium hydroxide is not very reliable; however, the possibility of determining a very low content of manganese is illustrated. The results for the other two samples show the reproducibility of this type of analysis (the two samples differ considerably, of course, in the type and amount of trace impurities).

TABLE II.—SUBSTOICHIOMETRIC DETERMINATION OF MANGANESE.

Material analysed	Chalk			Calcium carbonate		Potassium hydroxide
Weight of sample, *mg*	98·1*	116·4†	86·5^{b,c}†‡	101·6†‡	106·8†	59·2*
Amount (y_s) of Mn in irradiated standard sample, *μg*	1·2	0·80	0·80	0·80	0·80	1·2
Activity¶ obtained from standard sample (a_s)	4224	6063	6063	6063	6063	4224
Activity¶ obtained from test sample (a)	31261	84211	62065	902	910	190
Amount of manganese found, *μg*	8·89	11·11	8·19	0·119	0·120	0·054
%	$9·06 \times 10^{-3}$	$9·99 \times 10^{-3}$	$9·46 \times 10^{-3}$	$1·17 \times 10^{-4}$	$1·12 \times 10^{-4}$	$9·77 \times 10^{-5}$

* Sample irradiated simultaneously with 100 *μg* of manganese standard.

† Sample irradiated simultaneously with 60-*μg* manganese standard using a slightly higher neutron flux and shorter cooling period than in the previous case.

‡ Diethyldithiocarbamate preliminary separation step applied.

¶ Expressed in counts/100 sec and corrected for background and decay.

The radiochemical purity of the tetraphenylarsonium permanganate extracts has been checked by measurement of decay curves (Fig. 2). It follows from the decay measurements as well as from Table II (no differences found between samples analysed with and without the preliminary separation) that neither the chalk nor calcium carbonate contained interfering elements. The use of a multichannel analyser would probably avoid the necessity of using the preliminary separation step even in the analysis of more complicated materials.

CONCLUSION

A simple substoichiometric determination of manganese by neutron-activation analysis has been developed and previous theoretical considerations[1] are, therefore, confirmed. Consequently, it can be expected that it will definitely be possible in the same way to determine the other elements mentioned in the previous paper,[1] indeed, the work on one of them, rhenium, has just been successfully completed.[6]

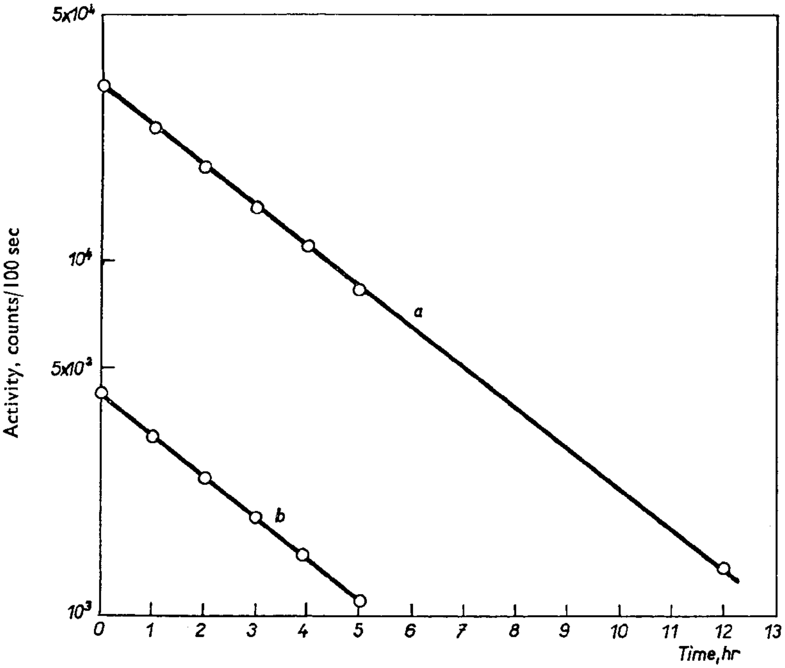

FIG. 2.—Typical decay curves of tetraphenylarsonium permanganate extracts:
(a) chalk,
(b) standard manganese sample.
In both cases the observed half-life was 2·6 hr.

Acknowledgment—The authors thank Professor V. Majer for his interest in this work and Dr. M. Williams for critical discussion.

Zusammenfassung—Eine einfache und schnelle Methode zur unterstöchiometrischen Bestimmung von Manganspuren in verschiedenen Materialien durch Neutronenaktivierungsanalyse wurde entwickelt. Nach Auflösung der bestrahlten Probe wird Mangan(II)-Träger zugegeben und mit Peroxodisulfat zur siebenwertigen Stufe oxydiert. Das gebildete Permanganat wird als Tetraphenylarsoniumpermanganat in Chloroform extrahiert, wobei Tetraphenylarsoniumchlorid in unterstöchiometrischer Menge angewandt wird. Bei der Analyse relativ einfachen Materials, das keine Störelemente (Gold, Rhenium usw.) enthält, liefert diese einfache Abtrennung radiochemisch reines Mangan-56. Ist dies nicht der Fall, muß Mangan zuerst aus der bestrahlten Probe abgetrennt werden durch Extraktion von Mangandiäthyldithiocarbamat in Chloroform und nachfolgende Rückextraktion in verdünnte Schwefelsäure. Ein gleichzeitig bestrahlter Manganstandard muß genau so wie die Probe behandelt werden. In den mit der neuen Methode analysierten Stoffen wurden 10^{-5} bis $10^{-3}\%$ Mangan bestimmt.

Résumé—On a élaboré une méthode simple et rapide pour le dosage substoechiométrique de traces de manganèse dans diverses substances au moyen de l'analyse par activation de neutrons. Après dissolution de la prise d'essai irradiée, on ajoute le manganèse(II) entraîneur puis oxyde à l'état heptavalent par le perdisulfate. Le permanganate ainsi formé est enfin extrait en chloroforme à l'état de permanganate de

tétraphénylarsonium, en utilisant une quantité substoechiométrique de chlorure de tétraphénylarsonium. Cet unique stade de séparation isole le manganèse-56 radiochimiquement pur à partir d'une substance relativement simple, où les éléments interférents (or, rhénium, etc . . .) sont absents. Lorsque ce n'est pas le cas, il faut procéder à une séparation préliminaire du manganèse de l'échantillon irradié, basée sur l'extraction en chloroforme du diéthyldithiocarbamate de manganèse suivie d'un lavage du manganèse à l'acide sulfurique dilué. Un étalon contenant du manganèse, et irradié simultanément, doit être traité exactement de même maniére que la prise d'essai. Dans les substances analysées selon la nouvelle méthode, on a dosé 10^{-5} à 10^{-3}% de manganèse.

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LUMINOL AS A FLUORESCENT ACID-BASE INDICATOR

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Summary—The acid and base dissociation constants of luminol are determined at various ionic strengths. The transition interval occurs at pH 7·7–9·0, therefore luminol is a fluorescent indicator for the titration of strong and weak acids and strong bases. Its value as an indicator is established by titrating milk, red wine and cherry juice.

THE intensive blue chemiluminescent and fluorescent light of luminol (3-aminophthalic hydrazide) stimulated many research workers to find analytical applications of the phenomenon. Chemiluminescence of luminol was used first for detection of heavy metal ions,[1,2] hydrogen peroxide[3–5] and hemine[6–8] and, later, for the end-point detection of acid-base titrations.[9–11]

Erdey and his coworkers developed, with the aid of luminol, many oxidation-reduction determinations which were previously impossible because of the dark colour of the solution to be titrated or of the reaction products.[12–14] It has been advantageously used recently also as a chelometric indicator.[15]

In an alkaline medium in the presence of oxidising agents luminol emits a chemiluminescent light which ceases in an acidic medium; it intensively fluoresces when irradiated with ultraviolet light in an acidic medium. This fluorescent light suddenly disappears in an alkaline medium, demonstrating that luminol has properties characteristic of fluorescent acid-base indicators. This is mentioned also by Birner and Perrottet[16] who measured the ultraviolet absorption of luminol as a function of pH when studying properties of luminol.

Fluorescent indicators, as is well known, are generally organic molecules whose π electrons are excited by ultraviolet light. Electrons of the excited molecules, being in the triplet state, fall into the singlet state by spin compensation while fluorescent light is emitted.

This process, however, depends on the state of acid dissociation of the molecule. There are substances whose ionic form emits fluorescent light, while others, like luminol, emit fluorescent light only in the undissociated state. A linear relationship between the fraction dissociated and intensity of the fluorescent light is found. In dilute solutions which absorb fluorescent light only to a negligible extent, the intensity of fluorescence changes linearly with the concentration of the fluorescent substance. This relation was used for determination of the dissociation constants of luminol.

EXPERIMENTAL

Apparatus

Fluorimeter. Pulfrich photometer with fluorescence attachment. An L3 filter and a D comparison standard colour were used.

pH meter. Polimetrom 42B.

Reagents

Luminol solution, 0·01%. An aqueous solution is stable for a long time.

Procedure

Transfer an aliquot of the strong or weak acid into a 200-ml titration flask, add 0·5 ml of 0·01% luminol solution and titrate the solution with sodium hydroxide (0·1N, 0·01N or 0·001N) under ultraviolet light until the disappearance of the blue fluorescent light. The end-point of the titration of strong bases is indicated by the sudden appearance of the fluorescent light. The variation of intensity of fluorescence with concentration is shown in Fig. 1. It can be seen that in the concentration range between 1×10^{-5} and $1{\cdot}5 \times 10^{-4}M$ the intensity of fluorescence increases linearly with increasing luminol concentration; for higher concentration values, however, after a maximum the intensity decreases. In subsequent experiments, therefore, a luminol solution of $10^{-4}M$ was used.

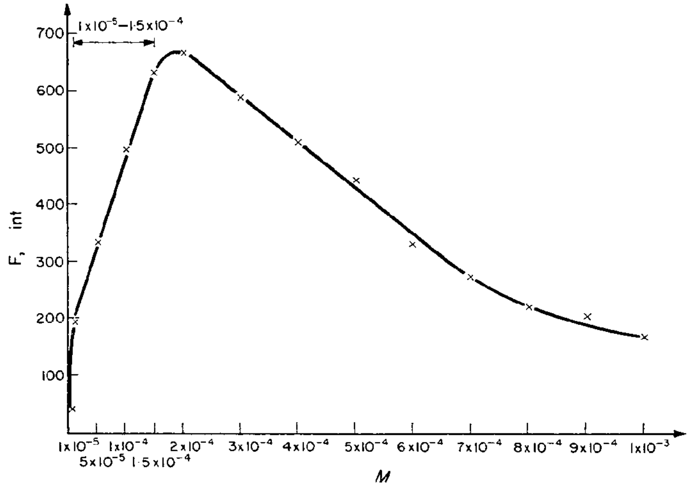


FIG. 1.—Fluorescence intensity of luminol as a function of luminol concentration.

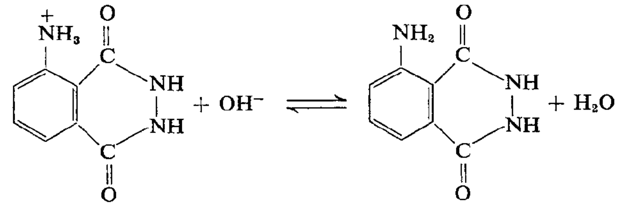
For the determination of dissociation constants Britton-Robinson buffer mixtures were used. It was established that these solutions and solutions of sodium chloride and sulphate do not influence the fluorescence of luminol.

The intensities of fluorescence of $10^{-4}M$ luminol solutions at various pH and ionic strengths are shown in Fig. 2, which shows that intensity of fluorescence goes through a maximum with increasing pH. Dissociation constants of luminol were calculated from the experimental data.

DISCUSSION

Because of the amphoteric character of luminol, the following equilibria must be considered:

at low pH:

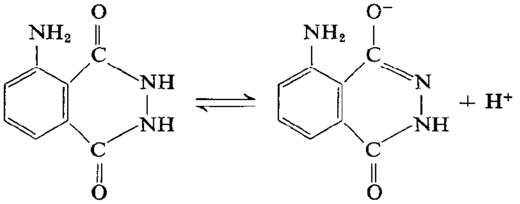


(1)

Luminol hydrochloride cation, does not fluoresce.

Luminol neutral molecule, fluoresces.

at higher pH (but pH < 10):



(2)

Neutral molecule, fluoresces.

Anion of luminol, does not fluoresce.

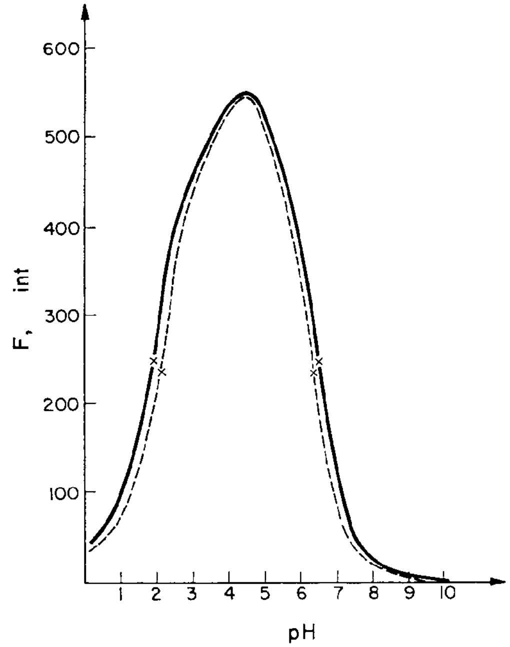


FIG. 2.—Fluorescence intensity of luminol as a function of pH at various ionic strengths.

Because only the neutral form fluoresces, the maximum intensity of fluorescence of luminol is at the pH corresponding to the greatest concentration of neutral luminol. The dissociation constant K_a of an indicator acid HI can be expressed as

$$K_a = \frac{[H^+][I^-]}{[HI]}$$

where $[I^-]$ is concentration of the indicator anion, [HI] that of the undissociated indicator. If the total concentration of acid is $[H^+]$, and the degree of dissociation is α, then

$$K_a = \frac{\alpha}{1-\alpha}[H^+].$$

If $\frac{\alpha}{1-\alpha} = 1$, *i.e.*, $\alpha = 0{\cdot}5$, then $K_a = [H^+]$.

Because the intensity of fluorescence is proportional to the concentration of the undissociated form, the pH value at which the intensity of fluorescence falls to half of its maximal value equals pKa.

At lower pH, where equilibrium (1) is valid, the neutral molecule taking part in the equilibrium behaves as a base. The corresponding equilibrium constant is given at half neutralisation by

$$K_b = \frac{K_\omega}{[H^+]}, \text{ where } K_\omega \text{ is the dissociation constant of water,}$$

and from this, at 25°

$$pK_b = -\log K_b = 14 - pH.$$

After the evaluation of curves plotted at various ionic strengths, the values presented in Table I were obtained. As can be seen and as was also to be expected, the values of pK_a and pK_b decrease slightly with increasing ionic strength. Our results are nearly identical with the values of Weber obtained by fluorometric techniques,[17] whereas those of Babko and Lukovskaya,[18] obtained by a spectrophotometer, differ by about one order of magnitude. The reason for the deviation can possibly be found in the difference between the two methods of measurement.

TABLE I.—DISSOCIATION CONSTANTS OBTAINED AT DIFFERENT IONIC STRENGTHS

Ionic strength	pK_a	K_a	pK_b	K_b
0·004	6·33	$4{\cdot}7 \times 10^{-7}$	—	—
0·01	6·26	$5{\cdot}5 \times 10^{-7}$	12·00	$1{\cdot}0 \times 10^{-12}$
0·07	6·23	$5{\cdot}9 \times 10^{-7}$	11·90	$1{\cdot}3 \times 10^{-12}$
0·1	6·20	$6{\cdot}3 \times 10^{-7}$	11·85	$1{\cdot}4 \times 10^{-12}$
0·5	6·12	$7{\cdot}6 \times 10^{-7}$	11·80	$1{\cdot}6 \times 10^{-12}$

Although the transition pH values of an indicator may be deduced from the acid and base dissociation constants, in the case of single coloured indicators the value of the transition interval is also given because concentration and solubility of the indicator affects the width of the transition interval.

For the purpose of approximate determination of this interval 0·01*M* hydrochloric acid was titrated potentiometrically with 0·01*M* carbonate-free sodium hydroxide, and meanwhile the intensity of fluorescence was observed. Fig. 3 shows the titration curve obtained and it is to be seen that at higher indicator concentration the transition pH interval is 7·5–8·2, and at lower indicator concentration it is 7·1–8·1.

For more precise determination of the transition interval a buffer series was made the pH of which increased by 0·1 pH unit. To this luminol solutions of known and increasing concentrations were added and the fluorescence of the solutions observed in ultraviolet light. In Table II the pH at which fluorescence suddenly decreased or ceased are presented. It is to be seen that the fluorescence changes between pH 7·2–7·8 and pH 8·3–9·0 between 1×10^{-6} and $2{\cdot}5\text{–}10^{-5}M$ concentrations, respectively. In practice 0·5 ml of 0·01 % indicator solution was used for one titration and the volume at the end of the titration was 10–60 ml, *i.e.*, luminol is $2{\cdot}5 \times 10^{-5}$–$5 \times 10^{-6}M$. Therefore, luminol can be used as a fluorescent indicator for the titration of strong and weak acids and strong bases.

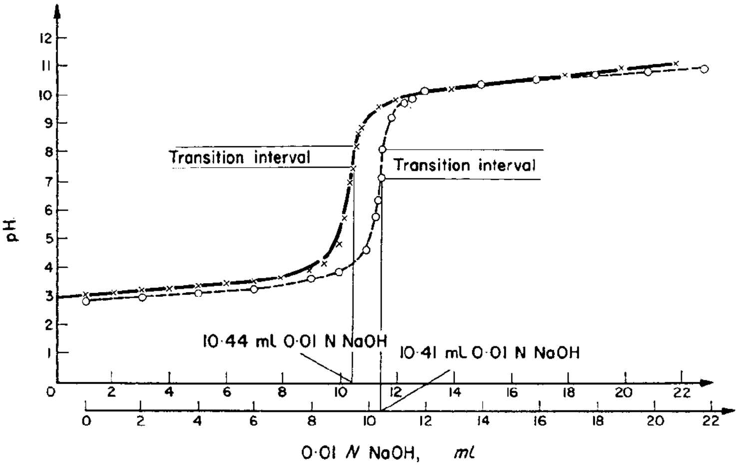


FIG. 3.—Determination of transition interval of luminol at various indicator concentrations.

TABLE II.—TRANSITION RANGE OF LUMINOL AS A FUNCTION OF INDICATOR CONCENTRATION

Luminol conc., *M*	Range, *pH*
$1{\cdot}0 \times 10^{-6}$	7·2–7·8
$2{\cdot}5 \times 10^{-6}$	7·6–8·2
$5{\cdot}0 \times 10^{-6}$	7·7–8·3
$7{\cdot}5 \times 10^{-6}$	8·0–8·6
$1{\cdot}0 \times 10^{-5}$	8·2–8·8
$2{\cdot}5 \times 10^{-5}$	8·3–9·0

TABLE III.—TITRATION OF VARIOUS ACIDS WITH NaOH IN THE PRESENCE OF LUMINOL AS INDICATOR

Acids	Concentration, *N*	Deviation from real value, %	Standard deviation,	
			ml	%
HCl	1·0	±0·0	±0·01	±0·06
	0·1	−0·10	±0·02	±0·08
	0·01	±0·0	±0·02	±0·10
	0·001	+2·4	±0·07	±0·36
CH_3COOH	1·0	±0·0	±0·01	±0·07
	0·1	+0·05	±0·01	±0·06
	0·01	+0·15	±0·02	±0·10
	0·001	+1·4	±0·13	±0·63
H_2SO_4	1·0	−0·20	±0·02	±0·08
	0·1	−0·35	±0·02	±0·08

TABLE IV.—TITRATION OF NaOH WITH VARIOUS ACIDS IN THE PRESENCE OF LUMINOL AS INDICATOR

Acid	Concentration, N	Deviation from real value, %	Standard deviation *ml*	Standard deviation %
HCl	1·0	+0·05	±0·02	±0·08
	0·1	−0·05	±0·01	±0·07
	0·01	−0·30	−0·03	−0·13
	0·001	−1·7	−0·10	±0·58
CH_3COOH	1·0	+0·20	±0·01	±0·07
	0·1	+0·05	±0·02	±0·09
	0·01	−0·25	±0·03	±0·16
	0·001	−0·88	±0·13	±0·64
H_2SO_4	1·0	+0·05	±0·01	±0·06
	0·1	−0·15	±0·02	±0·09

TABLE V.—PRACTICAL USE OF LUMINOL

0·1N NaOH required, *ml*						
by 20·00 ml of milk			by 20·00 ml of red wine		by 20·00 ml of cherry juice	
In presence of phenolphthalein	In presence of luminol	Potentiometrically	In presence of luminol	Potentiometrically	In presence of luminol	Potentiometrically
3·13	2·40	2·50	16·75	16·71	22·45	22·44
3·21	2·47	2·46	16·67	16·70	22·36	22·42
3·17	2·46		16·73		22·38	
3·17	2·44	2·48	16·72	16·71	22·40	22·43

Table III gives data about the errors of titration of strong and weak acids of various concentration. It is to be seen that the deviation from the real value is permissible even at 0·001N concentration.

Table IV shows results of the titration of sodium hydroxide with strong and weak acids. Both the standard deviation and deviation from the real value are small.

The advantage of fluorescent indicators over the usual dye indicators is that they can be used in the titration of dark, coloured and turbid solutions. We checked the practical value of luminol by determining the acid content of milk, red wine and cherry juice. In Table V are shown results obtained in titrations in the presence of luminol and in potentiometric titrations. It is clear that the two methods give practically the same results.

Zusammenfassung—Die Säure- und Basendissoziationskonstanten von Luminol wurden bei verschiedenen Ionenstärken ermittelt. Der Umschlagsbereich liegt bei pH 7·7–9·0, daher ist Luminol ein Fluoreszenzindikator zur Titration starker und schwacher Säuren und starker Basen. Seine Anwendbarkeit wurde durch Titration von Milch, Rotwein und Kirschsaft bestätigt.

Résumé—On a déterminé les constantes de dissociation acide et basique du luminol pour diverses forces ioniques. Le domaine de transition se situe à pH 7·7–9·0; par conséquent le luminol est un indicateur fluorescent pour le dosage des acides forts et faibles et des bases fortes. On établit ses possibilités d'application en dosant le lait, le vin rouge et le jus de cerises.

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INVESTIGATION OF THE SOLVENT EXTRACTION OF CALIFORNIUM, FERMIUM AND MENDELEVIUM

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Summary—The extraction constants for the systems di-(2-ethylhexyl)-orthophosphoric acid/toluene/hydrochloric acid and americium, curium californium and fermium have been determined. They have been used to select the best conditions for the separation of californium, fermium and mendelevium by extraction chromatography. The separation factors are much higher than the corresponding ion-exchange methods.

PREVIOUS work by Siekierski and Fidelis[1,2] on the separation of rare earths by means of extraction chromatography using tributyl phosphate has shown that this method can also be applicable for the separation of tervalent transuranic elements. The results of other investigations[3,4] confirmed the advantage of extraction chromatography, especially for separation of heavy transplutonic elements whose quantities are still very scarce.

Recently, work on the use of alkylphosphoric acids for the separation of lanthanides and light transuranic elements by means of extraction chromatography[5–9] has been reported. The interest in these acids is because they bring about the separation of lanthanides and actinides more effectively than organic reagents used in conjunction with an ion-exchange resin. One, in particular, which has found widespread use for the separation of tervalent metals by extraction is di-(2-ethylhexyl)orthophosphoric acid (HDEHP).[10]

The present paper deals with the static and dynamic extraction of californium, fermium and mendelevium in the system di-(2-ethylhexyl)orthophosphoric acid-hydrochloric acid with a view to determining extraction constants and to finding conditions for their separation.

THEORETICAL

Di-(2-ethylhexyl)orthophosphoric acid is present in organic solvents in the dimeric form.[11] The extraction of lanthanides and tervalent actinides in trace quantities is based on the following reaction:

$$M^{3+} + 3(H_2A_2)_{org} \rightleftharpoons M(HA_2)_{3org} + 3H^+ \qquad (1)$$

The equilibrium constant of this reaction (the extraction constant) is

$$K = \frac{[M(HA_2)_3]_{org}[H^+]^3}{[M^{3+}][H_2A_2]^3_{org}} = q\,\frac{[H^+]^3}{[H_2A_2]^3_{org}} \qquad (2)$$

where q is the distribution of the metal investigated.

The extraction constant can be determined readily by determining values of q at different hydrogen-ion concentrations and substituting into equation (2). The separation factor of different transuranic elements is determined by the ratio of their extraction constants.

The multiple repetition of extraction runs in extraction chromatography permits selective separation of transplutonic elements in quantities of several tens or hundreds of atoms. When such quantities of an element are present in the solvent ($<10^{-15}$ *M*), the ability to concentrate the element studied into the smallest volume without any contamination becomes very significant.

At the same time extraction chromotography makes it possible to determine the distribution ratios of such elements as mendelevium by the position of the elution peaks; such an identification is impossible under the conditions of static extraction.

EXPERIMENTAL

Transplutonium elements

The synthesis of ^{246}Cf, ^{252}Fm and ^{256}Md isotopes was performed in the 300-cm heavy-ion accelerator of the Laboratory of Nuclear Reactions (JINR) by means of the following reactions:

(I) $^{238}\mathrm{U}(^{14}\mathrm{N}, 6\mathrm{n})\ ^{246}\mathrm{Es} \xrightarrow[7\ \mathrm{min}]{\mathrm{e.c.}} {}^{246}\mathrm{Cf} \xrightarrow[35{\cdot}7\ \mathrm{hr}]{\alpha}$

(II) $^{238}\mathrm{U}(^{18}\mathrm{O}, 4\mathrm{n})\ ^{252}\mathrm{Fm} \xrightarrow[25\ \mathrm{hr}]{\alpha}$

(III) $^{238}\mathrm{U}(^{22}\mathrm{Ne}, \alpha 4\mathrm{n})\ ^{252}\mathrm{Fm} \xrightarrow{\alpha}$

(IV) $^{238}\mathrm{U}(^{22}\mathrm{Ne}, \mathrm{p}3\mathrm{n})\ ^{256}\mathrm{Md} \xrightarrow[90\ \mathrm{min}]{\mathrm{e.c.}} {}^{256}\mathrm{Fm} \longrightarrow$

The cross-sections for reactions (I) and (III) are $\sim 10^{-29}$ cm^2 and $\sim 2 \times 10^{-31}$ cm^2, respectively. The cross-section for reaction (IV) is very small (2×10^{-33} cm^2).[12] The irradiation of U_3O_8 deposited on a copper backing with internal water-cooling was performed in the internal beam of the accelerator. The energy of N, O and Ne ions was equal to about 110, 128 and 140 MeV, respectively. To increase the yield of ^{256}Md a 75–85 % enrichment of ^{22}Ne was used. About 10^7 atoms of ^{246}Cf, 10^5 atoms of ^{252}Fm and 10^2 atoms of ^{256}Md were obtained per cycle.

The processing of the irradiated targets and the separation of transplutonic elements were performed by methods previously described.[13,14]

Static extraction

Experiments on static extraction were performed as follows.

The mixture of transplutonic elements was dissolved in hydrochloric acid (of known concentration) in a quartz test-tube. One ml of the solution was transferred to a quartz test-tube (fitted with a ground stopper), then 0·5 ml of toluene and 0·5 ml of di-(2-ethylhexyl)phosphoric acid were added. The tube was shaken for 1-4 hr (extraction equilibrium is reached in several minutes) and 0·8 ml of aqueous phase was taken and deposited on a rhodium backing.

The deposition of the solution was performed by small portions to obtain a thin uniform layer. After drying and annealing of the backing at about 300°, the alpha-activity of the sample was measured. Because of difficulties connected with decomposition of the organic phase the transuranic elements after 5-fold dilution of the extract with toluene were quantitatively re-extracted in 1·00 ml of 3-4*M* hydrochloric acid and 0·90 ml of the re-extract was processed for activity measurements as above. The distribution coefficients for different transuranic elements were determined by the alpha-spectrum of the aqueous phase and the re-extract. By carrying out the experiment in this way it is possible not only to determine the extraction constants of several transplutonium elements per experiment, but to determine exactly the separation factors of these elements.

Extraction chromatography

The experiments on the separation of transplutonic elements were performed in a glass column, 2·5 mm in diameter, with a ground stopper. Hyflo-Super Cell silica gel, rendered hydrophobic by treatment with dimethyldichlorosilane, was packed into the column to give a column-height of 100 mm; the grain size was 12-18 μ. The silica-gel was saturated with a solution of di-(2-ethylhexyl)orthophosphoric acid in toluene (1 + 1) which was passed through the column; the amount of the extractant in the column was about 15 % of the weight of the silica gel.

The mixture of transplutonic elements together with rare-earth tracers and ^{137}Cs was dissolved in 3-4 drops of hydrochloric acid of certain concentration. This mixture was placed on the top of the column and elution with hydrochloric acid (saturated with working solution of the extractant) of the required concentration was performed. The speed of the elution was 1 drop per 25 sec at 64°. The high speed of elution was chosen because of the short half-life of ^{256}Md, though under these conditions the peaks of separate elements are not so sharp as those obtained at lower speeds of elution. Separate drops were collected on glass backings, dried, and the beta-activity of the rare earths and ^{137}Cs (as an indicator of a free volume of the column) measured by means of an end-window Geiger-Müller counter. The alpha-activity of ^{246}Cf and ^{252}Fm was measured by an ionisation chamber with 2π-geometry and a 100-channel amplitude analyser ("Rainbow").

^{256}Md was detected by the daughter nuclei of ^{256}Fm with a half-life of spontaneous fission equal to 2·7 hr. Fission fragments of ^{256}Fm were detected directly on glass backings as described previously.[4,15]

RESULTS AND DISCUSSION

The dependence of the distribution ratios for californium and fermium together with americium, curium, promethium, europium, gadolinium and terbium on the concentration of hydrochloric acid is shown in Fig. 1.

It is shown that the distribution ratio of all the studied elements is inversely proportional to the cube of the concentration of hydrochloric acid, *i.e.*, the extraction of these elements proceeds according to equation (1).

The results of the determination of extraction constants for californium and fermium are given in Table I. The mean value of the logarithm of the extraction constant is

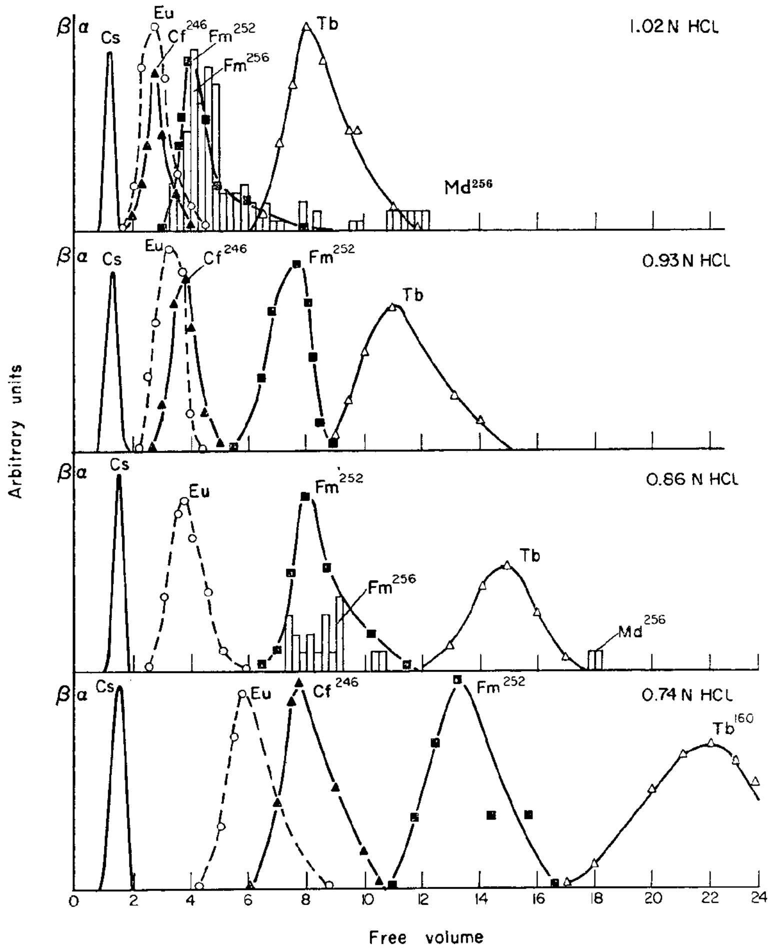

FIG. 1.—Separation of Cf, Fm and Md by means of extraction chromatography. (Hydrochloric acid concentration is equal to 0·74–1·02*M*)

equal to —0·17 for californium and to +0·49 for fermium, *i.e.*, the separation factor (F) of these elements is about 4·5. This value much exceeds the separation factor of the californium-fermium pair when the selective complexing agents in ion-exchange chromatography are used (for α-hydroxyisobutyric acid with F = 3·2).[16] It also exceeds the separation factor of the extraction by means of tributyl phosphate (F = 1·45),[3] thenoyltrifluoroacetone (F = 2·0)[17] and di-2-ethylhexylphenylphosphonic acid (F = 3·1).[18]

TABLE I.—DETERMINATION OF EXTRACTION CONSTANTS OF Cf AND Fm WITH DI(2-ETHYLHEXYL)ORTHOPHOSPHORIC ACID (TOLUENE AS A SOLVENT)

Element	Cf		Fm	
log[HCl]	log q	log K	log q	log K
0·18	—1·03	—0·13	—0·42	0·49
0·09	—0·83	—0·19	—0·11	0·53
0·06	—0·67	—0·12	—0·08	0·47
—0·01	—0·55	—0·22	0·12	0·48
—0·09	—0·19	—0·09	0·38	0·48
—0·10	—0·26	—0·20		
—0·13	—0·14	—0·17		
—0·24	0·26	—0·10		
—0·32	0·44	—0·16		
	aver.	—0·17	aver.	—0·49

The extraction constant of californium determined in the present paper is in good agreement with the data of Peppard *et al.*[19] (log K = 0·0).

The extraction constant of fermium has not been determined previously.

The values of the extraction constant of americium (log K = —1·67; according to Peppard *et al.*[20] log K = —1·53) and of curium (log K = —1·43; according to Peppard *et al.*[19] log K = —1·4) indicate that it is feasible to separate californium and heavier transplutonic elements from americium and curium by means of di-(2-ethylhexyl)orthophosphoric acid [the separation factor (F) is above 20, whereas F = 4·5 if these elements are separated by means of ion-exchange chromatography with α-hydroxyisobutyric acid[16]].

The results of the separation of the californium, fermium and mendelevium by means of extraction chromatography are given in Table II, where the positions of the peaks of the separated elements expressed in free volumes of the column at different concentrations of hydrochloric acid are shown. As the concentration of hydrochloric acid decreases, the values of the distribution ratio increase, which results in later elution

TABLE II.—POSITIONS OF PEAKS OF Eu, Tb, Cf, Fm AND Md AS A FUNCTION OF CONCENTRATION OF HYDROCHLORIC ACID*

HCl, *M*	Eu	Tb	Cf	Fm	Md
1·15	2·2	6	—	3·9	—
1·02	2·7	8·0	2·7	4·3	10–13
0·93	3·3	11	4·0	7·7	—
0·86	3·7	15	—	7·8	17–19
0·79	5·2	19	7	—	—
0·74	5·7	22	8	12	—

* Expressed as free volumes of column.

of separate elements and increase of the total time of separation. Hence, the optimum concentration of hydrochloric acid for the separation of a californium-fermium pair is equal to 0·7–0·9*M* and for the separation of a fermium-mendelevium pair is 0·9–1·0*M* (Fig. 2). At this concentration of hydrochloric acid the separation factor for fermium-mendelevium is equal to 2·5–3, which is much higher than in ion-exchange chromatography. Some disagreements between separation factors obtained under static and

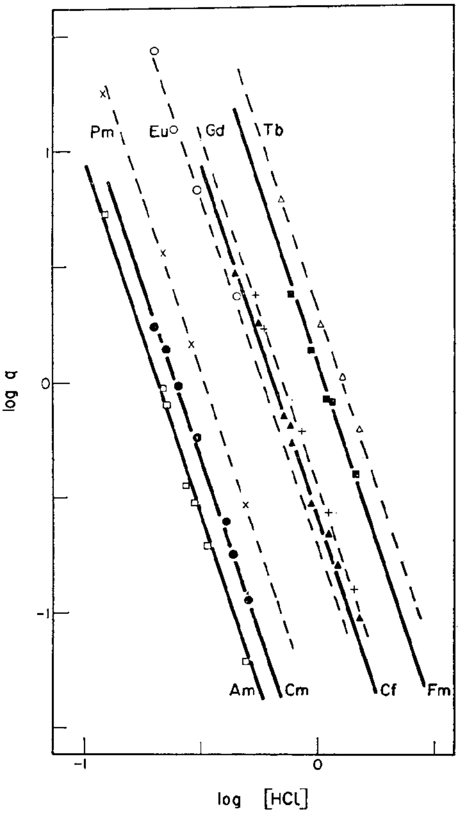

FIG. 2.—Distribution ratios (q) of transplutonium elements as functions of hydrochloric acid concentration:
Am(log K = −1·67), Cm(log K = −1·42), Cf(log K = −0·15), Fm(log K = 0·49), Pm(log K = −1·05), Eu(log K = −0·36), Gd(log K = −0·03) and Tb(log = +0·74).

dynamic conditions are the result of difficulties in the exact determination of the free volume in small columns and a partial elution of the extractant by hydrochloric acid.

The use of extraction chromatography permits the separation of transplutonic elements in a hydrochloric acid medium without contamination from organic complexing agents.

CONCLUSION

1. The extraction constants of americium, californium, curium and fermium in the system of di-(2-ethylhexyl)orthophosphoric acid/toluene/hydrochloric acid have been determined.

(2) The conditions for selective separation of californium, fermium and mendelevium by means of extraction chromatography have been found. The separation factors in this system are much higher than in the ion-exchange method.

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Zusammenfassung—Die Extraktionskonstanten für die Systeme Di-(2-äthylhexyl-)orthophosphorsäure/Toluol/Salzsäure und Americium, Curium, Californium und Fermium wurden bestimmt. Sie wurden verwendet, um die besten Bedingungen zur Trennung von Californium, Fermium und Mendelevium durch Extraktionschromatographie zu ermitteln. Die Trennfaktoren sind viel größer als bei den entsprechenden Ionenaustauschmethoden.

Résumé—On a déterminé les constantes d'extraction pour les systèmes acide di-(2-éthylhexyl)orthophosphorique/toluène/acide chlorhydrique et américium, curium, californium et fermium. Elles ont été utilisées pour sélectionner les meilleures conditions de séparation du californium, du fermium et du mendelevium par chromatographie d'extraction. Les facteurs de séparation sont beaucoup plus élevés que pour les méthodes correspondantes par échange d'ions.

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POTENTIOMETRIC DETERMINATION OF PLUTONIUM BY ARGENTIC OXIDATION, FERROUS REDUCTION AND DICHROMATE TITRATION

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Summary—A simple and rapid method is described for the routine determination of plutonium with a coefficient of variation of better than 0·2%. It is directly applicable to nitrate solutions containing a large amount of uranium; moderate amounts of iron, molybdenum, fluoride and phosphate do not interfere. Chromium, cerium and manganese interfere quantitatively, and the procedure may also prove convenient for the determination of these elements. The plutonium is oxidised to the sexivalent state with argentic oxide in nitric acid solution, and the excess of oxidant is destroyed by reaction with sulphamic acid. A weighed small excess of iron(II) solution is then added, and the excess is titrated potentiometrically with standard potassium dichromate solution using polarised gold indicator electrodes. The whole determination is performed in one vessel at room temperature, and takes about 20 min.

INTRODUCTION

METZ and Waterbury,[1] reviewing the analytical methods for plutonium determination published before 1962, recommended the following procedures for macro amounts of the element:—

- (a) Reduce with zinc amalgam and titrate from plutonium(III) to plutonium(IV) with cerium(IV) using a potentiometric end-point.[2]
- (b) As (a), but reduce with titanium(III).[3]
- (c) As (a), but reduce with chromium(II).[4]
- (d) Oxidise with perchloric acid, reduce from plutonium(VI) to plutonium(IV) with an excess of iron(II), and titrate the excess with cerium(IV) again using a potentiometric end-point.[5]
- (e) Titrate plutonium(VI) by constant current coulometry with electrogenerated iron(II).[6]
- (f) Titrate by controlled potential coulometry.[7]
- (g) Oxidise with argentic oxide, and titrate plutonium(VI) to plutonium(IV) amperometrically with iron(II).[8,9]
- (h) Titrate solutions of plutonium metal from plutonium(III) to plutonium (IV) with cerium(IV) to a spectrophotometric end-point.[10]

Jones,[11] in a more recent review, also selected most of these methods and reported the experimental procedures in detail.

Since Metz and Waterbury compiled their review, Corpel and Regnaud[12] have reported a simple method for determination of plutonium, uranium, or iron by reduction with an excess of titanium(III) in the presence of nitric acid, which destroys the excess reducing agent, followed by titration with cerium(IV). Also, Brown[13] has described a complexometric method for plutonium by titration with EDTA. Another relevant method, not included in Metz and Waterbury's recommended procedures, was the precise determination of plutonium reported by Pietri and Baglio[14] by titration from plutonium(III) to plutonium(IV) with dichromate, using polarised gold electrodes to detect the end-point.

At the Dounreay Experimental Reactor Establishment, precise methods were required for the analysis of plutonium/uranium ceramic fuels under development for the fast reactor, and of intermediates in the production of these materials from nitric acid solutions of the elements. Fuel materials which have been examined so far have included sintered mixed oxides and carbides containing from 10 to 50% of plutonium. They have normally been prepared for analysis by dissolution in nitric acid containing a small amount of hydrofluoric acid. Two general approaches were possible for the determination of plutonium in such solutions. Either the plutonium could be separated from the uranium before determination, *e.g.*, by the ion-exchange method reported by Kressin,[15] or the plutonium could be determined directly by a specific method. If a simple method suitable for routine use could be found, the latter approach was obviously preferable, because separation procedures are usually tedious and must contribute to the imprecision and bias of the whole method.

Many of Metz and Waterbury's recommended methods have been used with very high precision, but only under ideal conditions and usually only on relatively large samples of pure plutonium metal. The analysis of mixed oxides presents more formidable problems, and many of the methods cannot be used. Uranium interferes seriously with most procedures requiring reduction to plutonium(III), and when uranium is present as a major component it is almost essential to use the reduction of plutonium(VI) to plutonium(IV) as the fundamental reaction of the titration.

Further study of the methods listed above suggested that a hybrid, combining selected stages from several procedures, might be more generally applicable than any of the originals. Thus, comparing the oxidation stages of the two chemical methods using the plutonium(VI) to plutonium(IV) reaction, Waterbury[5] used fuming perchloric acid, and Seils[8] used argentic oxide. The former method appears to have two drawbacks. Fuming perchloric acid is a potentially hazardous reagent, particularly in a glovebox, and, in common with many workers on the determination of chromium,[16] Seils[8] found that errors could be introduced if the correct conditions for dilution of the fuming acid were not followed strictly. Because oxidation with argentic oxide was simple to perform and the excess reagent was readily destroyed by gentle heating, the argentic oxide method appeared preferable.

Comparing the reduction stages, Waterbury[5] added an excess of iron(II) and back-titrated the excess, whereas Seils[8] titrated with iron(II) directly to an amperometric end-point. In the latter procedure, the slow reaction between plutonium(VI) and iron(II) complicated the measurement of residual current just before the end-point. Seils[8] assumed that the residual current did not change during the whole titration, whereas Bergstresser[9] measured the residual current after adding 98% of the theoretical amount of iron (II) to a separate portion of sample. Such approximations may be justified in the case of pure plutonium metal samples; but there is more danger of error when analysing, routinely, samples of varying history. Reduction by adding an excess of iron(II) and back-titrating the excess therefore seemed preferable.

Comparison of procedures for titration of either the excess of iron(II) or of plutonium(III) to plutonium(IV) showed that all workers used cerium(IV) as titrant, except Pietri[14] who used dichromate. The advantage of using a primary oxidimetric standard are obvious, providing that the end-point is sufficiently sharp and robust. Pietri claimed that the potentiometric end-point using gold electrodes, polarised by passing a small constant current, satisfied these conditions.

The development of a method for plutonium determination based on the above considerations is described in this report. A direct and specific method for uranium in similar solutions has already been published.[17]

EXPERIMENTAL

Reagents

The following reagents were used, prepared from analytical-grade materials where available.

Argentic oxide. "Silver peroxide", 99% pure (Johnson Matthey and Co. Ltd., London, England).

Standard potassium dichromate solution (1 g ≡ 10·000 mg of plutonium). Weigh a clean, dry 2-l. volumetric flask to ± 0·01 g. Weigh out about 8·20 g of dried potassium dichromate to ± 0·1 mg (A g). (Use the 99·99% pure National Bureau of Standards sample No. 136a, and correct the weight for buoyancy, if maximum accuracy is required.) Dissolve the dichromate in water in the weighed flask and dilute to about 1990 ml. Weigh the flask plus solution, and add water from a weight burette until the weight of the solution is ($243{\cdot}82 \times A$) g (*i.e.*, for plutonium of typical isotopic composition, of Relative Atomic Weight = 239·10 on the 12-carbon scale). Shake the solution thoroughly.

0·5*M Ammonium iron(II) sulphate.* Dissolve 392 g of ammonium iron(II) sulphate in 2*N* sulphuric acid and dilute to 2 l. with the 2*N* acid. Remove dissolved air by sparging with nitrogen, and store the solution under xylene in an aspirator. To standardise, weigh out accurately about 4 g of the standard potassium dichromate solution (D g) into a 5-ml polythene sample tube, add 0·5-1 ml of concentrated nitric acid to simulate the acidity of a normal sample, and follow the experimental procedure using this solution in place of the sample, but adding about ($D/F + 0{\cdot}075$) g of iron(II) solution (G g). Assume $F = 5$ for the first attempt. If the dichromate titration obtained is Z Agla units (see *Apparatus*) then the iron factor (f) is given by:

$$f = \frac{D + 0{\cdot}02\,Z}{G}.$$

Standardise each batch daily until a graph of iron factor (f) *vs.* time can be constructed, then check as required. Read the daily iron factor (F) used in the plutonium determination from the smoothed curve.

1·5 *M Sulphamic acid.* Dissolve about 150 g of sulphamic acid in 1 l. of cold water. The solution is almost saturated.

2·5 *M Nitric acid*

2 *N Sulphuric acid*

Plutonium nitrate standard solution. Prepare a pure solution of plutonium(IV) nitrate, and assay for plutonium by evaporation with sulphuric acid and ignition to plutonium dioxide ($PuO_{2{\cdot}000}$) in air at 1250°.[18]

Apparatus

The following special apparatus was used.

Agla micro-burette (Burroughs Wellcome and Co., London, England). 0·5-ml capacity, graduated in 25·00 Agla units, subdivided to 0·01 Agla unit. If maximum accuracy is required, calibrate the Agla burette with standard dichromate solution by weighing the amount delivered. For most purposes, it is sufficient to assume that 1·00 Agla unit = 0·02 g of dichromate solution.

Millivoltmeter. Any direct-reading pH and millivoltmeter is suitable.

Magnetic-stirrer.

Gold electrodes. Make a pair of identical electrodes from 0·25 mm thick 99·6% pure gold sheet, 1·3 cm × 0·8 cm, flame-welded to a gold wire for making electrical connection. Rinse the electrodes after each titration with 2*N* sulphuric acid and water, and leave them in air.

Polarising circuit. Connect a 50 to 60-V dry battery in series with a 22-MΩ resistor across the electrodes to pass a constant current of 2 to 3 μA through the titration cell. Measure the potential difference between the electrodes with the millivoltmeter.

Weight burettes. Prepare from 5 to 10-ml capacity polythene vials by drawing out the necks to a fine jet over a small flame.

Sample preparation

The procedure is written for the determination of plutonium in nitric acid solutions of plutonium/uranium ceramic fuels. For example, weigh out accurately from 1 to 2 g of a 15% plutonium/uranium oxide specimen, and dissolve under reflux in 5 ml of 16*M* nitric acid containing 0·1 ml of 2% hydrofluoric acid. Dilute to about 20 ml and weigh the solution.

Recommended procedure

The following procedure is recommended for sample aliquots containing between 20 and 80 mg of plutonium. If the weight of plutonium is not known to within ±2 mg (to enable the correct excess of iron(II) solution to be added), carry out a preliminary titration.

Weigh out a suitable portion of the sample solution (W g) into a 5-ml polythene tube for transfer to the titration glove-box. Wash the sample into a squat 100-ml conical flask with 2·5*M* nitric acid, to give a total volume of about 20-ml and an acidity between 2·5 and 5*N*. Cover with a watch glass and place on the magnetic stirrer. Add small portions of solid argentic oxide from a micro spatula until the solution is dark brown; about 100 mg is normally adequate. Allow to stir for 5 min, after which the solution should still be brown. Meanwhile, weigh out accurately from a weight burette into a 5-ml polythene tube about ($P/10F + 0{\cdot}075$) g of iron(II) solution, where P mg is the estimated weight of plutonium taken and F is the iron factor. Let this weight of solution be H g. Rinse the watch-glass with 2*N* sulphuric acid into the titration flask, add about 1 ml of 1·5*M* sulphamic acid, and wash down the walls of the flask with 2*N* sulphuric acid to give a total volume of about 40 ml. Quantitatively transfer the weighed iron(II) solution into the sample solution with 2*N* sulphuric acid washes to give a total volume of 50–60 ml. Dip the spades of the electrodes into the solution and stir smoothly. Fill the Agla burette with standard potassium dichromate solution, and adjust to the 25·00 mark. Dip the burette tip into the solution and slowly titrate the excess of iron(II), waiting 5 sec between additions. Add only 0·1 Agla unit increments when the potential reading begins to rise. At the end-point, there is a steady increase in potential of several hundred millivolts over a period of about 3 min without adding any further titrant. As excess titrant is added the potential reaches a maximum, then falls slowly. Subtract the Agla burette reading at the end-point from 25·00 to obtain the dichromate titration (Y Agla units). If this titration is less than 5 Agla units, add another portion of iron(II) sulphate and repeat the titration (see *Results and Discussion*).

Calculate the plutonium concentration in the sample solution from the expression:

$$\mathrm{Pu} = \frac{10(FH - 0{\cdot}02\ Y)\ \mathrm{mg/g}}{W}$$

where F = daily iron(II) factor,
H = weight of iron(II) solution in g,
Y = dichromate titration in Agla units,
and W = weight in g of the portion of sample taken for the determination.

RESULTS AND DISCUSSION

Preparation of plutonium(VI)

Oxidation with argentic oxide. In early experiments the oxidation procedure used was similar to that of Seils,[8] using several small additions of argentic oxide in a dilute sulphuric medium, after removing any nitric acid by evaporation with sulphuric acid. However, the black solid which formed when an excess of argentic oxide* was added to dilute sulphuric acid solutions was sometimes slow to redissolve on heating, and caused erroneous titration results. Because Lingane and Davis[19] had used argentic oxide as the oxidimetric reagent for chromium and other elements in 2–5*M* nitric acid solutions, in which the excess reagent was readily soluble, similar conditions were tried for plutonium. The oxidation proceeded smoothly, and the dark brown colour of the argentic ion in nitric acid stronger than 2·5*M* conveniently indicated when an

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* The argentic oxide used for these early experiments was prepared by the method of J. C. Bailar, *Inorganic Syntheses*, Vol. IV, p. 12. McGraw-Hill, New York, 1953.

excess of reagent had been added, and the fading of the colour on heating showed that destruction of the excess was complete. Occasionally the brown colour faded within 1 min at room temperature, and plutonium results were low, showing that oxidation was incomplete. If the brown colour was maintained for a few minutes by adding more argentic oxide, such errors were avoided. No adverse effects have been noted on leaving plutonium(VI) solutions to stand for several hours in the presence of an excess of silver(II).

A theoretical study reported by Lloyd and Pickering,[20] since the bulk of this work was completed, confirms that the use of a nitric acid medium has many advantages for oxidations with argentic oxide.

Destruction of argentic nitrate with sulphamic acid. The usual procedure for removal of excess argentic oxide involves heating to about 80°, but the addition of a reagent of suitable redox potential was considered to be preferable in many ways.

Brasted[21] has reported that sulphamic acid reacts with strong oxidising agents, such as potassium chlorate, with evolution of nitrogen. It was found that a few drops of saturated sulphamic acid solution rapidly decolourised a typical excess of argentic oxide in nitric acid solution at room temperature. However, no effervescence was observed, and a brief study of the stoichiometry of the reaction suggested that the sulphamic acid was oxidised to sulphuric and nitric acids. Because the presence of sulphamic acid was required in later stages of the method, the addition of 1 ml of the saturated solution was adopted to ensure complete destruction of the silver(II) ions. The exact amount added was not critical. This modification enabled the whole oxidation, reduction and titration to be completed in a single vessel without heating and without any transfer operations other than the addition of solid and liquid reagents.

Stability of plutonium(VI). The stability of plutonium(VI) in this medium was tested by allowing solutions prepared by the recommended procedure to stand for up to 90 min after adding the sulphamic acid, but before adding the iron(II) solution. The results in Table I show that no errors were introduced on standing for up to 15 min, but for safety it was concluded that samples should not stand for more than 10 min after destroying the excess silver(II).

TABLE I.—PLUTONIUM(VI) STABILITY

Time of standing, *min*	Plutonium recovery, %
0·5	100·02
4	100·07
5	100·10
15	99·88
30	99·24
65	99·42
90	99·53

Reduction to plutonium(IV)

Reduction with iron(II). Seils[8] and Bergstresser[9] found that the reaction between plutonium(VI) and iron(II) was slow in dilute sulphuric acid solution. The reaction did not go to completion in the nitric-sulphuric acid solution used in this work. For example, when only 99 % of the theoretical amount of iron(II) was added to a 40-mg sample of plutonium(VI) and the solution was titrated after 2 min in the usual way, the titration proceeded to an apparently normal end-point, requiring 0·017 ml of the standard dichromate solution. Thus, a small amount of iron(II) remained unoxidised even though a greater amount of plutonium(VI) was still present. However, 99·5% of the added iron had been oxidised within 2 min. The incomplete reaction had two practical implications in the procedure recommended for plutonium determination.

Firstly, it was not possible to follow the addition of iron(II) to a plutonium(VI) solution with the indicator electrodes, to show when an excess had been added, under any acidity conditions tried. An initial potential between the electrodes of 400 mV in the plutonium(VI) solution fell to zero on adding the first drops of iron(II), showing that free iron(II) was already present. The amount of iron required to provide a suitable excess was, therefore, calculated from the estimated plutonium content, which must be known to within ±2 mg in order to produce a back-titration within one filling of an Agla burette with dichromate of the selected concentration.

TABLE II.—STABILITY OF THE EXCESS IRON(II)

Plutonium taken, *mg*	Nitric acid, *mequiv*	Standing time, *min*	Iron factor	Plutonium recovery, %
0	50	5	4·660	—
0	100	5	4·657	—
0	100	5	4·658	—
0	50	30	4·660	—
0	100	20	4·651	—
0	100	40	4·647	—
39·47	50	5	—	100·23
37·60	50	25	—	99·87
41·86	100	20	—	100·84
53·09	100	5	—	99·70

Secondly, at least a certain minimum excess of iron(II) was required to reduce the plutonium(VI) quantitatively, or false results were obtained, even though the titration curve appeared normal. Similarly, if an impurity causing quantitative interference was present, the amount of iron(II) added had to be an excess over the plutonium-plus-impurity equivalence; otherwise plutonium(VI) reduction was not complete, and interference did not appear to be quantitative. Fortunately, the size of the dichromate titration in the method provided a criterion that a sufficient excess of iron(II) had been added. No false results have been observed from this cause during development work when the titre was greater than one Agla unit (0·002 mequiv of dichromate). For routine use, a minimum of 5 Agla units has been adopted for safety. If the titre is less than 5 Agla units, another portion of iron(II) may be added and the titration continued, but some loss of precision must be expected due to the extra operations involved.

Stability of the excess of iron(II). It was appreciated that errors would arise if the excess of iron(II) was oxidised by nitric acid. Under the conditions prevailing in the recommended procedure, the autocatalytic reaction between iron(II) and nitric acid[22] was suppressed by the sulphamic acid, which had already been added to destroy the excess of silver(II); this acid also removed the nitrite calalyst produced in the reaction. The results of experiments to study the stability of the excess of iron(II) under these condition are given in Table II, both for iron standardisations and for plutonium determinations. Oxidation of iron by nitrate would cause a low iron factor or a high plutonium result. The method specifies that the sample should be diluted with about 50 mequiv of nitric acid; under these conditions, no loss of iron(II) was observed in 30 min. If the sample taken for analysis contained an additional 50 mequiv of acid, slight losses of iron(II) occurred on standing, leading to errors approaching 1 % after 20 min in an extreme case. Therefore, undue delays should be avoided before titrating, and when the sample taken contains much nitric acid, the solution to be oxidised should be adjusted to a volume of about 20 ml of 2·5 to 5*M* acid, instead of diluting with the 2·5*M* acid.

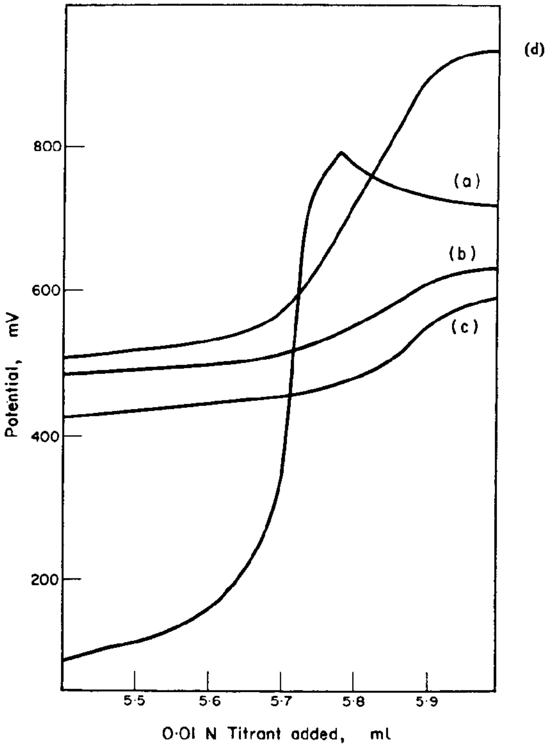

FIG. 1.—Comparison of methods of end-point detection: (a) Dichromate and polarised gold electrodes; (b) Dichromate and platinum/calomel electrodes; (c) As (b), but with phosphoric acid added; (d) Cerium(IV) sulphate and platinum/calomel electrodes.

Titration of the excess of iron(II)

Choice of titrant and end-point. A preliminary comparison was made between titration methods for iron(II), with the objective of using potassium dichromate, which is a primary standard, in preference to cerium(IV). In Fig. 1, several end-points obtained on titration of about 0·06 mequiv of iron(II) in about 50 ml of 2*N* sulphuric acid solution are superimposed on the same expanded scale; the absolute values of the titres have no meaning. 0·01*N* Potassium dichromate was the titrant in curves (a) and (b), and the end-points were detected potentiometrically with polarised gold electrodes[14] and with a conventional platinum/calomel electrode system, respectively. Curve (c) was a repeat of (b) but with the addition of phosphoric acid in an attempt to improve the end-point. In curve (d) a similar amount of iron(II) was titrated with 0·01N cerium(IV) sulphate, again with a platinum/calomel electrode system.

The very sharp end-point obtained with polarised gold electrodes obviously merited further work. Previously, Willard and Fenwick,[23] Van Name and Fenwick,[24] Reilley,[25] and others have studied in detail the use of two polarised metal electrodes in potentiometric analysis, and Lingane[26] reported that the system was particularly suitable for the titration of a reversible ion with a non-reversible oxidant.

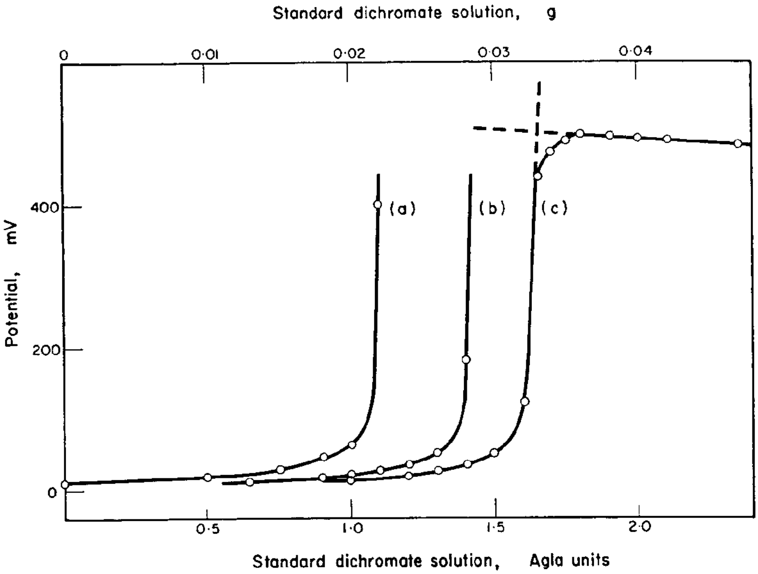

FIG. 2.—End-points with polarised gold electrodes: (a) Iron standardisation; (b) Plutonium determination; (c) Alternative location of end-point.

End-point detection with polarised gold electrodes. In the method finally adopted the same procedure was used for standardisation of the iron(II) solutions as for plutonium determination, by substituting an equivalent weighed portion of the standard dichromate solution for the plutonium sample. Hence, any bias due to the location of the end-point on the titration curve was eliminated, and automatic compensation was made for the small method blanks, *etc.* Curves (a) and (b) in Fig. 2 show on an arbitrary scale the end-points for iron standardisation and for plutonium determination, respectively, following the recommended procedure. The shape of the titration curve is similar in each case, and the steady rise in potential at the end-point is so marked that for rapid, routine use it is readily detectable without recording the readings. It should be noted that the portion of the titration plotted in Fig. 2 is equivalent to less than 1 % of the amount of plutonium normally taken.

The absolute value of the method blank was measured by comparing the iron standardisation as above with the direct titration of a similar amount of iron(II) with dichromate in 2N sulphuric acid only. It varied from zero to 0·02 g of dichromate solution, averaging about 0·2 % of the usual titre. This variation could well be the major source of imprecision in the method, but attempts to reduce it or make the blank more reproducible have not so far been successful.

Curve (c) in Fig. 2 illustrates an alternative method of locating the end-point of a plutonium titration which was used when maximum precision was required rather than speed. In this case, millivolt readings were allowed to become constant between additions and the titration was continued beyond the end-point, which was taken to be the point of intersection shown.

In normal use, a pair of electrodes has been employed without deterioration for hundreds of determinations over a period of months, providing that their polarity was not reversed. After prolonged use, and on certain isolated occasions, the electrode response has sometimes become sluggish, probably because of surface poisoning. In these cases, the response was fully restored either by heating both electrodes to red heat, or by anodising in 2*N* sulphuric acid followed by cathodising in 2*M* hydrochloric acid.

Selection of titration conditions. With a back-titration procedure, it was possible to combine high precision with simplicity by adding a small excess of the bulk reagent by weight. The dichromate and iron(II) standard solutions were, therefore, prepared by weight dilution, and the plutonium sample and excess of iron(II) were added by weight. The excess, which was less than 10% of the total titre, was conveniently titrated with dichromate from an Agla micro burette.

TABLE III.—PLUTONIUM CONCENTRATION RANGE

Plutonium taken, *mg*	Plutonium found, *mg*	Recovery, %	Error, *mg*
4·94	5·00	101·2	+0·06
9·79	9·85	100·61	+0·06
20·92	20·96	100·19	+0·04
41·31	41·27	99·90	−0·04
85·50	85·28	99·74	−0·22
124·79	124·10	99·45	−0·69
277·1	276·3	99·71	−0·8

Storage of iron(II) *solution.* In order to minimise the oxidation of the standard iron(II) solution it was stored in an aspirator under a layer of pure xylene to exclude air. Iron(II) solution was run off from below as required and used within a few hours. The change in iron factor when following this simple precaution was at a steady rate of less than 2% per month, and no inert blanketing gas was required.

Range of plutonium concentration. The final procedure was tested over a plutonium range from 5–280 mg per determination. With 280 mg of plutonium present, the potential at the end-point only rose to 160 mV instead of 500 mV or more. The results in Table III show that with the standard amount of reagents the procedure begins to break down with more than 80 mg of plutonium present, because above this level the small fixed excess of iron(II) is insufficient to reduce the plutonium(VI) quantitatively. With small amounts of plutonium, the relative errors become appreciable although the absolute errors are not changed significantly. Thus, the optimum concentration range for the method as written is from 20–80 mg of plutonium, but it seems certain that the range could be extended up or down by adjusting the reagent volumes and the excess of iron(II) in proportion to the plutonium. The method has already been used successfully on limited numbers of 2-mg samples of plutonium in a small volume and with more dilute dichromate.

Effect of foreign substances. Considerable information has been published by other workers[5,9] on the effect of foreign elements on methods involving similar chemical reactions to the present procedure. Attention was, therefore, concentrated on elements and radicals which were likely to be found in samples from processes at D.E.R.E. or which were most likely to interfere.

It was shown that the amounts of foreign substances given in Table IV did not interfere when added individually to the iron standardisations and plutonium determinations. Chloride formed a precipitate of silver chloride, but this did not affect the titration results. The oxidation with silver(II) to plutonium(VI) with 10 mg of fluoride present was not as rapid as usual, but was complete within the recommended 5-min period. It was also shown that the organic degradation products formed on dissolution of 0·3 g of uranium carbide in nitric acid were oxidised by the silver(II) nitrate; the solution was a clear uranium yellow after destroying the excess oxidant with sulphamic acid. The error introduced into a plutonium determination was less than 0·5%, a limit probably set by the impurities present in the uranium carbide used.

TABLE IV.—SUBSTANCES WHICH DO NOT INTERFERE

Substance	Amount, *mg*	Added as
Ammonium	18	Sulphate
Aluminium	27	Nitrate
Copper	6	Sulphate
Mercury(II)	20	Nitrate
Molybdenum	30	Ammonium molybdate
Nickel	10	Chloride
Tin(II)	12	Chloride
Titanium(III)	5	Sulphate
Tungsten	18	Sodium tungstate
Uranium(VI)	200	Nitrate
Chloride	35	Hydrochloric acid
Fluoride	10	Hydrofluoric acid
Phosphate	160	Orthophosphoric acid
Sulphate	250	Sulphuric acid
Peroxide	30	Hydrogen peroxide

A limited number of tests showed that chromium (2·9 mg), cerium (42 mg) and manganese (5·5 mg) all interfered essentially quantitatively both with and without plutonium present, and without affecting the end-point characteristics. It seems probable that the same general procedure can be applied with little modification as a convenient and precise method for the determination of any of these elements. For example, in the chromium system in the absence of plutonium, the iron(II)-dichromate reaction was sufficiently rapid and complete to give a clear potential break with the indicator electrodes on adding an excess of the iron(II) solution. In this case, therefore, preliminary knowledge of the approximate amount of iron required would not be essential.

Interference from vanadium (3·4 mg) in an iron standardisation was again essentially quantitative, but the end-point was poor, the potential rising to only 340 mV. No end-point at all was obtained with 3·4 mg of vanadium in a plutonium titration, but with 0·5 mg the end-point was tolerable and interference was quantitative.

Ruthenium also interfered in an iron standardisation, approximating to a two electron reaction, but the end-point deteriorated with more than 1 mg present. A synthetic mixed fission product solution equivalent to the stable products from the fission of 10 mg of 235-uranium caused interference approximating to the sum of the cerium and ruthenium present, equivalent to about 2 mg of plutonium. Interference would also be expected if significant amounts of neptunium or americium were present, but this has not been tested.

Precision and accuracy

Using the recommended procedure, which was designed as a rapid and convenient method for routine use, the coefficient of variation for a single result was 0·17% calculated from 24 determinations on a plutonium nitrate standard solution during the final testing of the method, which covered the extreme limits of experimental variables permitted by this report. The results were obtained by one operator working intermittently over a period of 5 months, using two batches each of dichromate and iron solutions. The bias of the method was less than 0·1% relative to plutonium dioxide ignited in air at 1250° taken as stoichiometric. The method has also been in routine use for 9 months by about six relatively inexperienced operators, who obtained a coefficient of variation of 0·26%.

It seems probable that even better precision could be obtained when required by specialist operators working under more closely controlled conditions, using a modified procedure with 200–400 mg portions of plutonium, correspondingly larger reagent volumes, and graphical location of the end-point. Whilst this may be worthwhile for the assay of pure plutonium metal[27] or solutions,[28] it should be remembered that the effect of trace impurities may limit the precision which can be obtained by any method of analysis for fuel materials of comparatively low plutonium content. For example, 100 ppm of chromium in a 15% plutonium/uranium oxide would be equivalent to 600 ppm with respect to plutonium, and would cause an error of almost 0·5% in the plutonium determination described here.

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Zusammenfassung—Eine einfache und schnelle Methode zur Routinebestimmung von Plutonium mit einem besseren Variationskoeffizienten als 0·2% wird beschrieben. Sie ist auf grosse Mengen Uran enthaltende Nitratlösungen direkt anwendbar. Mässige Mengen Eisen, Molybdän, Fluorid und Phosphat stören nicht. Chrom, Cer und Mangan werden quantitativ mitbestimmt; die Arbeitsvorschrift kann sich auch für die Bestimmung dieser Elemente als günstig erweisen. Das Plutonium wird mit Silberoxyd in salpetersaurer Lösung zum sechswertigen oxydiert und überschüssiges Reagens mit Sulfanilsäure zerstört. Dann wird ein gewogener geringer Überschuss an Eisen(II)-Lösung zugegeben und der Überschuss potentiometrisch mit eingestellter Kaliumdichromatlösung und polarisierten Gold-Indikatorelektroden titriert. Die ganze Bestimmung geht in einem Gefäss bei Zimmertemperatur vor sich und dauert etwa 20 Minuten.

Résumé—On décrit une méthode simple et rapide de dosage courant du plutonium avec un coefficient de variation inférieur à 0·2%. Elle est directement applicable aux solutions de nitrate contenant une forte quantité d'uranium; des quantités peu élevées de fer, molybdène, fluorure et phosphate n'interfèrent pas. Le chrome, le cérium et le manganèse interfèrent quantitativement, et la technique peut aussi se révéler convenable pour le dosage de ces éléments. On oxyde le plutonium à l'état hexavalent au moyen d'oxyde argentique en solution dans l'acide nitrique et détruit l'excés d'oxydant par reaction avec l'acide sulfamique. On ajoute alors un petit excès, pesé, de solution de fer(II) et l'excès est dosé potentiométriquement au moyen d'une solution étalon de bichromate de potassium en utilisant des éléctrodes indicatrices polarisées en or. Le dosage complet est effectué dans un seul récipient à température ordinaire, et nécessite environ 20 mn.

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DETERMINATION OF MANGANESE IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS WITH PAN

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Summary—A spectrophotometric method for the determination of 0·0005–0·10% of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals is described. The matrix materials are separated from the manganese by extraction as cupferrates, after sample dissolution, then the red complex formed between manganese(II) and 1-(2-pyridylazo)-2-naphthol, PAN, is extracted into chloroform from an ammoniacal tartrate-cyanide medium. The absorbance of the extract is determined at 562 mμ. With the exception of zinc and lead, other impurities present in the four high-purity metals described do not interfere with the proposed method.

INTRODUCTION

THE determination of impurities in high-purity niobium, tantalum, molybdenum and tungsten metals is a continuing analytical project of the Mines Branch laboratories concerning the properties of refractory metals. As part of this project, the present investigation was undertaken to develop a spectrophotometric procedure for determining trace amounts of manganese that would be applicable to all four metals.

Published information pertaining to the determination of small amounts of manganese in matrices of the above metals is meagre. Several spectrophotometric procedures have been applied to the determination of manganese in niobium,[1] molybdenum[2] and tungsten[3] metals, but none of these methods is directly applicable to all four metals under consideration.

The most widely used method for determining manganese spectrophotometrically is based on the oxidation of manganous to permanganate ion with a suitable oxidising agent. Because of its low sensitivity this method was not considered in the present investigation. Recently, methods[4–11] of considerably greater sensitivity than the permanganate method have been proposed for the determination of small amounts of manganese. Methods involving 1-(2-pyridylazo)-2-naphthol, PAN, as the chromogenic reagent have been reported in which the molar absorptivities for the manganese(II) PAN complex in chloroform[4] and in ether[5,6] have been found to be 4×10^4 and $5{\cdot}85 \times 10^4$ at 550 and 560 mμ, respectively. Because of the high sensitivity inherent in the use of PAN it was decided to investigate its possible application in the present work.

This paper describes a procedure for determining manganese spectrophotometrically in high-purity niobium, tantalum, molybdenum and tungsten metals with PAN after the matrix materials have been removed by extraction of their cupferrates. The procedure used for dissolution of the samples is essentially that previously reported in methods for determining iron,[12] copper[13] and nickel.[14] Zinc and lead interfere in this method, but quantities up to 50 and 100 μg, respectively, can be tolerated in the aliquot taken for analysis without causing appreciable error in the manganese determination.

EXPERIMENTAL

Apparatus

Spectrophotometer. Unicam Model SP 500.

pH meter. Leeds and Northrup.

Centrifuge. Canlab clinical type.

Teflon (tetrafluoroethylene) beakers. 250- and 400-ml; Dynalab Corp., Rochester, N.Y., U.S.A.

Separatory funnels (Nalgene). 500-ml pear shape type; The Nalge Co., Inc., Rochester, N.Y., U.S.A.

Reagents

Water. De-ionise by passing distilled water through a column of Dowex 50W-X8 resin.

Standard manganese solution. Dissolve 0·1000 g of electrolytic manganese in 10 ml of 1 + 1 sulphuric acid and dilute to 500 ml with water. Dilute 5 ml of this stock solution to 500 ml with water. Prepare fresh as needed (1 ml of this diluted solution = 2 μg of manganese).

PAN, 0·1% solution. Dissolve 0·100 g of 1-(2-pyridylazo)-2-naphthol (J. T. Baker Chemical Co.) in ethyl alcohol and dilute to 100 ml with ethyl alcohol.

Ammonium tartrate, 10% solution, w/v.

Hydroxylamine hydrochloride, 20% solution, w/v. Prepare a fresh solution daily.

Buffer solution. Dissolve 10 g of ammonium chloride in water and add 100 ml of concentrated ammonia solution. Dissolve 1·200 g of potassium cyanide in this solution, dilute to 200 ml with water and store in a polyethylene bottle.

Cupferron, 9% solution. Prepare a fresh solution as required.

Chloroform. Analytical reagent, obtained from Mallinckrodt Chemical Works.

Isoamyl alcohol. Analytical reagent, obtained from Fisher Scientific Company.

Colour development and preparation of calibration curve

Add 1 ml of 10% ammonium tartrate solution to each of seven 60-ml separatory funnels that are marked at 25 ml; then, by burette, add to the last six funnels 1, 2, 3, 4, 5 and 6 ml, respectively, of standard manganese solution (*i.e.*, 1 ml = 2 μg of manganese). (The stem of each funnel is first rinsed with ethyl alcohol to remove water droplets.) The first funnel contains the blank. Add to each funnel 5 ml of 20% hydroxylamine hydrochloride solution, dilute to the 25-ml mark with water, stopper and mix. (Because chloroform is soluble to a certain extent in water, *i.e.*, 10 g/l. at 15°, the total volume should be kept relatively constant.) Then, working with one solution at a time, add 5 ml of buffer solution and 3 ml of 0·1% PAN solution, and mix well after each addition. Allow exactly 45 seconds to elapse (timed from the start of the addition of PAN solution), then add, by pipette, 10 ml of chloroform, stopper and shake for 2 min. Allow 3 min for the layers to separate, then drain the chloroform extract into a 15-ml centrifuge tube and centrifuge for 30 sec. (If the aqueous phase remains too long in contact with the organic phase low results will be obtained.) Determine the absorbance of each extract against the blank as the reference solution, using 1-cm cells, at a wavelength of 562 mμ. Plot μg of manganese *vs.* absorbance.

Procedure

In the following procedures a reagent blank is carried along with the samples.

Niobium and tantalum metals. Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker, add 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon cover. Through the lip of the beaker add concentrated nitric acid slowly, approximately 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. Add 3 ml of formic acid to destroy excess nitric acid and heat gently until the evolution of brown oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water, evaporate to approximately 5 ml and add 1 ml of hydrofluoric acid and 20 ml of 1 + 1 sulphuric acid. (If the solution remains slightly cloudy at this stage, warm gently until it clears.) Wash down the sides of the beaker with 1 + 1 hydrochloric acid and transfer the resulting solution to a 500-ml Nalgene separatory funnel. Dilute to approximately 100 ml with water, stopper, mix and cool on ice for about 1 hr. Then add 100 ml of cold, freshly prepared 9% cupferron solution, mix, add 50 ml of cold chloroform and shake for 1 min. Allow 5 min for the layers to separate, then drain off and discard the organic layer. Repeat the extraction with 20 ml of cupferron solution and 25 ml of chloroform, and, finally, with four successive 10-ml portions of chloroform. Transfer the aqueous phase to a 400-ml Teflon beaker, cover, heat gently to remove excess chloroform, then evaporate the solution to fumes of sulphur trioxide with the addition of 20 ml each of concentrated nitric and hydrochloric acids to destroy residual organic material. Cool, wash down the sides of the beaker with water, evaporate to fumes again, and repeat to ensure complete removal of hydrofluoric acid. Dilute the solution with approximately 10 ml of water, wash down the sides of the beaker with 1 + 1 hydrochloric acid, transfer to a 250-ml Pyrex beaker and evaporate to dryness. Again, wash down the sides of the beaker with 1 + 1 hydrochloric acid and evaporate to dryness. Add 5 ml of 10% ammonium tartrate solution and 20 ml of water to the residue in the beaker and heat gently until the solution is clear. Then add 1 ml of hydrochloric acid and dilute to approximately 35 ml with water. Using a pH meter, adjust the pH of the resulting solution to 3·5 ± 0·2 with concentrated ammonia solution, transfer to a 100-ml volumetric flask and dilute to volume. Transfer a suitable aliquot (2–20 ml) of both sample and blank solutions, depending on the manganese content of the sample, to 60-ml separatory funnels and analyse the solution for manganese by the procedure given under "Calibration Curve". When 20-ml aliquots of sample solution are taken:

$$1\ \mu g \text{ of manganese} = 0{\cdot}001\%.$$

Molybdenum metal. Decompose a 0·5000-g sample of the powdered metal in a 250-ml Pyrex beaker with 20 ml of 1 + 1 sulphuric acid and 2 ml each of concentrated nitric and hydrochloric acids. Evaporate the resulting solution to fumes of sulphuric acid, cool, wash down the sides of the beaker with water, and again evaporate to fumes to ensure complete removal of nitric acid. Proceed with the cupferron–chloroform extraction of molybdenum and the subsequent determination of manganese as described above for niobium and tantalum metals, using glass funnels and beakers and omitting the procedure for the removal of hydrofluoric acid.

Tungsten metal. Decompose a 0·5000-g sample of the powdered metal as described above for niobium and tantalum metals. After removal of excess nitric acid with formic acid, add 1 ml of hydrofluoric acid and 70 ml of 1 + 1 sulphuric acid. Then proceed with the extraction of tungsten cupferrate as described above, using in succession 100, 50, 25, 15, 15 and 15 ml of a 2:1 mixture of chloroform and isoamyl alcohol as extractant instead of chloroform. Gently evaporate the aqueous phase until approximately 150 ml remain. (The solution will be black at this stage because of the large quantity of organic material present.) Cool on ice, add 20 ml each of nitric and hydrochloric acids and let stand at room temperature until most of the organic material has decomposed. Then proceed with the determination of manganese according to the method described for niobium and tantalum metals.

RESULTS

Extraction of the coloured complex

Shibata[5,6] showed that the manganese(II)-PAN complex can be extracted into various organic solvents, but stated that it is extracted most efficiently with ether or chloroform. Tests carried out in this laboratory with *n*-amyl alcohol, chloroform, benzene and carbon tetrachloride yielded considerable differences in the absorption maximum of the complex in these solvents, *i.e.*, 558, 562, 568 and 570 mμ, respectively. Ether was not included in these tests because Shibata[5] had already shown that the absorption maximum of the complex in ether occurs at 560 mμ. The results of these tests showed that chloroform and benzene are equally efficient extractants and also indicated that the molar absorptivity of the complex varies considerably with the solvent employed. The molar absorptivities in ether, chloroform and benzene were $5{\cdot}85 \times 10^4$,[5] $4{\cdot}8 \times 10^4$ and $4{\cdot}7 \times 10^4$, respectively. Although the molar absorptivity of the complex is greatest in ether, chloroform was chosen for the present investigation because it is less noxious than ether or benzene.

Preliminary experiments carried out at pH 9 with test solutions containing ammonium chloride, hydroxylamine hydrochloride and potassium cyanide showed that up to at least 12 μg of manganese contained in approximately 25 ml of solution can be extracted quantitatively in a single stage with 10 ml of chloroform. The extraction of larger amounts was not attempted because of the high absorbance of the resulting extract. Beer's Law is obeyed over the range investigated. The absorbance of the chloroform extract of the manganese(II)-PAN complex remains constant for hours after extraction and only decreases slightly if allowed to stand for 24 hr.

Factors influencing formation and subsequent extraction of manganese(II)-*PAN complex*

Effect of reductant. Erratic results were obtained in preliminary experiments carried out at approximately pH 9 when the PAN reagent was added to ammoniacal test solutions containing ammonium chloride and potassium cyanide (to complex copper and other impurities present in the water and reagents used). It was considered that this effect could be caused by partial air-oxidation of the manganese, because previous investigators[15,16] have shown that atmospheric oxidation of manganese(II) to manganese(III) takes place in alkaline media. Oelschläger[17] and Starý[18] state that this effect can be prevented by the addition of hydroxylamine hydrochloride, and subsequent tests performed in the presence of an excess of this reducing agent yielded consistent and reproducible results.

Effect of pH. Previous investigators have used slightly different systems so that the optimum pH range for the complete formation of the manganese(II)-PAN complex under our conditions had to be determined. The results obtained by Shibata,[5] Betteridge *et al.*[19] and Berger and Elvers[4] indicate pH ranges of approximately 9 to 11, 8·5 to 9·6 and 8 to 10, respectively. To define this range more precisely, pH experiments were carried out on test solutions containing 10 μg of manganese, using 5 ml each of a series of buffer solutions of increasing pH (prepared by dissolving 5 g of ammonium chloride and 100 mg of potassium cyanide in water, adding varying quantities of concentrated ammonia solution and diluting to 100 ml). The pH at which the complex was formed in these test solutions was determined by measuring the pH of the aqueous phase after the complex was extracted. The results of these tests showed that, for the pH range tested (approximately 6 to 10), the manganese(II)-PAN complex is completely formed and extracted in a single stage with 10 ml of chloroform in the pH range 8·8 to 9·6.

On the basis of these results, an intermediate pH of 9·2 was chosen for the present work. This pH was obtained in the above tests with a buffer solution containing 50 ml of concentrated ammonia solution in a volume of 100 ml.

Effect of PAN concentration. Shibata[6] states that 1 ml of 0·1% PAN solution suffices to complex 10 μg of manganese, but this amount was not sufficient under the conditions of the present investigation, in which the PAN solution was added after the buffer solution. This order of addition of reagents was chosen to complex copper and other impurities present in the water and reagents used with potassium cyanide at pH 9·2 before formation of the manganese(II)-PAN complex. Tests performed with varying amounts of PAN solution showed that at least 3 ml of 0·1% PAN solution are required to complex 10 μg of manganese under the above conditions.

Effect of potassium cyanide and ammonium tartrate. Although PAN is known to form extractable complexes with a great number of metallic ions,[20] previous investigators of PAN reactions have shown that cyanide and citrate are effective complexing agents for many of these metals.[20,6] Therefore, tests were undertaken to determine the maximum amounts of these complexing agents that could be present during extraction of the manganese(II)-PAN complex without appreciably affecting the manganese result. The effect of potassium cyanide alone was first tested on solutions containing 10 μg of manganese, using a series of buffer solutions of varying potassium cyanide content (otherwise prepared as described under "Reagents"). The results of these tests showed that up to 30 mg of potassium cyanide can be present during extraction without affecting the determination of manganese.

Preliminary tests, carried out with ammonium citrate, yielded low results for manganese. However, similar tests with ammonium tartrate indicated that its inhibiting effect on the manganese-PAN reaction is considerably less than that of citrate. This result is corroborated by Jones[21] who showed that, during extraction of the manganese-diethyldithiocarbamate complex with chloroform, the competitive complexing action of citrate is much greater than that of tartrate.

The effect of varying amounts of ammonium tartrate was tested on solutions containing the maximum tolerable amount of potassium cyanide (*i.e.*, 30 mg) found previously. The results of these tests showed that, although ammonium tartrate interferes slightly, up to 100 mg can be present in the solution taken for extraction without causing excessive error in the manganese result.

Effect of time. Although the results obtained by Shibata[6] indicate that the manganese(II)-PAN complex remains stable in solution (presumably before extraction) over a time interval of 2 to 60 min, this is not true in the present investigation under the competitive complexing influence of cyanide and tartrate ions. The results (Table I) of tests carried out in *media* containing cyanide alone and cyanide plus tartrate, in

TABLE I.—EFFECT OF TIME ON THE STABILITY OF THE MANGANESE(II)-PAN COMPLEX*

Time	Absorbance	
	I Potassium cyanide taken, 5 *mg*	II Potassium cyanide taken, 30 *mg*
30 sec	0·874	0·868
45 sec	—	0·873
1 min	0·879	0·854
2 min	0·847	0·787
3 min	0·834	0·750
5 min	0·813	0·750
15 min	0·781	0·655
30 min	0·781	0·597
	III Potassium cyanide taken, 5 *mg* Ammonium tartrate taken, 100 *mg*	IV Potassium cyanide taken, 30 *mg* Ammonium tartrate taken, 100 *mg*
30 sec	0·852	0·868
45 sec	—	0·867
1 min	0·867	0·853
2 min	0·824	0·758
3 min	0·807	0·731
5 min	0·787	0·685
15 min	0·752	0·621
30 min	0·765	0·562

* Manganese taken, 10 μg.

which the time interval from the beginning of the addition of PAN solution to the start of the chloroform addition was varied from 30 sec to 30 min, show the effect of time on the stability of the manganese complex. The results also show that the rate of dissociation of the complex is dependent on the concentration of cyanide and tartrate ions present in solution. Relatively consistent results were obtained for the 30 and 45 sec time intervals; consequently, the latter was chosen for the present work mainly for convenience.

Separation of niobium, tantalum, molybdenum and tungsten by extraction of their cupferrates

Preliminary experiments to determine the applicability of the manganese-PAN-chloroform extraction procedure to the determination of manganese in solutions of the four high-purity metals were carried out on a synthetic sample of each metal decomposed according to the procedure described for niobium and tantalum metals. In these tests, boric acid and ammonium tartrate were used to complex excess hydrofluoric acid and the matrix elements, respectively. The results of these tests showed that incomplete recovery of the added manganese was obtained from all four solutions. Further investigation showed that this was caused by the presence of boric acid and also by the excessive amount of ammonium tartrate required to complex the matrix elements. (Although boric acid alone does not interfere in the manganese determination, low results are obtained if both boric acid and ammonium tartrate are present in the solution taken for extraction.) Consequently, it was considered that the separation of the matrix materials from the manganese might provide a more effective means of determining manganese in the four metals under consideration. Other investigators[22,23] have shown that the cupferrates of niobium, tantalum and molybdenum can be extracted with chloroform from a strong sulphuric acid medium; consequently, this separation technique was used in the present investigation.

Tungsten is precipitated by cupferron from strongly acid solution[22] but its cupferrate is relatively insoluble in chloroform. Allen and Hamilton[24] investigated the partition of small amounts of tungsten cupferrate (20 μg of tungsten) between aqueous solutions and a series of immiscible organic solvents and showed that it is most efficiently extracted with isoamyl alcohol. They also studied the effect of sulphuric acid concentration on the extraction with isoamyl alcohol and concluded that a concentration of $6N$ is satisfactory for 98–100% extraction of tungsten when four extractions are performed. The applicability of their procedure to the separation of large amounts of tungsten was investigated in the present work.

Experiments were performed with tungsten solutions prepared by decomposing 0·5000 g of tungsten metal according to the procedure described for niobium and tantalum metals. A 2:1 mixture of chloroform and isoamyl alcohol was employed as extractant in these tests. The results of these tests showed that large amounts of tungsten cupferrate can be extracted by the above solvent mixture, but because of the large volume of cupferron solution required to complex 0·5000 g of tungsten, the initial concentration of sulphuric acid has to be increased to approximately $12N$ before the addition of cupferron solution. Under these conditions chemical analysis showed that between 14 and 21 mg of tungsten remained in the aqueous phase after extraction and this amount does not interfere in the determination of manganese.

Effect of diverse ions

Previous investigators[4-6,20] have shown that the following ions also form coloured metal complexes with PAN: bismuth(III), cadmium(II), copper(II), palladium(II), platinum, tin(IV), uranium(VI) (UO_2^{2+}), mercury(II), thorium(IV), cobalt(II), lead(II), iron(II), iron(III), nickel(II), zinc(II), lanthanum(III), cerium(III), cerium(IV), indium(III), scandium(III), europium(III), gallium(III), yttrium(III), vanadium(V) and gold. These authors investigated qualitatively the effect of various complexing agents (*i.e.*, ethylenediaminetetra-acetic-acid, cyanide, fluoride and citrate) on the formation of some of the above PAN complexes. Because the formation and stability of PAN complexes and also the effectiveness of cyanide as a complexing agent are greatly influenced by pH, it was considered expedient to investigate the possible interference effects of those of the above ions plus other ions that could occur as impurities in samples of the four high-purity metals.

The results of these tests showed that 1 mg each of nickel(II), copper(II), cadmium(II), phosphorus(V), chromium(III), vanadium(V), aluminum(III), zirconium(IV), iron(III), arsenic(V), antimony(III), antimony(V), tin(IV), titanium(IV), silicon(IV) and bismuth(III) (added in the valence states shown) do not interfere in the determination of manganese by the proposed method. However, 1-mg quantities of zinc(II), lead(II) and cobalt(II) do interfere. Zinc is ineffectively complexed with small amounts of cyanide under the described experimental conditions but forms a very stable, extractable PAN complex (formation constant $10^{21\cdot8}$).[19] Test solutions containing lead (or bismuth) turned a dark reddish-brown colour on addition of PAN but cleared up on shaking with chloroform. Low results were obtained with test solutions containing 1 mg of cobalt, even though the cobalt appeared to be completely complexed with cyanide. However, up to at least 50, 100 and 500 μg of zinc, lead and cobalt, respectively, can be tolerated separately in the proposed method without causing an appreciable error in the manganese result.

Application to synthetic niobium, tantalum, molybdenum and tungsten samples

To determine the accuracy of the proposed method, it was applied to the analysis of a series of synthetic samples in which the added manganese varied from 0·001 to 0·10%. The standard manganese solution was added directly to the powdered metal samples. The results obtained are given in Table II.

DISCUSSION

Table II shows that the results obtained by the proposed method agree favourably with the total calculated percentage of manganese in the range of values up to approximately 0·1%.

Although tests were performed to determine the possible interference effects of various impurities that could occur in samples of the four high-purity metals under consideration, some of these impurities (*i.e.*, copper, vanadium, zirconium, iron, antimony, tin and titanium) are partially or completely removed in the proposed method by extraction of their cupferrates.

In preliminary tests carried out to determine the applicability of cupferron-chloroform extraction to the separation of niobium, tantalum and molybdenum from small amounts of manganese, slightly low results were obtained for the added manganese. This error was found to be caused by partial oxidation of manganese to manganese dioxide during evaporation to dryness of the aqueous phase remaining after the extraction. However, this problem was avoided by dissolving the manganese dioxide adhering to the sides of the beaker with hydrochloric acid.

The pH range required for quantitative extraction of the manganese(II)-PAN complex in a single stage with 10 ml of chloroform is approximately 8·8 to 9·6, but complete extraction can also be obtained at higher pH (approximately 10) by performing three extractions. However, because of the solubility of PAN in chloroform and the instability of the manganese complex in ammoniacal tartrate-cyanide media, additional PAN solution must be added before each extraction step in order to recomplex the residual manganese resulting from the dissociation of its PAN complex.

TABLE II.—RECOVERY OF MANGANESE BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Mn present, %	Mn found, %	Sample	Total Mn present, %	Mn found, %
Nb + 0·0010% Mn	0·0011	0·0011	Ta + 0·0010% Mn	0·0010	0·0010
Nb + 0·0050% Mn	0·0051	0·0050	Ta + 0·0050% Mn	0·0050	0·0048
Nb + 0·0100% Mn	0·0101	0·0101	Ta + 0·0100% Mn	0·0100	0·0099
Nb + 0·0250% Mn	0·0251	0·0249	Ta + 0·0250% Mn	0·0250	0·0250
Nb + 0·0500% Mn	0·0501	0·0504	Ta + 0·0500% Mn	0·0500	0·0502
Nb + 0·1000% Mn	0·1001	0·0998	Ta + 0·1000% Mn	0·1000	0·1005
Mo + 0·0010% Mn	0·0013	0·0013	W + 0·0010% Mn	0·0010	0·0009
Mo + 0·0050% Mn	0·0053	0·0052	W + 0·0050% Mn	0·0050	0·0049
Mo + 0·0100% Mn	0·0103	0·0103	W + 0·0100% Mn	0·0100	0·0100
Mo + 0·0250% Mn	0·0253	0·0253	W + 0·0250% Mn	0·0250	0·0248
Mo + 0·0500% Mn	0·0503	0·0507	W + 0·0500% Mn	0·0500	0·0497
Mo + 0·1000% Mn	0·1003	0·1017	W + 0·1000% Mn	0·1000	0·0988

Duplicate determinations of manganese in the above Nb, Ta, Mo and W metals by the proposed method gave average results of 0·0001 %, none detected, 0·0003 % and none detected, respectively.

The combined extracts may then be diluted to a definite volume with chloroform before spectrophotometric measurement. Low results are obtained if ethyl alcohol is used as diluent.

The method presented in this paper is suitable for samples containing 0·0005–0·10% of manganese, but manganese contents below 0·0005% can be determined fairly accurately because the reagent blank contains approximately 0·5 μg or less of manganese. The precision is such that the error in the determination of 100 μg of manganese is not greater than ∓1·5 μg. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Es wird eine spektralphotometrische Methode zur Bestimmung von 0,0005–0,10% Mangan in hochreinem metallischem Niob, Tantal, Molybdän und Wolfram beschrieben. Die Matrix-Metalle werden nach Lösen der Probe durch Extraktion als Cupferrate vom Mangan getrennt, dann wird der rote Komplex aus Mangan(II) und 1-(2-Pyridylazo)-2-naphthol (PAN) aus ammoniakalischem Tartrat-Cyanid-Medium in Chloroform extrahiert. Die Extinktion des Extraktes wird bei 562 mμ gemessen. Außer Zink und Blei stören andere Verunreinigungen in den beschriebenen vier hochreinen Metallen bei der vorgeschlagenen Methode nicht.

Résumé—On décrit une méthode spectrophotométrique de dosage de 0,0005–0,10% de manganèse dans les niobium, tantale, molybdène et tungstène métalliques de haute pureté. On sépare les substances de la matrice du manganèse par extraction à l'état de cupferrates, après dissolution de l'échantillon, puis le complexe rouge formé entre le manganèse(II) et le 1-(2-pyridylazo) 2-naphtol, PAN, est extrait en chloroforme à partir d'un milieu ammoniacal tartrate-cyanure. On détermine l'absorption de l'extrait à 562 mμ. Dans la méthode proposée, et à l'exception du zinc et du plomb, les autres impuretés présentes dans les quatre métaux de haute pureté décrits n'interfèrent pas.

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MILLIGRAM DETERMINATION OF PRIMARY AMIDES

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Summary—An accurate and selective milligram procedure for the determination of primary amides is described. About 3–4 mg of sample are hydrolysed with a concentrated solution of sodium hydroxide and the resulting ammonia is distilled into dilute sulphuric acid. The ammonium sulphate thus obtained is converted into ammonium iodide by passing it through hydroxide- and iodide-form resins. This iodide is oxidised to iodate with bromine, then titrated iodometrically. Determinations carried out on a number of primary amides, ureas and thioureas show a deviation of about 0·3% from full recovery of the compounds.

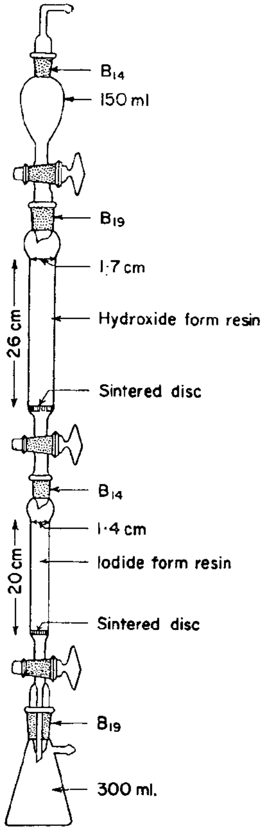
THE usual basic properties of the nitrogen atom in an amide function are effectively neutralised by the presence of the acyl group and, therefore, the determination of amides as bases by direct titrimetry is not possible. For similar reasons they also cannot be titrated as acids. Though the usual alkali saponification procedure[1] is applicable for the gram determination of amides, the method is seldom used because of the excessive reaction time required and the possible loss of the reagent by interaction with the glass vessel. Moreover, the sensitivity of the procedure decreases with increasing molecular weight of the sample in a homologous series unless a very large excess of the reagent is used, in which case the error from the loss of the reagent by interaction with the glass container becomes very significant. Recently, Bednarski and Hume[2] attempted to overcome this difficulty by saponifying the samples (about 150 mg or more) using a large excess of concentrated aqueous alkali and removing the excess alkali by neutralising with a cation-exchange resin (H-form). Carboxylic acid salts, formed during the hydrolysis, are thereby converted to the corresponding free acids and titrated directly against standard alkali solution.

It is important to note that neither of the above two procedures is specific for primary amides and their adaptation to the milligram scale is rather difficult. In the procedure of Bednarski and Hume[2] the error from inconsistent and unusually high blank values, probably arising from thermal degradation of the resin by maintaining it at 80°, is quite significant. There are only a few methods for the selective determination of primary amides. Indirect titrimetry by measuring the ammonia evolved on alkaline hydrolysis[3] and the 3,5-dinitrobenzoyl chloride procedure[4] are available for the determination of primary amides on the gram scale. A non-aqueous procedure has also been described by Fritz.[5]

Other compounds containing amide groups, like ureas and thioureas, can be determined by a number of procedures,[6–12] but some of them can only be applied on the gram scale while others are not fairly simple and accurate.

For the determination of total nitrogen in organic compounds by the Kjeldahl procedure, Shah and Qadri[13] have replaced the distillation step by converting ammonium sulphate to iodide with the use of ion-exchange resins.

By the combined use of the principles of alkali saponification and the conversion of ammonium sulphate to iodide by ion exchangers, we have developed a simple and accurate [within ±0·2–0·4%(abs.) in most cases] milligram procedure for the selective determination of primary amides, ureas and thioureas. The sample is hydrolysed using a large excess of alkali and the resulting ammonia distilled into dilute sulphuric acid. The ammonium sulphate so formed is then passed through hydroxide- and iodide-form resins to convert it to ammonium iodide, which is subsequently oxidised to iodate by bromine and titrated iodometrically. The procedure gives a six-fold amplification and high accuracy is achieved.



EXPERIMENTAL

Apparatus

Ion-exchange columns. Two columns are fixed one above the other through B_{14} ground joints (Fig. 1). Hydroxide-form resin (26 cm length) is filled into the upper column and iodide-form resin (20 cm length) into the lower column. A separatory funnel of 150-ml capacity may be employed as the reservoir on top of the upper column.

Reagents

Resins. Hydroxide-form resin (Amberlite IR 401, analytical-reagent grade, B.D.H., England) is thoroughly washed with water before use. The resin is regenerated after use with 500 ml of 10% sodium hydroxide solution.

About 12 g of the hydroxide-form resin are converted to the iodide form by treating it with 30 g of potassium iodide in 80 ml of water, then thoroughly washing with water.

Bromine solution. 1% (v/v) bromine solution in 10% sodium acetate in acetic acid.

Formic acid. Analytical-reagent grade 90% acid (B.D.H., England).

Procedure

Before use the resin columns are washed with 100 ml of water and the effluent titrated against 0·025*M* sodium thiosulphate solution for free iodine. If the titre exceeds 0·6 ml, further washing of the columns is essential.

About 3–4 mg of sample are accurately weighed and transferred to a 200-ml conical flask containing about 100 ml of sodium hydroxide solution (2% for simple primary amides and 8-10% for other compounds) and a few boiling stones. The contents are boiled and the resulting ammonia is simultaneously distilled into 5 ml of 0·066*N* sulphuric acid. Ammonium sulphate plus the excess sulphuric acid is passed through the resin columns under gentle suction and eluted with 100 ml of water. The eluate is treated with a slight excess of bromine solution, then allowed to stand for 2 min. Excess bromine is destroyed by the dropwise addition of formic acid till a clear solution is obtained. About 1 g of potassium iodide and 5 ml of 4*N* sulphuric acid are added to the bromine-free solution and the liberated iodine titrated against the standard 0·025*N* sodium thiosulphate solution.

A blank determination should be carried out under identical conditions except for the absence of a sample.

RESULTS AND DISCUSSION

Taking acetamide as the test sample, the indirect titrimetric procedure, involving direct distillation of ammonia into standard acid solution and back-titration of the excess acid, has been compared for accuracy with the present method. It is evident from Table I that with decreasing sample size the accuracy of the method also decreases, and in the sample range of 3–4 mg the accuracy of the procedure described by us is three times (Table II) better than that of the indirect titrimetric method.

TABLE I.—DETERMINATION OF ACETAMIDE BY THE INDIRECT TITRIMETRIC PROCEDURE USING DIFFERENT SAMPLE SIZES.

Sample, *mg*	No. of determinations	Recovery, %	Deviation, %
15	3	99·70	0·30
10	3	99·66	0·34
8	3	99·45	0·55
6	4	99·36	0·64
3	5	99·21	0·79

For the present method, 100 ml of a 2% solution of sodium hydroxide are found to effect complete hydrolysis of many primary amides within 30 min. Compounds which resist hydrolysis under these conditions require a higher concentration of alkali (8–10%) and treatment for 60–80 min. Although the determination of allylthiourea is fairly quantitative, phenyl and naphthylthioureas give a recovery of only 30%.

One filling of the hydroxide-form resin is sufficient for about four actual and four blank determinations. The iodide-form resin, however, requires fresh regeneration each time. The time required for the distillate and the washings to pass through the columns should be adjusted to about 15–20 min.

The results of the determinations of some primary amides, ureas and thioureas are given in Table II.

TABLE II.—DETERMINATION OF PRIMARY AMIDES, UREAS AND THIOUREAS

*Compound	Reaction time, *min*	No. of determinations	Recovery, %	Deviations, %
Acetamide	30	4	99·75	0·25
Benzamide	30	5	99·65	0·35
Oxamide	30	6	99·75	0·25
Succinimide	30	4	99·65	0·35
Salicylamide	60	5	99·75	0·25
Phthalamide	60	4	99·72	0·28
Dicyandiamidine	60	5	99·41	0·59
Urea	70	5	99·71	0·29
Phenylurea	75	4	99·15	0·85
Thiourea	80	6	99·65	0·35
Allylthiourea	80	6	99·45	0·55

* All compounds were of analytical-reagent grade (B.D.H., England) or recrystallised samples from appropriate solvents.

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Zusammenfassung—Eine genaue und selektive Vorschrift zur Bestimmung von Milligrammen primärer Amide wird beschrieben. Etwa 3–4 mg Probe werden mit konzentrierter Natronlauge hydrolysiert und der gebildete Ammoniak in verdünnte Schwefelsäure destilliert. Das erhaltene Ammonsulfat wird durch Ionenaustausch an Harzen in Hydroxyd- und Jodidform in Ammoniumjodid überführt. Das Jodid wird mit Brom zu Jodat oxydiert und dann jodometrisch titriert. Bestimmungen von primären Amiden, Harnstoffen und Thioharnstoffen zeigen eine Abweichung von etwa 0,3% vom theoretischen Wert.

Résumé—On décrit une technique précise et sélective de dosage des amides primaires à l'échelle du milligramme. On hydrolyse environ 3–4 mg d'échantillon au moyen d'une solution concentrée de soude et l'ammoniac résultant est distillé dans de l'acide sulfurique dilué. Le sulfate d'ammonium ainsi obtenu est converti en iodure d'ammonium par passage sur résines sous formes hydroxyde et iodure. Cet iodure est oxydé en iodate par le brome, puis titré par iodométrie. Les dosages d'amides primaires, d'urées et de thiourées montrent un écart d'environ 0,3% par rapport aux quantités de composés mises en jeu.

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EIN VORSCHLAG ZUR DARSTELLUNG DER ANALYSEERGEBNISSE IN "IONENFORM" SCHON VOR DER AUSARBEITUNG DER IONENTHEORIE

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Zusammenfassung—1865 schlug Karl Than, Professor der Chemie in Budapest vor, dass die Analysenergebnisse nicht in der Berzeliusschen dualistischen Form, sondern in der Form dargestellt werden sollen, wie sie durch die Analyse bestimmt werden. Es wurde verfolgt, wie sich dieser anfänglich nicht beachtete Vorschlag durch die Ionentheorie und Wilhelm Ostwalds Tätigkeit einführte.

VOR 100 Jahren, im Jahr 1865 erschien eine Veröffentlichung in einer ungarischen pharmazeutischen Zeitschrift des damals noch sehr jungen, neu ernannten Professors für Chemie der Universität Budapest, Karl Than (1834–1908) unter dem Titel "Über die Zusammenstellung der Analyse von Mineralwässern".[1] Die Publikation betraf eigentlich einen Vortrag, den Than schon ein Jahr früher, 1864 auf der X. Wanderversammlung der ungarischen Ärzte und Naturforscher in Marosvásárhely (Siebenbürgen) hielt. Auf der Sitzung vom 20 April 1865 der mathematisch-naturwissenschaftlichen Klasse der kaiserlichen Akademie in Wien legte Thans ehemaliger Lehrer, Redtenbacher diese Abhandlung vor. Sie erschien bald auch in deutscher Sprache in den Sitzungsberichten.[2] Obwohl der Verfasser darin wichtige chemische Dinge abhandelte, und Vorschläge machte, die uns heute selbstverständlich erscheinen sowie auch dafür sorgte, dass seine Feststellungen und Vorschläge zur Kenntnis des in-und ausländischen Chemikerpublikums gelangten, muss man feststellen, dass er einstweilen keinen Erfolg verbuchen dürfte. Zweilfellos waren Thans Gedanken deshalb erfolglos, weil er der wissenschaftlichen Erkenntnis voraneilte und noch keine theoretische Begründung seiner Vorschläge vorlegen konnte. Es dauerte noch etwa ein Vierteljahrhundert bis sich herausstellte, dass er auch aus theoretischem Gesichtspunkt Recht hatte.

Zu jener Zeit war es üblich die Ergebnisse von Analysen nach der Berzeliusschen dualistischen Lehre in Basen- bzw. Säureanhydriden anzugeben (welche Gepflogenheit sich in der Mineralanalyse bis heute hält) bzw. im Fall von Lösungen u.a. auch bei Mineralwässern die Analyseergebnisse zu Salzem zusammenzustellen.

Than fand dieses Vorgehen prinzipiell schlecht:

"Wenn man das übliche Verfahren bei der Zusammenstellung der Mineralwasseranalysen einer objektiven Kritik unterzieht, so gelangt man zu der Überzeugung, dass durch eine derartige Zusammenstellung die wirkliche Constitution eines Wassers nicht ausgedrückt wird, ja sogar, dass sie eine Zusammensetzung darstellt, welcher sowohl in qualitativer, als auch insbesondere in quantitativer Beziehung unrichtig ist."

Mit den analytischen Methoden lässt sich nur feststellen welche Mengen eines Elements, im Fall gewisser Nichtmetalle einer Elementengruppe zugegen sind. Alle auf Affinität, Löslichkeit und ähnliche Betrachtungen beruhenden Aussagen zur Ermittelung der Salzkombinationen sind unzuverlässig, haben keine wissenschaftliche Grundlage und sind deshalb willkürlich.

Mit verschiedenen eigenen Versuchen und unter Berufung auf Grahams Versuche über die Diffusionsgeschwindigkeit unterstützte Than dann ausführlich seine obigen Behauptungen.

Dann fuhr er weiter fort:

"Meines Erachtens kann der Zweck derartiger Zusammenstellungen bei dem gegenwärtigen Stande unserer Kenntnisse ein zweifacher sein u.z.

1. Dass durch dieselben die in verschiedenen Mineralwässern enthaltenen Bestandteile exact verglichen werden können.
2. Dass durch dieselben die chemische Constitution des Wassers richtig dargestellt werde."

Zur Erfüllung des ersten Zieles.

"schlage ich vor, dass die in 1000 (oder 10000) Gewichtstheilen des Wassers enthaltenen Gesamtmengen der Elementarbestandtheile ausgedrückt werden sollen, so wie diese aus den directen Ergebnissen der Analyse berechnet werden, ohne dass sie unter sich zu imaginären Salzen eingetheilt wären."

"Es ist klar, dass bei einer derartigen Zusammenstellung die Resultate der Analyse auf den ersten Blick in exacter Weise verglichen werden können, da die Daten, aus welchen eine solche Zusammenstellung hervorgeht, die unmittelbaren Thatsachen der Analyse und daher von jeder Hypothese unabhängig sind."

Hinsichtlich der zweiten Zielsetzung d.h. der Erkenntnis wie sich die elementaren Bestandteile nun tatsächlich kombinieren, musste Than feststellen, dass sich dafür bei dem damaligen wissenschaftlichen Stand der Chemie keine Möglichkeit boten. (Dass die zukünfliche Chemie die Existenz von Salzmolekeln in Lösungen überhaupt bestreiten wird, konnte er natürlich nicht ahnen.) Er schlug jedoch eine Methode vor, womit sich dieses Ziel annähern lässt und durch welche man ein klareres Bild über die Reaktionen des Wassers bekommt als durch die bis dahin üblichen Zusammenstellungen.

"Damit man die wahre chemische Constitution eines Wassers beurtheilen könne, schlage ich vor, dass bei der Zusammenstellung ausser den in 1000 Theilen enthaltenen Mengen auch die relativen Äquivalente der elementaren Bestandtheile ausgedrückt werden sollen."

Diese relativen Mengen erhält man nach Than indem die Gewichtsmengen der einzelnen Elemente in 1000 Gewichtsteilen Wasser durch ihre Äquivalentgewichte dividiert werden. Die so erhaltenen Werte informieren einerseits gut über die Zusammensetzung eines gegebenen Wassers und ermöglichen anderseits auch die Kontrolle der Analyse, da die Summen der einzelnen relativen Äquivalente der Metalle und der Nichtmetalle bei richtigen Analysen übereinstimmen müssen. Stimmen sie nicht überein, so deutet dies bei alkalischem Wasser was zumeist vorliegt auf die Anwesenheit von Hydrogencarbonaten hin, deren Menge sich aus der Differenz errechnen lässt. Zum Vergleich verschiedener Wässer wurde noch vorgeschlagen, die relativen Äquivalente in Prozenten auszudrücken, indem man die Summe der relativen Äquivalente der Metalle = 100 setzt. Diese Prozente zeigen auf den ersten Blick deutlich, in welche Gruppe der Mineralwässer das entsprechende Wasser gehört:

"Ein unbestreitbarer Vorzug dieser Zusammenstellung ist es, dass durch sie der chemische Charakter irgend eines Wassers sicherer beurtheilt weredn kann . . . und, dass die chemischen Charaktere der verschiedenen Mineralwässer ebenfalls mit Präzision verglichen werden können."

Mit Beispielen schloss Than seine Erörterung.

Die Ergebnisse de Analysen von Lösungen in Ionenform darzustellen wurde erst selbstverständlich als die Theorie der elektrolytischen Dissoziation von Arrhenius, die zwischen 1884–1887 ausgearbeitet und veröffentlicht wurde, sich am Beginn unseres Jahrhunderts durchgesetst hatte. Bis dahin musste Thans Vorschlag ziemlich Zweifelhaft erscheinen. Besonders waren die Ärzte dagegen, da sie die Wirkung der Mineralwässer nach Salzen zu beurteilen gewohnt waren und sich auch nicht durch die Irrealität der Angaben davon abbringen liessen. Wir fanden bis zur Jahrhundertswende kein analytisches Buch dass den Vorschlag Thans auch nur erwähnt hätte. In Ungarn allein hat man hier und da, in Thans Institut und unter seinen ehemaligen Schülern diese Darstellungsweise benutzt, doch weder allgemein noch regelmässig.

Than gehörte zu den ersten Verfechtern der neuen physikalisch-chemischen Anschauungen. Die Arrheniussche Lehre gab die theoretische Begründung seiner Ansichten und Entwürfe.

Im Jahre 1890 berichtete er in einer Veröffentlichung über die neuen Lehren von Raoult, van't Hoff, Arrhenius sowie Ostwald und zeigte ihre Übereinstimmung mit seinen vor 25 Jahren gemachten Vorschlägen.[3] Er hatte ja eigentlich schon damals die Ergebnisse in Ionenform zusammengestellt.

"Die Berechtigung meines vor 26 Jahren gemachten Vorschlages haben die neuesten grossen Errungenschaften der Wissenschaft glänzend und unzweifelhaft dargethan."

Er gab allerdings zu, dass sein Vorschlag sich bis dahin nicht durchgesetzt hatte. Man schrieb noch immer nach der alten Gepflogenheit.

"Wie die meisten Vorurtheile, hat sich auch diese Gewohnheit so tief eingewurzelt, dass obwohl namentlich hierzulande einige meinen Vorschlag angenommen haben, in Grossen und Ganzen die alte Gewohnheit sich aufrecht erhalten hat."

Auf Grunde der neuen Tatsache ging mun Than erneut auf dem alten, und scheinbar auch schon von ihm aufgegebenen Gebiet an die Arbeit. Mit seinem Assistenten, Geysa Karlovszky analysierte er 76 europäische Mineralwässer (43 ungarische und 31 ausländische) und rechnete die Ergebnisse in Äquivalentprozente um.[3]

Die Analytiker waren aber konservativ. Die neuen Auflagen der klassischen Bücher (Fresenius, Böckmann) hielten auch noch in den ersten Jahren unseres Jahrhunderts an den alten Ansichten fest und erwähnten weder Ionentheorie, noch Thans Vorschlag.

Wilhlem Ostwald, der die analytische Chemie auf Grund der neuen physikalisch-chemischen Kenntnisse bearbeitete, kam in seinen "Wissenschaftlichen Grundlagen der analytischen Chemie" zum selben Vorschlag wie Than ein Vierteljahrhundert zuvor. Er schrieb: In den Analysen soll man "die Aufführung der einzelnen Elemente in den Mengen darstellen in denen sie vorhanden sind" um "den analytischen Ergebnissen ihren hypothesenfreien Charakter zu wahren." Obwohl man damit "in den Ergebnissen nicht zum Ausdruck bringen kann, in welcher Form die verschiedenen Elemente in der Verbindung enthalten sind."[4]

Es lässt sich gewiss nicht leugnen, dass die alten Ansichten in der analytischen Chemie durch Wilhelm Ostwald durchgebrochen wurden. Gewiss hat sich die

Darstellung der Analyseergebnisse in Ionenform auch in erster Linie durch sein Werk verbreitet.

Obwohl Ostwald ohne Kenntnis der Thanschen Arbeit zu seiner Folgerung kam, wurde er später darüber unterrichtet und erkannte Thans Priorität in den weiteren Ausgaben seines Werks[5] an. Auch findet man in gewissen damaligen analytischen Büchern eine diesbezügliche Berufung, auf Than allerdings erst im Wunschform, d.h. dass es gut wäre, wenn man den Than-Ostwaldschen Vorschlag in der Praxis verwenden würde.

Summary—In 1865 Karl Than, Professor of Chemistry in Budapest, suggested that analytical results should not be given in the dualistic form of Berzelius, but rather they should be given in the form in which they are determined by the analysis. The manner in which this suggestion, originally ignored, was adopted as a result of the ionic theory and activity of Wilhelm Ostwald is traced.

Résumé—En 1865 Karl Than, professeur de chimie à Budapest, a suggéré que les résultats analytiques ne devraient pas être donnés sous la forme dualistique de Berzelius, mais plutôt sous la forme où ils sont déterminés par l'analyse. On met en évidence la manière selon laquelle cette suggestion, ignorée à l'origine, a été adoptée comme un résultat de la théorie ionique et de l'activité de Wilhelm Ostwald.

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SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY WITH BROMOPYROGALLOL RED

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Summary—Bromopyrogallol Red may be used as a reagent for the spectrophotometric determination of antimony(III) in the range 10–100 μg. The colour system, in the presence of EDTA, cyanide ion or fluoride ion as masking agents, is unaffected by 200-fold molar excesses of 18 cations examined, and a further 5 cations can be tolerated at lower concentrations. The procedure is simple and rapid, and with a molar absorptivity coefficient in excess of 35,000, it compares favourably with the most sensitive of the techniques used at present.

INTRODUCTION

Bromopyrogallol Red (BPR) has previously been used as a reagent for the spectrophotometric determination of trace amounts of silver[1] and niobium.[2] During the investigation of the reaction with niobium it was observed that the reagent yielded a blue complex with antimony(III), at pH 5·8, and that this reaction was unaffected by the presence of conventional masking agents such as EDTA. This reaction has been further investigated and a simple and sensitive procedure has now been developed for the spectrophotometric determination of antimony.

The blue colour was found to form by the addition of a solution of potassium antimonyl tartrate to the reagent, buffered within the pH range 5–8, but a pH range between 6·6 and 6·8 was found to be optimal for colour development.

Initially an ammonium acetate buffer was used to maintain the pH within this optimal range, but because relatively small fluctuations in pH occurred, which in turn produced considerable changes in the absorbance values, this buffer was found to be unsatisfactory and a more stable phosphate buffering system was employed. The presence of phosphate had no adverse effect on the colour system itself, and as will be seen below, no difficulties were experienced from the precipitation of metal phosphates whilst studying cationic interferences.

Preliminary absorption spectra were plotted for the reagent and for an equimolar mixture of reagent and antimony(III) at pH 6·6–6·8 (Fig. 1). The reagent shows maximum absorbance at 560 mμ. The effect of the antimony(III) is to cause a decrease in the absorbance of the reagent at 560 mμ, accompanied by an absorbance increase for the complex which exhibits a maximal value at 615 mμ. It is worthy of note that only a poorly defined broad absorption band is formed at the longer wavelength. This may be attributed to partial dissociation of the complex under these conditions.

The reaction was found to be instantaneous, and the solutions showed no significant change for up to 2·5 hr after colour development, though extensive fading, because of oxidation of the reagent, occurred on prolonged standing. This could, however, readily be minimised by the addition of a small amount of hydroxylamine hydrochloride, the latter having no adverse effect on the colour system. The order of addition of the reagents was found to be of no significance.

Preliminary calibration curves showed linearity in the range 10–100 μg of antimony, with effective molar absorptivities at 560 mμ and 615 mμ of 39×10^3 and 7×10^3, respectively. It was decided to make all subsequent absorbance measurements at the shorter wavelength because of the greater sensitivity offered.

It was observed that a minimal 4-fold excess of reagent was required for maximal absorbance values, but that a reagent concentration in excess of $4 \times 10^{-5}M$ in the final solution provided a colour too intense for measurement in 1-cm cells at 560 mμ. All solutions were made $3{\cdot}5 \times 10^{-5}M$ with respect to BPR, allowing a maximum concentration of antimony in the final solution of $9 \times 10^{-6}M$; *i.e.*, the upper limit corresponds to 9 ml of $10^{-4}M$ antimony(III) or 110 μg of antimony.

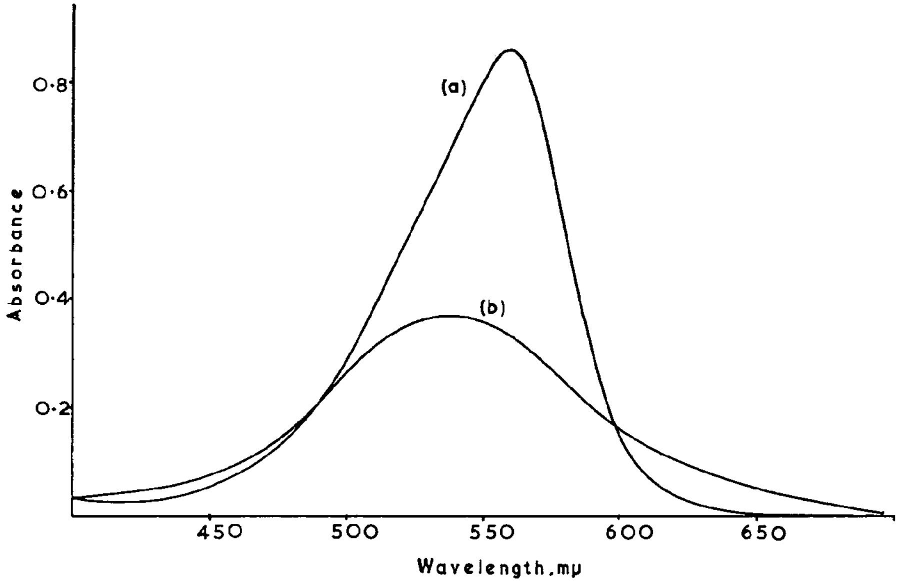

FIG. 1.—Absorption spectra:
(a) 5 ml of 5×10^{-4} *M* Bromopyrogallol Red + 5 ml of phosphate buffer diluted to 100 ml with water.
(b) As (a) plus 5 ml of 10^{-4} *M* potassium antimonyl tartrate.
(Measurements made in 1-cm cuvettes with Beckman DB spectrophotometer)

An examination of the effects on the colour system of a number of potential masking agents showed that the absorbance of a solution containing 60 μg of antimony and made $3{\cdot}5 \times 10^{-5}M$ with respect to BPR was unaffected by 1000-fold molar excess quantities of nitrilotriacetic acid, fluoride, iodide or oxalate. Similar quantities of EDTA or cyanide caused a slight (*ca.* 5%) decrease in absorbance, but CDTA, citrate and tartrate interfered extensively.

The tartrate effect was further studied because potassium antimonyl tartrate was being used as a source of antimony for all experimental work. A concentration of 0·1% of tartrate in the final solution could be tolerated, but this represents a considerable excess (*ca.* 1000-fold) over that directly bound up with antimony when the latter is used as potassium antimonyl tartrate. There was no significant difference in the absorbance of tartrate-free solutions and those which contained $\leqslant 0{\cdot}1\%$ tartrate. Thus, it would appear that tartrate plays little part in the constitution of the complex.

In view of the number of masking agents available and of their effects, no extensive search was made for an organic extractant to increase the selectivity of the procedure. Apart from involving unnecessary complications, extraction of the antimony complex itself was certain to prove difficult because of the presence of the sulphonic acid grouping in the reagent molecule. A brief examination showed that neither the reagent nor the antimony complex could be extracted into any of the following solvents: benzene, chloroform, isopropyl ether, methyl t-butyl ketone, methyl ethyl ketone, t-butanol, iso-amyl alcohol and nitrobenzene.

Final calibration curves for the system in the presence of the three masking agents selected for use, *viz.* EDTA, cyanide ion and fluoride ion, were plotted. All showed linearity in the range 10–100 μg of antimony with molar absorptivities and sensitivity indices as shown below.

TABLE I.—MOLAR ABSORPTIVITIES AND SENSITIVITY INDICES FOR THE SYSTEM IN THE PRESENCE OF SELECTED MASKING AGENTS

Masking agent	Molar absorptivity (ϵ)	Sensitivity index
None	39,200	0·0031
EDTA (10^{-2} *M*)	37,400	0·00325
Cyanide (10^{-2} *M*)	37,400	0·00325
Fluoride (10^{-2} *M*)	39,000	0·00312

The reproducibility of the colour system is indicated by the mean absorbance and standard deviation obtained from 12 solutions each containing 60 μg of antimony(III), buffered at pH 6·7 in the presence of a 1,000-fold molar excess of EDTA and rendered $3{\cdot}5 \times 10^{-5}M$ with respect to BPR. The mean absorbance was equal to 0·166, standard deviation 0·003.

Examination of interferences

All solutions for the interference studies contained 60 μg of antimony, together with a 1,000-fold molar excess over antimony of the masking agent employed. Ions were deemed to interfere if their presence caused an absorbance change greater than that of the standard deviation shown above.

In the presence of EDTA, a 200-fold molar excess over antimony of the following ions showed no interference: Al, Ba, Ca, Cd, Ce(III), Co, Fe(II), Fe(III), Mg, Mn, Ni, Pb, Sr, Tl, V(IV) and Zn. The EDTA complexes of both chromium(III) and copper(II) caused additive spectral interference, but a 100-fold molar excess of chromium(III) could be tolerated, and copper(II) showed no interference in the presence of cyanide ion provided it was added before the EDTA. The extensive interference of silver(I) was also eliminated in the presence of cyanide ion. Arsenic(III) did not interfere at the 100-fold molar excess level in the presence of EDTA, but slight interference was observed at twice this concentration. Some of the above ions in their higher oxidation states caused interference because of decolorisation of the reagent, but this was readily eliminated by the addition of sufficient hydroxylamine hydrochloride to reduce the respective ions to the lower oxidation state. Thorium, thallium and beryllium interfered extensively, but all could be tolerated at moderate concentrations (10-fold molar excess) in the presence of fluoride ion. The following cationic interferences could not be masked: Bi, Hg(II), Mo, Pt, W(VI), U(VI), Au, Nb and Zr.

Of the anions, none of the common ones (halides, sulphate, nitrate) showed interference. Readily reduced anions (permanganate, dichromate) can be expected to cause decolorisation of the reagent, unless a suitable reductant (hydroxylamine or ascorbic acid) is employed, while readily oxidised ions will merely serve to stabilise the reagent.

Reaction mechanism

Unlike the niobium-BPR system,[2] the antimony-BPR complex is not stabilised and intensified by the addition of gelatin and no coagulation occurs at an aqueous-organic interface, indicating that the complex is not colloidal in nature.

It was observed that the antimony complex, unlike the reagent itself, was unaffected by mild oxidising agents. This indicates that complex formation occurs through interaction between the antimony and the (readily oxidised) vicinal dihydroxy grouping in the reagent molecule.

A comparison of this reaction with that between antimony(III) and pyrocatechol[3] suggests that the complex formed has an empirical composition corresponding to that of a Bromopyrogallol Red ester of antimonous acid (Fig. 2).

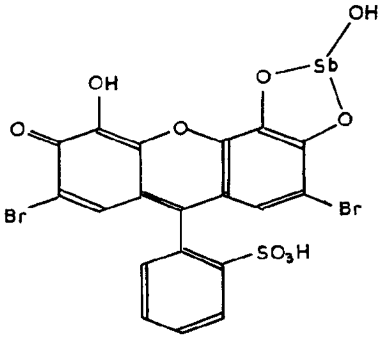

FIG. 2

Job plots and slope ratio curves (Fig. 3) confirm the existence of a fairly stable 1:1 complex. The conditional instability constant of the complex obtained by calculations based on the mole ratio data has an approximate value of $4{\cdot}85 \times 10^{-6}$.

DISCUSSION

With an extinction coefficient of about 35,000 the technique compares favourably with the most sensitive of those at present in use for the spectrophotometric determination of antimony. Principally, this new method offers considerable advantage, however, in that the technique is simple to operate, and is readily reproducible, while still preserving a high degree of selectivity.

For example, the well established Rhodamine B technique,[4] whilst being both highly selective and sensitive, involves initial oxidation of the antimony(III) to the quinquevalent state to form the unstable $SbCl_6^-$ ion, and the subsequent extraction of the ion-association system into an organic solvent. We have found it difficult to obtain reproducible results with this method, using both benzene and isopropyl ether as extractants.

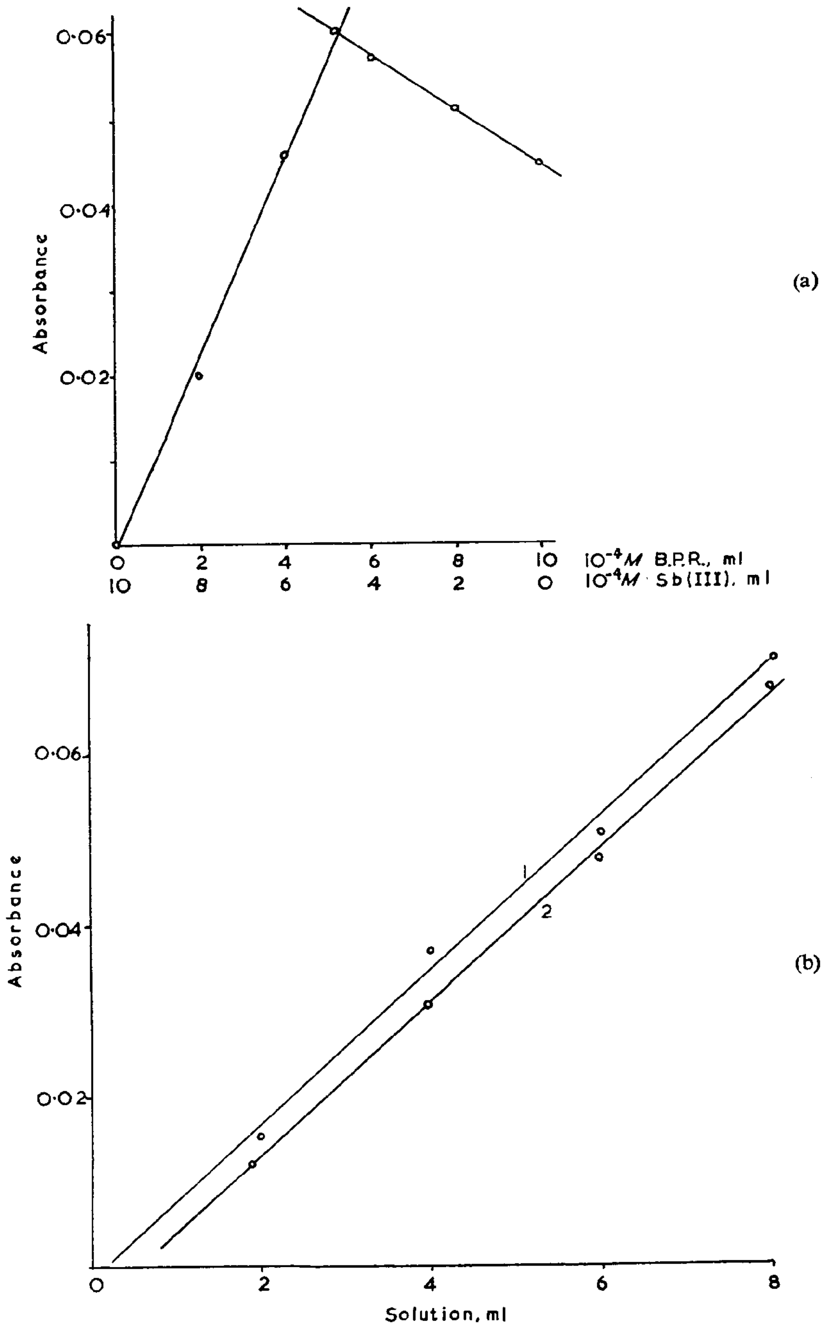

FIG. 3.—Structural data:–

(a) *Job plot:* Varying ratios of 10^{-4} M Bromopyrogallol Red + potassium antimonyl tartrate + 5 ml of phosphate buffer diluted to 100 ml with water.

(Absorbance measured at 615 mμ; 1-cm cuvettes)

(b) *Slope Ratio Curves:* (1) 5 ml of 10^{-3} M potassium antimony tartrate + 5 ml of phosphate buffer + x ml of 10^{-4} M Bromopyrogallol Red diluted to 100 ml with water. (2) 5 ml of 10^{-3} M Bromopyrogallol Red + 5 ml of phosphate buffer + x ml of 10^{-4} M potassium antimony tartrate diluted to 100 ml with water.

(Absorbance measured at 615 mμ in 1-cm cuvettes)

Extraction is also necessary in the sodium diethyldithiocarbamate method, which, while being very selective (only Be, Te, Tl^{3+} and larger amounts of As, Se and Cu interfere), has limited sensitivity. The iodide method, based on the formation of $HSbI_4$, while being relatively straightforward in application, is only sensitive when measurements are made at 330 mμ and, unfortunately, at this wavelength many other ions interfere.

The BPR method described here has been simplified by the use of a composite buffer and masking agent solution. The only difficulties experienced in using this system arose with aluminium and copper. The aluminium is initially precipitated by the phosphate ions of the buffer but redissolves following dilution and standing for some time. When copper is present, the blue EDTA-copper(II) chelate is formed in preference to the colourless copper(I) cyanide and causes interference. This problem was readily eliminated by addition of excess of $10^{-1}M$ potassium cyanide before the buffer solution.

TABLE II.—A COMPARISON OF VARIOUS REAGENTS FOR THE SPECTROPHOTOMETRIC DEFINITION OF ANTIMONY[5]

Antimony as	Reagent	Solvent	Molar absorptivity (ε)	Wavelength, mμ
Sb^{3+}	Bromopyrogallol Red	Water	39,200	560
Sb^{3+}	Hydrochloric acid	Water	18,000	228
Sb^{3+}	Sodium diethyldithiocarbamate	Carbon tetrachloride	3,700	350
Sb^{3+}	Potassium iodide	Water	4,400	425
	Potassium iodide	Water	32,000	330
Sb^{5+}	Hydrochloric acid	Water	8,100	272
$SbCl_6^-$	Rhodamine B	Benzene	28,000	565
		Isopropyl ether	34,000	545

Because the order of addition of reagents, apart from the above exceptions, does not appear to be critical it should also be possible to use a single solution containing BPR as well as buffer and masking agent.

All the chemicals used are inexpensive and readily obtained and the method is ideally suited to the rapid repetitive analysis of antimony.

Whilst extraction methods usefully provide a separation stage, they do involve an extra operation and it has been shown that the present procedure, which achieves selectivity by simple addition of masking agents, is at least equally selective.

Table II compares the performance of the proposed procedure with the most commonly applied methods for antimony.

EXPERIMENTAL

Preparation of Calibration Curve

Reagents

10^{-4} M *Potassium antimonyl tartrate.* Prepared by dilution of standardised (bromate method) 10^{-2} *M* potassium antimonyl tartrate.

7×10^{-4} M *Bromopyrogallol Red.* 0·390 g of BPR dissolved in and diluted to 1 litre with 50% v/v aqueous ethanol. This solution is stable for several weeks.

Buffer solution (pH 6·6–6·8). 37·23 g of EDTA disodium salt (analytical-reagent grade), 6·15 g of potassium cyanide (analytical-reagent grade), 4·2 g of sodium fluoride 37·5 g of disodium hydrogen phosphate and 13·6 g of potassium dihydrogen phosphate dissolved in and diluted to 1 litre with water.

Apparatus

Hilger Uvispek spectrophotometer with 1-cm and 4-cm cuvettes.
Beckman DB recording spectrophotometer with 1-cm cuvettes.

Procedure

Pipette 0–10 ml of the 10^{-4} *M* antimony solution and 10 ml of the buffer solution into 100-ml volumetric flasks. Add 5·0 ml of 7×10^{-4} *M* BPR solution, dilute to 100 ml and immediately, or within 2·5 hr, measure the absorbance of the blank solution against each of the antimony solutions in turn, at 560 mμ using 1-cm cuvettes. A plot of absorbance *vs.* concentration gives a straight line graph over the range 10–100 μg of antimony.

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Zusammenfassung—Brompyrogallolrot kann als Reagens zur spektralphotometrischen Bestimmung von Antimon(III) im Bereich von 10–100 μg verwendet werden. Die Farbe wird in Gegenwart von EDTA, Cyanid oder Fluorid zur Maskierung durch 200-fache molare Überschüsse von 18 geprüften Kationen nicht beeinflußt, weitere 5 Kationen können bei niedrigeren Konzentrationen zugelassen werden. Die Vorschrift ist einfach und schnell auszuführen; mit einem molaren Absorptionskoeffizienten von über 35000 ist sie mit Vorteil unter die empfindlichsten der heute angewandten Methoden einzureihen.

Résumé—On peut utiliser le Rouge de Bromopyrogallol comme réactif pour le dosage spectrophotométrique de l'antimoine(III) entre 10 et 100 μg. Le système coloré, en présence d'EDTA, de cyanure ou d'ion fluorure comme agents dissimulants, n'est pas affecté par des quantités molaires 200 fois supérieures de 18 cations examinés, et 5 autres cations peuvent être tolérés à de plus faibles concentrations. La technique est simple et rapide, et avec un coefficient d'absorption molaire excédant 35000, elle peut être comparée favorablement à la plus sensible des techniques utilisées actuellement.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXI*

DETERMINATION OF NICKEL IN THE PRESENCE OF COBALT

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Summary—A new method for the determination of nickel in the presence of cobalt, based on the masking of the cobalt with potassium cyanide and hydrogen peroxide, is proposed. The yellow, or orange-yellow, complex of cobalt(III) is formed, from which cobalt is not displaced upon the addition of silver nitrate. Tetracyanonickelate, however, reacts quantitatively with silver nitrate, and the displaced nickel can be determined directly with EDTA, using Murexide as indicator. Up to 30 mg of cobalt can be tolerated in the solution.

THE direct determination of nickel without previous separation from cobalt is still a difficult problem in complexometry, as the masking of cobalt can only be carried out when it is in the tervalent form. The earliest proposal was based on the formation of the blue $Co(H_2O)$-EDTA complex in alkaline medium, which unlike nickel-EDTA complex, does not react with potassium cyanide.[1] Because of the intense coloration of this cobalt complex, however, the amount of cobalt taken is restricted to a few milligrams. The red-violet complex CoY^- is also highly coloured in acidic medium so that nickel can only be determined in the presence of small amounts of cobalt even when a fluorescent indicator such as Calcein (Fluorexone) is used.[2] This principle has been applied for the analysis of some iron–nickel–cobalt alloys.[2] Recently we have found that triethanolamine (TEA) with hydrogen peroxide is more suitable for masking cobalt than EDTA + hydrogen peroxide.[3] In this case the red coloration is not so intense, so that 15–20 mg of cobalt in 500 ml of the solution can be tolerated. In addition, iron and aluminium are also masked by the triethanolamine. Nickel is determined directly with EDTA in an ammoniacal solution with Murexide as indicator.

All these above mentioned complexes of tervalent cobalt exhibit very similar absorption maxima (520–580 mμ) in comparison with free Murexide (540 mμ) (Figs. 1 and 2). It would therefore be more convenient, and not only for visual titrations, to mask cobalt as another complex having an absorption maximum in a different region, *e.g.*, in the near ultraviolet. For this reason potassium cyanide has been chosen as the masking agent for tervalent cobalt. The yellow to pink-yellow complex $Co(CN)_6^{3-}$ (Fig. 2) is formed quantitatively in ammoniacal medium by the addition of hydrogen peroxide and potassium cyanide. Cobalt is not displaced from this complex upon careful addition of silver nitrate, whereas nickel is displaced from $Ni(CN)_4^{2-}$. The displacement of nickel is quantitative when the first cloudiness due to silver

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* Part XX: *Talanta*, 1966, **13**, 233.

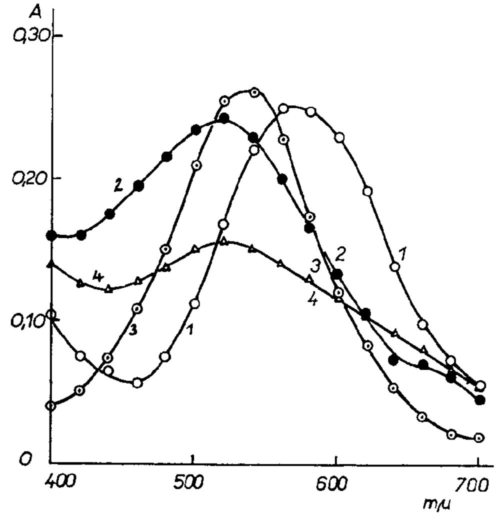

FIG. 1.—Absorption spectra of cobalt complexes:
1—1·5 × $10^{-4}M$ $Co(H_2O)Y^-$
2—1·5 × $10^{-4}M$ CoY^-
3—4 × 10^{-3}% Murexide + EDTA (0·1 ml of 0·05*M* EDTA)
4—15 × $10^{-4}M$ Co — TEA complex (TEA = triethanolamine).

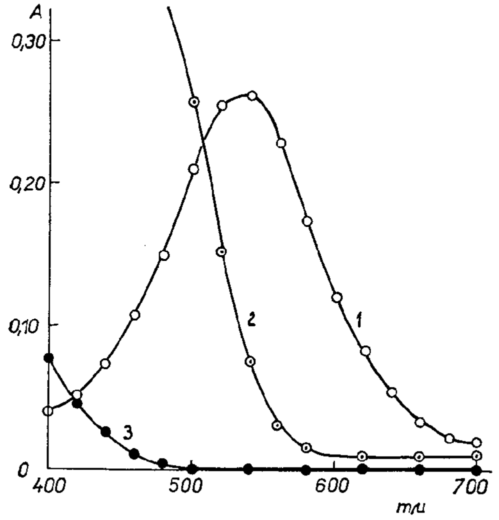

FIG. 2.—Absorption spectra of nickel and cobalt complexes:
1—4 × 10^{-3}% Murexide + EDTA (0·1 ml of 0·05*M* EDTA)
2—4 × 10^{-3}% Murexide + Ni (0·1 ml of 0·05*M* Ni)
3—1·5 × $10^{-4}M$ $Co(CN)_6^{3-}$.

cyanide appears. The nickel can then be determined by direct titration with EDTA with Murexide as indicator, or indirectly by back-titration of the excess EDTA with calcium using Methylthymol Blue as indicator.

EXPERIMENTAL

Reagents

EDTA, 0·05*M*.
Calcium chloride, 0·05*M*.
Potassium cyanide, 5% *solution*.
Hydrogen peroxide, 2%.
Potassium iodide solution, 5%.
Silver nitrate solution, 10%.
Ammonia, *conc. and* 1 + 9 *solution*.
Murexide, 1% *in potassium nitrate*.
Methylthymol Blue, 1% *in potassium nitrate*.

Apparatus

Spectrophotometer. SFM-2 RUKOV, Rumburk, ČSSR; cylindrical cuvettes, 17 mm diameter.

Procedure A

Direct titration of nickel. To the solution containing nickel and cobalt add 25–35 ml of concentrated ammonia and dilute to 200–250 ml. Then add 10–15 ml of 5% KCN solution and 5–10 ml of 3% hydrogen peroxide and allow the solution to react for 3–5 min with occasional stirring. Add 10% silver nitrate from a burette with vigorous stirring until the solution shows a slight but permanent turbidity. Allow the solution to stand for 1–2 min and then titrate slowly, after addition of Murexide, with 0·05*M* EDTA from yellow or yellow-orange to bright violet. By this method up to 50 mg of nickel in the presence of up to 30 mg of cobalt (in a volume of 300–500 ml) can be satisfactorily determined (Table I).

TABLE I.—DETERMINATION OF NICKEL IN THE PRESENCE OF COBALT (DIRECT TITRATION)

Taken, *mg*		0·05*M*	Ni found,	
Ni	Co	EDTA, *ml*	*mg*	Difference, *mg*
2·89	2·95	0·92	2·72	−0·17
5·78	5·90	1·85	5·43	−0·35
2·89	14·74	0·98	2·89	0
2·89	29·47	0·95	2·80	−0·09
2·89	44·20	1·05–1·15*	2·35–2·55	−0·46 to −0·66
2·89	57·82	1·10–1·40†	—	—
14·46	14·74	4·88	14·32	−0·14
28·91	29·47	9·80	28·70	−0·15
57·82	2·95	19·80	58·11	+0·29
57·82	29·47	19·93	58·48	+0·66

* Indistinct end-point
† Very unsharp colour change

Remarks. A large excess of silver nitrate must be avoided because the intense turbidity obscures the end-point. After a while (5–15 min) Murexide is destroyed by hydrogen peroxide.

Procedure B

Indirect determination of nickel. It has been found that in the presence of excess EDTA a small amount of cobalt is cotitrated, owing to the displacement reaction between AgCN and $Co(CN)_6^{3-}$. If the solution contains iodide, however, the more insoluble silver iodide is formed before AgCN (the classic Liebig-Denigès method for the determination of cyanide) and no displacement of cobalt occurs. The procedure is very similar to the previous one. After oxidation of the cobalt, 5 ml of potassium iodide solution are added and 10% silver nitrate until a permanent turbidity occurs. After 1–2 min a measured volume of 0·05*M* EDTA is added, the solution diluted to 300–500 ml, Methylthymol Blue added and the solution titrated with 0·05*M* calcium chloride until the smoke grey colour changes to intense blue. Some results are summarised in Table II.

TABLE II.—DETERMINATION OF NICKEL IN THE PRESENCE OF COBALT (BACK-TITRATION WITH CALCIUM)

Taken, *mg*		Added 0·05*M* EDTA, *ml*	Back-titration 0·05*M* Ca, *ml*	Ni, found *mg*	Difference, *mg*
Ni	Co				
2·89	2·95	5·00	4·01	2·91	+0·02
2·89	29·47	5·00	4·00	2·94	+0·05
8·67	8·84	5·00	1·97	8·89	+0·22
14·46	14·74	10·00	4·95	14·83	+0·37
28·91	29·47	12·00	2·06	29·17	+0·26
57·82	29·47	25·00*	5·30–5·40	57·79–57·52	−0·03–0·30
57·82	2·95	25·00	5·32	57·75	−0·07

* Indistinct end-point; high concentration of Ni and Co.

Zusammenfassung—Eine neue Methode zur Bestimmung von Nickel in Gegenwart von Kobalt wird vorgeschlagen, die auf der Maskierung von Kobalt mit Kaliumcyanid und Wasserstoffperoxyd beruht. Der gelbe oder orange-gelbe Komplex von Kobalt(III) wird gebildet, aus dem Kobalt durch Zusatz von Silbernitrat nicht verdrängt wird. Tetracyanonickelat jedoch reagiert quantitativ mit Silbernitrat, und das verdrängte Nickel kann direkt mit EDTA und Murexid als Indikator bestimmt werden; bis 30 mg Kobalt können in der Lösung geduldet werden.

Résumé—On propose une nouvelle méthode de dosage du nickel en présence de cobalt, basée sur la dissimulation du cobalt au moyen de cyanure de potassium et d'eau oxygénée. On forme le complexe jaune ou orangé-jaune du cobalt (III), dont le cobalt n'est pas déplacé par addition de nitrate d'argent. Le tétracyano nickelate, toutefois, réagit quantitativement avic le nitrate d'argent, et l'on peut doser directement le nickel déplacé par l'EDTA, en présence de Murexide comme indicateur; on peut tolérer jusqu'à 30 mg de cobalt dans la solution.

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A NEW METHOD FOR THE TITRIMETRIC DETERMINATION OF PERCHLORATE

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Summary—A new method for the titrimetric determination of perchlorate has been developed, based on its reduction to chloride by iron(II) in a strong sulphuric acid medium at high temperature. The effect of variables, such as the sulphuric acid concentration, the temperature and the period of heating, on the extent of reduction has been studied and the optimal conditions for analytical determination of perchlorate derived.

INTRODUCTION

A RAPID and at the same time accurate method is lacking for the determination of perchlorate. Analysis of perchlorate is generally carried out by converting it to chloride and determining the latter either gravimetrically or titrimetrically. The conversion occurs by heating the perchlorate with sodium carbonate (in the presence of platinum),[1] sodium nitrite,[2] ammonium chloride[3] or potassium carbonate-manganous nitrate mixture;[4] copper powder,[5] sodium oxalate,[6] manganese dioxide[7] and sodium peroxide[8] have also been recommended as matrices for conversion. The reduction of perchlorate to chloride in the solution phase has also been reported using titanium(III) sulphate,[9] zinc amalgam[10] and tin(II) chloride in presence of molybdate as catalyst.[11] Sjollema[12] reported that incomplete reduction (90–94%) of perchlorate to chloride occurred on boiling with a mixture of iron(II) sulphate and sodium hydroxide for an extended period of 2–3 hr. On heating with fuming sulphuric acid,[13] perchlorate is converted to chlorine which can be determined. Amongst the direct gravimetric methods,[14] precipitation of the potassium salt has been studied most extensively but the results obtained are seldom accurate unless solubility losses are compensated.

The rapid titrimetric method described in this paper was evolved from consideration of the somewhat similar aqueous behaviour of the nitrate and perchlorate ions. Nitrate ion is reduced quantitatively to nitric oxide[15,16] by boiling with excess of iron(II) ions for 3–5 min in a 13–15N sulphuric acid medium. Similarly, it appeared that perchlorate might undergo reduction to chloride according to

$$ClO_4^- + 8H^+ + 8e \rightarrow Cl^- + 4H_2O$$

which might be put to analytical use. The conditions required for the reduction of perchlorate are, however, found to be more drastic than those for nitrate reduction. Titanium(III) salts reduce perchlorate to chloride when heated in acidic solution and in an inert atmosphere[17–22] under conditions less drastic than required by iron(II). However, the use of titanium(III) is to be favoured less because of the considerable excess of the reagent that has to be employed and the problems associated with the instability of the reagent and the need for maintenance of an inert atmosphere.

EXPERIMENTAL

Reagents

Iron(II) sulphate solution. Ferrous sulphate heptahydrate (B.D.H. England, analytical-reagent grade) was used to prepare 0·1–0·3M solutions in 4N sulphuric acid and these solutions were standardised with dichromate.

0·1–0·2N *Potassium permanganate solution.* Prepared and its strength determined using sodium oxalate. Standard solutions of cerium(IV) sulphate and dichromate, with the aid of suitable indicators, were also used in the determination of iron(II) during the study.

Ammonium perchlorate. Prepared from aqueous ammonia and perchloric acid (both analytical-reagent grade), then recrystallised thrice from water and dried at 110° before use.

All other reagents used were of accepted grades of purity and contained no impurities which would interfere with the course of the investigation.

In order to test whether any oxidation of iron(II) by perchlorate occurred, the two species, taken in various ratios with the iron(II) in excess, were heated for various periods at different temperatures using a wide range of sulphuric acid concentrations. The iron(II) remaining in the experiments was determined by titration with permanganate. The exact details are elaborated below.

RESULTS AND DISCUSSION

Preliminary experiments indicated that perchlorate ion was completely unaffected by iron(II) under the conditions specified for the reduction of nitrate to nitric oxide. Therefore, the concentration of sulphuric acid was raised gradually and also the temperature of boiling. It was observed that in the temperature range 150–155° (685 mm) reduction of perchlorate occurred rapidly. The acid concentration in the hot liquid at this stage corresponded to 65–70% by weight, *i.e.*, about 11–12M in the cold. No reduction of perchlorate occurred, however, at lower temperatures even in 65–70% sulphuric acid. At temperatures higher than 160°, there was appreciable oxidation of iron(II) by the sulphuric acid itself. Therefore, rise of temperature beyond 160° (685 mm) must be avoided during the determination of perchlorate according to the present method.

The time taken for complete reduction of perchlorate by iron(II) at 150–155° was about 10 min. Variation of the excess of iron(II) taken within the range 10–100% had apparently no influence in decreasing the minimum period of heating required for complete reduction. The extent of reduction of perchlorate for different periods of heating was ascertained as follows:

20 ml of ammonium perchlorate solution (containing 0·09178 g of the salt), 20 ml of 0·4966M iron(II) sulphate solution and about 20 ml of 13M sulphuric acid were taken in a conical flask, a few glass beads added, a thermometer introduced, a small funnel placed over the flask and the contents were boiled over a sand bath whose temperature could be controlled to within 2°. The temperature of the boiling liquid increased gradually from about 105° as water was continuously lost; when the temperature reached 150–155°, a stop watch was started. After 60 sec the flask was removed from the sand bath, cooled, the contents diluted and the flask again cooled. The amount of unreacted iron(II) was determined by titration with permanganate. Similar experiments were carried out for heating periods of 3, 5, 7, 10, 15 and 20 min at 150–155°.

The results obtained are presented in Table I. It is seen that quantitative reduction of perchlorate is completed in about 10 min, but a period of 15 min is suggested in the recommended procedure to allow a reasonable margin of safety.

During reduction of the perchlorate, most of the iron(III) formed crystallises out as ferric sulphate (exact hydrate composition not determined) at the high temperature and acid concentration obtaining. Therefore, it is desirable that the heat distribution to the flask containing the reactants is made as uniformly as possible in order to avoid spurting by localised heating. If the temperature of the liquid should slightly exceed 155°, careful introduction of a few drops of water prevents further rise of

TABLE I.—EFFECT OF TIME ON THE EXTENT OF REDUCTION OF PERCHLORATE BY IRON(II)

[temperature of reaction: 150–155°; medium-strong sulphuric acid (about 65–70 wt. %); ammonium perchlorate taken: 0·09178 g]

Time of heating, *min*	NH_4ClO_4 reduced, *g*	Reduction, %
1	0·01247	13·58
3	0·04326	47·15
5	0·06852	74·64
7	0·07400	80·61
10	0·09180	100·0
15	0·09190	100·1
20	0·09178	100·0

temperature. Even though the conditions specified appear to be stringent, in actual practice it is found that the temperature is easily maintained.

Molybdenum(VI) is known to sensitise the reaction between nitrate and iron(II).[23] Rechnitz and Laitinen[24] and Haight[25] have reported on the molybdenum-catalysed reduction of perchlorate at the dropping mercury electrode. However, it was observed in the present investigation that neither the time factor nor the drastic conditions of temperature and acid concentration required for the reduction of perchlorate could be minimised by the presence of molybdenum(VI), tungsten(VI), osmium tetroxide, chromium(III), vanadium(IV), chloroplatinate or palladium chloride.

Recommended procedure for determination of perchlorate

20 ml of 0·1–0·3*N* ammonium perchlorate solution and 20 ml of 0·2–0·4*M* iron(II) sulphate solution are taken in a conical flask. About 20 ml of 13*M* sulphuric acid are added, a few glass beads and a short-bulb thermometer introduced, a small funnel placed at the mouth and the contents are boiled briskly till a temperature of 150–155° is gradually reached. The conical flask is then kept over a sand bath and the temperature of the liquid maintained at 150–155° for about 15 min, after which the flask is rapidly cooled, the contents diluted well and the flask again cooled. The unreacted excess of iron(II) is titrated with permanganate. A blank with 20 ml of iron(II) solution is preferably run under similar conditions. However, it is interesting to note that the titre of an iron(II) solution after it is subjected to the conditions specified for perchlorate reduction was found not to differ from the value obtained when the iron(II) solution was titrated directly in the cold, *i.e.*, no atmospheric oxidation of iron(II) occurs under the conditions specified for the reduction of perchlorate.

The amount of perchlorate ion (X) in the test solution is given by the equation

$$X = 99{\cdot}47N(v_1 - v_2)/8 \times 1000 \text{ g}$$

where N is the normality of the permanganate solution, v_1 is the volume of permanganate consumed in the blank, and v_2 is the volume of permanganate accounting for the excess of iron(II) left over after the complete reduction of perchlorate.

TABLE II.—DETERMINATION OF PERCHLORATE BY REDUCTION WITH IRON(II)

[temperature of reaction: 150–155°; medium-strong sulphuric acid (about 65–70 wt. %); period of reaction: 15 min]

NH_4ClO_4 taken, *g*	NH_4ClO_4 found, *g*	Error, %
0·03200	0·03205	+0·15
0·04600	0·04600	0·00
0·06902	0·06920	+0·29
0·08540	0·08535	−0·06
0·1160	0·1168	+0·71
0·1708	0·1703	−0·30

The results of some typical analyses are given in Table II. It is seen that the results obtained are accurate to within 0·3 %. The interference of nitrate and chlorate ions in the determination could easily be avoided because these ions are reduced by iron(II) at much lower temperatures and sulphuric acid concentrations at which there is no reduction whatsoever of the perchlorate ion. Because perchlorate is reduced only under drastic conditions, it should be possible to eliminate the interference of the more easily reduced species by their initial reduction with iron(II) under mild conditions.

Zusammenfassung—Eine neue Methode zur titrimetrischen Bestimmung von Perchlorat auf Grund der Reduktion zu Chlorid mit Eisen(II) in starker Schwefelsäure bei hoher Temperatur wurde entwickelt. Es wurde der Einfluß von Änderungen in der Schwefelsäurekonzentration, Temperatur und Erhitzungszeit auf den Reduktionsgrad studiert und die besten Arbeitsbedingungen zur analytischen Bestimmung von Perchlorat ermittelt.

Résumé—On a élaboré une nouvelle méthode de dosage titrimétrique du perchlorate, basée sur sa réduction en chlorure par le fer (II) en milieu acide sulfurique fort à température élevée. On a étudié l'influence, sur le degré de réduction, de variables telles que la concentration en acide sulfurique, la température et le temps de chauffage et on en a déduit les conditions optimales de dosage du perchlorate.

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SHORT COMMUNICATIONS

Rapid iodometric determination of copper in some copper-base alloys

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In recent years a mixture of hydrofluoric and nitric acids has occasionally been used for the dissolution of alloys. Thus, Garate and Garate[1] have described the dissolution of friction alloys, containing tin, antimony and lead, in such a mixture before the determination of the alloying constituents. The present authors found[2] that alloys of bismuth, tin, lead and cadmium are also readily dissolved in this mixture of acids.

Dozinel[3] noted that copper-tin alloys may be dissolved in a mixture of hydrofluoric and nitric acids, but no detailed directions could be found in the literature by the present authors on the dissolution procedure or on the possibility of applying conventional means of completing the analysis of such alloys. It seemed useful to investigate this analysis of copper-tin alloys further; conventional procedures are laborious because copper is adsorbed on the precipitate of hydrated tin(IV) oxide formed during dissolution of the alloys in nitric acid alone.

According to the British[4] and American[5] standard procedures, in which the copper is eventually determined electrolytically, tin should first be removed by volatilisation as tin(IV) bromide if more than 1–1·5% of this element is present. A similar procedure is recommended in the more or less official German standard.[6]

Kühnel-Hagen and Salomonson[7] claim that good results are obtained by iodometric titration of copper in its alloys after dissolution in nitric acid alone and digestion for 10–30 min. In their procedure up to 20% of tin apparently gives no error, but much lead should not be present. Orlik and Tietze[8] dissolve copper-base alloys in a mixture of nitric and sulphuric acids, evaporate until crystals of copper sulphate appear and eventually titrate the copper iodometrically. From their paper it is not clear how much tin may be present.

The iodometric finish was also employed in our investigations. Bromine was used to oxidise arsenic and antimony to the quinquevalent form, when both metals may be masked by fluoride if one works at a suitable pH.[9] Iron(III) may also be masked with fluoride.

EXPERIMENTAL

General

The solvent mixture is prepared by mixing 3 volumes of 40% hydrofluoric acid, 14 volumes of 65% nitric acid and 5 volumes of water. In a first series of experiments, polypropylene beakers were heated in a water-bath because it was feared that the solvent attack on glass might be disadvantageous in analysis. In later experiments it was, however, found that Pyrex vessels could be used if they were heated gently during the dissolution procedure. If the vessels are heated too vigorously an insoluble compound is formed and erroneous results are obtained.

With the final procedure, in each experiment the vessels lost only about 150 mg of their weight. This proved to have no unfavourable effect on the results. The standard deviation was even decreased compared with results obtained when polypropylene beakers were used, possibly because the excess of bromine and the nitric oxides are expelled more completely at the temperature used in the Pyrex vessels.

In all experiments described below 150-ml Pyrex Erlenmeyer flasks were used, covered with a polypropylene watch-glass during heating. The vessels were heated gently on an electric hot-plate. The power-supply was regulated to bring the content of the vessels just to, or slightly below its boiling point. The time required for dissolution did not exceed 2 min in all experiments described below. In one experiment the influence of the presence of much lead was investigated, because lead fluoride is slightly soluble. An (slightly inhomogeneous) alloy, containing about 30% of lead and 5% of tin, was attacked in the way described below and this alloy, was dissolved in about 5 min.

Procedure

Weigh exactly a quantity of alloy, containing about 200 mg of copper, in a 150-ml Pyrex Erlenmeyer flask, add 5 ml of solvent mixture, cover the vessel with a polypropylene watch-glass and heat it gently. After dissolution add saturated bromine solution until a distinctly brown colour is seen. Continue heating for 5 min, add about 200 mg of urea, then heat 1 min more. Cool to room temperature, add 25 ml of water, 25 ml of 20% ammonium acetate solution (giving a pH of about 4), 1 ml of 40% hydrofluoric acid and 3 g of potassium iodide. Titrate with 0·1*M* sodium thiosulphate solution. Add starch solution just before the end-point, titrate further until the colour bleaches, then add 2 g of ammonium thiocyanate and finish the titration. Standardise the sodium thiosulphate solution against electrolytic copper, using the same procedure.

RESULTS AND DISCUSSION

The procedure was checked with four standard samples and with some mixtures of electrolytic copper with pure tin or antimony. Results are given in Table I. The results show a standard deviation of about 0·1%, and the systematic error seems well below this value.

TABLE I.—ANALYSIS OF COPPER-BASE ALLOYS AND "SYNTHETIC" MIXTURES AFTER DISSOLUTION IN A MIXTURE OF HYDROFLUORIC AND NITRIC ACIDS

Expt.	Sample	Copper content, % (certificate value)	Other important constituents, %	Copper found, %	Error, %
1	NBS 52 c	89·25	Sn 8	89·37; 89·13; 89·42	+0·1; −0·1; +0·2
2	BCS 207/1	88·1	Sn 10; Sb 0·1; As 0·1	88·15; 88·09; 88·14	+0·1; 0·0; 0·0
3	BCS 183/1	84·8	Sn 5; Sb 0·2; As 0·1 Pb 4; P 0·5	84·87; 85·00; 84·80	+0·1; +0·2; 0·0
4	NBS 63	78·05	Sn 10; Sb 0·5; As 0·2 Pb 10; P 0·6	78·02; 78·07; 77·97	0·0; 0·0; −0·1
5	Electrolytic copper	*ca.* 200 mg	*ca.* 100 mg of tin added	recovery 99·96; 99·92; 99·88; 99·90	0·0; −0·1; −0·1 −0·1
6	Electrolytic copper	*ca.* 200 mg	*ca.* 10 mg of antimony added	recovery 99·82; 99·98	−0·2; 0·0

Similar experiments were carried out in which a mixture of 3 ml of 65% nitric acid and 2 ml of water was used as solvent, and 2 ml of 40% hydrofluoric acid were used after ammonium acetate was added. The thiosulphate used here, was standardised after dissolution of copper in nitric acid alone. When duplicating experiments 1, 2, 3 and 6 (Table I) with this modification, the results seemed as good as when a mixture of hydrofluoric and nitric acid was employed. Standard NBS 63 dissolved, however, with great difficulty and the results were 0·5%, 0·3% and 0·2% low; also, if 30–35% of tin was added (similar to experiment 5) the results were 0·2%, 0·7%, 1·1% and 0·9% low.

It should be pointed out that some difference is possible in the results obtained with alloys, when compared with results obtained with "synthetic" mixtures of the same composition. It seems probable, however, that this difference may be neglected in cases where the sample is completely dissolved. It may be expected, therefore, that alloys containing up to 35% of tin or up to 5% of antimony (and possibly more of these elements) will give good results when dissolved in a mixture of hydrofluoric and nitric acids. In cases when nitric acid alone is used as a solvent, residues are left and the amount of copper adsorbed may be different for alloys and mixtures. It cannot be assumed, however, that this amount may be neglected if much tin is present in an alloy. A final conclusion, therefore, may be that the use of a hydrofluoric-nitric acid solvent mixture gives good results in many cases where the use of nitric acid alone cannot be recommended.

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Summary—Copper-base alloys, especially those containing tin, are readily dissolved in a mixture of hydrofluoric and nitric acids. In the resulting solution copper can be titrated iodometrically in the conventional manner.

Zusammenfassung—Legierungen auf Kupferbasis, besonders zinnhaltige, lösen sich leicht in einer Flußsäure-Salpetersäure-Mischung. In der erhaltenen Lösung kann Kupfer in üblicher Weise jodometrisch titriert werden.

Résumé—Les alliages à base de cuivre, spécialement ceux contenant de l'étain, se dissolvent aisément dans un mélange d'acides fluorhydrique et nitrique. Dans la solution résultante, on peut doser le cuivre de façon usuelle par iodométrie.

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A simplified sampling technique for use with the Weisz ring oven: Application to qualitative analysis of some gold and silver alloys

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INTRODUCTION

Applications of the ring oven technique have been described for microchemical qualitative and semiquantitative analysis of several types of alloy.[1–3] Separation schemes and identification reactions specially designed for ring oven work have also been published.[4,5] Nevertheless, detailed procedures of analysis are still missing for certain alloys.

Apart from direct chemical attack on the specimen, two main types of sampling procedure have so far been suggested. One method, proposed by Stephen,[2] depends on electrolytic dissolution of the sample in combination with ring oven technique and was applied to the analysis of several non-ferrous alloys. Nall and Scholey[3] used the same procedure but for the sampling of steel. As far as electrolytic sampling is concerned, no positive evidence has so far been presented as to whether the composition of the dissolved sample is strictly equivalent to that of the original specimen. Where figures of a more quantitative nature are desired, there would be a definite risk of biased results, because the normal potential values of the constituents cover a wide range.

The second method of sampling is based on mechanical abrasion, as described by Strebinger and Holzer,[6] who rubbed the specimen with a microscope slide having a circular roughened section, and that mentioned by Ballczo[7] who applied a 2-mm corund stick in the manner of a file. These two procedures suffer from the disadvantage that only convex or protruding parts of the specimen can be sampled.

The present authors have overcome the disadvantages of the above sampling procedures by introducing a simplified technique of mechanical abrasion for sampling some gold and silver alloys. This was achieved by using a 4-mm Pyrex glass rod with a hemispherical tip which was ground on a carborundum disc to provide a rough surface of about 25 mm^2. Up to 100 μg of sample can be obtained by rubbing the tip under gentle pressure, rotating it against the sample and also tilting it at various angles, until most of the rough surface is coated with abraded material. In this way it is possible to obtain a sample from almost any part of a specimen, including concave or curved surfaces, inner surfaces of vessels or other parts of special interest, such as welded seams.

Complete dissolution of most alloys, except for those of gold, can be carried out by exposing the sample on the glass rod tip to the vapours of suitable acids of sufficient volatility, *e.g.*, concentrated nitric acid, concentrated hydrochloric acid alone or saturated with bromine or with some potassium chlorate added, or *aqua regia*. Because the sample is finely dispersed, its dissolution is completed in a very short time without accumulating an unnecessary excess of acid. After drying, the metal salts obtained are dissolved in water, which is condensed on the glass rod tip by exposing it to steam until a small droplet forms; the droplet is then removed on the centre of a filter paper disk. Quantitative sample transfer can be completed by repeating the vapour phase and steam treatments as required. For gold alloys, a sample on the glass rod tip must be dissolved in potassium cyanide-hydrogen peroxide solution contained in the depression of a white porcelain spot plate (see later).

EXPERIMENTAL

Apparatus

Ring oven with accessories.[4,5]

Gas treatment device for filter paper disks, or wide necked bottles for vapour phase treatment.

Sprayers for application of reagent solutions.

White porcelain spot plate.

Filter paper disks, 5·5 cm in diameter, of Whatman No. 41 or 42, Schleicher and Schüll 589^2 white ribbon or similar papers.

Reagents

Potassium cyanide. 0·5% w/v solution, containing 0·1% of 100 vol. hydrogen peroxide.

Bromine water

Ammonia solution. Sp. gr. 0·88; one portion must be freed from silica and carbonate by isothermal distillation.

Benzidine. 0·5% w/v solution in 10% v/v acetic acid.

Hydrochloric acid. 0·1 *M*, containing 0·1% v/v of 100 vol. hydrogen peroxide, added immediately before use.

α-Benzoin oxime. 5% w/v solution in ethanol.

Dimethylglyoxime. 2% w/v solution in ethanol.

Nitric acid. Sp. gr. 1·42.

Hydrogen sulphide. Gaseous, and a saturated solution in water (or acetone).

Sodium hydroxide. 0·1*M* solution.

Procedures

Gold alloys (*Au-Ag-Cu*). For proper detection of the alloying elements (Ag and Cu), which are usually present in lower percentages, it is essential to obtain dissolution of all three components. *Aqua regia* is, therefore, not suitable, because it will precipitate silver chloride which adheres firmly on the rough glass surface and is difficult to redissolve. The sample can be dissolved in 50 μl of potassium cyanide-hydrogen peroxide solution contained in the depression of a white porcelain spot plate. Dissolution is enhanced by ready access of atmospheric oxygen. The glass rod is dipped into the solution and repeatedly stirred and rotated until the sample is completely dissolved. Water is added, if necessary, to replace that lost by evaporation.

The sample solution, containing $K[Au(CN)_4]$, $K[Ag(CN)_2]$ and $K_3[Cu(CN)_4]$, is transferred to the centre of a filter paper disk, using a capillary pipette. A total of about 100 μl of water, in several portions, is used, first for rinsing the spot plate depression to ensure complete sample transfer, then for full washing of the complex cyanides of the three metals to Ring I. After drying, the ring is oxidised by exposing the filter successively to bromine and ammonia vapours. Hypobromite ion is formed, which destroys all cyanide. The filter is kept in the oven for some minutes to destroy the excess of oxidant. Ring I will contain $CuBr_2$, $K(AuBr_4)$ and AgBr. It is cut into three sectors, which are tested as follows:

1. Gold(III). One sector is treated with benzidine reagent. After fuming over ammonia solution, benzidine blue will form if gold(III) is present. Limit of identification: 0·1 μg.
2. Silver. The second sector is bathed in 0·1*M* hydrochloric acid containing hydrogen peroxide, then rinsed under the tap. A small part of this sector is cut off and tested for the absence of gold. Bathing and rinsing are repeated if necessary. It can be assumed that copper will also be absent when the gold has been completely removed, because copper(II) bromide is more stable and soluble in water than its gold analogue. The remaining part of the sector is tested for silver by bathing for 5 min in saturated aqueous hydrogen sulphide. Limit of identification: 0·5 μg (we have not been able to confirm the far lower limit of identification previously reported[4]).

Other tests for silver, based on *p*-dimethylaminobenzylidenerhodanine, coprecipitation of MnO.OH, or a replacement reaction using $K_2Ni(CN)_4$ and dimethylglyoxime, were also examined but none of them proved superior to the simple sulphide precipitation. It has to be considered, however, that under the conditions of this test silver is present as insoluble silver bromide (K_{sp} 7·7 × 10^{-13}) so that only silver sulphide as the most insoluble known compound of silver (K_{sp}1 × 10^{-50}) provides a suitable test.

3. Copper. α-Benzoin oxime solution is applied to the third sector which is then fumed over ammonia solution. A green line indicates the presence of copper. Limit of identification: 0·1 μg.

It appeared more convenient to use a test for copper in the same range of sensitivity as those employed for the other two alloying elements and at the same time was not subject to interference from gold and silver. The dithio-oxamide test is far too sensitive for copper contents above 1%. Furthermore, the inevitable copper content of filter paper and reagents, including distilled water, results in a strong blank.[8] It is, therefore, even difficult to establish whether copper is completely absent or present in low amount if a specially designed procedure is not applied.

The above procedure for gold alloys was successfully applied to the detection of gold, silver and copper in some alloys containing from 58·3 to 87·5% of gold, up to 41·7% of silver and up to 41·7% of copper.

Silver alloys (Ag—Cu—Ni—Zn—Mn). The procedure for an alloy consisting of the five stated elements is here considered as the only example. Other elements present in a silver alloy could presumably be identified after applying well-known general separation schemes.[4,5]

After collecting the sample on the glass rod tip, it is dissolved by vapour phase treatment over hot concentrated nitric acid. The sample solution is allowed to dry in order to remove excess acid and the residue dissolved by condensing steam on the glass rod. The resulting solution is transferred to a filter paper disk and dried again. The spot is treated with 10 μl of 0·1*M* hydrochloric acid, followed by gaseous hydrogen sulphide, which is sucked through the filter using one of the previously mentioned devices.[4] Silver and copper will precipitate, and nickel, zinc and manganese can subsequently be washed to the ring (Ring I) using 0·1*M* hydrochloric acid. After drying, the central disk is punched out, oxidised by successive vapour phase treatments over bromine and ammonia solutions, placed on a new filter paper and washed out fully to the ring (Ring II) using ammonia solution (free from silicate and carbonate) containing 0·1% v/v of 100 vol. hydrogen peroxide in order to prevent partial reduction of silver. Ring II is cut into two sectors, which are tested as follows:

1. Silver. The first sector is bathed in 0·1*M* hydrochloric acid, then rinsed under the tap until all the copper is removed. Silver sulphide is developed by bathing the sector for several minutes in saturated aqueous hydrogen sulphide. Limit of identification: 0·5 μg.
2. Copper. The second sector is tested with α-benzoin oxime solution as described under *Gold alloys.*

Ring I is cut into three sectors which are tested as follows:

1. Nickel. The first sector is sprayed with dimethylglyoxime solution, then fumed over ammonia solution. A red line indicates nickel. Limit of identification: 0·1 μg.
2. The second sector is examined by the cobalt mercury(II) thiocyanate coprecipitation test.[4,8] Limit of identification: 0·075 μg.
3. Manganese(II). The third sector is moistened with 0·1*M* sodium hydroxide solution, then sprayed with benzidine reagent. A blue line indicates manganese. Limit of identification: 0·05 μg. Manganese can also be detected successfully using the periodate-tetrabase test.[8,9]

The above procedure for silver alloys was applied satisfactorily to the detection of silver, copper, nickel, zinc and manganese in some alloys containing from 50 to 90% of silver, 10 to 40% of copper, up to 5% of nickel and of zinc, and up to 1·5% of manganese.

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Summary—Up to 100 μg of sample can be collected from gold or silver alloys by rubbing the specimen with the ground hemispherical tip of a 4-mm Pyrex glass rod. Gold alloys are then dissolved in potassium cyanide solution containing hydrogen peroxide; silver alloys are exposed to vapours of nitric acid. Procedures for transfer, ring oven separation and identification of alloy constituents in the sample solutions are described.

Résumé—On peut recueiller jusqu'à 100 μg de prise d'essai à partir d'alliages d'or ou d'argent en frottant l'échantillon avec l'extrêmité hémisphérique rodée d'une baguette en verre Pyrex de 4 cm. On dissout alors les alliages d'or dans une solution de cyanure de potassium contenant de l'eau oxygénée; les alliages d'argent sont exposés aux vapeurs d'acide nitrique. On décrit les techniques de transfert, séparation au four annulaire et identification des constituants de l'alliage dans les solutions d'essai.

Zusammenfassung—Bis 100 μg Probe können von Gold- oder Silberlegierungen genommen werden durch Reiben des Materials mit dem geschliffenen halbkugeligen Ende eines 4 mm-Pyrexglasstabes. Goldlegierungen werden dann in wasserstoffperoxydhaltiger Kaliumcyanidlösung gelöst; Silberlegierungen werden Salpetersäuredämpfen ausgesetzt. Es werden Arbeitsvorschriften zur Überführung, Ringofentrennung und Identifizierung der Legierungsbestandteile in den Probelösungen angegeben.

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Amperometric titration of mercury with a stationary platinum electrode in stirred solutions

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THE present communication describes a rapid method for the determination of mercury by amperometric titration with 2-mercaptobenzoxazole in stirred solution with a stationary platinum electrode utilising the same technique as reported in a previous communication.[1] Bera and Chakrabartty used this reagent in the gravimetric determination of palladium and silver,[2] and in amperometric determination of palladium, copper and silver.[3] It was reported[3] that mercury was quantitatively precipitated with 2-mercaptobenzoxazole from an acetate buffer solution in the pH region 4–5. Although the precipitate conformed approximately to a metal to ligand ratio of 1:2, the formula could not be ascertained definitely. The present investigation was undertaken to acquire further information on the composition of the mercury complex.

The nature of the electrode reactions exhibited by the reagent and the mercury(II) ions was studied in a sodium acetate–acetic acid buffer medium in the pH range 4–5 (Fig. 1) at room temperature (25 ± 1°). The reagent did not produce any current at an applied potential of zero potential *vs.* saturated calomel electrode, but from $-0{\cdot}1$ V onwards it produced a large current. On the other hand, mercury ions diffused towards the cathode, producing a large current even at an applied potential of zero potential. The current was proportional over the concentration range of $0{\cdot}4 \times 10^{-4}$ to $2{\cdot}5 \times 10^{-4}$ *M* mercury(II). For the subsequent experiments, a potential of zero potential with respect to a calomel electrode was chosen. Deoxygenation was unnecessary because dissolved oxygen did not undergo any cathodic reaction at the applied potential selected for titration. Different supporting electrolytes, *e.g.*, ammonium nitrate, potassium nitrate, ammonium chloride and potassium chloride, were tried, but steady current values were obtained only in the presence of potassium chloride. The current gradually decreased with time at the beginning, but towards the equivalence point the values remained almost constant. For satisfactory titration curves, the current readings were noted 30 sec after each addition of an aliquot of titrant.

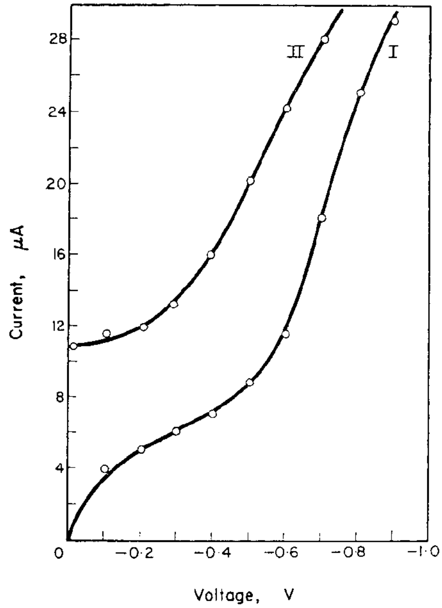

Fig. 1.—Current-voltage curves of the reagent and mercury(II) in acetate buffer solution:
I. 1·5000 × 10^{-3} *M* 2-mercaptobenzoxazole,
II. 1·3068 × 10^{-4} *M* mercury(II).

EXPERIMENTAL

Solutions of 2-mercaptobenzoxazole were prepared by dissolving the reagent in the minimum quantity of dilute potassium hydroxide solution and diluting to the desired volume. The reagent solution was standardised with a standard mercury(II) solution. The concentration of the titrant was about fifty times that of the mercury(II) solution. The reagent solution could be preserved in a refrigerator for 2 days. Sodium acetate acetic-acid buffer was used. A stock solution of mercury(II) was prepared by dissolving pure mercuric oxide in dilute nitric acid and expelling excess acid. The mercury content of this solution was determined by a standard method.[4]

The electrode was constructed in such a way that about 5 mm of platinum wire (0·5 mm diam.) protruded vertically from the wall of the glass tubing. It was mounted over the centre of the stirrer bar so that the gap between electrode and bar was about 1 cm. The amperometric assembly consisted of a stationary platinum electrode as the polarisable electrode, a saturated calomel electrode with a potassium chloride-agar salt bridge as the reference electrode, a potentiometer and a microammeter. The titration vessel was a 200-ml tall-form beaker fitted with a rubber stopper. Holes were drilled in the stopper to accommodate the salt bridge, the platinum electrode and the burette delivery tip. The solution was stirred with a magnetic stirrer and the speed of rotation was maintained effectively between 230 and 235 rpm.

Procedure

An aliquot of standard mercury solution was placed in the titration vessel followed by 5 ml of buffer solution, 5 ml of 1*M* potassium chloride solution and water to adjust the final volume to 50 ml. The vessel was then placed over the stirrer and the electrodes were assembled. The circuit was then closed with an applied potential of zero volt. After about 1 min the value of the current was noted. The titrant was gradually run into the solution from a microburette and the current readings were noted 30 sec after each addition of the titrant. Titration was continued till no current flowed. Some typical titration curves are depicted in Fig. 2.

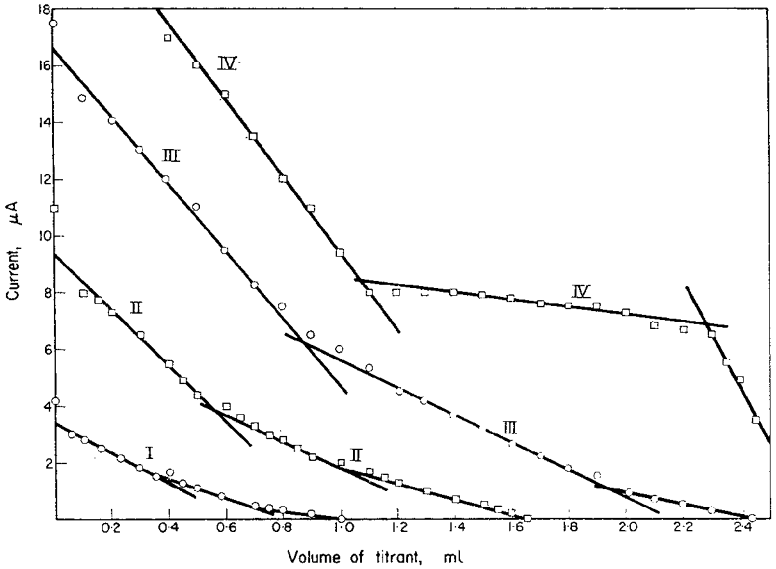

FIG. 2.—Titration of mercury(II) with 2-mercaptobenzoxazole:
I. 0·4356 × 10^{-4} *M* (0·437 mg) mercury(II) with 0·6622 × 10^{-2} *M* reagent,
II. 1·3068 × 10^{-4} *M* (1·311 mg) mercury(II) with 1·3244 × 10^{-2} *M* reagent,
III. 2·6136 × 10^{-4} *M* (2·622 mg) mercury(II) with 1·3244 × 10^{-2} *M* reagent,
IV. 3·9204 × 10^{-4} *M* (3·496 mg) mercury(II) with 1·3244 × 10^{-2} *M* reagent.

RESULTS AND DISCUSSION

Each set of titrations resulted in three straight lines and showed two intersections. The second or final intersection was taken as indicating the end-point and corresponded to a metal to ligand ratio of 1:2. The first or the intermediate intersection corresponded appoximately to a metal to ligand ratio of 1:1. Reproducible results were obtained when the amount of mercury varied between

TABLE I.—DETERMINATION OF MERCURY(II)

Hg taken, *mg*	Hg found, *mg*	Average error, *mg*
0·4370	0·4383	
	0·4400	+0·0038
	0·4443	
1·3110	1·3000	
	1·3080	+0·001
	1·3280	
2·6220	2·5820	
	2·5900	−0·022
	2·6300	
3·4960	3·0200	
	3·0400	−0·439
	3·1120	

0·4 and 2·5 mg. With higher amounts of mercury, the intermediate straight line gradually became parallel to the volume axis, consequently leading to erroneous results. The above phenomenon can be explained by the stepwise complex formation of mercury with the ligand. Evidently, at the lower ligand concentration a 1:1 complex is formed, and this changes to a 1:2 complex when the reagent is in excess. Some results are tabulated in Table I.

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Summary—Amperometric titration of mercury (in the range of 0·4 to 3·5 mg) has been carried out with 2-mercaptobenzoxazole with a stationary electrode in stirred solution in a sodium acetate-acetic acid medium.

Zusammenfassung—Quecksilber (0,4–3,5 mg) wurde mit einer ruhenden Elektrode in gerührter Natriumacetat-Essigsäure-Lösung mit 2-Mercaptobenzoxazol amperometrisch titriert.

Résumé—On a réalisé le dosage ampérométrique du mercure (de 0,4 à 3,5 mg) au moyen de 2-mercaptobenzoxazole avec une électrode stationnaire dans une solution sous agitation, en milieu acétate de sodium-acide acétique.

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Determination of orthoesters by hydrolysis and Karl Fischer titrimetry

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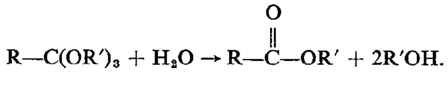
A simple, rapid analytical method for orthoesters was needed. To meet this need, a titrimetric method based on the acid hydrolysis of orthoesters was developed.

Orthoesters can be quantitatively hydrolysed to carboxylic esters by shaking with water:[1]



$$R{-}C(OR')_3 + H_2O \rightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR' + 2R'OH.$$

The reaction is catalysed by acid.[2,3]

The method we have developed involves adding an orthoester sample to a standard solution of water in trichloroacetic acid-methyl alcohol. After a timed reaction period, unreacted water is determined by Karl Fischer titration. This method is an alternative to the aquametric procedure described by Smith *et al.*[4] which involves water formation by reaction with a boron trifluoride-acetic acid reagent. Our method is faster and requires no heating.

EXPERIMENTAL

Reagents and apparatus

All of the orthoesters and the trichloroacetic acid used in this work were obtained from the J. T. Baker Chemical Company. Karl Fischer stabilised reagent was obtained from Fisher Scientific Company. A water solution was prepared by pipetting 10·0 ml of distilled water into a one l. volumetric flask and diluting to volume with dry methyl alcohol. A trichloroacetic acid solution was prepared by weighing 125 g of reagent-grade trichloroacetic acid into a 500-ml volumetric flask, and dissolving and diluting to volume with dry methyl alcohol. All flasks were dried at 110° for 30 min before use.

Procedure

Pipette 10·0 ml of trichloroacetic acid-methyl alcohol solution and 20·0 ml of water-methyl alcohol solution into a 125-ml glass stoppered Erlenmeyer flask. Add 1–1·5 g of the orthoester sample, stopper the flask and allow the solution to stand 45 min with occasional swirling. Titrate the solution with Karl Fischer reagent. Also, titrate a reagent blank which has also stood for 45 min. Calculate the percentage of orthoester as follows:

$$\% = \frac{(V_b - V_s)(f)(M)}{180{\cdot}2(n)(W)}$$

where: V_b = volume of Karl Fischer reagent required to titrate blank (ml),
V_s = volume of Karl Fischer reagent required to titrate sample (ml),
f = Karl Fischer reagent standardisation factor (mg of H_2O/ml of reagent),
M = molecular weight of orthoester,
n = orthoester groups per molecule,
and W = weight of sample used (g).

RESULTS AND DISCUSSION

This procedure was used in the analysis of four commercially available orthoesters. The results are shown in Table I.

TABLE I.—ASSAY OF ORTHOESTERS

Compound	Orthoester, *Wt.%*
Triethyl orthoacetate, practical grade	95·2
Triethyl orthopropionate, practical grade	94·8
Trimethyl orthoformate, reagent grade	98·8
Triethyl orthoformate, reagent grade	99·2

The trichloroacetic acid-methyl alcohol reagent undergoes a slow esterification, producing a very small amount of water in the system. It is, therefore, important that blanks and samples stand the same length of time before titration. If this is done, no significant error is introduced. Because carboxylic esters are most likely impurities in orthoesters, several were checked for interferences. No interference was found.

Acknowledgement—The authors wish to thank Mr. I. Saleh and Mr. D. A. Danald for making many of the determinations used in this work.

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Summary—The acid hydrolysis of orthoesters has been made the basis of a titrimetric method. The method involves reaction of an orthoester with a known excess of water in a trichloroacetic acid-methyl alcohol system, followed by determination of unreacted water by Karl Fischer titration.

Zusammenfassung—Die saure Hydrolyse von Orthoestern wurde zu einer titrimetrischen Bestimmungsmethode verwertet. Man läßt den

Orthoester mit einem bekannten Wasserüberschuß in einem Trichloressigsaure-Methanol-System reagieren und bestimmt das nicht umgesetzte Wasser durch Karl Fischer-Titration.

Résumé—L'hydrolyse acide des orthoesters a été prise pour base d'une méthode titrimétrique. La méthode comprend la réaction d'un orthoester avec un excès connu d'eau dans un système acide trichloracétique-méthanol, suivie du dosage de l'eau qui n'a pas réagi par titrage selon Karl Fischer.

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Talanta, 1966, Vol. 13, pp. 535 to 537. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Trivial names of analytical reagents

SIR,

The susceptibility of chemists to store up trouble for themselves in the trivial names that they bestow on unsuspecting reagents is well known. After having once established the trivial name, they often insist on the use of it in the description of its derivatives, salts and complexes, without considering whether the original reason for giving the trivial name is still valid, *i.e.*, to identify the compound more concisely. In many instances, this extended usage merely leads to verbose, tongue-twisting, odd or even incorrect terminology. A particularly bad example that came to my notice recently is *cupferron*. This is the ammonium salt of *N*-nitrosophenylhydroxylamine. The insistence on the use of cupferron, rather than the correct chemical name, in all compounds in which it is involved, leads to such expressions as "the free acid of cupferron", and to the metal complexes of this acid being termed "cupferrates", clearly a misnomer because they contain no ammonium.

A brief glance through the literature reveals other examples—edetates, and the various expressions for 8-quinolinol and its complexes—to name but two. Surely persons in positions of influence, such as editors of journals and authors of standard text-books, could take the lead and avoid the perpetuation of irritating nomenclature. Perhaps they could also decide on the suitability of new trivial names when they are first suggested.

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During the I.U.P.A.C. Conference in Paris, July, 1965, an Interdivisional Committee on Nomenclature was formed, consisting of representatives from all the Nomenclature Commissions of the various Divisions (see *Talanta*, 1965, **12**, 785). The purpose of this new Committee—Convenor, Professor K. A. JENSEN (Copenhagen); Recorder, Professor R. BELCHER (Birmingham)—is to ensure complete liason by interchange of documents at various stages between the various Nomenclature Commissions. At the instigation of this new Committee, the Nomenclature Commission of the Analytical Chemistry Division of I.U.P.A.C. is compiling a list of trivial names of analytical reagents. When this list is complete, the Interdivisional Committee, as part of the next stage of the process, will arrange for some uniformity to be brought into the field.

EDITOR-IN-CHIEF

Selectivity index[1,2]

SIR,

The following observations are extracted from a private letter sent by Professor H. Flaschka to one of us. Professor Flaschka left it in our hands whether or not this should be published, but because it is a valuable contribution to the discussion we reproduce the pertinent paragraphs:

"First I may mention that the term G = gravimetric is not very good. What it obviously intends is to indicate a precipitation. A precipitation is, however, not necessarily made with a gravimetric finish in mind; nowadays, at least, it is frequently undertaken as a means of separation. Consequently, it seems to me that "gravimetric" would be better replaced by "precipitation".

The greatest trouble the scheme may run into rests in the fact that an assignment of an interference number (in Betteridge's proposal[2] the Greek letter) makes only *complete* sense and has *complete* validity after *all* elements have been investigated. In practice this is rather difficult because how many investigators have all the materials at hand and further how many are willing to do the work? In most cases a procedure is worked out for the analysis of an element in a certain material or group of materials; someone investigating a new reaction and applying it to steel analysis will hardly test for noble metals and rare earths. In the illustration quoted[2] for the spectrophotometric determination of niobium by 4-(2-pyridylazo)resorcinol (PAR),[3] β refers to the interference of uranium(VI), vanadium(V) and tantalum. However, we are at present working on a determination of palladium in which PAR takes the palladium out of an EDTA complex.

Thus, it seems to be necessary to put some additional requirements or limitations or whatever the correct word is, into effect. One possibility would be to group metals or elements into groups, *e.g.*, according to their frequency. Then Group I may be the 'most common metals', Group II these and some more rare ones, *etc.* Alternatively, a grouping according to analytical aspects would be more convenient and realistic. That is a matter you may discuss with your group next meeting and maybe some reasonable improvement can be made. To illustrate my idea the left superscript of the scheme might then read, for example, β(i), indicating that 2 elements from the metals in Group 1 interfere. Maybe "interfere" is not the correct term and it would be better to say that it also gives a positive reaction. An interference might be termed a substance that did not give the reaction *per se* but may prevent or foul up the positive reaction which is under test.

A scheme must be capable of giving all or nearly all the details so that one can actually read from the notation what is known and what one wants to know; otherwise we have made little progress other than to have replaced, to use your own words, a nebulous scheme by a nebulous term. Because for a good job and looking for a good reaction it is not enough to know only how many other compounds react, one may for the good reaction write, instead of a number or a Greek letter, the symbols for the compound giving the test also in a positive way.

The biggest problem seems to be, however, not merely that everybody accepts the scheme and learns how to read it, but that anyone investigating a new reaction does a complete job and tests all elements or ions and reports accordingly or at least within a group whatever that group might be."

In addition to the above comments from Professor Flaschka, we have received some verbal comments from colleagues and acquaintances. Some of these have been general in nature; some have suggested that more, and some that less, detail should be supplied. One specific objection has been made about the simpler system.[1]

Some reagents of wide application may have a different degree of selectivity, depending on the conditions of reaction and the ion examined. Thus, the same reagent might have different Selectivity Index Numbers. This is quite true (but not so general as might be thought), and the simpler system could be easily modified to accommodate such a reagent, by inserting the particular ion concerned in brackets after the reagent. For example, "diethyldithiocarbamate (ε)" would become "diethyldithiocarbamate (Cu^{2+})(α)".

Professor Flaschka's point about a method which employs precipitation but does not use a gravimetric finish can be met by using P for the centre letter of the Index. For a reaction which is carried out in concentrated acid solution, it may be better to specify the acid rather than the pH, *e.g.*, for trioctylphosphine oxide

$$\begin{matrix} \beta & & \mathrm{Au} \\ & \mathrm{Sx} & \\ \mathrm{HBr} & & \mathrm{PO_4} \end{matrix}$$

His other suggestion involves putting a subscript on a superscript and is thus somewhat awkward.

The remaining comments deal with interference and are thus not central to the issue of the Index. The broader question of what elements could usefully be examined before a degree of selectivity can be obtained is an interesting one. Obviously, when a method for a particular element is developed one would first examine the elements most likely to interfere. If the method looks promising one can at this stage either claim a degree of selectivity and publish, or examine more elements to substantiate the claim completely. We would accept editorial guidance on this point but, in general, feel that the greater the number of interferences examined the stronger the claim for selectivity.

Mr. Wilson's concern[4] over the concentration of the determinant is appreciated, but raises too many complications for the limited aims of the Index. Basically one wishes to know only whether an element or species is going to interfere excessively or negligibly: the details are of real concern when the method is being critically studied before use.

We accept that interfering species is preferable but feel that the definition of interference proposed by Mr. Wilson begs the question. What is a systematic error? We proposed arbitrary limits that are frequently used by other authors.

Returning to the Index, we reject the suggestion that we are proposing a nebulous scheme to replace a nebulous term. The definition of the degree of selectivity, *i.e.*, α, β, γ, is a precise statement and the addition of the nature and major conditions of reaction results in the abstraction of the most important information. If the original work is well carried out and presented it is a matter of minutes to compile the Index. If the original work is vague, both the Index and the term "selective" are ill advised. The Index was not meant to displace the literature but to improve the term "selectivity"; we believe that it does this.

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10 *December* 1965

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[4] A. L. Wilson, *ibid.*, 1965, **12**, 707.

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NOTICE

UNITED STATES OF AMERICA

Wednesday–Friday 11–13 *May* 1966: **Twelfth National ISA Analysis Instrumentation Symposium:** Hosted by *Houston Section of Instrument Society of America* and programmed by *ISA's Analysis Instrumentation Division.* Shamrock Hilton Hotel, Houston, Texas.

The theme of the Symposium is *Instrumental Methods for Trace Analysis*, featuring air and water purity measurements. Interested authors are invited to submit papers in the following analysis instrumentation areas: laboratory and/or process chromatography; radiation, optical, electro-mechanical, chemical or physical methods; and sample handling technique. Those desiring to present papers should submit a 300-word abstract to: George I. Doering, Technical Programme Chairman, Industrial Nucleonics Corporation, 650 Ackerman Road, Columbus, Ohio 43202. Advance registration information may be obtained from: L. B. Fields, Beckman Instruments, Inc., 5810 Hillcroft, Houston, Texas 77036.

Talanta, 1966, Vol. 13, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Jodemetrische Selenbestimmung nach vorausgegangener Extraktionstrennung mit Diisopropylketon: L. Futekov and N. Jordanov. (29 *November* 1965.)

Prediction of standard transition metal salts from the crystal structure: Kenneth G. Stone and Joseph T. Lundquist. (13 *December* 1965.)

Quantitation of thin-layer chromatograms: D. A. Keyworth and R. F. Swensen. (16 *December* 1965.)

Selection of the optimum range for reflectance spectrophotometric analysis: Van T. Lieu and Michael M. Frodyma. (20 *December* 1965.)

Radiochemical separation of antimony by isotopic exchange: Iqbal H. Qureshi and Muhammad Shabbir. (23 *December* 1965.)

Mechanism of the reaction between Hg(II) and iodide ion and the possibility of a volumetric determination of Hg(II): G. C. Jain and Y. K. Gupta. (29 *December* 1965.)

Some uses of ascorbic acid in the analytical chemistry of iron: M. L. Richardson and P. E. Luton. (4 *January* 1966.)

Spectrophotometric extractive titrations—III: Simultaneous determination of silver and copper in high purity lead: Aftanas Galík and Miroslav Knízek. (6 *January* 1966).

Teflon chains for use with the Foulk chain hydrometer: G. F. Smith. (6 *January* 1966.)

Inorganic polarography in organic solvents—I: Preliminary observations on the use of water-immiscible solvents: B. F. Afghan and R. M. Dagnall. (8 *January* 1966.)

Separation and determination of radioactive cesium in milk: R. B. Hahn, J. L. Johnson and J. B. McKay. (12 *January* 1966.)

3-Methyl-5 hydroxy-5-(D-arabino-tetrahydroxybutyl)-thiazolidine-2-thione as a reagent for the spectrophotometric determination of copper: J. A. Corbett. (14 *January* 1966.)

Separation of sugars by circular thin-layer chromatography: M. H. Hashmi and N. A. Chughtai. (19 *January* 1966.)

Remarks on hexamminecobalt (III) carbonatoberyllate: A. V. Vinogradov. (19 *January* 1966.)

Substoichiometric separation for activation analysis by coordinative extraction of unsolved salts: I. P. Alimarin and G. A. Perezhogin. (19 *January* 1966.)

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PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"**Precipitation of Metal Chelates from Homogeneous Solution**" by F. H. Firsching.

"**Recent Developments in the Ring Oven Technique**" by H. Weisz.

"**Adsorption Indicators in Precipitation Titrations**" by R. C. Mehrotra and K. N. Tandon.

"**Radiometric Titrations**" by T. Braun and J. Tölgyessy.

"**Recent Uses of Liquid Ion Exchangers in Inorganic Analysis**" by H. Green.

"**Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry**" by B. D. Flockhart and R. C. Pink.

"**A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum**" by F. E. Beamish.

"**A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold**" by F. E. Beamish.

"**Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals**" by Rudolf Přibil.

"**Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique**" by F. Girardi.

"**Separation of Transplutonium Elements**" by J. Starý.

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SUMMARIES FOR CARD INDEXES

Electrometric indicators in the amperometric titration of cations and acids: WALENTYNA RUSKUL, *Talanta*, 1966, **13**, 333. (Department of Inorganic Chemistry, University of Lodz, Poland.)

Summary—Amperometric titration is carried out at zero potential in the presence of hydroquinone and *p*-aminophenol as electrometric indicators. Solutions of sodium carbonate, sodium arsenite, sodium tetraborate and potassium cyanide have been used as reagents in neutralisation, precipitation and complex formation reactions for the determination of cations separately, the simultaneous determination of several cations in one sample and of acid and cations present simultaneously. After the equivalence point has been reached, hydroxyl ions appear in the solution as a result of salt hydrolysis and a considerable increase in the current voltage occurs. The indicator in alkaline solution induces the depolarisation of the electrode.

Determination of potassium by titrimetry: TADASHI IWACHIDO, *Talanta*, 1966, **13**, 341. (Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama, Japan.)

Summary—Epp's method modified by the addition of solid calcium hydroxide to the sample solution. This simplified the procedure, increased the rapidity and lessened the sources of error. With samples containing various ions except ammonium ion, potassium (conc. of KCl $0{\cdot}25$ to $1{\cdot}8 \times 10^{-2}M$) was determined within 0·4% of error, by means of corrections for the existence of a large quantity of sodium chloride and for the solubility of potassium tetraphenylborate.

Spectrophotometric determination of cerium with sulphanilic acid: P. L. SARMA and LOWELL H. DIETER, *Talanta*, 1966, 13, 347. (Department of Chemistry, University of North Dakota, Grand Forks, North Dakota, U.S.A.)

Summary—In the presence of other rare earths, cerium(IV) can be determined spectrophotometrically by its reaction with sulphanilic acid with which it produces a red colour. Solutions containing 28-210 ppm of cerium absorb at 495 mμ according to Beer's law. Other rare earths, except neodymium, and many common ions do not interfere. Strong oxidising agents and neodymium in greater than fifty times the concentration of cerium interfere with this method. The precision depends on the control of pH and time. Cerium alloys have been analysed by this method and the results are compared with those obtained by another spectrophotometric method.

ЭЛЕКТРОМЕТРИЧЕСКИЕ ИНДИКАТОРЫ В АМПЕРОМЕТРИЧЕСКОМ ТИТРОВАНИИ КАТИОНОВ И КИСЛОТ:

WALENTYNA RUSKUL, *Talanta*, 1966, **13**, 333.

Резюме—Амперометрические титрования проводится при потенциале нуль в присутствии гидрохинона и п-аминофенола в качестве злектрометрических индикаторов. Растворы карбоната натрия, арсенита натрия, тетрабората натрия и цианида калия были использованы как реагенты для нейтрализации, осаждения и образования комплексов при отдельном определении катионов, при одвонременном определении кислот и катионов и при одновременном определении нескольких катионов в одной пробе. После достижения точки зквиваленции в растворе появляются гидроксилионы в результате гидролиза соли и напряжение тока значительно повышается. Индикатор в щелочном растворе вызывает деполяризацию злектрода.

ОПРЕДЕЛЕНИЕ КАЛИЯ ТИТРИМЕТРИЧЕСКИМ МЕТОДОМ:

TADASHI IWACHIDO, *Talanta*, 1966, **13**, 341.

Резюме—Видоизменен метод Эппа добавлением твёрдой гидроокиси кальция к раствору пробы. Таким путем процедура упрощается и ускоряется, а источники ошибок уменьшаются. В пробах, содержающих различные ионы, исключая аммоний, определен калий (при концентрациях 0,25–1,8 × $10^{-2}M$ KCl) с ошибкой меньше 0,4%, вводя поправку в случае больших количеств хлорида натрия и поправку на растворимость тетрафенилборкалия.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦЕРИЯ СУЛЬФАНИЛОВОЙ КИСЛОТОЙ:

P. L. SARMA and LOWELL H. DIETER, *Talanta*, 1966, **13**, 347

Резюме—В присутствии других редкоземельных элементов можно определить церий(IV) спектрофотометрическим методом на основании его реакции с сульфаниловой кислотой, с которой образует красную окраску. Растворы содержающие 28–210 мг/л церия поглощают свет при 495 ммк, соблюдая закон Бера. Другие редкоземельные элементы, за исключением неодима, и многочисленные обыкновенные ионы не мешают. Сильные окислители и неодим в концентрации пятьдесят раз больше чем концентрация церия мешают етому методу. Точность метода зависит от регулирования pH и времени. Сплавы церия были анализированы этим методом и результаты сръвнены с данными полученными другим спектрофотометрическим методом.

Direct potentiometric titration of chlorite in presence of chlorate, chlorine dioxide and chloride: J. KĘPIŃSKI and G. BŁASZKIEWICZ, *Talanta*, 1966, **13**, 357. (Department of Inorganic Chemical Technology, Technical University, Szczecin, Poland).

Summary—A direct potentiometric titration of chlorite in the presence of chlorate, chlorine dioxide and chloride is described. Chlorite is determined in 0·01–0·0005M sodium chlorite at pH 2·0–3·5 using hypochlorite solution. The course of the reaction is followed potentiometrically using saturated calomel and platinum electrodes; the end-point is indicated by a potential jump of about 230 mV. Under these conditions no reaction takes place with chlorate, chlorine dioxide or chloride. Previously, the determination of chlorite in such mixtures was only possible by difference from several oxidimetric titrations.

Fluorometric titration of calcium, magnesium and iron using Calcein Blue as indicator: A. M. ESCARRILLA, *Talanta*, 1966, **13**, 363. (Utica College of Syracuse University, Utica, New York, U.S.A.).

Summary—Calcium, magnesium and iron can be determined by successive fluorometric titration without separation. Calcium is titrated directly with EGTA at a pH $\geqslant$ 13; magnesium is determined by a substitution reaction with copper-EDTA complex at a pH of about 11; and iron is titrated directly with EDTA in the presence of hydrogen peroxide at a pH of 10·5, after destroying its triethanolamine complex. Calcein Blue serves as an indicator in all of the titrations and as a fluorescent standard. The end-points are sharp and the accuracy is good for various proportions of the metal ions. The method is simple, reproducible and inexpensive. Standard solutions of ions, limestone, cement and serum samples have been analysed by the proposed method.

A high-temperature inert gas fusion apparatus: A. W. MOSEN, R. E. KELLEY and H. P. MITCHELL, JR., *Talanta*, 1966, **13**, 371. (General Atomic Division of General Dynamics Corporation, John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California, U.S.A.).

Summary—A high-temperature inert gas fusion apparatus capable of operating at crucible temperatures as high as 3100° is described. While this apparatus has been used primarily for the determination of oxygen in pyrolytic carbon-coated uranium carbide particles, its usefulness is not limited to this type of material. It can be generally applied to the determination of oxygen and nitrogen in metals, alloys and other materials amenable to analysis by vacuum-fusion techniques. Analytical results obtained on steel and uranium carbide samples are presented. The apparatus, in its present form, has been in daily use for nearly 2 years. Down time during this period has been negligible. A total of 20 samples can be run in duplicate in an 8-hr shift.

ПРЯМОЕ ПОТЕНЦИОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ХЛОРИТА В ПРИСУТСТВИИ ХЛОРАТА, ДВУОКИСИ ХЛОРА И ХЛОРИДА:

J. Kępiński and G. Błaszkiewicz, *Talanta*, 1966, **13**, 357.

Резюме—Описано прямое потенциометрическое определение хлорита в присутствии хлората, двуокиси хлора и хлорида. Хлорит определяют в 0,01–0,0005*M* растворе хлорита натрия при pH 2,0–3,5 с использованием раствора гипохлорита. Течение реакции обнаруживают потенциометрическим методом пользуясь насыщенным каломельевым и платиновым электродами; конец титрования означен скоком потенциала от 230 mV. В этих условиях нет реакции с хлоратом, двуокисью хлора или хлоридом. До сих пор в таких смесях определение хлорита было возможно только на основании разницы между несколькими оксидиметрическими титрованиями.

ФЛУОРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ КАЛЬЦИЯ, МАГНИЯ И ЖЕЛЕЗА С ИСПОЛЬЗОВАНИЕМ КАЛЬЦЕИНСИНЕГО В КАЧЕСТВЕ ИНДИКАТОРА:

A. M. Escarrilla, *Talanta*, 1966, **13**, 363.

Резюме—Кальций, магний и железо можно определить последовательным фдуорометрическим титрованием без выделения. Кальций титруют прямо с ЭДТА при pH $\geqslant$ 13; магний определяют реакцией замещения с комплексом меди и ЭДТА при pH около 11; железо титруют прямо с ЭДТА в присутствии перекиси водорода при pH 10,5 после разорения его комплекса с триэтаноламином. Кальцеинсиний служит в качестве индикатора во всех титрованиях, также как и в качестве флуоресцентного стандарта. Концы титрования острые и точность доволна для различных размеров ионов металлов. Метод несложный, точный и дешевый. Титрованные растворы ионов также как и растворы известняка, цемента и сыворотки были анализированы этим методом.

ПРИБОР ДЛЯ ПЛАВЛЕНИЯ В ИНЕРТНОМ ГАЗЕ ПРИ ВЫСОКОЙ ТЕМПЕРАТУРЕ:

A. W. Mosen, R. E. Kelley and H. P. Mitchell, Jr., *Talanta*, 1966, **13**, 371.

Резюме—Описан прибор для плавления при высоких температурах в атмосфере инертного газа, которым можно пользоваться всё до температур в тигле около 3100°. Этот прибор был использован в первую очередь для определения кислорода в частицах покрытых пиролитическим углеродом, но его применяемость не ограничивается только на этот тип материала. В общем можно пользоваться этим прибором для определения кислорода и азота в металлах, сплавах и других материалах анализируемых методом плавления в вакууме. Приводятся результаты полученные в пробах стали и карбида урана. Прибором в его нынешней форме пользовались ежедневно почти через два года. В этом периоде, потерянное на ремонт время было незначительно. В 8 часовой смене можно анализировать в целости 20 двойных проб.

Determination of certain trace impurities in uranium concentrates by activation analysis: A. A. Abdel-Rassoul, S. S. Wahba and A. Abdel-Aziz, *Talanta*, 1966, **13**, 381. (Nuclear Chemistry Department, Atomic Energy Establishment, Inchass, U.A.R.)

Summary—A method is presented for the simultaneous determination of chromium, iron, cobalt and zinc in samples of uranium concentrates, oxides and metallic uranium by neutron-activation analysis. The method involves adequate decontamination of gross fission product activities by adsorption on silica gel, removal of uranium by solvent extraction, separation of most carrier-free rare-earth activities by coprecipitation with aluminium chloride, and, finally, fractional separation of the elements concerned by ion-exchange chromatography. The method can assay ppm of such elements in limited quantities of samples by scintillation γ-ray spectrometric analysis with a reproducibility of 10–15%.

A comparison of neutron-activation analysis and hot extraction analysis of the oxygen content of steel: L. C. Pasztor and D. E. Wood, *Talanta*, 1966, **13**, 389. (Kaman Nuclear, Division of Kaman Aircraft Corporation, Colorado Springs, Colorado, U.S.A.)

Summary—A system developed for the fast neutron-activation analysis of the oxygen content of metals has been tested comparatively with the conventional vacuum fusion and carrier-gas fusion techniques. The results of these tests indicate that neutron-activation analysis is much faster (the total analysis takes only 2 min or less), and more reliable than vacuum fusion and carrier-gas fusion methods because all oxygen present is analysed. Samples can be much larger than the 0·2–3 g commonly used for the fusion methods. Furthermore, the analysis is non-destructive—the same samples can be re-analysed as often as desired. The fast neutron-analysis system includes a 14-MeV neutron generator producing 10^{11} neutrons/sec, a dual-tube pneumatic transfer system, a 5 × 5 inch NaI(Tl) crystal, a single-channel analyser, two scalers, and timers and switch-gear. A sample, in a polyethylene bottle, and a Lucite reference are irradiated simultaneously, after which the sample is returned to a detector for counting the ^{16}N gammas from the ^{16}O(n, p)^{16} N reaction. The reference is then counted in a second detector; the ratio of the sample counts to the reference counts is proportional to the oxygen content of the sample. Samples with oxygen contents from 0·002 to 0·1% of oxygen have been analysed by neutron activation, then cut in several pieces for hot extraction analysis of the total sample.

ОПРЕДЕЛЕНИЕ НЕКОТОРЫХ СЛЕДОВЫХ ПРИМЕС В УРАНОВЫХ КОНЦЕНТРАТАХ МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА:

A. A. ABDEL-RASSOUL, S. S. WAHBA and A. ABDEL-AZIZ, *Talanta*, 1966, **13**, 381.

Резюме—Приведен метод для одновременного определения хрома, железа, кобальта и цинка в урановых концентратах, в окисях и в металлическом уране методом радиоактивационного анализа. Метод включает соответствующую деконтаминацию грубой активности, продуктов расщепления адсорбированием на силикагеле, устранение урана экстрагированием с растворителем, выделение большинства редкоземельных активностей свободных от носителей соосаждением с хлоридом алюминия и, в конце, фракционное выделение миллиграммовых количеств этих элементов в ограниченных пробах, с использованием сцинтиллационной спектрометрии рентгеновских лучей с точностью 10–15%.

СРАВНЕНИЕ МЕТОДОВ РАДИОАКТИВАЦИОННОГО АНАЛИЗА И ГОРЯЧЕГО ЭКСТРАГИРОВАНИЯ ДЛЯ ОПРЕДЕЛЕНИЯ КИСЛОРОДА В СТАЛИ:

L. C. PASZTOR and D. E. WOOD, *Talanta*, 1966, **13**, 389.

Резюме—Процедура, разработанная для определения кислорода в металлах методом радиоактивационного анализа с использованием быстрых нейтронов, была испытана в сравнении с обыкновенными методами плавления в вакууме и плавления в газе-носителе. Результаты этих опытов показывают что метод радиоактивационного анализа гораздо быстрее (совокупный анализ продолжается только 2 минуты или меньше) и надежнее чем плавление в вакууме и плавление в газе-носителе, потому что анализируется весь присутствующий кислород. Пробы могут быть значительно больше чем 0,2–3 г, взятых обыкновенно для методов плавления. Кроме того анализ недеструктивный—те же пробы могут снова быть анализированы столько, сколько раз желается. Прибор для радиоактивационного анализа включает в себя генератор нейронов 14 MeV, производящий 10^{11} нейтронов (сек, пневматическую пеоеносную систему с двойными трубками, кристалл NaI(Tl) 5 × 5 дюймов, два шкалера, таймеры и переключающий механизм. Пробу в полиэтиленовой склянке и эталон Люцита облучают одновременно, после чего пробу возвращают детектору и считают ^{16}N гамма лучи из реакции $^{16}O(n, p)^{16}N$. Эталон потом считают в другом детекторе; отношение между отсчетом образца и эталона пропорционально содержанию кислорода в образце. Образцы содержающие 0,002–0,1% кислорода были анализированы радиоактивационным методом, затем были разрезаны в несколько части для анализа целого образца методом горячего экстрагирования.

Precise titrimetric determination of uranium in high-purity uranium compounds: LEON PSZONICKI, *Talanta*, 1966, **13**, 403. (International Atomic Energy Agency, Seibersdorf Laboratory, Vienna, Austria).

Summary—A procedure has been developed for the very precise determination of uranium in high-purity uranium compounds. Uranium(VI) is reduced in a strong hydrochloric acid solution with aluminium in the presence of cadmium ions to uranium(III). It is oxidised to uranium(IV) in the presence of excess orthophosphoric acid and then quantitatively oxidised to uranium(VI) with potassium dichromate using a potentiometric end-point detection. The coefficient of variation based on 20 analyses is $\mp 0{\cdot}003\%$.

Microdetermination of oxygen, carbon and water in inorganic materials using a carrier-gas technique: J. J. ENGELSMAN, A. MEYER and J. VISSER, *Talanta*, 1966, **13**, 409. (Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven-Netherlands).

Summary—A description is given of the accurate determination of small quantities of oxygen, carbon and water in inorganic compounds. Oxygen and carbon are determined by a conductimetric technique and water by a coulometric technique. The limits of detection of the different methods are: 0·1 μg of oxygen, 0·1 μg of carbon and 0·03 μg of water. This is accomplished by taking special care to obtain a low blank and by using stable instruments. A suggestion is made for the simultaneous determination of water and hydrogen.

Separation of transplutonium elements: J. STARÝ, *Talanta*, 1966, **13**, 421. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehova 7, Czechoslovakia).

Summary—A critical review of the group separation of tervalent lanthanides and actinides and of the separation of individual transplutonium elements is presented. The theoretical principles involved are also discussed.

Amperometry with two polarisable electrodes—VII: Chelometric determination of indium: F. VYDRA and J. VORLÍČEK, *Talanta*, 1966, **13**, 439. (Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Analytical Laboratory, Prague 1, Jilská 16, Czechoslovakia).

Summary—Optimum conditions have been found for the chelometric determination of indium by biamperometric titration with EDTA. Two stationary platinum electrodes (Pt-Pt) or two graphite electrodes (C-C) may be used to indicate the end-point of the titration. At pH 1–1·5 the determination is highly selective. The applied potential only influences the absolute value of the current; the accuracy of the determinations remains constant over a wide interval of applied potential. At a potential of 1·0–1·7 V the change of current during a titration with 0·05M EDTA solution is of the order of 10 μA. Analytical applications of the method are discussed.

ТОЧНОЕ ТИТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ УРАНА В СОЕДИНЕНИЯХ УРАНА ВЫСОКОЙ ЧИСТОТЫ:

LEON. PSZONICKI, *Talanta*, 1966, **13**, 403

Резюме—Разработана процедура для аккуратного определения урана в соединениях урана высокой чистоты. Уран(VI) восстанавливают алюминием в уран(III) в присутствии ионов кадмия, в силнокислом растворе соляной кислоты. Уран(III) окисляют в уран%(IV) в присутствии избытка ортофосфорной кислоты и затем окисляют количественно в уран(VI) с бихроматом калия, с использованием потенциометрического обнаружения конца титрования. Коэфициент вариации равен ∓0,003%, вычислен на основе 20 анализов.

МИКРОМЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ КИСЛОРОДА, УГЛЕРОДА И ВОДЫ В НЕОРГАНИЧЕСКИХ ВЕЩЕСТВАХ С ИСПОЛЬЗОВАНИЕМ ГАЗА НОСИТЕЛЯ:

J. J. ENGELSMAN, A. MEYER and J. VISSER, *Talanta*, 1966, **13**, 409.

Резюме—Описан точный метод для определения небольших количеств кислорода, углерода и воды в неорганических соединениях. Кислород и углерод определяют кондуктометрическим, а воду кулонлметрическим методом. Пределы чувствительности методов равны 0,1 мкг кислорода, 0,1 мкг углерода и 0,03 мкг воды. Эта чувствительность получена обращая особенное внимание на низкие слепые пробы и на использование устойчивых приборов. Предложено одновременное определение воды и водорода.

ВЫДЕЛЕНИЕ ТРАНСПЛУТОНИЕВЫХ ЭЛЕМЕНТОВ:

J. STARÝ, *Talanta*, 1966, **13**, 421.

Резюме—Приведен критический обзор методов для группового выделения трехвалентных лантанидов и актинидов и методов для выделения отдельных трансплутониевых элементов. Также обсуждены теоретические принципы этих выделений.

АМПЕРОМЕТРИЯ С ДВУМЯ ПОЛЯРИЗИРУЮЩИМИСЯ ЭЛЕКТРОДАМИ—VII: ХЕЛАТОМЕТРИЧЕСКОЕ ОПРЕДЕЛНИЕ ИНДИЯ:

F. VYDRA and J. VORLÍČEK, *Talanta*, 1966, **13**, 439.

Резюме—Определены оптимальные условия для хелатометрического определения индия биамперометрическим титрованием с ЭДТА. Можно пользоваться двумя стационарными платиновыми (Pt-Pt) или графитовыми электродами для обнаружения конца титрования. Определение обладает высокой избирательностью при pH 1–1,5. Приложенный потенциал действует только на абсолютное значение тока; точность определения постоянная в широком пределе потенциалов. При потенциале 1,0–1,7 V перемена тока в течение титрования с 0,05*M* раствором ЭДТА равна приблизительно 10 мкА. Обсуждается использование этого метода в анализе.

Determination of iron, copper and aluminium by gas-liquid chromatography: R. W. MOSHIER and J. E. SCHWARBERG, *Talanta*, 1966, **13**, 445. (Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, U.S.A.)

Summary—Gas chromatography has been utilised in the analysis of two National Bureau of Standard alloys for quantitative determination of aluminium, iron and copper. In the analysis of N.B.S. 162a the relative mean errors were 3·13% for aluminium, 2·06% for iron and −1·72% for copper and for N.B.S. 164a the relative mean errors were −1·39%, −0·19% and −0·89% for aluminium, iron and copper, respectively. The procedure for analysis involves solution of the alloy, conversion of the metal ions to trifluoroacetylacetonates by solvent extraction and, finally, complete separation of the metal chelates and quantitative determination by gas chromatography using a column containing Gas Pack F coated with Tissuemat E, a polyethylene wax. Other metals present in the N.B.S. samples did not interfere with the determination of aluminium, iron and copper.

Substoichiometric determination of manganese by neutron-activation analysis: A. ZEMAN, J. PRÁŠILOVÁ and J. RŮŽIČKA, *Talanta*, 1966, **13**, 457. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia.)

Summary—A simple and rapid method for the substoichiometric determination of traces of manganese in various materials by neutron-activation analysis has been developed. After dissolution of the irradiated test sample, manganese(II) carrier is added and subsequently oxidised by peroxodisulphate to the heptavalent state. The permanganate thus formed is finally extracted into chloroform as tetraphenylarsonium permanganate using a substoichiometric amount of tetraphenylarsonium chloride. This single separation step isolates radiochemically pure manganese-56 in the analysis of a relatively simple material in which interfering elements (gold, rhenium, *etc.*) are absent. When this is not true, a preliminary separation of manganese from the irradiated sample, based on the extraction of manganese diethyldithiocarbamate into chloroform and followed by stripping of the manganese with dilute sulphuric acid, must be used. A simultaneously irradiated standard containing manganese must be treated in exactly the same way as a test sample. In the materials analysed by the new method 10^{-5} to 10^{-3}% of manganese has been determined.

Luminol as a fluorescent acid-base indicator: L. ERDEY, I. BUZÁS and K. VIGH, *Talanta*, 1966, **13**, 463. (Institute for General Chemistry, Technical University, Budapest XI, Hungary.)

Summary—The acid and base dissociation constants of luminol are determined at various ionic strengths. The transition interval occurs at pH 7·7–9·0, therefore luminol is a fluorescent indicator for the titration of strong and weak acids and strong bases. Its value as an indicator is established by titrating milk, red wine and cherry juice.

КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ ЖЕЛЕЗА, МЕДИ И АЛЮМИНИЯ МЕТОДОМ ГАЗО-ЖИДКОСТНОЙ ХРОМАТОГРАФИИ:

R. W. Moshier and J. E. Schwarberg, *Talanta*, 1966, **13**, 445.

Резюме—Метод газо-жидкостной хроматографии был использован для количественного определения алюминия, железа и меди в анализе двух сплавов из National Bureau of Standards. В анализе образца N.B.S. 162a относительнйе средные ошибки были 3,13% для алюминия, 2,06% для железа и −1,72% для меди, а в анализе образца N.B.S. 164a относительные средные ошибки были −1,39%, −0,19% и −0,89% для алюминия, железа и меди, соответственно. Анализ включает в себя растворение сплава, перєведение ионов металлов в трифторацетилацетонаты экстрагированием с растворителем, и в конце, полное выделение хелатов металлов и количественное определение методом газовой хроматографии, с использованием колонки содержающей Gas Pack F, пропытанный с Tissue-mat E (полиэтиленовым воском). Другие металли присутствующие в образцах N.B.S. не влияли на определение алюминия, железа и меди.

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАРГАНЦА МЕТОДОМ РАДИОАКТИВАЦИОННОГО АНАЛИЗА:

A. Zeman, J. Prasilova and J. Ruzicka, *Talanta*, 1966, **13**, 457.

Резюме—Разработан быстрый и несложный метод для определения следов марганца в различных веществах. После растворения облученному образцу добавляется носитель марганец(II) и проводится окисление пероксодисульфатом до семивалентного состояния. Перманганатион, образован этой реакцей, экстрагируется хлороформом в форме перманганата тетрафениларсония, с использованием субстехиометрического количества хлорида тетрафениларсония. Этой операцией выделяется марганец-56 радиохимической чистоты в анализе сравнительно несложного материала, который не содержит мешающих элементов (золота, рения и т.д.). В случае присутствия мешающих элементов надо провести предварительное выделение марганца из облученного образца, основывающиеся на экстрагировании диэтилдитиокарбамата марганца хлороформом и последующем извлечении марганца разбавленной серной кислотой. Одновременно облученный эталон надо обрабатывать таким же образом, как и исследованный образец. В анализированных материалах определено новым методом 10^{-5} до 10^{-3}% марганца.

ЛЮМИНОЛ В КАЧЕСТВЕ ФЛУОРЕСЦИРУЮЩЕГО КИСЛОТНО-ЩЕЛОЧНОГО ИНДИКАТОРА:

L. Erdey, I. Buzás and K. Vigh, *Talanta*, 1966, **13**, 463.

Резюме—Определены постоянные диссоциации водородных ионов люминола при разлиных ионных концентрациях. Переходный интервал при pH 7,7–9,0; поэтому можно считать люминол как флуоресцирующий индикатор для титрования сильных и слабых кислот и сильных оснований. Применимость этого индикатора проверена в титровании молока, красного вина и вишнёвого сока.

Investigation of the solvent extraction of californium, fermium and mendelevium: K. A. Gavrilov, E. Gvuzdz, J. Starý and Wang Tung Seng, *Talanta*, 1966, **13**, 471. (Joint Institute for Nuclear Research, Dubna, Moscow, USSR)

Summary—The extraction constants for the systems di-(2-ethylhexyl)-orthophosphoric acid/toluene/hydrochloric acid and americium, curium californium and fermium have been determined. They have been used to select the best conditions for the separation of californium, fermium and mendelevium by extraction chromatography. The separation factors are much higher than the corresponding ion-exchange methods.

Potentiometric determination of plutonium by argentic oxidation, ferrous reduction and dichromate titration: J. L. Drummond and R. A. Grant, *Talanta*, 1966, **13**, 477. (U.K.A.E.A., Reactor Group, Dounreay Experimental Reactor Establishment, Thurso, Caithness, Scotland.)

Summary—A simple and rapid method is described for the routine determination of plutonium with a coefficient of variation of better than 0·2%. It is directly applicable to nitrate solutions containing a large amount of uranium; moderate amounts of iron, molybdenum, fluoride and phosphate do not interfere. Chromium, cerium and manganese interfere quantitatively, and the procedure may also prove convenient for the determination of these elements. The plutonium is oxidised to the sexivalent state with argentic oxide in nitric acid solution, and the excess of oxidant is destroyed by reaction with sulphamic acid. A weighed small excess of iron(II) solution is then added, and the excess is titrated potentiometrically with standard potassium dichromate solution using polarised gold indicator electrodes. The whole determination is performed in one vessel at room temperature, and takes about 20 min.

Determination of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals with PAN: Elsie M. (Penner) Donaldson and W. R. Inman, *Talanta*, 1966, **13**, 489. (Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.)

Summary—A spectrophotometric method for the determination of 0·0005–0·10% of manganese in high-purity niobium, tantalum, molybdenum and tungsten metals is described. The matrix materials are separated from the manganese by extraction as cupferrates, after sample dissolution, then the red complex formed between manganese(II) and 1-(2-pyridylazo)-2-naphthol, PAN, is extracted into chloroform from an ammoniacal tartrate-cyanide medium. The absorbance of the extract is determined at 562 mμ. With the exception of zinc and lead, other impurities present in the four high-purity metals described do not interfere with the proposed method.

ИЗУЧЕНИЕ ЭКСТРАКЦИИ КАЛИФОРНИЯ, ФЕРМИЯ И МЕНДЕЛЕВИЯ РАСТВОРИТЕЛЯМИ:

K. A. Gavrilov, E. Gvuzdz, J. Starý and Wang Tung Seng, *Talanta*, 1966, **13**, 471.

Резюме—Определены постоянные экстракции для системы ди-(2-этилгексил)ортофосфорная кислота—толуол—соляная кислота для америция, кюрия, калифорния и фермия. Эти постоянные служили для отбора оптимальных условий для выделения калифорния, фермия и менделевия методом экстракчионной хроматографии. Коэффициенты разделения значительно выше чем в соответствующих ионообменных методах.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПЛУТОНИЯ ОКИСЛЕНИЕМ С СЕРЕБРОМ, ВОССТАНОВЛЕНИЕМ С ЖЕЛЕЗОМ(II) И ТИТРОВАНИЕМ С БИХРОМАТОМ:

J. L. Drummond and R. A. Grant, *Talanta*, 1966, **13**, 477.

Резюме—Описан быстрый и несложный метод для серийного определения плутония с козфициентом вариации лучше чем 0,2%, которым можно прямо пользоваться в анализе растворов нитратов, содержающих больщие количества урана. Умеренные количества железа, молибдена, фторидиона и фосфатиона не мешают определению. Хром, церий и марганец мешают количественным образом, поэтому зта процедура могла бы служить для определения зтих злементов. Плутоний окисляют до шестивалентного состояния с окисью серебра в азотнокислом растворе и избыток окислителя уничтожают реагированием с сульфаминовой кислотой Затем добавляют отвешенный небольший избыток раствора железа(II) и определяют избыток потенциометрическим титрованием с титрованным раствором бихромата калия, с использованием поляризованных золотых индикаторных злектродов. Целое определение проводится в одном сосуде при комнатной температуре и продольжается около 20 мин.

ОПРЕДЕЛЕНИЕ МАРГАНЦА В МЕТАЛЛИЧЕСКОМ НИОБИЕ, ТАНТАЛЕ, МОЛИБДЕНЕ И ВОЛЬФРАМЕ ВЫСОКОЙ ЧИСТОТЫ С ИСПОЛЬЗОВАНИЕМ ПАН:

Elsie M. (Penner) Donaldson and W. R. Inman, *Talanta*, 1966, **13**, 489.

Резюме—Описан спектрофотометрический метод для определения 0,9995–0,10% марганца в металлическом ниобие, тантале, молибдене и вольфраме высокой чистоты. Матричные материалы отделяются от марганца зкстрагированием в форме купферратов, после растворения пробы; потом красный комплекс, образующийся между марганцем(II) и 1-(2-пиридилазо)-2-нафтолом, (ПАН), зкстрагируется хлорофомом из аммиячного раствора тартрата-цианида. Светопоглощение зкстракта измеряется при 562 ммк. Примеси присутствующие в четыре упомянутых металлах высокой чистоты—кроме цинка и свинца—не мешают описанном определению.

Milligram determination of primary amides: R. D. Tiwari, J. P. Sharma and I. C. Shukla, *Talanta*, 1966, **13**, 499. (Department of Chemistry, University of Allahabad, Allahabad, India.)

Summary—An accurate and selective milligram procedure for the determination of primary amides is described. About 3–4 mg of sample are hydrolysed with a concentrated solution of sodium hydroxide and the resulting ammonia is distilled into dilute sulphuric acid. The ammonium sulphate thus obtained is converted into ammonium iodide by passing it through hydroxide- and iodide-form resins. This iodide is oxidised to iodate with bromine, then titrated iodometrically. Determinations carried out on a number of primary amides, ureas and thioureas show a deviation of about 0·3% from full recovery of the compounds.

A suggestion for presentation of analytical results in "ionic form" made before development of the ionic theory: Z. Szökefalvi-Nagy and F. Szabadváry, *Talanta*, 1966, **13**, 503. (Institute for General Chemistry, Technical University, Budapest, Hungary.)

Summary—In 1865 Karl Than, Professor of Chemistry in Budapest, suggested that analytical results should not be given in the dualistic form of Berzelius, but rather they should be given in the form in which they are determined by the analysis. The manner in which this suggestion, originally ignored, was adopted as a result of the ionic theory and activity of Wilhelm Ostwald is traced.

Spectrophotometric determination of antimony with Bromopyrogallol red: D. H. Christopher and T. S. West, *Talanta*, 1966, **13**, 507. (Chemistry Department, Imperial College, London S.W.7, England.)

Summary—Bromopyrogallol Red may be used as a reagent for the spectrophotometric determination of antimony(III) in the range 10–100 μg. The colour system, in the presence of EDTA, cyanide ion or fluoride ion as masking agents, is unaffected by 200-fold molar excesses of 18 cations examined, and a further 5 cations can be tolerated at lower concentrations. The procedure is simple and rapid, and with a molar absorptivity coefficient in excess of 35,000, it compares favourably with the most sensitive of the techniques used at present.

ОПРЕДЕЛЕНИЕ МИЛЛИГРАММОВЫХ КОЛИЧЕСТВ ПЕРВЫЧНЫХ АМИДОВ:

R. D.Tiwari, J. P. Sharma and I. C. Shukla, *Talanta*, 1966, **13**, 499.

Резюме—Описана точнаяи избирательная процедура для определения миллиграммовых количеств первычных амидов. 3–4 мг пробы гидролизуют концентрированным раствором гидроокиси натрия и образованный аммияк перегоняют в разбавленную серную кислоту. Полученный сульфат аммония превращают в иодид аммония пропусканием через слои ионообменных смол в форме гидроокиси и иодида. Иодид окисляется в иодат бромом, после чего титруется иодометрическим методом. Определения первычных амидов, мочевин и тиомочевин показывают отклонение от полного возвращения зтих соединений равно 0,3%.

ПРЕДСТАВЛЕНИЕ РЕЗУЛЬТАТОВ АНАЛИЗА В «ИОННОЙ ФОРМЕ» ПРЕДЛОЖЕНО ПЕЕЖДЕРЧЕМ САМОЕ РАЗВИТИЕ ИОННОЙ ТЕОРИИ:

Z. Szökefalvi-Nagy and F. Szabadváry, *Talanta*, 1966, **13**, 503.

Резюме—1865 года Карл Тан, профессор химии в Будапесте, предложил что результаты анализа не нада представлять в дуалистической форме Берцелиуса но в форме в которой они получены в анализе. Выследован способ которым зто первоначально игнорированное предложение было усвоено в результате ионной теории и деятельности Вильгельма Оствалда.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СУРЬМЫ С БРОМПИРОГАЛЛОЛКРАСНЫМ:

D. H. Christopher and T. S. West, *Talanta*, 1966, **13**, 507.

Резюме—Бромопирогаллолкрасным можно пользоваться в качестве реагента для спектрофотометрического определения сурьмы(III) в области 10–100 мкг. В присутствии ЭДТА, цианидили фторидионов в качестве маскирующего агента 18 исследованных катионов не влияют на окраску даже при 200 кратном молярном избытке, а следующих 5 катионов не мешают в нижих концентрациях. Процедура несложна и быстра; на основании молярного коефициента поглощения большего чем 35,000 ее можно сравнивать с самыми чувствительными методами, существующими в настоящее время.

Contributions to the basic problems of complexometry—XXI: Determination of nickel in the presence of cobalt: RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1966, **13**, 515. (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—A new method for the determination of nickel in the presence of cobalt, based on the masking of the cobalt with potassium cyanide and hydrogen peroxide, is proposed. The yellow, or orange-yellow, complex of cobalt(III) is formed, from which cobalt is not displaced upon the addition of silver nitrate. Tetracyanonickelate, however, reacts quantitatively with silver nitrate, and the displaced nickel can be determined directly with EDTA, using Murexide as indicator. Up to 30 mg of cobalt can be tolerated in the solution.

A new method for the titrimetric determination of perchlorate: G. ARAVAMUDAN and V. KRISHNAN, *Talanta*, 1966, **13**, 519. (Department of Chemistry, Indian Institute of Technology, Madras-36, India.)

Summary—A new method for the titrimetric determination of perchlorate has been developed, based on its reduction to chloride by iron(II) in a strong sulphuric acid medium at high temperature. The effect of variables, such as the sulphuric acid concentration, the temperature and the period of heating, on the extent of reduction has been studied and the optimal conditions for analytical determination of perchlorate derived.

Rapid iodometric determination of copper in some copper-base alloys: J. AGTERDENBOS and P. A. ELBERSE, *Talanta*, 1966, **13**, 523 (Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands.)

Summary—Copper-base alloys, especially those containing tin, are readily dissolved in a mixture of hydrofluoric and nitric acids. In the resulting solution copper can be titrated iodometrically in the conventional manner.

ДОКЛАДЫ К ОСНОВНЫМ ПРОБЛЕМАМ КОМПЛЕКСОМЕТРИИ—XXI: ОПРЕДЕЛЕНИЕ НИКЕЛЯ В ПРИСУТСТВИИ КОБАЛЬТА:

RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta* 1966, **13**, 515.

Резюме—Предложен новый метод для определения никеля в присутствии кобальта, основывающийся на маскированию кобальта с цианидом калия и перекисью водорода. Образуется желтый или оранжевожелтый комплекс кобальта(III), из которого кобальт не вытеснен при добавлении нитрата серебра. Между тем, тетрацианоникелят реагирует количественно с нитратом серебра и освобожденный никель определяется прямо с ЭДТА, с использованием Мурексида в качестве индикатора. Можно допустить все до 30 мг кобальта в растворе.

НОВЫЙ МЕТОД ДЛЯ ТИТРОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ПЕРХЛОРАТА:

G. ARAVAMUDAN and V. KRISHNAN, *Talanta*, 1966, **13**, 519.

Резюме—Разработан новый метод для титрометрического определения перхлоратиона, основывающийся на его восстановлении вохлоридион железом(II) в сильно сернокислой среде и при высокой температуре. Изучено влияние концентрации серной кислоты, температуры и продолжительности нагревания на степень восстановления и определены оптимальные условия для анализа перхлората.

БЫСТРОЕ ИОДОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ В НЕКОТОРЫХ СПЛАВАХ:

J. AGTERDENBOS and P. A. ELBERSE, *Talanta*, 1966, **13**, 523.

Резюме—Сплавы на основе меди содержающие олово хорошо растворяются в смеси фтористоводородной и азотной кислот. В полученном растворе мед титруется обыкновенным иодометрическим методом.

A simplified sampling technique for use with the Weisz ring oven: Application to qualitative analysis of some gold and silver alloys: L. J. Ottendorfer, Y. A. Gawargious and S. S. M. Hassan, *Talanta*, 1966, **13**, 525 (Microanalytical Chemistry Unit, National Research Centre, Dokki, Cairo, U.A.R.)

Summary—Up to 100 μg of sample can be collected from gold or silver alloys by rubbing the specimen with the ground hemispherical tip of a 4-mm Pyrex glass rod. Gold alloys are then dissolved in potassium cyanide solution containing hydrogen peroxide; silver alloys are exposed to vapours of nitric acid. Procedures for transfer, ring oven separation and identification of alloy constituents in the sample solutions are described.

Amperometric titration of mercury with a stationary platinum electrode in stirred solutions: B. C. Bera, M. M. Chakrabartty, S. P. Bag and K. L. Mallik, *Talanta*, 1966, **13**, 528 (Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.)

Summary—Amperometric titration of mercury (in the range of 0·4 to 3·5 mg) has been carried out with 2-mercaptobenzoxazole with a stationary electrode in stirred solution in a sodium acetate-acetic acid medium.

Determination of orthoesters by hydrolysis and Karl Fischer titrimetry: Donald J. Clancy and David E. Kramm, *Talanta*, 1966, **13**, 531. (Research Division, W. R. Grace & Company, Clarksville, Maryland, 21029, U.S.A.)

Summary—The acid hydrolysis of orthoesters has been made the basis of a titrimetric method. The method involves reaction of an orthoester with a known excess of water in a trichloroacetic acid-methyl alcohol system, followed by determination of unreacted water by Karl Fischer titration.

УПРОЩЕННАЯ ПРОЦЕДУРА ВЗЯТИЯ ПРОБЫ ДЛЯ КОЛЬЦЕВОЙ ПЕЧИ ВАЙСА. ПРИМЕНЕНИЕ В КАЧЕСТВЕННОМ АНАЛИЗЕ НЕКОТОРЫХ СПЛАВОВ ЗОЛОТА И СЕРЕБРА:

L. J. Ottendorfer, Y. A. Gawargious and S. S. M. Hassan, *Talanta*, 1966, **13**, 525.

Резюме—Можно собрать все до 100 мкг мробы трением сплавов .золота и серебра с шлифованным полушаровым верхом на палке из стекла пайрекс толщины 4 мм. Сплавы золота потом растворяются в растворе цианида калия, содержающем перекись водорода; сплавы серебра подвергают действию паров азотной кислоты. Описываются процедури для переноса, разделения на кольцевой печи Вайса и отождествления компонентов в растворе пробы.

АМПЕРОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ РТУТИ В ПЕРЕМЕЩИВАННЫХ РАСТВОРАХ С ИСПОЛЬЗОВАНИЕМ СТАЦИОНАРНОГО ПЛАТИНОВОГО ЭЛЕКТРОДА:

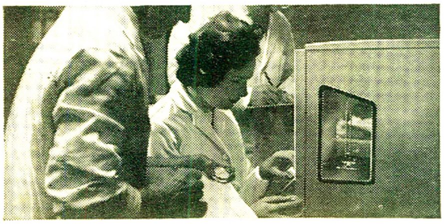
B. C. Bera, M. M. I. Chakrabartty, S. P. Bag and K. L. Mallik, *Talanta*, 1966, **13**, 528.

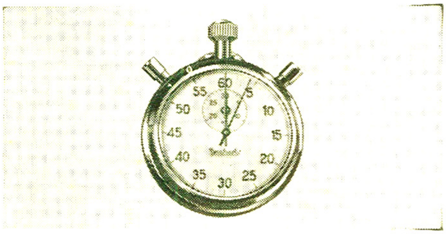
Резюме—Проведено амперометрическое титрование ртути (в области 0,4–3,5 мг) с 2-меркаптобензоксазолом в перемешиванном растворе ацетата натрия и уксусной кислоты, с использованием стационарного электрода.

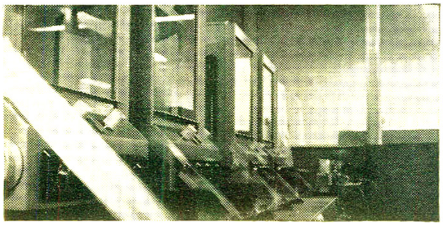
ОПРЕДЕЛЕНИЕ ОРТОЭФИРОВ ГИДРОЛИЗОМ И ТИТРОВАНИЕМ С РЕАГЕНТОМ КАРЛ ФИЩЕРА:

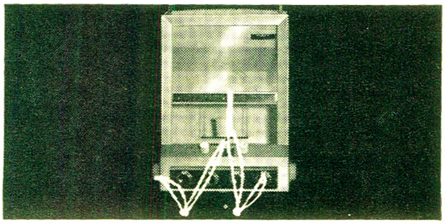
Donald J. Clancy and David E. Kramm, *Talanta*, 1966, **13**, 531.

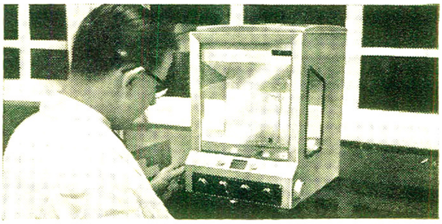
Резюме—Разработан титриметрический метод для определения ортоэфиров основывающийся на гидролизе в кислой среде. Метод включает в себя реакцию ортоэфира с знакомым избитком воды в растворе трихлоруксусной кислоты и метилового спирта, и определение нереагированной воды титрованием с реагентом Карл Фишера.

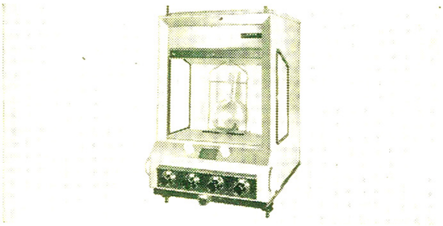












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