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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 30, No. 2, February 1964

THE DETERMINATION OF URANIUM IN THE PRESENCE OF PLUTONIUM BY CONTROLLED POTENTIAL COULOMETRY

APPLICATION TO THE ANALYSIS OF FUEL ELEMENT PROCESSING SOLUTIONS

A controlled potential coulometric method is described for the determination of uranium in the presence of plutonium and iron based on the reduction of uranium(VI) to uranium(IV) at a mercury cathode, after reduction of plutonium to plutonium(III) with hydrazine. The application of this procedure to the analysis of fuel element processing solutions in nitric acid is discussed and a precision of 0.2% has been obtained. A brief description of the controlled potential coulometer is given.

G. C. GOODE, J. HERRINGTON AND G. HALL,
Anal. Chim. Acta, 30 (1964) 109–113.

THE INFLUENCE OF SOME MASKING AGENTS ON THE SOLVENT EXTRACTION OF ZINC OXINATE

An investigation of the extraction of radio-labelled 10^{-6} M zinc from various aqueous solutions into chloroform containing oxine has been carried out. The effects of pH value, oxine concentration, and 10 aqueous masking agents have been studied. The experimental results have been compared with theoretically calculated values, allowing some conclusions with regard to the participating species to be drawn.

G. K. SCHWEITZER AND W. VAN WILLIS,
Anal. Chim. Acta, 30 (1964) 114–118.

THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

Fourteen different chelating reagents have been investigated as possible extractants for radiolabelled 10^{-6} M thallium(I) from aqueous solutions into chloroform. The data have been analyzed theoretically to identify the predominant species involved and to estimate association and distribution constants.

G. K. SCHWEITZER AND A. D. NORTON,
Anal. Chim. Acta, 30 (1964) 119–125.

THE SEPARATION OF TITANIUM FROM VANADIUM AND MOLYBDENUM BY CUPFERRON SOLVENT EXTRACTION

The isolation of small amounts of titanium from vanadium and molybdenum before the spectrophotometric determination of titanium as the "pertitanate" complex has been achieved by a solvent extraction procedure using cupferron and chloroform at pH 6 in the presence of EDTA.

J. A. CORBETT,
Anal. Chim. Acta, 30 (1964) 126–130.

RARE EARTH CHELATES DERIVED FROM 8-QUINOLINOL

The composition and heat stabilities of trivalent lanthanide oxinates prepared by homogeneous precipitation (urea hydrolysis in the presence of acetic acid) have been studied. The products contain acetate ion; and the molar ratio oxinate/metal is less than three. Polymeric structures are proposed for these materials. Heat stability in an inert atmosphere, as determined by thermogravimetric, thermomanometric and differential thermal analyses, decreases with increasing atomic weight of the metal.

R. G. Charles and A. Perrotto,
Anal. Chim. Acta, 30 (1964) 131–138.

ANION-EXCHANGE PAPER CHROMATOGRAPHY OF METAL IONS

The migration of 26 ions on anion-exchange paper is studied with five different complexing solvents. The results are reported as a function of the sign of the charge on each ion determined electrochromatographically. Several possible separations, are presented, but it is shown that the prediction of separations, knowing only the charge on several substances, is impossible. It is also demonstrated that ion-exchange column experiments and ion-exchange paper experiments do not necessarily yield identical results.

J. Sherma and C. W. Cline,
Anal. Chim. Acta, 30 (1964) 139–147.

HIGH SPEED SEPARATION OF THE LIGHT RARE EARTHS ON CENTRIFUGALLY ACCELERATED ION-EXCHANGE PAPER

The separation of the rare earths, La, Ce, Pr, Nd, Sm and Y on centrifugally accelerated Amberlite SA-2 cation-exchange paper was studied. All combinations of the elements can be completely separated except the Pr–Nd pair by using as eluant glycolic acid of a properly-chosen concentration (0.30 or 0.40 *M*) and pH (3.0 to 4.5). The Pr–Nd pair can be partially separated. The average number of ligand glycolate ions per rare earth ion in the resin phase was determined for each rare earth over the pG range 0.7 to 1.0.

C. Heininger, Jr. and F. M. Lanzafame,
Anal. Chim. Acta, 30 (1964) 148–154.

USE OF PYRIDINIUM BROMIDE PERBROMIDE AS AN ANALYTICAL REAGENT

Pyridinium bromide perbromide has been shown to be a satisfactory reagent for the bromination of phenols, unsaturates and aromatic ethers. The color of the reagent permits the spectrophotometric detection of the end-point. Most phenols and unsaturates react fast enough, in the presence of a catalyst, to permit titration within 10 min. The aromatic ethers, in general, react very slowly but yield accurate results. The reagent has the advantage over the conventional bromate-bromide that the titrations are fast and the stoichiometry exact. The speed of reaction of PBPB with many functional groups may permit the use of automatic titration procedures with this reagent.

T. Williams, J. Krudener and J. McFarland,
Anal. Chim. Acta, 30 (1964) 155–162.

SEMIQUANTITATIVE ANALYSIS BY MEASUREMENT OF THE DECOLORIZATION TIMES OF SPOT REACTIONS

(in German)

A rapid semiquantitative method is described based on measurement of the time required for decolorization of spot reactions on filter paper strips by suitable reagents. This very simple method yields results which are accurate to ± 10%. The method has been verified for several ions (Ag^+, Pb^{2+}, IO_3^-, Cu^{2+}, CrO_4^{2-}). The utility of this method for the characterization and differentiation of filter papers is indicated.

H. WEISZ,

Anal. Chim. Acta, 30 (1964) 163–166.

DETERMINATION OF MANGANESE IN URANIUM BY ION EXCHANGE AND SQUARE-WAVE POLAROGRAPHY

Traces of manganese in uranium and its compounds can be determined by ion-exchange separation and square-wave polarography. When a 9 *M* hydrochloric acid solution of the sample is introduced into a column of strongly basic anion-exchange resin, manganese can be quantitatively separated from uranium by eluting with 9 *M* hydrochloric acid. The determination of the separated manganese by square-wave polarography is performed in 1 *M* potassium hydroxide–0.4 *M* triethanolamine solution with an excellent sensitivity. The lower limit of the method is 0.5 p.p.m. of manganese.

F. NAKASHIMA,

Anal. Chim. Acta, 30 (1964) 167–175.

DETERMINATION OF THORIUM IN ROCKS

THE ARSENAZO III REACTION IN PERCHLORATE MEDIUM

SAVVIN's reagent, arsenazo III, has been examined for the determination of traces of thorium in rocks. The superior sensitivity and selectivity of the arsenazo III reaction over the thorin reaction have been confirmed. Sensitivity and stability have been improved by working in a perchlorate medium. Anomalous effects were observed in the presence of relatively large amounts of titanium. Silicate samples are decomposed by RAFTER's peroxide sinter, the sinter cake leached with water, and the residue dissolved in acid. Thorium is collected on a calcium oxalate precipitate and determined photometrically in perchlorate medium at 660 mμ. The normal working range is 0 to 25 μg of thorium on a 0.5-g sample.

S. ABBEY,

Anal. Chim. Acta, 30 (1964) 176–187.

DETERMINATION OF CALCIUM, STRONTIUM AND BARIUM IN SINGLE CRYSTALS OF ALKALI HALIDES BY NEUTRON ACTIVATION

The determination by neutron activation of trace quantities of calcium, strontium and barium in single crystals of alkali halides has been studied. The matrix is eliminated before the irradiation by an ion-exchange procedure. Gamma spectroscopy after radiochemical separation is used to determine strontium and barium. Calcium is determined by measuring the β-activity of ^{49}Sc formed by the decay of ^{49}Ca. Long-lived radioactive tracers are used to determine the chemical yields.

F. GIRARDI AND R. PIETRA,

Anal. Chim. Acta, 30 (1964) 188–199.

THEORY OF TITRATION CURVES

IV. POINTS OF MINIMUM SLOPE ON POTENTIOMETRIC STRONG ACID–STRONG BASE AND PRECIPITATION TITRATION CURVES

Strong acid–strong base and precipitation titration curves, like other kinds of potentiometric titration curves, inherently possess an inflection point where the slope is a minimum as well as one where it is a maximum. In any kind of titration the first of the inflection points can be caused to occur earlier, and can eventually be made to disappear altogether, by adopting certain expedients. For a weak acid–strong base titration, for example, these include decreasing the concentration of the acid titrated and titrating in the presence of an excess of its conjugate base. For strong acid–strong base and precipitation titrations they include decreasing the concentration of the substance titrated and increasing the concentration of the titrant. The conditions under which a physically significant inflection point of minimum slope can exist are defined, and explicit equations are given from which its position can be calculated under various experimental conditions, for strong acid–strong base and for both isovalent and heterovalent precipitation titrations.

L. MEITES AND J. A. GOLDMAN,
Anal. Chim. Acta, 30 (1964) 200–208.

THE POLAROGRAPHIC BEHAVIOUR OF DIAZOACETOPHENONE

(Short Communication)

D. M. COOMBS AND L. L. LEVESON,
Anal. Chim. Acta, 30 (1964) 209–210.

PAPER CHROMATOGRAPHIC SEPARATION OF SOME LESS FAMILIAR TRANSITION METALS USING A SOLVENT CONTAINING CHLOROFORM

(Short Communication)

R. P. BHATNAGAR AND N. S. POONIA,
Anal. Chim. Acta, 30 (1964) 211–212.

THE DETERMINATION OF URANIUM IN THE PRESENCE OF PLUTONIUM BY CONTROLLED POTENTIAL COULOMETRY

APPLICATION TO THE ANALYSIS OF FUEL ELEMENT PROCESSING SOLUTIONS

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(Received July 2nd, 1963)

Controlled potential coulometry has become a well-established analytical technique in recent years and has found particular application in the determination of uranium and plutonium[1-3].

In the production of fuel element systems containing uranium and plutonium, the concentration of these elements in solutions at various stages of processing is required and controlled potential coulometry is applicable to this problem. In particular, there is a requirement for the determination of the ratio of plutonium to uranium in 2–4 M nitric acid solutions containing approximately 50 mg per ml of plutonium and 100 mg per ml of uranium. SHULTS[3] has described a controlled potential coulometric procedure for the accurate determination of plutonium in such systems and this paper is concerned with the development of a method for the coulometric determination of uranium.

EXPERIMENTAL

Controlled potential coulometer

Since the design of the original controlled potential coulometer by BOOMAN[4], a number of modifications have been made[5-7], and more recently, work has been directed towards the application of transistor circuits. PROPST[8] has described a transistorised power amplifier for a controlled potential coulometer and ROCKETT[9] has published full details of completely transistorised equipment designed at A.E.R.E. Harwell.

The apparatus used in the present work was designed and constructed at the Atomic Weapons Research Establishment and has functioned satisfactorily for a considerable time. The following is a brief description of the apparatus.

Potentiostat. This is a fully transistorised unit capable of controlling the working electrode potential to within ±2 mV in the range +2 to −2 V and is designed to work at a maximum current of 100 mA. The ripple voltage across the cell does not exceed 5 mV peak to peak. The circuit is arranged so that oxidation and reduction processes can be selected using a single switch, and electrolysis currents are indicated on a centre zero milliammeter showing oxidation on one side and reduction on the other. The output stages consist of two p–n–p, n–p–n transistors controlling the electrolysis current, and at very low currents a cross-over action is obtained whereby the uncontrollable minimum current I_{c_0} for either transistor is backed off automatically by current from the other, enabling the instrument to function down to zero background current.

Iu early designs of apparatus, difficulties arose due to transient currents produced at the start of the electrolysis. These are due to potential overshoot inherent in this type of servo system and have been eliminated by supplying the control transistors with a slowly increasing current, over a period of several seconds when the instrumedt is switched on. The output stages of the instrument are shown in Fig. 1. TR3 and TR4 are the control transistors and in the "Balance" and "Calibrate" positions positiions B and C in Fig. 1) are isolated by transistors TR1 and TR2. On switching to the "Run" position (position R in Fig. 1), TR1 and TR2 supply current to TR3 and TR4 at a slowly increasing rate as their base voltages increase by the charging of the 70 μF capacitors through the 100 K resistors. The DC amplifier has a gain of approximately 3000 and is of conventional design employing transistors. It is mounted on a heat sink to maintain stability of the reference potential at the input.

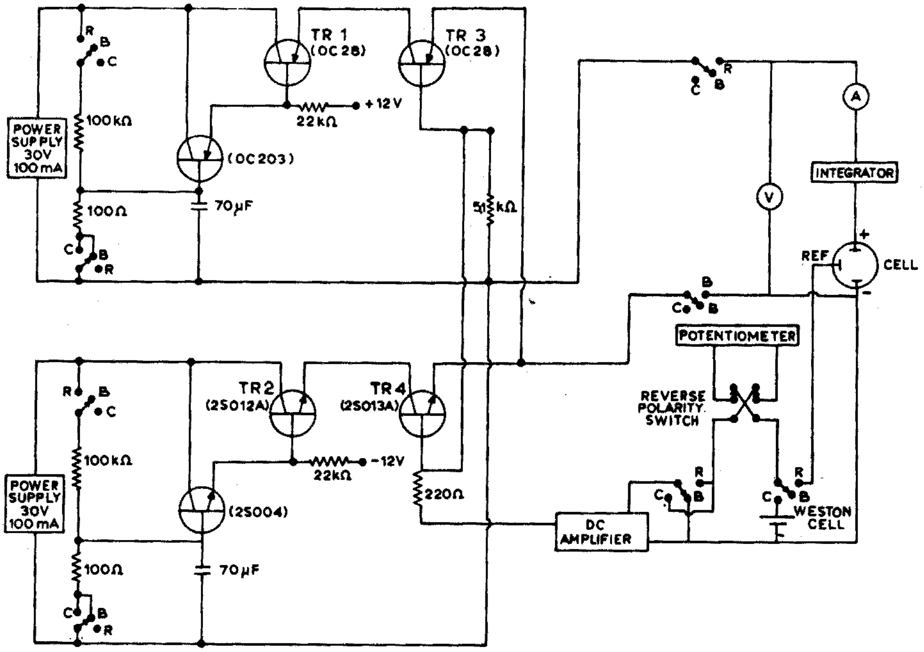

Fig. 1. Output stages of potentiostat.

Integrator. This is a "Miller" resistance–capacitance integrator incorporating a drift-corrected Solatron chopper amplifier (Type A900), high quality resistances and plastic condensers and has five working ranges of 0.1, 1, 10, 50 and 500 coulombs. The instrument is calibrated by means of a high precision constant current unit and timer and has been shown to have a precision of better than 0.05% on all ranges. The integrator output voltage is conveniently measured by means of a Solatron type 1010 digital voltmeter, and for routine operation one such voltmeter is used to determine the readout voltages for a number of coulometers using a suitable switching system.

Electrolysis cell. The cell consists of a flat bottomed glass vessel 35 mm internal diameter, 40 mm in height, and fitted with a polythene stopper. This supports two Corning 7930 Vycor unfired glass tubes, one of 1/8″ internal diameter containing a Ag/AgCl, saturated KCl reference electrode and the other of 1/4″ internal diameter containing a 16 SWG platinum wire anode immersed in 0.5 *M* sulphuric acid. In addition, there is a glass disc stirrer, a nitrogen inlet tube and a 5-mm glass tube containing a platinum wire sealed through the lower end and making electrical connection with the mercury cathode. The latter is used in preference to a platinum seal through the side of the cell, in order that a large number of interchangeable cells may be used and transference of solutions during determinations avoided.

Preliminary experiments

Since the coulometric determination of uranium necessitates a prior reduction of plutonium to plutonium(III), some consideration was given to the possible methods available for this.

Electrolytic methods appeared to be the most convenient and some preliminary experiments were carried out in which plutonium(IV) nitrate solutions were allowed to react with mercury in the electrolysis cell and the mercury(I) produced was then reduced electrolytically at a potential sufficiently positive to prevent reduction of uranium(VI). It was found that with electrolysing at +0.05 V the reduction was very slow and background currents obtained were too high to be satisfactory. In other experiments, specially designed electrolysis cells were used in which a platinum cathode could be used to reduce plutonium to plutonium(III) and this could then be covered with mercury for the subsequent determination of uranium. This technique was abandoned, however, because of difficulties in constructing cells of satisfactory geometry.

The application of chemical reductants was thus considered and ascorbic acid which reduces plutonium to plutonium(III) rapidly at room temperature was examined. It was found that, although the reduction of plutonium was rapid, the time required for the subsequent reduction of uranium(VI) was roughly doubled, presumably due to the effect of some oxidation product of ascorbic acid.

Hydrazine has been used as a reducing agent for plutonium in the polarographic determination of uranium in plutonium metal[10]. This reagent was shown to reduce 10 mg of plutonium to plutonium(III) in 0.5 *M* sulphuric acid by heating on a boiling water bath for 15 min, and uranium determinations could be made satisfactorily in the normal time. It was found convenient to carry out a pre-reduction at +0.05 V before the uranium determination in order to ensure that complete reduction of plutonium had been effected.

To determine the correct potential for reduction of uranium(VI) in this medium and the possible effects of nitric acid, half-wave potentials were determined polarographically for 100 μg U(VI) in a solution of 3 ml of saturated hydrazine sulphate and 4 ml of 1 *M* sulphuric acid in the presence of varying quantities of nitric acid. It was shown that for nitric acid concentrations below 4 *M*, $E_{\frac{1}{2}}$ was 0.245 V *vs.* S.C.E.

Reagents

Hydrazine sulphate. A saturated solution in 0.5 *M* sulphuric acid.

Mercury, trebly distilled. Rinse with 1:1 nitric acid and wash thoroughly with water. Store under 0.5 *M* sulphuric acid.

Nitrogen. Remove any oxygen present by passage through two washing bottles containing 0.5 *M* chromous chloride in 1 *M* hydrochloric acid kept over zinc amalgam.

Procedure

Introduce a suitable volume of the mixed plutonium–uranium solution (containing approximately 10 mg uranium) into a clean electrolysis cell using an "Agla" micro-syringe pipette, add 3 ml of saturated hydrazine sulphate solution and place in a boiling water bath for 30 min. Add 4 ml of 0.5 *M* sulphuric acid and 7 ml of mercury, attach the cell to the electrode assembly, ensuring that the glass disc stirrer is positioned correctly at the mercury–solution interface and start the stirrer motor and nitrogen flow. Pass nitrogen through the solution for 5 min and then electrolyse at $+0.05$ V until a background current of less than 30 μA is obtained. Zero the integrator, reset the cathode voltage to -0.35 V and repeat the electrolysis until background current is again reached; record the duration of the electrolysis, the background current and integrator readout voltage. Correct the total readout voltage for background current and integrator drift and subtract the reagent blank, corrected in the same way. Determine the concentration of uranium using the integrator calibration factor obtained by electrical calibration.

RESULTS

The precision of the procedure in the absence of plutonium was first established, using 10 mg of uranium for each determination. A standard deviation of 0.09% was obtained for 10 results.

Further determinations in the presence of 5 mg of plutonium(IV) dispensed from a solution containing 2–5 mg per ml in 4 *M* nitric acid gave the results shown in Table I.

TABLE I

DETERMINATION OF URANIUM IN THE PRESENCE OF PLUTONIUM

Determination	*Uranium taken (mg)*	*Uranium found (mg)*	*% Recovery of uranium*
1	9.001	9.012	100.12
2	10.892	10.873	99.83
3	9.017	9.043	100.29
4	8.656	8.648	99.90
5	8.438	8.470	100.38
6	10.197	10.173	99.77
7	8.851	8.852	100.01
8	10.332	10.322	99.90
9[a]	11.221	11.221	100.00
10[a]	13.761	13.790	100.21
			Mean = 100.04 σ = 0.20%

[a] Results 9 and 10 were obtained in the presence of 10 mg of Fe(III).

CONCLUSIONS

The procedure described for the coulometric determination of uranium in the presence of plutonium has been shown to give satisfactory results. Although the precision obtained is slightly less than that in the absence of plutonium, it is entirely adequate for the analysis of fuel element processing solutions. Under routine operating conditions, the precision has been maintained and a complete determination can be made in 30 min. It has also been shown that moderate quantities of iron do not interfere with the procedure.

We wish to thank Mr. C. FOSTER for carrying out some of the experiments.

SUMMARY

A controlled potential coulometric method is described for the determination of uranium in the presence of plutonium and iron based on the reduction of uranium(VI) to uranium(IV) at a mercury cathode, after reduction of plutonium to plutonium(III) with hydrazine. The application of this procedure to the analysis of fuel element processing solutions in nitric acid is discussed and a precision of 0.2% has been obtained. A brief description of the controlled potential coulometer is given.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'uranium, en présence de plutonium et de fer, par coulométrie à potentiel contrôlé. Elle est basée sur la réduction de l'uranium(VI) en uranium(IV), à la cathode de mercure, après réduction du plutonium en plutonium(III) au moyen d'hydrazine. Cette méthode peut s'appliquer à l'analyse de "fuels". Une brève description du coulomètre à potentiel contrôlé est donnée.

ZUSAMMENFASSUNG

Zur Bestimmung von Uran in Gegenwart von Plutonium und Eisen wird eine coulometrische Methode mit kontrolliertem Potential beschrieben. Sie beruht auf der Reduktion des Uran(VI) zum Uran(IV) an einer Quecksilberkathode, nach Reduktion des Plutoniums mit Hydrazin zum Plutonium(III). Die Anwendung dieses Verfahrens zur Analyse von Brennstoffelementen und das benutzte Coulometer werden beschrieben.

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THE INFLUENCE OF SOME MASKING AGENTS ON THE SOLVENT EXTRACTION OF ZINC OXINATE

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(Received June 17th, 1963)

Oxine, one of the most widely employed chelating reagents, has been used for the solvent extraction of many metals. Surveys of much of this work have been provided by MORRISON AND FREISER[1]. In a recent work, STARY[2] has extracted 32 metals into chloroform containing oxine. He has varied the oxine concentration and has introduced several masking agents into the aqueous phase. UMLAND[3] has also made a recent report in which he describes the solvent extraction of 37 metal oxinates into chloroform. He has investigated the effects of added alcohols and amines on the extractions, and has determined the stoichiometries of metal-containing species separated from these systems. All of these works report studies on zinc. The purpose of this present investigation has been to expand the work on the influence of various masking agents on the extraction of zinc from aqueous solutions into chloroform containing oxine.

THEORETICAL BACKGROUND

An equation that has been found quite useful in describing solvent extractions of chelates from aqueous solutions containing masking agents[4] may be written for zinc oxinate extractions as follows:

$$D = E/(100 - E) = K_cP_c(\mathrm{HR})_o^{2+a}/K_r^2P_r^{2+a}(\mathrm{H})^2Q = K(\mathrm{HR})_o^{2+a}/(\mathrm{H})^2Q \qquad (1)$$

In this relationship, D is the organic/aqueous distribution ratio of the total metal concentration, E is the percent of the metal extracted from the aqueous into the organic phase when equal phase volumes are used, K_c is the stability constant of the extracting species $\mathrm{ZnR_2(HR)}_a$, P_c is the organic/aqueous distribution constant of this species, $(\mathrm{HR})_o$ is the equilibrium concentration of oxine in the organic phase, K_r is the acid association constant of the oxine, P_r is the organic/aqueous distribution constant of the oxine, (H) is the equilibrium activity of the hydrogen ion in the aqueous phase, Q is a term known as the complexing term, and K is equal to $K_cP_c/K_r^2P_r^{2+a}$. The term Q is intended to account for water-soluble complexes formed in the aqueous phase by hydroxide ion, oxinate ion, and masking agent ions. It may be written

$$Q = 1 + \sum_0^h \sum_0^r \sum_0^x K_{hrx}(\mathrm{OH})^h(\mathrm{R})^r(\mathrm{X})^x \qquad (2)$$

The letters h r x refer to the number of hydroxide, oxinate, and masking agent ions complexed with the zinc in the aqueous phase, and K_{hrx} signifis the appropriatee cumulative association constants. Since the masking agent ion is often the anion of a weak acid, its concentration has to be calculated from a relationship of the following type:

$$X = \frac{[\mathrm{X}]}{1 + K_a(\mathrm{H}) + K_b(\mathrm{H})^2 + K_c(\mathrm{H})^3 + K_d(\mathrm{H})^4} \qquad (3)$$

In the equation, [X] represents the total concentration of the masking agent in the system regardless of its precise forms, and K_a, K_b, K_c, and K_d indicate the cumulative acid association constants of the masking agent acid.

PROCEDURES

In each experiment, 10 ml of aqueous phase was stirred with 10 ml of chloroform phase for 4 h at 30.0 ± 0.5°. The aqueous phase had been pre-saturated with chloroform, contained 10^{-6} M zinc as the perchlorate, was labelled with zinc-65, made up to a desired concentration in masking agent, and was brought to an ionic strength of 0.1 with sodium perchlorate if necessary. The organic phase had been pre-saturated with 0.1 M sodium perchlorate solution, and was made up to a desired concentration in oxine. After the 4-h equilibration, which had been demonstrated to provide equilibrium conditions, the phases were sampled, their radioactivities determined, and E values were calculated. Doubly distilled water was used throughout, redistilled chloroform was employed, and all chemicals were reagent grade. Measurements of pH were conducted with a Beckman Model H2 pH Meter equipped with a Beckman 41252 Glass Electrode and a Beckman 41239 Calomel Reference Electrode.

RESULTS

The experimental results are provided in Table I. The first column gives the system number; the second and third columns define the system; the fourth column reports the data, the pH value in each instance followed by the E value in parentheses; in the fourth column there is a star by the $\mathrm{pH}_{1/2}$ value, this value being defined as the pH at which E equals 50 or D equals 1; and the fifth column indicates the instantaneous slope of the curve at the $\mathrm{pH}_{1/2}$ value.

TREATMENT OF DATA

Systems 1–4 report the data obtained with four concentrations of HR and in the absence of any masking agent. The best fit of the data is found when one assumes a to be equal to unity (that is, $ZnR_2(HR)$ to be the extracting species) and when one assumes Zn^{2+} to be the predominant aqueous species in the region of pH 3.0, ZnR_2 in the region of pH 6.0, and $ZnR(OH)_2^-$ in the region of pH 10.0. It is probable that the sixth coordination position in the extracting species is filled by water. STARY[2] states that the extracting species is $ZnR_2(HR)_2$, but it appears that he decides on the basis of only two HR concentrations, 0.1 and 0.01 M. As can be seen in this work, the curve at 0.01 M is not regular, whereas those at 0.6, 0.1 and 0.06 are. This would seem to make a stoichiometry determination on the basis of the 0.01 M curve questionable, since obviously effects are present which are not of import in the other cases. UMLAND[3]

TABLE I

EXPERIMENTAL DATA

System[a]	*log (HR)*$_o$	*Aqueous phase*[b]	*Data* ($pH_{1/2}$ *starred*)[c]	*Instantaneous slope at* $pH_{1/2}$	*Calculated* $pH_{1/2}$
1	−0.2	10^{-1} *M* $NaClO_4$	pH (*E*), 1.5 (1), 2.3* (50), 2.5 (70), 3.4 (94), 4.3 (97), 4.8 (99), 5.2 (99), 9.1 (99), 9.6 (98)	120	2.3
2	−1.0		2.0 (1), 2.3 (1), 2.6 (2), 2.7 (8), 3.3 (28), 3.5* (50), 3.8 (68), 4.0 (82), 4.7 (96), 5.0 (98), 5.2 (99), 5.3 (99), 6.4 (99), 6.5 (99), 7.1 (99), 7.9 (99), 9.3 (95), 9.9 (75), 10.7 (21)	120	3.5
3	−1.2		2.7 (1), 3.1 (4), 3.4 (19), 3.6 (21), 3.8 (35), 4.1* (50), 4.3 (67), 4.8 (97), 5.7 (98), 5.8 (99), 8.0 (97), 8.4 (94), 9.2 (88), 9.4 (80)		
4	−2.0		3.5 (1), 4.6 (25), 5.6* (50), 6.6 (75), 7.8 (82), 8.6 (57), 9.3 (2)	30	5.0
5		10^{-1} *M* NaBr	3.4 (8), 4.2* (50), 4.3 (56), 4.8 (75), 5.3 (89), 5.7 (95), 6.6 (98)	60	3.5
6		10^{-1} *M* NaCl	2.8 (3), 3.7 (19), 4.0 (28), 4.1* (50), 4.5 (69), 5.3 (97)	80	3.5
7		10^{-1} *M* KSCN	2.7 (2), 3.0 (11), 3.3 (21), 3.6 (40), 3.7* (50), 3.8 (55), 4.2 (77), 5.0 (91), 6.0 (96)	90	3.8
8		10^{-1} *M* $Na_2S_2O_3$[d]	3.4 (1), 3.8 (3), 5.0 (9), 4.4 (17), 4.6 (33), 4.9* (50), 5.3 (69), 5.6 (80), 6.4 (91), 7.6 (97)	50	4.8
9		10^{-4} *M* EDTA	No extraction below pH 11.0, 11.2 (3), 11.5 (10)	—	9.6
10		10^{-1} *M* Glycine	2.7 (4), 3.4 (14), 3.8 (41), 3.9* (50), 4.0 (74), 5.0 (95)	80	3.5
11	−1.0	10^{-1} *M* Malonate	2.8 (3), 3.5 (16), 3.9 (36), 4.1 (35), 4.3* (50), 4.5 (55), 4.8 (65), 5.0 (72), 5.3 (80), 5.6 (89)	30	4.2
12		10^{-1} *M* Glycollate	3.4 (4), 3.7 (10), 4.3 (34), 4.5* (50), 4.6 (57), 4.8 (64), 6.9 (94)	110	4.0
13		10^{-4} *M* NTA	3.3 (4), 3.7 (10), 4.0 (15), 4.7 (22), 4.9 (42), 5.0* (50), 5.5 (68), 7.2 (95)	30	4.5
14		10^{-3} *M* NTA	3.6 (1), 3.9 (1), 4.3 (3), 4.8 (6), 5.1 (10), 5.5 (15), 5.9 (23), 6.7 (43), 7.1 (48), 7.3* (50), 7.6 (51), 9.0 (52), 10.9 (16)	10	6.2
15		10^{-2} *M* NTA	5.0 (2), 5.9 (2), 6.3 (6), 7.0 (9), 7.6 (10), 8.2 (10), 8.6 (12), 8.9 (13), 9.2 (15), 9.5 (15), 9.8 (22)	—	8.3
16		10^{-1} *M* NTA	No extraction below pH 11.5	—	9.3

TABLE I (continued)

System[a]	*log (HR)*$_o$	*Aqueous phase*[b]	*Data (pH*$_{1/2}$ *starred)*[c]	*Instantaneous slope at pH*$_{1/2}$	*Calculated pH*$_{1/2}$
17		10^{-4} *M* Citrate	3.2 (5), 3.6 (25), 3.7* (50), 3.8 (64), 5.1 (97), 7.2 (97)	120	3.5
18		10^{-3} *M* Citrate	2.9 (7), 3.4 (20), 3.7* (50), 4.0 (66), 4.5 (80), 5.1 (90), 5.6 (95), 5.9 (95), 6.7 (96), 7.2 (97), 7.4 (97)	50	3.5
19		10^{-2} *M* Citrate	3.9 (19), 4.4 (27), 4.9 (35), 5.5* (50), 5.6 (52), 6.0 (75), 6.7 (92), 7.0 (95), 7.3 (95), 7.6 (95), 7.8 (95), 8.0 (94), 9.6 (78), 10.2 (61)	30	3.5
20		10^{-1} *M* Citrate	5.2 (8), 5.6 (9), 6.0 (11), 7.0 (43), 7.5 (90), 8.0 (94), 8.5 (95)	80	3.9

[a] All systems are $2 \cdot 10^{-6}$ *M* in $Zn(ClO_4)_2$.
[b] Made up to an ionic strength of 0.1 *M* with $NaClO_4$ where necessary.
[c] Error: ± 0.1 pH unit.
[d] Reagent tends to decompose.

TABLE II

LOGARITHMS OF CONSTANTS

Reagent	*Constants (values)*	*Reference*
Hydroxide	$K_{100}(4.4)$, $K_{300}(14.4)$, $K_{400}(15.4)$	6
Chloride	$K_{001}(-0.3)$, $K_{002}(0.0)$, $K_{003}(-0.3)$, $K_{004}(-0.1)$	5
Bromide	$K_{001}(-0.6)$, $K_{002}(-1.0)$, $K_{003}(-1.7)$, $K_{004}(-1.3)$	5
Thiocyanate	$K_{001}(1.7)$	5
Thiosulfate	$K_{001}(2.4)$, $K_{002}(4.6)$	5
Citrate	$K_{001}(10.7)$, $K_a(16.0)$, $K_b(21.9)$, $K_c(26.1)$, $K_d(29.0)$	7
Glycollate	$K_{001}(1.9)$, $K_a(3.7)$	5
Glycinate	$K_{001}(5.3)$, $K_{002}(9.7)$, $K_a(9.8)$	5
Malonate	$K_{001}(3.3)$, $K_a(5.2)$, $K_b(7.9)$	5
Nitrilotriacetate	$K_{001}(10.7)$, $K_{002}(13.5)$, $K_a(9.7)$, $K_b(12.2)$, $K_c(14.1)$	5
Ethylenediamine-tetraacetate	$K_{001}(16.5)$, $K_a(10.3)$, $K_b(16.4)$, $K_c(19.1)$, $K_d(21.1)$	5

reports that in the presence of certain amines, a species corresponding to $ZnR_2(RNH_2)(H_2O)$ can be isolated from the organic phase. This bears some similarity to the extracting species assumed in this study.

With the assumptions of the species as indicated above, the value of log *K* may be calculated from systems 1–3 and eqn. (1) to be −4.0. The values of the calculated pH$_{1/2}$, for systems 1–4, as reported in column six of Table I, are ascertained by using this value of log *K*, by setting *D* equal to one, and by setting *Q* equal to one in eqn. (1). Agreement appears to be good, except in the case of system 4 where the slope is also irregular.

To attempt to provide calculated pH$_{1/2}$ values for the masked systems, a number of constants are needed for substitution into eqns. (2) and (3) so that *Q* can be determined for substitution into eqn. (1). A number of available constants are indicated in Table

II. The subscripts of the constants with three subscripts correspond to the proper values of h, r and x. As can be seen, the experimental and the theoretical values in systems 7, 8, 10, 11, 12, 13, 14, 17 and 18 agree fairly well (within 0.5). However, it is important to realize that agreement in some cases may not constitute unequivocal evidence of the precise character of the system. There is less agreement in systems 5, 6, 9, 15, 16, 19 and 20. Included among these are systems involving relatively high concentrations of the masking reagent (15, 16, 19, 20) and systems involving polydentate masking reagents (9, 15, 16, 19, 20). The lack of constants for some other possible complexes in several of these cases may account for the failure to calculate the $\mathrm{pH}_{1/2}$ values. Another complicating factor concerns the hydrolysis of the zinc ion. Although the values given[5] for log K_{100} range from 3.8 to 5.8, DYRSSEN AND SEKINE[8] have recently concluded that the value should be around 9.5 based on some solvent extraction experiments they have carried out. If they are correct, then the situations involved in systems 4, 5, 6 and 10 might become clearer. Finally, it is generally recognized that ionic strength effects on the association constants of several zinc complexes are rather large[9]. These effects may be operating in some of the systems (5, 6).

SUMMARY

An investigation of the extraction of radio-labelled 10^{-6} M zinc from various aqueous solutions into chloroform containing oxine has been carried out. The effects of pH value, oxine concentration, and 10 aqueous masking agents have been studied. The experimental results have been compared with theoretically calculated values, allowing some conclusions with regard to the participating species to be drawn.

ZUSAMMENFASSUNG

Es wurden Versuche zur Extraktion von radioaktiv markiertem Zink (10^{-6} M) aus wässrigen Lösungen mit in Chloroform gelöstem Oxin durchgeführt. Dabei wurde der Einfluss des pH-Wertes, der Oxin-Konzentration und einer Anzahl maskierender Reagenzien geprüft. Ein Vergleich der experimentellen Ergebnisse mit theoretisch berechneten Werten erlaubte Folgerungen über den Mechanismus der Reaktion.

RÉSUMÉ

Une recherche a été effectuée sur l'extraction du zinc marqué (10^{-6} M), en solutions aqueuses diverses, au moyen de chloroforme renfermant de l'oxine. Les auteurs ont examiné l'influence du pH, de la concentration en oxine et de dix agents de masquage. Les résultats expérimentaux ont été comparés avec les valeurs calculées théoriques, permettant ainsi quelques conclusions au sujet du mécanisme des réactions.

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THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

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Thallium(I) extractions

Very little detailed attention has been paid to the solvent extraction of chelates of the thallium(I) ion. Some reagents which have been employed in such extractions include thenoyltrifluoroacetone, diphenylthiocarbazone, sodium diethyldithiocarbamate, mercaptobenzothiazole, and thiosalicylideneethylenediimine[1].

The purpose of this study was to conduct an exploratory investigation of the potential of a number of types of reagent for use in extracting thallium(I). Based on a chart presented by MORRISON AND FREISER[2], 14 reagents having different chelate ring size possibilities and different bonding atoms were selected. Bi-, tri-, and tetradentate reagents were included; 4-, 5-, and 6-membered chelate ring possibilities were included; and oxygen, nitrogen, and sulfur as bonding atoms were included.

Theoretical considerations

In the extraction of the thallium(I) ion from aqueous solutions containing the noncomplexing perchlorate ion into chloroform containing a chelating reagent HR, two variables are of great importance. These are the pH and the concentration of the HR in the organic phase $[\mathrm{HR}]_o$. When proper experiments are run, the distribution coefficient of the thallium(I), D, can be measured as a function of pH at constant $[\mathrm{HR}]_o$, and as a function of $[\mathrm{HR}]_o$ at constant pH. The data are then plotted in terms of curves of log D against pH and log D against $[\mathrm{HR}]_o$. These curves usually show regions of constant slope and regions of changing slope. The regions of constant slope generally describe conditions in which one species predominates in each phase. The D value in such regions may be approximated by

$$D = [\mathrm{MR(HR)_a}]_o/[\mathrm{MR_r(OH)_h}] \qquad (1)$$

where the subscript "o" indicates the organic phase and the unsubscripted brackets refer to the aqueous phase. By proper substitution of constants, this equation may be made to read

$$\begin{aligned} D &= K_c P_c [\mathrm{HR}]_o{}^{1-r+a}/K_r{}^{1-r} P_r{}^{1-r+a} K_t K_w{}^h [\mathrm{H}]^{1-r-h} \\ &= K[\mathrm{HR}]_o{}^{1-r+a}/[\mathrm{H}]^{1-r-h} \qquad (2) \end{aligned}$$

where K_c is the association constant of the $\mathrm{MR(HR)_a}$, P_c is the organic–aqueous distribution constant of the $\mathrm{MR(HR)_a}$, K_r is the acid association constant of the HR, P_r

is the organic–aqueous distribution constant of the HR, K_t is the association constant of $MR_r(OH)_h$, K_w is the ion product of water, and K is $K_cP_c/K_r^{1-r}P_r^{1-r+a}\,K_tK_w^h$.

In regions of changing slope the D value may be represented by the sum of several terms of the type of (1), or $1/D$ may be represented by the sum of several terms of the form of reciprocals of (1). These expressions may then be transformed into equations containing terms of the type of (2). The two variables in eqn. (2), namely $[HR]_o$ and $[H]$, lead to the possibility of analyzing extraction data as set out in plots of log D against log $[HR]_o$ and log D against pH. By observation of the slopes and by curve fitting, the various constants in eqn. (2), particularly K_c, P_c, K_t, r, a, and h, may often be estimated.

EXPERIMENTAL

Thallium-204 in nitric acid, as obtained from the Oak Ridge National Laboratory, was converted to the perchlorate by successive evaporations with perchloric acid. From this a stock solution was prepared. All chelating reagents and other chemicals were either reagent grade or were purified by recrystallization procedures. Water and chloroform were purified by double distillation.

Ten-ml portions of the aqueous phase were stirred with 10-ml portions of the chloroform phase in each experiment for 3 h at 30.0° ± 0.5°. In all cases the original thallium concentration in the aqueous phase was $10^{-6.0}$ M and the aqueous phase was $10^{-1.0}$ M in sodium perchlorate. The pH was adjusted by addition of sodium hydroxide and perchloric acid solutions, and pH measurements were made on a Beckman Model H pH Meter equipped with a Beckman Combination Electrode. The instrument was frequently calibrated with Coleman buffers at pH values of 2.0, 4.0, 7.0, 9.0, and 11.0. Calibrations at pH values of 1.0 and 13.0 were done with 0.1 N perchloric acid and 0.1 N sodium hydroxide solutions.

After equilibration, pH values were measured, and 100-μl samples taken from each phase. These samples were placed on planchets, dried, and counted with a Tracerlab Beta Scintillation Counter.

For several reagents, determinations of P_r and K_r values had to be made, since no such data were available in the literature. Ten ml of the reagent at a known concentration in chloroform was placed in each of 12 to 20 bottles. To each bottle was added 10 ml of $10^{-1.0}$ M sodium perchlorate solution, the pH of which had been adjusted to a predetermined value, ranging from 1.0 to 13.0. After stirring to equilibrium at 30.0° ± 0.5°, the two phases were sampled, and the percentage reagent in each was determined spectrophotometrically. The per cent reagent in the organic phase E was plotted against pH.

From this plot, the pH of maximum extraction into the organic phase was selected. Thirty ml of the organic phase containing the known concentration of HR was equilibrated with 1 l of $10^{-1.0}$ M sodium perchlorate solution at this pH. The phases were then separated and the organic phase was sampled to determine the amount of reagent present. The aqueous phase was then equilibrated with 30 ml of pure chloroform, the phases separated, and the amount in the organic phase was again determined. Using the equation of SCHWEITZER AND MOTTERN[3], the P_r value was determined. The distribution of the reagent, d, can be calculated from the relation $d = E/(100—E)$, and this can be related to the expression $d = K_rP_r\,[H]/(1 + K_r\,[H])$. This allowed K_r to be calculated.

In some systems, the value of P_c was quite large. In these instances, larger volumes of the aqueous phase were employed to allow more accurate determination of the distributions.

RESULTS AND DISCUSSION

The results of the numerous experiments are presented in Table I. In system 1 (diethyldithiocarbamate), the curve rises with a slope of one (pH 4.0 to 9.0 approximately), levels off to a slope of zero (pH 9.5 to 11.5), and then falls with a slope of minus one (pH 11.5 to 12.5). The pH at which log D equals zero, known as the pH′, is

TABLE I

EXPERIMENTAL RESULTS

System[a]	*Data*
1. 10^{-1} M sodium diethyldithiocarbamate	pH(log D), 5.2(−2.87), 6.1(−1.60), 7.2(−0.46), 8.1(0.79), 8.9(1.81), 9.7(2.44), 10.1(2.53), 10.5(2.49), 11.5(2.48), 12.1(1.82), 12.6(1.31)
2. 10^{-2} M potassium xanthate	pH(log D), 3.1(−2.79), 4.0(−1.63), 4.6(−1.16), 5.2(−0.53), 6.3(0.61), 6.9(0.78), 7.4(0.86), 7.7(0.87), 8.3(0.88), 8.5(0.87), 10.0(0.86), 11.5(0.72), 12.1(0.15)
3. 10^{-3} M potassium xanthate	pH(log D), 4.1(−2.73), 5.0(−1.85), 5.5(−1.14), 6.1(−0.71), 6.7(−0.17), 7.5(0.74), 7.8(0.87), 8.7(0.88), 9.8(0.84), 11.0(0.86), 11.5(0.86), 11.7(0.87), 12.1(0.86)
4. 10^{-2} M mercaptobenzothiazole	pH(log D), 3.8(−4.22), 5.2(−2.71), 6.4(−1.35), 6.9(−0.89), 7.2(−0.80), 7.4(−0.49), 7.7(−0.29), 8.0(−0.12), 8.7(0.03), 9.6(0.00), 10.1(0.01), 11.0(−0.01)
5. 10^{-1} M 8-hydroxyquinoline	pH(log D), 7.5(−2.85), 8.0(−2.34), 8.5(−1.89), 9.1(−1.31), 9.2(−1.22), 9.8(−0.72), 10.0(−0.53), 10.2(−0.39), 10.3(−0.25), 10.5(−0.17), 10.8(−0.13), 11.2(0.00), 11.4(0.06), 11.7(0.05), 12.4(−0.05)
6. 10^{-1} M benzoylphenylhydroxylamine	pH(log D), 5.8(−2.47), 6.7(−1.64), 7.1(−1.18), 7.6(−0.70), 8.3(−0.01), 8.4(0.16), 8.8(0.65), 9.3(0.99), 9.8(1.18), 10.1(1.22), 10.4(1.21), 10.8(1.19), 11.2(1.21), 11.6(1.20), 11.9(1.00), 12.2(0.78)
7. 10^{-2} M benzoylphenylhydroxylamine	pH(log D), 5.5(−3.66), 7.0(−2.21), 8.2(−1.13), 9.2(−0.09), 9.5(0.12), 9.8(0.49), 10.6(1.17), 10.8(1.21), 11.0(1.20), 11.8(1.20), 12.0(1.19), 12.1(1.21)

TABLE I (continued)

System[a]	*Data*
8. 10^{-2} *M* diphenylthiocarbazone	pH(log *D*), 3.5(−2.30), 4.9(−0.77), 5.8(0.08), 6.3(0.51), 7.0(1.27), 7.5(1.78), 7.9(2.20), 8.2(2.37), 8.4(2.61), 8.8(2.52), 9.1(2.96), 9.7(3.25), 10.9(3.32)
9. 10^{-3} *M* diphenylthiocarbazone	pH(log *D*), 3.7(−3.14), 4.5(−2.36), 5.4(−1.48), 6.9(0.04), 7.5(0.76), 7.8(0.98), 8.0(1.18), 8.8(1.96), 9.2(2.35), 10.0(3.00), 10.6(3.15), 11.7(3.14), 11.9(3.18)
10. 10^{-1} *M* cupferron	pH(log *D*), reagent decomposed in acid region, 7.8(−0.02), 8.2(−0.05), 8.5(−0.04), 8.6(−0.03), 9.0(−0.03), 9.4(−0.04), 10.0(−0.03), 10.7(−0.04), 11.1(−0.05), 11.4(−0.05)
11. 10^{-2} *M* thionalide	No extraction; precipitate formed at interface
12. 10^{-2} *M* thenoyltrifluoroacetone	pH(log *D*), 3.0(−3.16), 4.0(−2.49), 5.4(−1.69), 5.7(−1.78), 6.5(−1.38), 8.0(−0.57), 8.9(−0.31), 10.1(−0.41), 11.5(−1.48)
13. 10^{-2} *M* acetylacetone	pH(log *D*), 6.9(−3.47), 7.9(−2.87), 8.2(−2.74), 9.1(−2.24), 9.7(−2.10), 10.6(−1.66), 11.0(−1.57), 11.4(−1.53), 11.7(−1.55), 12.1(−1.54), 12.8(−1.50)
14. 10^{-2} *M* salicylaldoxime	pH(log *D*), 7.9(−3.70), 8.7(−3.38), 9.2(−2.93), 10.0(−2.90), 11.1(−2.40), 11.8(−2.00), 12.2(−1.85)
15. 10^{-2} *M* 2-nitroso-1-naphthol	pH(log *D*), 2.5(−2.22), 2.7(−1.64), 3.7(−0.97), 4.2(−0.85), 4.9(−0.22), 6.5(0.45), 7.4(0.58), 8.7(1.02), 9.8(1.26), 11.0(1.41), 11.3(1.14), 12.1(0.54)
16. 10^{-2} *M* 1-nitroso-2-naphthol	pH(log *D*), 5.1(−3.02), 5.8(−2.31), 6.7(−1.80), 6.9(−1.79), 7.1(−1.55), 7.7(−1.29), 7.8(−1.26), 8.6(−1.09), 9.7(−0.94), 10.8(−0.88), 11.9(−0.76), 12.0(−0.74)
17. 10^{-2} *M* 1-(2-pyridylazo)-2-naphthol	pH(log *D*), 9.6(−3.09), 9.9(−2.68), 10.3(−2.37), 10.7(−1.98), 11.2(−1.48), 11.9(−0.79), 12.1(−0.58), 12.7(0.05)
18. 10^{-3} *M* glyoxalbis (*o*-hydroxyanil)	No extraction between pH 2.0 and 12.3 gave a log *D* greater than −1.70.

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[a] In all systems the original aqueous phase was $10^{-6.0}$ *M* in thallium and 0.1 *M* in sodium perchlorate.

7.5, and the log P_c was determined to be 2.5. In this system the reagent exists almost completely in the aqueous phase, its P_r being very low, and its log K_r value is reported to be 4.0 (ref. 4). Equation (2) would take the following form in such an instance:

$$\begin{aligned} D &= K_c P_c [\mathrm{HR}]^{1-r+a} / K_r{}^{1-r} K_t K_w{}^h [\mathrm{H}]^{1-r-h} \\ &= K[\mathrm{HR}]^{1-r+a}/[\mathrm{H}]^{1-r-h} \end{aligned} \tag{3}$$

Therefore 1−r−h would be equal to 1, 0, and −1 in the 3 constant-slope portions of the curve. Since the association constant for the monohydroxothallium(I) species has a logarithm of less than 1 (ref. 5), it can be assumed that h = 0. Hence the extracting species in all three regions is probably $\mathrm{TlR(HR)_a}$, and the predominant aqueous species are successively $\mathrm{Tl^+}$, TlR, and $\mathrm{TlR_2^-}$. These yield the proper slopes, but the HR concentration dependence would be necessary to determine a.

In systems 2 and 3 (xanthate), the curves go through successive constant slopes of 1, 0, and −1. The pH′ values are 5.7 for the 10^{-2} *M* system and 6.7 for the 10^{-3} *M* system. The HR concentration dependence indicates that 1−r+a has values of 1, 0, and −1 in regions where the pH is around 5.0, 9.0, and 12.0. The xanthate, like the diethyldithiocarbamate, has a very small P_r. The logarithm of P_c for the extracting compound is seen to be 0.9. The extracting species under all conditions is thus TlR, and the predominating aqueous species are successively as the pH rises $\mathrm{Tl^+}$, TlR, and $\mathrm{TlR_2^-}$. The logarithm of K_r is reported to be 1.5 (ref. 6), but this value will not allow a theoretical interpretation of the data.

In system 4 (mercaptobenzothiazole), the curve indicates that 1−r−h takes a value of one (pH 3.0 to 7.0) or zero (pH 8.5 to 11.0). The log P_c is 0.0. For this reagent, log P_r is 2.2 and log K_r is 7.8 (ref. 7). The probable extracting species is $\mathrm{TlR(HR)_a}$ and the involved aqueous species are $\mathrm{Tl^+}$ (at slope of one) and TlR (at slope of zero). Assuming a = 0, log K_c is 4.2, and log K calculates to be −5.8. In system 5 (oxine), the curve indicates again that 1−r−h takes a value of one (pH 7.0 to 10.0) or zero (pH 11.0 to 12.5). The log P_c is 0.0, and for oxine log P_r is 2.6 and log K_r is 9.7 (ref. 7). The probable extracting species is $\mathrm{TlR(HR)_a}$ and the involved aqueous species are $\mathrm{Tl^+}$ and TlR. Assuming a = 0, log K_c is 2.8, and log K is −9.5.

In systems 6 and 7 (benzoylphenylhydroxylamine), a situation quite similar to that of the xanthate systems (2 and 3) is seen. The pH′ values are 8.3 for the 10^{-1} *M* system and 9.3 for the 10^{-2} *M* system. The values of 1−r−h go from one to zero to minus one, and the values of 1−r+a in the corresponding pH regions are 1, 0, and −1. The extracting species is thus TlR and the aqueous species are $\mathrm{Tl^+}$, TlR, and $\mathrm{TlR_2^-}$ as the pH rises. Knowing log P_r to be 2.3 and log K_r to be 8.5 (ref. 8), and reading log P_c as 1.2, log K_c calculates to be 2.3, and log K is −7.3. In systems 8 and 9 (diphenylthiocarbazone), both curves rise with a slope of one, then level off to a slope of zero; hence 1−r−h has values of 1 and 0. Analysis of the curves with regard to HR concentration dependence leads to the observation that 1−r+a is one on the rising portions of the curves and is about 0.2 on the zero-sloped portions. This implies that the main extracting species is probably TlR with some TlR(HR) forming and extracting at the higher HR concentration. The main aqueous species are $\mathrm{Tl^+}$ and TlR. Neglecting the small difference in zero-sloped portions, K_c for TlR can be estimated by using log P_r to be 5.1, log K_r to be 5.7 (ref. 9), and reading log P_c as 3.1. The log of K_c turns out to be about 3.9, and K calculates to have a logarithm of −3.8.

System 10 (cupferron) was difficult to work with since the reagent decomposed in the acid range. From pH 7.0 to 11.5 consistent values could be obtained. These values indicate a log P_c of about 0.0. A few indications were given that the curve rises with a slope of one from a log D value of -3.00 around a pH of 2.0 to a log D of about -0.50 around a pH of 4.5. This would make it comparable to system 5 in its general behavior. The behavior in system 11 (thionalide) apparently reflects an insolubility of some compound, probably TlR, in both phases. The data in system 12 (thenoyltrifluoroacetone) were somewhat irregular, showing only one region of constant slope, that region being from pH 4.0 to 9.0 with a slope of about 0.5. The results did not lend themselves readily to theoretical interpretation. System 13 (acetylacetone) showed a slope of about 0.5 from pH 7.0 to 10.5, then a slope of zero from pH 11.0 to 12.5. The P_c value is quite low, its logarithm being -1.5. System 14 (salicylaldoxime) evidenced a slope of 0.5 from pH 8.0 to 12.2, while system 15 (2-nitroso-1-naphthol) gave a slope of about 0.5 from pH 4.0 to 10.0 and a slope of minus one from pH 11.0 to 12.0.

System 16 (1-nitroso-2-naphthol) rose with a slope of one from pH 5.0 to 7.0, then levelled off with a slope of zero from pH 9.5 to 12.5. The log P_c was about -0.8. These results indicate the extracting species to be $\mathrm{TlR(HR)}_a$ and the aqueous species to be Tl^+ and TlR. Assuming $a = 0$, and knowing log P_r to be 2.5 and log K_r to be 7.6 (ref. 10), log K_c is 4.6, and log K is -6.3. System 17 {1-(2-pyridylazo-2-naphthol)} shows a slope of one from pH 9.5 to 12.5, the predominating species probably being $\mathrm{TlR(HR)}_a$ and Tl^+.

In summary, the extractions with sodium diethyldithiocarbamate, potassium xanthate, and diphenylthiocarbazone occur at the lowest pH values, and extractions with sodium diethyldithiocarbamate and diphenylthiocarbazone give the largest P_c values. In most instances the extracting species appears to be $\mathrm{TlR(HR)}_a$, with a equal to 0 or 1, and the aqueous species appear to be Tl^+, TlR, and $\mathrm{TlR_2}^-$. The use of adducts with some of the systems might possibly enhance the extractions, since low P_c values are probably due to coordinated waters on the thallium(I) complex.

SUMMARY

Fourteen different chelating reagents have been investigated as possible extractants for radio-labelled 10^{-6} M thallium(I) from aqueous solutions into chloroform. The data have been analyzed theoretically to identify the predominant species involved and to estimate association and distribution constants.

RÉSUMÉ

Quatorze composés différents, susceptibles de former des chélates, ont été examinés comme réactifs d'extraction dans le chloroforme, pour le thallium radioactif (10^{-6} M). Les résultats ont été analysés théoriquement pour identifier les espèces prédominantes, en jeu, et pour estimer les constantes d'association et de distribution.

ZUSAMMENFASSUNG

Es wurden 14 verschiedene chelatbildende Reagenzien auf ihre Anwendbarkeit zur Extraktion von radiomarkiertem Thallium(I) (10^{-6} M) aus wässriger Lösung mit Chloroform untersucht. Die Ergebnisse wurden theoretisch analysiert, um die vorwiegend extrahierten Verbindungen zu identifizieren und Assoziations- und Verteilungskonstanten abzuschätzen.

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THE SEPARATION OF TITANIUM FROM VANADIUM AND MOLYBDENUM BY CUPFERRON SOLVENT EXTRACTION

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The determination of titanium by measuring the absorption of the "pertitanate" yellow complex formed with hydrogen peroxide in a strongly acid solution is a standard procedure. Both vanadium and molybdenum form coloured complexes under the same conditions and interfere with the absorption measurement for titanium causing a high result. The colour given by vanadium is of a similar intensity to that given by titanium but the molybdenum colour is much weaker. It is possible to determine titanium in the presence of vanadium and molybdenum by measuring the absorption at 410 mμ, 460 mμ and 330 mμ, the respective absorption maxima[1]. However, this is only possible when the vanadium and molybdenum are present in similar amounts to the titanium. BAGSHAWE[2] has reported a method of separation of titanium from vanadium for the analysis of steels, in which the titanium is precipitated with cupferron at high acid concentration (2–3 *N*) after reduction of vanadium with sulphurous acid. This separation is not complete as some vanadium contaminates the precipitate.

Titanium cupferrate is soluble in chloroform and can be extracted with this solvent from an acid aqueous solution[3]. Vanadium and molybdenum are also extracted along with other elements such as iron and zirconium[3]. In the present work, a study was made of the conditions under which titanium, vanadium and molybdenum are precipitated with cupferron and a method of separating the two elements from titanium by solvent extraction is suggested.

EXPERIMENTAL

Apparatus

Unicam 600 Spectrophotometer and matched glass cells. Exelo non-grease separating funnels. Jones Model "B" pH meter (glass electrode).

Reagents

All chemicals were of the best analytical grade; the cupferron (ammonium N-nitrosophenylhydroxylamine) was Analar grade and rejected unless pure white in colour.

Stock solutions of titanium(IV) were prepared by dissolving high purity titanium metal in dilute sulphuric acid and oxidizing with nitric acid; of molybdenum by solution of molybdenum trioxide (MoO_3) in sodium hydroxide and acidification with sulphuric acid; and of vanadium by dissolving vanadium pentoxide in sodium hydroxide and acidification with sulphuric acid.

Precipitation with cupferron

Vanadium can be precipitated with cupferron and the resultant cupferrate extracted with chloroform at pH 2 in a mineral acid medium[4]; even higher acid concentrations have been recommended by others[5]. Obviously under these conditions titanium would also be extracted.

The effect of pH on the precipitation of vanadium with cupferron alone and in the presence of chelating and reducing agents was studied; 5 mg of vanadium was used in 50 ml of aqueous solution, buffered with 5 ml of sodium acetate (50%), the pH was adjusted with dilute sulphuric acid and ammonia solution, and 10 ml of cupferron (5%) was added. It was found that above pH 3.5 with or without EDTA, vanadium(V) was not precipitated, but that when ascorbic acid (1 g), sulphurous acid or citric acid (5 g) was added, vanadium was precipitated up to pH 5.

Molybdenum can be precipitated and the resultant cupferrate extracted with chloroform[6] at pH 1.6 and higher acid concentrations[7]. Under these conditions titanium would also be extracted. Tests were made as described for vanadium; it was found that molybdenum(VI) was not precipitated above pH 3.0 with or without EDTA, but that when the other reagents were added, some molybdenum was precipitated at pH 5.0.

Titanium can be precipitated with cupferron and the precipitate extracted with chloroform from 2.5 *N* sulphuric or hydrochloric acid[3]. Visual tests as described for vanadium and molybdenum showed that titanium was precipitated with cupferron in the presence of EDTA up to pH 6.5; at pH 7 only a faint precipitate was obtained. In the absence of EDTA, titanium hydroxide precipitates above pH 3 before cupferron is added.

Tests were performed to find if titanium could be extracted completely at a pH where (from the previous results) vanadium and molybdenum would not interfere, *i.e.* above pH 3.5. Aliquots of the titanium solution were treated as described under RECOMMENDED PROCEDURE for calibration purposes, and further aliquots were treated by the extraction procedure described under RECOMMENDED PROCEDURE. These results showed that titanium in amounts up to 5 mg per 100 ml could be extracted completely in solutions containing EDTA in the pH range 3–6.5.

Separation of titanium from vanadium and molybdenum

The recovery of 1 mg of titanium per 50 ml in the presence of varying amounts of vanadium was investigated using the method as described under RECOMMENDED PROCEDURE over a range of acid concentrations. The optical density of the final solution was measured at 400 mμ for titanium*, and at 460 mμ to give an indication of the amount of vanadium present. The results showed that co-precipitation of vanadium occurred with the titanium at pH 3.5 where vanadium alone did not precipitate. However, at a titanium to vanadium ratio of 1 : 20 a separation could be

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* When potassium sulphate and phosphate are present in the final colour solution, the absorption maximum is changed to 400 mμ.

effected at pH 5–6.0. A higher ratio (1 :25) could be tolerated at pH 6.5.

The separation of titanium from molybdenum was investigated in the same manner as for the titanium–vanadium separation. The results showed that separation of titanium from molybdenum could be achieved readily at pH 5–6 at a ratio of titanium to molybdenum of 1 :50.

Table I shows the separation of titanium achieved from solutions containing all three ions, under the conditions found suitable in the previous results. It can be seen that 1 mg of titanium could be separated from solutions containing up to 20 mg of vanadium and 25 mg of molybdenum at pH 6.0; up to 50 mg of molybdenum could be tolerated for many purposes. At pH 6.3–6.4, up to 25 mg of vanadium and 50 mg of molybdenum could be present and did not interfere, but at pH 6.5 the recoveries of titanium were slightly low. When no vanadium or molybdenum was present at pH 6.5 titanium was recovered quantitatively.

TABLE I

SEPARATION OF TITANIUM FROM VANADIUM AND MOLYBDENUM

(1 mg titanium, optical density measured in 2-cm cell, volume 50 ml)

pH	*V (mg)*	*Mo (mg)*	*O.D. (400 mμ)*	*Ti equivalent (mg)*	*O.D. (460 mμ)*	*V equivalent (mg)*
5	10	25	0.320	1.08	0.142	0.06
5	15	25	0.326	1.10	0.146	0.09
5	20	25	0.346	1.17	0.154	0.18
5	25	25	0.358	1.22	0.156	0.20
5.5	10	25	0.296	1.00	0.136	Nil
6.0	10	25	0.296	1.00	0.136	Nil
6.0	20	25	0.298	1.00	0.138	0.01
6.0	10	25	0.296	1.00	0.136	Nil
6.0	20	50	0.306	1.04	0.140	0.03
6.1	20	25	0.296	1.00	0.137	Nil
6.2	20	25	0.297	1.00	0.137	Nil
6.3	25	50	0.296	1.00	0.136	Nil
6.4	25	50	0.296	1.00	0.138	0.01
6.5	20	50	0.292	0.97	0.134	Nil
6.5	25	50	0.290	0.95	0.134	Nil
6.5	35	50	0.294	0.98	0.140	0.03
6.5	50	50	0.306	1.04	0.158	0.22

An investigation of the recovery of titanium between pH 6.0 and 6.5 is shown in Table II; in this case the titanium concentration was varied from 0.2 mg to 5.0 mg. When 2 mg of titanium was present, it was necessary to add 10 ml of 5% EDTA to prevent precipitation. Above pH 6.0 with amounts of titanium above 2 mg, the recovery was low and there was contamination with vanadium. The actual recoveries were lower than shown in the Table, as the "Titanium equivalent" figure would also include vanadium. At this pH (above 6) the interface between the two phases was indistinct when more than 2 mg of titanium was present, and the separation was slow. Further tests were done by filtering the precipitated cupferrate[8], igniting the precip-

TABLE II

SEPARATION OF TITANIUM FROM VANADIUM AND MOLYBDENUM

(Conditions as noted in Table I, except that 10 ml of 5% EDTA solution was added, 1-cm cell)

pH	*V (mg)*	*Mo (mg)*	*Ti (mg)*	*O.D. (400 mμ)*	*Ti equivalent (mg)*	*O.D. (460 mμ)*	*V equivalent (mg)*
6.3	25	50	3.00	0.447	3.01	0.268	1.2
6.3	25	50	4.00	0.610	4.15	0.372	1.9
6.3	25	50	5.00	0.740	5.02	0.444	2.0
6.3[a]	25	50	0.20	0.059	0.20	0.028	Nil
6.0	20	25	3.00	0.443	3.00	0.209	Nil
6.0	20	25	4.00	0.595	4.00	0.275	Nil
6.0	20	25	5.00	0.730	4.98	0.340	Nil
6.0[a]	20	25	0.20	0.059	0.20	0.028	Nil

[a] 2-cm cell, 5 ml EDTA solution (5%).

itate and continuing as described under RECOMMENDED PROCEDURE. These results showed low recovery of titanium, and more contamination than in the extraction process.

DISCUSSION

The conditions chosen for a particular separation will be governed by the amounts of vanadium and molybdenum present. However at pH 6 a clean separation is obtained of up to 5 mg of titanium from up to 20 mg of vanadium and 25 mg of molybdenum. Above pH 6.0 the precipitation of vanadium and molybdenum is further prevented, but the titanium recoveries are doubtful. When no vanadium and molybdenum are present, the recovery at pH 6.5 is satisfactory, and even with 25 mg of vanadium alone a satisfactory recovery is obtained. KEMP[9] has discussed the distribution of cupferron between an aqueous solution and chloroform, and has shown that as a result of the ionization of cupferron the pH is increased and thus the distribution is affected. At pH 5–7 the amount of cupferron extracted is reduced considerably. It would appear that the amount of acid cupferron is insufficient to react with all the titanium, molybdenum and vanadium above pH 6.0. However, when the amounts of molybdenum and vanadium are reduced sufficiently, cupferron is available to react with all the titanium. This matter was not pursued further, because the poor interface at this pH made the separation impracticable.

RECOMMENDED PROCEDURE

Transfer a suitable aliquot of the titanium solution (approximately 40 ml) to a 100-ml beaker, and add 5 ml of 5% EDTA solution. Adjust the pH to 6.0 with dilute ammonia solution using a glass electrode pH meter. Cool to 10° and pour into a separating funnel, add 5 ml of 5% cupferron solution slowly and mix. Stand for 10 min, agitating the funnel frequently, but not necessarily continuously. Add 10 ml of chloroform and mix for 30 sec. Stand until the layers are separated (5–10 min)* and pour the chloroform layer into a platinum dish. Repeat the separation with another

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* If a higher pH is used (6.5) a definite separation is more difficult to obtain and it may be necessary to allow the solutions to stand for periods up to 30 min for the first separation. Subsequent separations can be stood for 10 min.

5 ml of chloroform, mixing and standing as before, and add the chloroform layer to the platinum dish. Repeat the separation with further 5-ml aliquots of chloroform until the chloroform layer is colourless after mixing.

Evaporate the chloroform to dryness, by directing a flow of warm air over the surface. Heat gently and finally ignite at a red heat. Cool, add 1 g of potassium bisulphate and fuse gently. Cool, add 20 ml of dilute (1 : 1) sulphuric acid, heat until all the salts are dissolved, and cool.

To a 100-ml standard flask add 15 ml of dilute (1 : 1) phosphoric acid, and using a pipet, 5.0 ml of 20-vol. hydrogen peroxide. Add the titanium solution, mix and dilute to the mark. Cool to room temperature, stand 10 min and measure the optical density of the solution at 400 mμ in a suitable size cell.

SUMMARY

The isolation of small amounts of titanium from vanadium and molybdenum before the spectrophotometric determination of titanium as the "pertitanate" complex has been achieved by a solvent extraction procedure using cupferron and chloroform at pH 6 in the presence of EDTA.

RÉSUMÉ

La séparation de faibles quantités de titane, d'avec le vanadium et le molybdène, en vue de son dosage spectrophotométrique sous forme de "pertitanate" complexe, a été effectuée par extraction au moyen d'un solvant. On utilise le cupferron et le chloroforme, au pH 6, en présence d'EDTA.

ZUSAMMENFASSUNG

Kleine Mengen Titan wurden durch Extraktion mit Kupferron und Chloroform beim pH-Wert 6 und in Gegenwart von EDTA vom Vanadium und Molybdän abgetrennt. Anschliessend wurde das Titan als "Pertitanat"-Komplex spektralphotometrisch bestimmt.

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RARE EARTH CHELATES DERIVED FROM 8-QUINOLINOL

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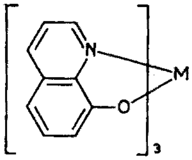
Although the trivalent lanthanide elements would be expected to form chelates of structure I with 8-quinolinol (oxine), several authors have pointed out that it is actually quite difficult to achieve the simple 1 : 3 stoichiometry required[1-4].



I

Specific data on the composition of the products obtained have for the most part, however, not been published.

As part of a program dealing with the properties of rare earth chelates, we have reexamined the composition and thermal properties of the products formed between oxine and all the available lanthanide elements, utilizing a fixed set of reaction conditions for their preparation. We have employed homogeneous precipitation (by ammonia generated through hydrolysis of urea) since this procedure has been shown to minimize coprecipitation of excess oxine, at least in the case of lanthanum[5].

The techniques of thermogravimetric analysis (TGA), differential thermal analysis (DTA), and thermomanometric analysis (TMA)[6], have been employed in the present work, both as aids in characterizing the products obtained, and to obtain thermal stability data for comparison with available information on other metal oxinates.

RESULTS AND DISCUSSION

Composition of compounds

Oxinates of each of the trivalent lanthanide ions were readily obtained by homogeneous precipitation from aqueous solution. By the procedure used, each of the metals heavier than samarium was quantitatively precipitated. Recovery of the lighter rare earths, however, varied from only 81% (Ce) to 95% (La). The precipitates were conveniently dried *in vacuo* at room temperature. Most of the dried precipitates did not gain appreciable weight when exposed for prolonged periods to air of normal humidity. The oxinates of Er, Tm, Yb and Lu, however, gained approximately 2% in weight under these conditions, indicating that relatively unstable hydrates may be formed by these 4 compounds.

Analytical data for the precipitates are given in Table I. The metal contents, though fairly reproducible from preparation to preparation, are greater than required by the 3 : 1 compounds I for all the products, except those derived from Yb and Lu. Also the experimental molar ratios, bound oxinate/metal, are considerably below three. The precipitates therefore cannot consist exclusively of species I. In order to maintain charge balance, the average composition of the products must be $M(C_9H_6NO)_yX_{3-y}$, where X is a monovalent anion.

TABLE I

COMPOSITION OF RARE EARTH 8-QUINOLINOLATES

Metal	*% M*[a]	*% C_9H_6NO*[b]	*C_9H_6NO/M molar ratios*	
			Total[b]	*Corrected*[c]
La	26.0, 25.8	66.8	2.48	2.48
Ce	26.8	66.2	2.41	2.41
Pr	27.0	62.8	2.27	2.27
Nd	27.2, 27.1	63.7	2.34	2.32
Sm	28.2, 28.6	62.2	2.30	2.27
Eu	28.6, 28.7	69.6	2.57	2.53
Gd	28.8	61.2	2.32	2.26
Tb	29.2	59.4	2.24	2.18
Dy	30.2, 30.3	61.9	2.31	2.22
Ho	28.6	62.4	2.50	2.34
Er	28.2	64.5	2.64	2.48
Tm	30.4	66.3	2.56	2.49
Yb	27.0	66.3	2.95	2.69
Lu	27.0, 27.4	68.3	3.08	2.81

[a] Where more than one number is given, the values refer to separately prepared samples.
[b] Includes contribution due to occluded oxine.
[c] Corrected for occluded oxine based on results of thermogravimetric determinations.

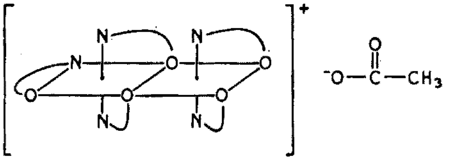
TABLE II

ELEMENTAL ANALYSES FOR RARE EARTH 8-QUINOLINOLATES

Metal	*% C*	*% H*	*% N*	*% Cl*
La	53.8	3.47	5.6	0.2
Sm	50.5	3.32	5.2	0.0
Dy	48.7	3.32	5.8	0.1
Lu	51.5	3.08	6.8	0.1

Under the experimental conditions used here, X could reasonably be chloride, hydroxide, acetate or nitrate. That X is predominately acetate is shown by the following evidence. (*1*) The pH of the reaction mixtures at the conclusion of the reactions is in the range 5 to 6. In each case it was below the pH region of hydrolysis for the respective trivalent lanthanide cation[7]; thus it is unlikely that the oxinate precipitates contain appreciable hydroxide. (*2*) Additional elemental analyses for several of the products are given in Table II. The precipitates are seen to contain little chloride. Carbon, hydrogen, and nitrogen results agree well with the theoretical values for $M(C_9H_6NO)_y(C_2H_3O_2)_{3-y}$, when allowance is made for occluded oxine. (The subscript y is taken equal to the corrected ratio C_9H_6NO/M, from Table I.) (*3*) Thermal decomposition studies (*vide infra*) indicate the presence of acetate.

The precipitation of the rare earth oxinates may involve the formation of polymeric species such as II.



II

Fisher–Hirschfelder molecular models show such structures to be sterically feasible. The average molecular weight of such species would probably be determined by the number of units necessary to give an insoluble product under the experimental conditions employed. The dimer II requires a mole ratio (C_9H_6NO/M) = 2.50 while the corresponding trimer and tetramer require 2.33 and 2.25, respectively. Most of the corrected experimental ratios (Table I) fall in this general range.

Structures somewhat analogous to II, involving the sharing of phenolic oxygens between two metal atoms, have been proposed for certain copper complexes derived from oxine[8].

TABLE III

INFRARED SPECTRA OF RARE EARTH OXINATES

Metal	*Absorption peaks (cm^{-1})*
La	726, 747, 788, 806, 822, 898, 1103, 1272, 1312, 1496, 1572
Sm	726, 748, 787, 804, 822, 900, 1103, 1268, 1310, 1496, 1571
Dy	727, 752, 788, 806, 823, 902, 1104, 1268, 1310, 1501, 1575
Lu	730, 745, 788, 804, 822, 905, 1106, 1274, 1316, 1502, 1577

Infrared spectra of some of the lanthanide oxinates are shown in Fig. 1. The spectra are all very similar to each other (Fig. 1 and Table III) but differ significantly from that of oxine itself. The spectra of the oxinates all show the strong, sharp absorption peak at about 9 μ which is characteristic of other metal oxinates[9].

Thermogravimetric measurements

Weight-loss curves (obtained in flowing argon) are given for each of the oxinates in

Fig. 2. The absence of appreciable weight loss below 150° indicates that none of the vaccum-dried products are hydrated. Weight loss for the oxinates of the heavier rare earths in the temperature range 150–200° appears to be due to loss of occluded excess oxine. Coprecipitation of oxine is not appreciable for the oxinates of the rare earths lighter than Gd.

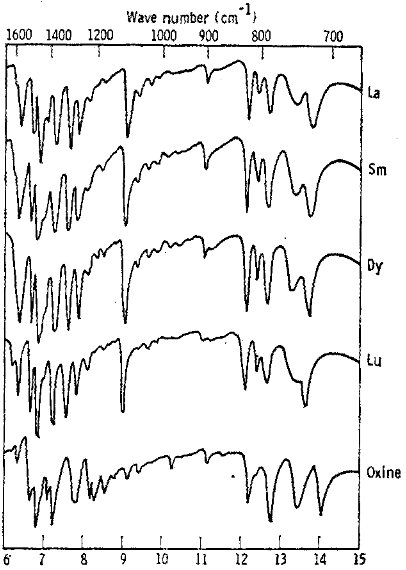


Fig. 1. Infrared absorption spectra for oxine and rare earth oxinates (Nujol mull).

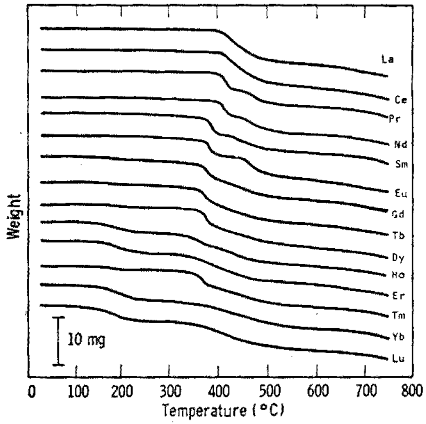


Fig. 2. Thermogravimetric curves for rare earth oxinates heated in a stream of argon. Fifty-mg samples. The curves are displaced along the ordinate.

Weight loss at temperatures higher than 250° is due to thermal decomposition. In contrast to certain of the divalent metal oxinates[6], the rare earth oxinates are not, themselves, volatile under the conditions used, as shown by metal analyses of the residues remaining at 750°.

Weight losses due to decomposition first became detectable in the temperature range 325–400°. For most of the compounds the onset of weight loss was rather abrupt, but for the Yb and Lu oxinates it was much more gradual. To establish the temperature region in which pyrolysis of the bonded 8-quinolinol anions occurs, a separate series of TGA runs was carried out with Eu oxinate. Each of the runs was terminated at a separate temperature and the residue remaining in the sample container was dissolved in acid. The optical absorbance (at 252 mμ) of the resulting solution gave a measure of the remaining undecomposed oxinate. The results plotted in Fig. 3 show that nearly complete decomposition occurs in the range 400 to 500°, coinciding with the region of weight loss marked B–C. The initial region of weight loss A–B does not involve appreciable decomposition of oxinate anions, but may represent pyrolysis of bonded acetate ions.

It is evident from Fig. 2 that there is a trend toward lower heat stabilities with increasing atomic weight of the metal, although there is little difference in heat stabilities between adjacent members of the series.

WENDLANDT[5] has investigated the thermogravimetric behavior of some of the rare earth oxinates in an atmosphere of air. He found very much larger weight losses than those shown in Fig. 2; but weight loss occurred in the same general temperature regions observed here. In air, oxidation due to atmospheric oxygen and hydrolysis due to water vapor can be of great importance in determining the thermal behavior of a material. Hence weight losses obtained in air for organic materials cannot in general be attributed to pyrolysis alone.

Thermomanometric determinations

Thermomanometric analysis[6] provides a direct measure of those decomposition products gaseous at room temperature. In Fig. 4, TMA curves are given for each of the rare earth oxinates. The initial horizontal portion of the curves corresponds to zero gas evolution. The lack of any rise in the curves in the range 150 to 200° is consistent with the evolution of occluded oxine in this region (Fig. 2), since oxine is not sufficiently volatile at room temperature to contribute significantly to the pressure in the system.

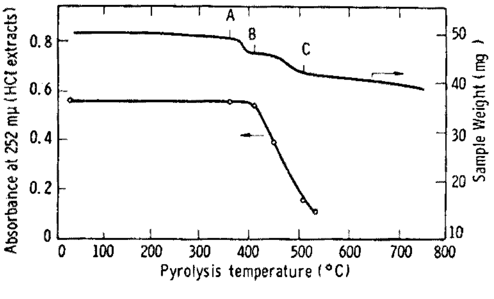


Fig. 3. Weight loss and optical absorbance as functions of pyrolysis temperature for europium(III) oxinate.

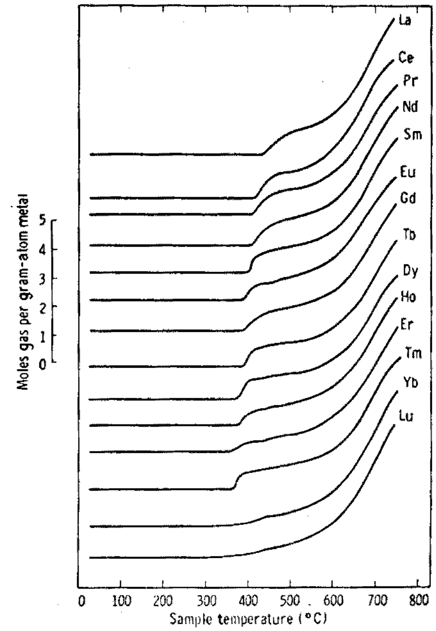


Fig. 4. Thermomanometric curves for rare earth oxinates.

The onset of gas evolution, as shown in Fig. 4, occurs rather abruptly, for most of the oxinates, at temperatures corresponding reasonably well with the onset of weight loss in Fig. 2. The beginning of gas evolution is much more gradual for the Yb and Lu oxinates and, as with the weight-loss curves (Fig. 2), it is difficult to assign a specific temperature for the onset of decomposition. The same trend of decreasing heat stability with increasing atomic weight of the metal is observed in Fig. 4 as in Fig. 2.

In separate experiments (Table IV) the gaseous products for 3 of the oxinates at 450° were identified by mass spectrometer determinations. The principal products were H_2, CO ,CO_2, and acetone. Except for acetone, these products are also produced by the divalent metal oxinates[6]. Acetone has not been observed as a pyrolysis product from other oxinates[6,10] but it is a decomposition product from metal acetates[11]. The presence of acetone is therefore additional evidence for the presence of acetate ions in the oxinate precipitates.

TABLE IV

GASEOUS PRODUCTS FROM RARE EARTH OXINATES
(15 min at 450°)

Oxinate	*Gas (mole %)*			
	H_2	*CO*	*CO_2*	*Acetone*
La	41	4	28	26
Eu	18	4	40	38
Dy	24	3	37	36

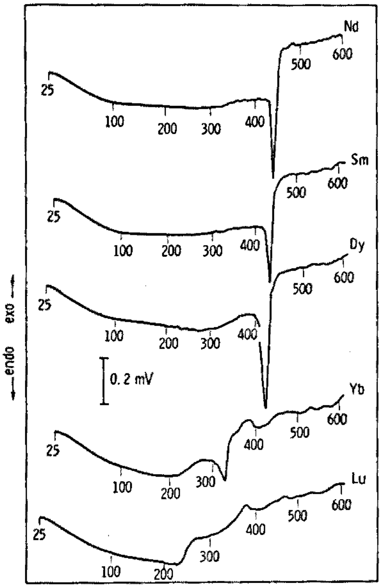


Fig. 5. Differential thermal analysis curves for rare earth oxinates; numbers refer to furnace temperature.

Differential thermal analysis

Differential thermal analysis curves were obtained for several of the lanthanide oxinates, heated in an argon atmosphere. Results are shown in Fig. 5. The Nd, Sm and Dy oxinates give sharp endotherms due to melting (verified by visual observation in a high temperature melting point apparatus). The DTA curves for these 3 oxinates are very similar to the curves from those divalent metal oxinates for which decomposition accompanies melting[12]. The endotherm for Yb oxinate is much less sharp. For this compound some decomposition evidently occurs prior to melting. No well-defined endotherm due to melting is observed for Lu oxinate, although visual observation indicates that melting occurs at about 310°. For Lu oxinate, extensive decomposition probably takes place before the normal melting point can be reached, as indicated by the broad and ill-defined endotherm in the 200–300° temperature region. In general, thermal decomposition occurs at higher temperatures for the DTA than for the TGA and TMA runs, due to the higher heating rates employed with the DTA determinations[12].

Melting points, for those rare earth oxinates examined, decrease with increasing atomic weight of the metal. Corrected[12] melting points (as determined by DTA) of the Nd, Sm, Dy and Yb oxinates are, respectively, 422, 417, 395 and 316°.

EXPERIMENTAL

Preparation of compounds

The procedure was similar to that described by WENDLANDT[5]. To a solution of 1×10^{-3} moles of rare earth chloride (Lindsay 99.9%, added as a standardized 0.5 *M* solution) in 180 ml of water was added 0.75 ml of concentrated nitric acid, followed by a solution of 800 mg of 8-quinolinol in 40 ml of 1 *M* acetic acid. Six grams of solid urea were added and the mixture was heated for 17 h at about 80°. For most of the experiments, heating was accomplished by means of a combination magnetic stirrer–thermostated hot plate. In a few instances, a steam bath was substituted. After cooling, the precipitate was filtered off on a sintered glass crucible, washed repeatedly with hot water and dried in a vacuum desiccator.

Carbon, hydrogen and chlorine analyses were carried out by the Galbraith Laboratories, Knoxville, Tennessee. Metal analyses were performed by igniting the compounds to the oxides, followed by dissolution in acid and titration with ethylenediaminetetraacetate. (In a few instances the metal content was calculated from the weight of the oxide directly.)

To determine the oxinate content, a weighed sample of the compound was dissolved in dilute hydrochloric acid and the optical absorbance determined at 252 mμ by means of a Beckman model DU spectrophotometer[6,10]. One-cm quartz cells were employed. To obtain the data shown in Fig. 3, the residue remaining from 50 mg of sample was extracted with 20 ml of 1 *M* hydrochloric acid and the extract was diluted successively 20 : 200 and 1 : 100 with 0.1 *M* hydrochloric acid.

Thermogravimetric analysis

The thermobalance has been described elsewhere[13]. Samples (50 mg) were heated in small open platinum crucibles in a stream (50 ml/min) of argon at atmospheric pressure. Weight loss–temperature curves were recorded directly by means of a Moseley X–Y recorder. The rate of temperature increase was 2°/min.

Thermomanometric analysis

The technique, except for the following changes, was the same as that previously described[6]. The apparatus was modified to decrease the fraction of the gas in the heated zone. This decreased the pressure rise due to heating the inert gas alone and allowed a simpler correction procedure to be made to the results obtained in a run. This procedure consisted of subtracting, point by point, the pressure rises obtained in a blank run (argon but no sample). The initial pressure of argon for all runs was 550 mm Hg. Pressures were measured by means of a sensitive Bourdon gauge rather than by the mercury manometer used previously. The rate of temperature increase was 3°/min. One hundred mg samples of metal oxinate were used.

Differential thermal analysis

The apparatus and procedure have been described elsewhere[12]. Three hundred to 400 mg samples were used.

The authors are grateful to Mr. I. Kesse for providing the infrared curves given herein. We also thank Mr. W. M. Hickam for the mass spectrometer results.

SUMMARY

The composition and heat stabilities of trivalent lanthanide oxinates prepared by homogeneous precipitation (urea hydrolysis in the presence of acetic acid) have been studied. The products contain acetate ion; and the molar ratio oxinate/metal is less than three. Polymeric structures are proposed for these materials. Heat stability in an inert atmosphere, as determined by thermogravimetric, thermomanometric and differential thermal analyses, decreases with increasing atomic weight of the metal.

RÉSUMÉ

Les auteurs ont effectué une étude sur la composition et la stabilité thermique d'oxinates de lanthanides trivalents, préparés par précipitation homogène en milieu acétique. Les produits obtenus renferment l'ion acétate; le rapport molaire oxinate/métal est inférieur à trois. Des structures polymères sont proposées. La stabilité thermique, en atmosphère inerte (déterminée par l'analyse thermogravimétrique, l'analyse thermomanométrique et l'analyse thermique différentielle) diminue avec l'augmentation du poids atomique du métal.

ZUSAMMENFASSUNG

Die Zusammensetzung und Wärmestabilität von Oxinaten der 3-wertigen Lanthaniden, die durch homogene Fällung hergestellt waren (Harnstoff-Hydrolyse in der Gegenwart von Essigsäure) wurden untersucht. Die Produkte enthalten Acetationen. Das molare Verhältnis Oxinat/Metall ist kleiner als 3. Polymere Strukturen werden für diese Materialien vorgeschlagen. Die Wärmestabilität in inerter Atmosphäre fällt mit steigendem Atomgewicht des Metalls. Die Bestimmung geschah thermogravimetrisch, thermomanometrisch und mit der Differentialthermoanalyse.

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ANION-EXCHANGE PAPER CHROMATOGRAPHY OF METAL IONS

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In previous reports we have demonstrated the separation of silver or thallium[1], and antimony or arsenic[2] from multicomponent mixtures of various ions by development with complexing solvents on ion-exchange papers. While performing these separations, we were able to study the mode of migration of many ions on strong-acid cation-exchange paper as a function of the sign of the charge on these ions, determined electrochromatographically[2].

This paper describes the results of similar migration studies of the same ions on strong-base anion-exchange paper with the same complexing solvents. Comparisons between the modes of migration of the ions on the two types of paper are made, and it is shown that it is not always possible to predict separations by ion-exchange paper chromatography knowing the charges on the constituents of the mixture. It is also demonstrated that the results presented can be used as the basis for many separations of pairs or groups of ions; also offered is conclusive proof of a fact mentioned only in passing in our earlier paper[2]: that contrary to the impression created by much of the research in the field, ion-exchange resin papers do not necessarily produce results identical to those obtained with columns of the same resin.

EXPERIMENTAL

Migration studies on anion-exchange paper

Migrations were performed in a conventional chamber according to the standard procedures recommended for the downward development of paper chromatograms. The exact details, developing solvents, ions studied, and method of zone detection are described elsewhere[1,2]. Test solutions (0.050 *M*) were prepared by dissolving the reagent-grade nitrate, chloride, sulfate, or acetate in water. Mercury(I) nitrate was stabilized with 48 ml of nitric acid per liter of solution. Platinum(IV) and gold(III) were prepared as the usual chloro complexes. To the uranium(VI) acetate solution was added the minimum necessary amount of glacial acetic acid. Vanadium(V) was a saturated solution of vanadium pentoxide in 0.10 *M* sulfuric acid. Antimony(III), tin(IV), and arsenic(III) chloride solutions were stabilized with 6 *M* hydrochloric acid. Bismuth chloride was dissolved in 1 :5 hydrochloric acid. To the cerium(IV) sulfate solution was added the minimum necessary amount of sulfuric acid. Amberlite SB-2 ion-exchange papers, containing about 45% by weight of Amberlite IRA-400 strong-base anion-exchange resin in the chloride form, were used (control A-10297,

H. Reeve Angel & Co.). The paper was converted to the required form by soaking overnight in a 4% (by weight) solution of an appropriate salt, washing with water and air drying. With the size of paper employed[1], the distance of migration was about 36 cm in all cases; development times were about 2 h.

Electrochromatographic studies

Again, the complete details of the experimental procedures used for these studies have been previously reported[2-4]. Each ion was studied in an electrochromatographic system in which each of the developing solvents was in turn the background electrolyte which was stabilized on Eaton-Dikeman Grade 301 cellulose paper. The direction of migration of each zone revealed the sign of the charge on each substance. Zones which did not migrate (after correction for electroosmotic flow) were either precipitated or nonionic. To differentiate these, each was spotted on E.D.-301 paper and developed by downward flow of solvent. Zones which migrated with R_F close to 1 were considered to be nonionic. Zones which remained in a compact zone at the origin were considered to be precipitated and held mechanically by the paper. Zones which streaked considerably over much of the length of the paper could be either; test-tube experiments with sample solution and developing solvent were performed to see which, if any, of these ions were probably precipitated on the paper.

We would like to emphasize that a simple chromatographic test with flow of background electrolyte does not always differentiate nonionic and precipitated substances by itself; that is, precipitates usually, but not necessarily, remain mechanically imbedded in the paper at the origin; and nonionic substances usually, but not necessarily, migrate with the solvent front, even though cellulose paper does not adsorb ions in the normal sense. For example, if one spots a copper salt on cellulose paper and washes with ammonia, the zone remains fixed. This is because the copper ions form a stronger complex with the hydroxy groups of the cellulose than with the developing solution. Likewise, precipitates may or may not yield small zones at the point of application. The size of the zone, its length, and its movement will depend upon a variety of conditions inherent in the particular chromatographic system employed[5].

Separation studies on cation-exchange paper

Attempts were made to separate binary mixtures of tin and each of the following metals in turn: Cu(II), Ni(II), Co(II), Cd(II), Zn(II), and Fe(II). Ten μl of sample, 0.050 M in tin, 0.050 M in one of the other ions, and 0.33 M in tartaric acid were spotted on sheets of Amberlite SA-2 strong-acid cation-exchange paper in the ammonium form and developed with 0.33 M tartaric acid as above. Reference zones of each metal were developed on the same sheet, and detected by spraying with aqueous hydrogen sulfide. Identical experiments were also performed on sheets of Whatman No. 1 cellulose paper.

In a separate series of experiments to prove that the method of sample preparation was not critical, the two ions were mixed on the paper by successively spotting 10 μl of the respective test solutions with drying in between. The same results were obtained after development with 0.33 M tartaric acid as with the runs above.

RESULTS AND DISCUSSION

Results are interpreted using the familiar R_F notation which is the distance traveled by the leading edge of the solute zone divided by the distance traveled by the solvent front. All R_F (and distance) values reported are the average of at least three experiments with an average deviation of ± 0.03 R_F unit or less.

Migration studies on anion-exchange paper

The results of migrations on SB-2 paper in the tartrate form with 0.05 M tartaric acid (system 1) as the wash liquid are presented in Table I. As might be expected, the 4 anionic substances underwent ion exchange and did not migrate from the origin. This same behavior was exhibited by the precipitated Ce(IV), which must have been mechanically held by the paper, and two of the nonionic substances, which could have been retarded by ion exchange or by several possible nonionic interactions[6]. The ion exchange would be because of the presence of anions (usually in equilibrium with cationic and neutral species) in the apparently neutral zone. The other two nonionic substances partially left the origin, but still showed conside-

TABLE I

RESULTS OF MIGRATIONS OF THE IONS ON SB-2 PAPER IN THE TARTRATE FORM WITH 0.05 M TARTARIC ACID (pH = 2.2) AS THE DEVELOPING SOLVENT

Ion	*Sign of charge in the system*[a]	*Mode of migration*[b]	R_F	*Length of zone*
Ag	+	a	0	—
Al	+	a	0	—
Ba	+	c	1.0	6.0
Cd	+	c	0.54	4.5
Ce(III)	+	a	0	—
Co	+	c	1.0	7.0
Cr	+	b	1.0	36
Cu	+	c	0.62	1.0
Fe	+	b	0.10	3.5
Mg	+	c	1.0	2.0
Mn	+	c	1.0	2.0
Ni	+	c	0.87	8.0
Pb	+	b	0.62	23
Tl	+	c	0.97	4.0
U	+	a	0	—
V	+	a	0	—
Zn	+	c	0.87	8.0
Au	—	a	0	—
Pt	—	a	0	—
Sb	—	a	0	—
Sn	—	a	0	—
As	0	b	0.19	6.5
Bi	0	b	0.070	2.5
Hg(I)	0	a	0	—
Hg(II)	0	a	0	—
Ce(IV)	p	a	0	—

[a] + = cation, — = anion, o = nonionic compound, p = precipitate.

[b] a = substance fixed at origin in compact zone, b = substance streaked in long zone trailing back to the origin, c = substance migrated in more or less distinct, compact zone; tail of zone left the origin.

rable affinity for the resin paper. The cations exhibited all 3 possible types of migration. Some remained fixed at the origin, probably due to the possible nonionic interactions mentioned above. Others migrated in diffuse zones trailing back to the origin, indicating these same types of interactions occurred but to a lesser degree, or that equilibrium conditions did not obtain in the chromatographic system composed of the solvent, paper, and these solutes. Still others moved as might be expected in more or less compact zones, the degree of this movement being the probable result of differences in these nonionic interactions with the stationary phase.

The results of migrations on SB-2 paper in the fluoride form with 0.50 *M* ammonium fluoride (system 2) as the wash liquid are presented in Table II. In this system, several of the anions migrated as distinct zones instead of remaining at the origin. This was not surprising because of the natural differences in selectivity of ion-exchange resins for different ions. Again, the cations exhibited all possible modes of migration. Nonionic arsenic migrated with $R_F = 0.75$ in a compact zone, indicating little interaction with the resin paper as exhibited by the other nonionic substances in this and the last system. The precipitates again remained at the origin.

TABLE II

RESULTS OF MIGRATIONS OF THE IONS ON SB-2 PAPER IN THE FLUORIDE FORM WITH 0.50 *M* AMMONIUM FLUORIDE (pH = 6.5) AS THE DEVELOPING SOLVENT

Ion	*Sign of charge in the system*[a]	*Mode of migration*[b]	R_F	*Length of zone*
Ag	+	a	0	—
Au	+	a	0	—
Ba	+	c	1.0	5.0
Cd	+	b	0.10	3.5
Co	+	c	0.59	12
Cr	+	a	0	—
Cu	+	b	0.060	2.0
Mn	+	b	0.65	23
Ni	+	c	0.51	8.5
Pb	+	a	0	—
Tl	+	c	0.76	3.5
Zn	+	c	0.21	6.0
Al	—	c	0.37	10
Bi	—	a	0	—
Fe	—	c	0.30	2.5
Pt	—	a	0	—
Sb	—	c	0.31	5.0
Sn	—	a	0	—
U	—	a	0	—
V	—	a	0	—
As	0	c	0.75	2.0
Hg(I)	0	b	0.070	2.5
Hg(II)	0	b	0.060	2.0
Mg	0	a	0	—
Ce(III)	p	a	0	—
Ce(IV)	p	a	0	—

[a] See Table I.
[b] See Table I.

The results of migrations on SB-2 paper in malonate form with 0.050 M malonic acid (system 3) as the wash liquid are presented in Table III. The fact that the only anion remained at the origin, while the cations and nonionic compounds underwent various modes of migration is not surprising compared with systems (1) and (2). The interesting result in this system is that precipitated antimony did not remain in a compact zone at the origin but moved in a zone trailing back to the origin. The fact that precipitated substances do not necessarily remain in compact zones at the origin was mentioned before in connection with migrations on cellulose paper. Chromium was discovered in two distinct zones on the paper: one compact zone at the origin, and one fairly diffuse zone near the solvent front. This zone at the origin could result if the chromium were partly precipitated by the solvent or partly in the form of a charged colloid electrostatically attracted to the resin-paper surface.

The results of migrations on SB-2 paper in the chloride form with 0.020 M di-

TABLE III

RESULTS OF MIGRATIONS OF THE IONS ON SB-2 PAPER IN THE MALONATE FORM WITH 0.050 M MALONIC ACID (pH = 2.2) AS THE DEVELOPING SOLVENT

Ion	*Sign of charge in the system*[a]	*Mode of migration*[b]	R_F	*Length of zone*
Au	+	a	0	—
Ba	+	c	0.94	20
Cd	+	c	0.63	4.5
Ce(III)	+	c	0.84	9.5
Co	+	c	0.85	6.0
Cr	+	a	0	—
		c	0.84	9.0
Cu	+	c	0.23	3.0
Mg	+	c	1.0	3.0
Mn	+	c	1.0	2.0
Ni	+	c	0.79	5.5
Pb	+	c	0.45	9.0
Pt	+	a	0	—
Tl	+	c	0.88	4.5
U	+	a	0	—
V	+	a	0	—
Zn	+	c	0.74	4.0
Fe	—	a	0	—
Ag	0	a	0	—
Al	0	a	0	—
As	0	c	0.81	2.5
Sn	0	b	0.090	3.1
Bi	p	a	0	—
Ce(IV)	p	a	0	—
Hg(I)	p	a	0	—
Hg(II)	p	a	0	—
Sb	p	b	0.20	7.5

[a] See Table I.

[b] See Table I.

ethylenetriamine (system 4) as the wash liquid are presented in Table IV. In this solvent, the anions showed all three possible modes of migration while the cations all migrated in distinct, compact zones. Thallium yielded two distinct zones as shown. The nonionic compounds, except for arsenic, streaked from the origin. More ions were precipitated in this solvent than in any of the others because of the relatively high pH value. The precipitated zones showed all three possible modes of migration, including migration of cobalt with the solvent front in an exceptionally compact zone. This was the only example of such behavior noted in any of the systems.

The results of migrations on SB-2 paper in the chloride form with 0.020 *M* diethylenetriamine–0.080 *M* hydrochloric acid (system 5) as the wash liquid are presented in Table V. All the anionic substances remained at the origin, as did the only precipitate. All the cations except one migrated in a distinct zone. Nonionic arsenic migrated as usual, while tin streaked from the origin. Mercury(I) disproportionated into Hg° and Hg(II), both of which remained at the origin. Antimony was not studied

TABLE IV

RESULTS OF MIGRATIONS OF THE IONS ON SB-2 PAPER IN THE CHLORIDE FORM WITH 0.020 *M* DIETHYLENETRIAMINE (pH = 11) AS THE DEVELOPING SOLVENT

Ion	*Sign of charge in the system*[a]	*Mode of migration*[b]	R_F	*Length of zone*
Ag	+	c	0.19	4.5
Ba	+	c	1.0	9.0
Cd	+	c	0.47	2.5
Cu	+	c	1.0	7.5
Hg(II)	+	c	0.28	4.0
Mg	+	c	1.0	3.5
Ni	+	c	1.0	4.5
Pb	+	c	0.56	19
Tl	+	c	0.22	5.5
			0.83	4.5
Zn	+	c	0.62	4.0
Al	−	c	0.55	12
Au	−	b	0.20	7.5
Pt	−	a	0	—
U	−	b	0.060	2.0
V	−	b	0.14	5.0
As	o	c	0.82	2.0
Hg(I)	o	b	0.31	11
Sb	o	b	0.080	3.0
Sn	o	b	0.17	6.5
Bi	p	a	0	—
Ce(III)	p	b	0.20	8.0
Ce(IV)	p	a	0	—
Co	p	c	1.0	1.0
Cr	p	a	0	—
Fe	p	b	0.27	10
Mn	p	b	0.31	11

[a] See Table I.
[b] See Table I.

electrochromatographically in this solution; it streaked on the anion-exchange paper and was therefore probably present in a nonionic form.

Comparing the results of the five systems, we see that a substance of any given condition is liable to migrate in any of the three possible modes mentioned above.

Table VI summarizes the migration of all species as a function of the sign of the charges. The most that can be said in the way of generalization is that a cation will probably

TABLE V

RESULTS OF MIGRATIONS OF THE IONS ON SB-2 PAPER IN THE CHLORIDE FORM WITH 0.020 *M* DIETHYLENETRIAMINE–0.080 *M* HYDROCHLORIC ACID (pH = 1.7) AS THE DEVELOPING SOLVENT

Ion	*Sign of charge in the system*[a]	*Mode of migration*[b]	R_F	*Length of zone*
Al	+	c	0.26	1.7
Ba	+	c	0.89	3.0
Cd	+	c	1.0	3.6
Ce(III)	+	c	1.0	3.0
Ce(IV)	+	a	0	—
Co	+	c	1.0	3.6
Cr	+	c	1.0	4.0
Cu	+	c	1.0	8.7
Fe	+	c	0.92	17
Mg	+	c	1.0	2.0
Mn	+	c	1.0	3.0
Ni	+	c	1.0	3.5
Pb	+	c	0.52	3.8
Tl	+	c	0.81	13
U	+	c	0.61	12
V	+	c	0.61	2.5
Zn	+	c	0.57	5.0
Au	—	a	0	—
Bi	—	a	0	—
Hg(I)	—,p	a	0	—
Hg(II)	—	a	0	—
Pt	—	a	0	—
As	0	c	0.83	1.7
Sn	0	b	0.12	4.0
Ag	p	a	0	—

[a] See Table I.
[b] See Table I.

TABLE VI

NUMBER OF SUBSTANCES MIGRATING IN A GIVEN FASHION AS A FUNCTION OF CONDITION

Condition of substance	*Number migrating in mode a*[a]	*Number migrating in mode b*[a]	*Number migrating in mode c*[a]
Cationic	14	6	51
Anionic	15	3	3
Nonionic	5	9	4
Precipitate	11	4	1

[a] See Table I.

migrate in a more-or-less compact, distinct zone; and that an anion or a precipitate will probably remain at the origin in a compact zone. Analogous results were found for the same systems employing strong-acid cation-exchange paper[2].

This means that predicting the results of separations to be attempted by ion-exchange paper chromatography is virtually impossible. For example, one would predict that cationic nickel would migrate and separate from anionic platinum with solvent (4) as the developer. Table IV shows that in fact this separation could be accomplished. However, with solvent (1), cationic aluminum could not be separated from anionic tin because both remain at the origin (Table I). In solvent (2), anionic iron migrates and separates from cationic lead which remains at the origin (Table II); one would predict a separation based on the movement of lead. Antimony is precipitated in solvent (3) while copper remains cationic (Table III); one might predict a separation of these, but none is possible. Finally, in solvent (5), cerium (IV) and copper are both cations (Table V). Separation is easily achieved, however, because the cerium remains at the origin.

By referring to the results presented in Tables I–V many analytically useful separations of two, three, or four components can be designed. We performed one such separation in each solvent by preparing the respective mixtures on the paper by multiple spotting on the same area of paper. Reference zones of each ion were developed on the same paper. These separations were: U, Cu, and Mn in solvent (1); Cr, Sb, and As in solvent (2); V, Tl, and Cd in solvent (3); Bi, Ag, Zn, and Co in solvent (4); and Hg(II), Al, and Mg in solvent (5).

Separation studies on cation-exchange paper

Recent reports[7,8] have described the separation of tin(IV) from various metals by elution of the mixture with aqueous tartaric acid through a column of cation-exchange resin. The tin is complexed as an anion and is not sorbed by the resin, while the other metals are retained in a narrow band at the top of the column. Attempts to reproduce these separations on ion-exchange papers containing the same resin in the same ionic form by development with the same solvent as used in the column studies were completely unsuccessful. The tin, as well as the other metals, remained at the origin. The tin zone did streak from the origin a few centimeters in every case, but most of it remained at the point of application. When developed similarly on Whatman No. 1 cellulose paper, the tin zone migrated with $R_F = 1$ in a compact zone.

This lack of sorption on columns of resin and on cellulose paper, and presence of sorption on resin-loaded paper means that the tin must be retarded by the binder chemicals that are added to the cellulose pulp in the production of commercial ion-exchange paper[9]. Test migrations on papers containing only resin and cellulose would prove the accuracy of this explanation.

It is clear that resin papers and columns of the same resin can produce entirely different results in certain cases.

Mr. C. W. CLINE, was a participant in Lafayette's National Science Foundation Undergraduate Research Program. This work was performed in part at the Argonne National Laboratory, Argonne, Ill., in the Laboratory of Dr. H. H. STRAIN. The author is also indebted to Lafayette College for a Summer Faculty Research Grant which allowed the work to be completed.

SUMMARY

The migration of 26 ions on anion-exchange paper is studied with five different complexing solvents. The results are reported as a function of the sign of the charge on each ion determined electrochromatographically. Several possible separations are presented, but it is shown that the prediction of separations, knowing only the charge on several substances, is impossible. It is also demonstrated that ion-exchange column experiments and ion-exchange paper experiments do not necessarily yield identical results.

RÉSUMÉ

L'auteur a effectué une étude sur la migration de 26 ions sur papier échangeur d'anions, en utilisant 5 solvants complexants différents. Les résultats sont reportés en fonction du signe de la charge de chaque ion, déterminé électrochromatographiquement. Plusieurs séparations sont ainsi possibles. Les essais effectués sur colonne et sur papier ne donnent pas nécessairement des résultats identiques.

ZUSAMMENFASSUNG

Die Wanderung von 26 Ionen auf Anionenaustauscherpapier mit 5 verschiedenen komplexbildenden Lösungsmitteln wurde untersucht. Die Ergebnisse werden als Funktion des Ladungsvorzeichens eines jeden Ions wiedergegeben. Mehrere mögliche Trennungen werden erläutert. Es zeigt sich jedoch, dass eine Vorhersage von Trennungen, wenn man nur die Ladung von verschiedenen Substanzen kennt, unmöglich ist. Es wird darauf hingewiesen, dass Versuche mit Ionenaustauscherkolonnen und solche mit Ionenaustauscherpapier nicht unbedingt zu den gleichen Ergebnissen führen müssen.

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HIGH SPEED SEPARATION OF THE LIGHT RARE EARTHS ON CENTRIFUGALLY ACCELERATED ION-EXCHANGE PAPER*

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In an attempt to develop a rapid, clean separation applicable to the lighter rare earths (La to Sm), the technique of high speed, centrifugal chromatography[1] on ion-exchange paper[2] was investigated. It was possible to separate completely the elements in any combination except the pair Pr and Nd. It was also possible to calculate from the data the average number of glycolate anions held in the resin-plus-paper phase per rare earth ion so held.

EXPERIMENTAL

The apparatus used was a Hi-Speed Chromatograph manufactured by Precision Scientific Company. In this apparatus, circular sheets of ion-exchange paper are mounted on the shaft of a variable speed motor (300–1500 rev./min). Four metal spokes are used to support the paper; the spokes are best coated with a plastic tape in order to prevent attack of the metal by the eluant. The eluant is delivered under pressure in a fine stream through a 0.1-mm diameter orifice in a stainless steel disk and directed onto the paper inside the point at which the ion mixture was applied. In our arrangement, the eluant was delivered from a 100-ml gas buret so that the flow rate could be determined.

The ion-exchange paper was Amberlite SA-2, which is a paper containing about 50% by weight of Amberlite IR-120 sulfonic acid resin in the Na^+ form.

The rare earth solutions were made from oxides obtained from Lindsay Chemical Company and said to be at least 99.9% pure. The eluant solutions were prepared from Fisher Scientific Company glycolic acid and brought to the desired pH by addition of ammonia. They were filtered before use to eliminate clogging of the orifice. The indicator solution was 0.1% PAN (1-(2-pyridylazo)-2-naphthol from J. T. Baker Chemical Company) by weight in ethyl alcohol.

The paper was placed on the apparatus and washed with eluant. The rotation was stopped and the rare earth solutions were spotted on the wet paper in a circle 4 cm from the center of rotation with a 2-μl pipet. The quantity of rare earth ion applied was about 0.02 mg, which does not exceed the exchange capacity of the resin at the point of application. The stated capacity is 0.025 meq./cm^2.

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The chromatogram was eluted for 1 to 12 min at 5 ml/min and 1500 rev./min. The paper was then dried, sprayed with PAN solution, and exposed to ammonia vapor. Red spots appeared because of formation of a PAN–rare earth complex in ammoniacal medium. These fade on drying and therefore must be outlined in pencil.

The distance traveled was measured from the point of application to the center of the spot. R_F values could not be determined because the solvent front washed off the edge of the 32-cm diameter paper circles.

RESULTS

Obvious variables to be considered when developing a separation method using the

TABLE I

MOVEMENT OF METAL IONS DURING HIGH SPEED CHROMATOGRAPHIC ELUTION

Glycolic acid solution			*Time (min)*	*Distance traveled (cm)*					
M	*pH*	*pG*		*La*	*Ce*	*Pr*	*Nd*	*Sm*	*Y*
0.25	4.0	0.84	5	0.6	1.0	1.5	2.0	2.0	3.3
	4.0	0.84	10	1.1	1.8	2.5	3.1	5.1	4.8
	4.5	0.68	10	3.0	5.6	7.0	9.1	11.8	11
0.30	3.50	1.01	3	0.2	0.4	0.5	0.7	0.8	0.9
			6	0.2	0.5	1.0	1.5	2.2	2.2
			9	0.4	1.0	1.6	1.9	2.9	3.2
	3.75	0.86	3	0.6	1.0	2.1	2.6	3.5	3.7
			6	1.2	2.2	3.5	4.4	5.4	5.4
			9	1.5	3.0	4.1	5.1	8.7	8.4
	4.0	0.74	3	1.0	2.1	3.6	4.2	5.4	5.0
			6	2.3	4.3	6.0	6.8	9.6	9.4
			9	3.4	5.7	7.9	10.0	>12	>12
	4.5	0.60	3	2.9	4.7	6.5	7.5	9.6	—
			6	5.0	8.4	10.6	11.8	>12	>12
			9	6.7	9.5	>12	>12	>12	>12
0.40	3.0	1.28	3	0.1	0.2	0.2	0.3	0.4	0.4
			6	0.1	0.2	0.4	0.4	0.5	0.5
	3.25	1.07	1	—	0.2	0.2	0.2	0.3	0.4
			3	0.1	0.3	0.3	0.6	0.7	1.0
			6	0.2	0.5	0.6	1.0	1.5	1.3
			9	0.3	0.6	1.2	1.5	2.5	2.5
			12	0.4	0.9	1.7	1.8	3.4	2.9
	3.50	0.89	1	0.2	0.4	0.4	0.6	0.7	0.7
			3	0.4	0.7	1.5	2.0	3.1	3.3
			6	1.0	1.1	2.8	4.2	5.8	6.3
			9	1.2	2.2	3.3	4.6	8.2	7.2
			12	1.6	3.2	4.3	5.7	9.1	7.7
	3.75	0.74	1	0.7	1.2	1.2	1.8	2.2	2.3
			3	1.2	2.0	3.1	4.4	6.4	7.7
			6	2.6	4.2	5.7	7.6	9.2	9.7
			9	3.7	6.1	8.5	10	10.8	>12
	4.0	0.62	1	1.0	2.0	2.2	2.5	3.1	3.4
			3	2.9	5.7	5.8	6.8	9.3	9.9
			6	4.9	9.0	10.4	10.5	>12	>12

technique described here are eluant flow rate, amount of sample, speed of rotation, type of paper and ion-exchange resin, separation time, temperature, and identity, concentration, and pH of the eluant solution.

The ion-exchange papers show good wet strength in addition to having the conventional ion-exchange properties. Because most ion-exchange separations of the rare earths have been made on strong acid cation exchangers[3], the one commercially available paper of this type known to us was chosen for study.

An eluant flow rate of 5 ml/min was chosen because greater flow rates led to excessive tailing and smaller flow rates were difficult to achieve and reproduce. The maximum rotation speed, 1500 rev./min, was chosen in order to give the fastest possible separation.

Preliminary runs using solutions of glycolic, lactic, α-hydroxyisobutyric, and citric acids of varying concentrations and pH suggested that glycolic acid would be most likely to give satisfactory separations. Determinations of the distance traveled by the elements La, Ce, Pr, Nd, Sm and Y were made for glycolic acid concentrations of 0.25 to 0.40 *M*, a pH range of 3.0 to 4.5, and running times of 1 to 12 min. The glycolate anion concentration varied from 0.053 to 0.25 *M*. The results are given in Table I.

A typical plot of distance traveled as a function of elution time is shown in Fig. 1. In general, it can be said that velocity is constant at the lower velocities and distances, but that the velocity decreases as time increases. In other words, as the ion approaches the edge of the paper, its velocity decreases. The best time intervals to be used for separations appear to be 3 to 6 min. The ions are able to move a good distance from their point of origin but in general have not begun to bunch at the outside edge.

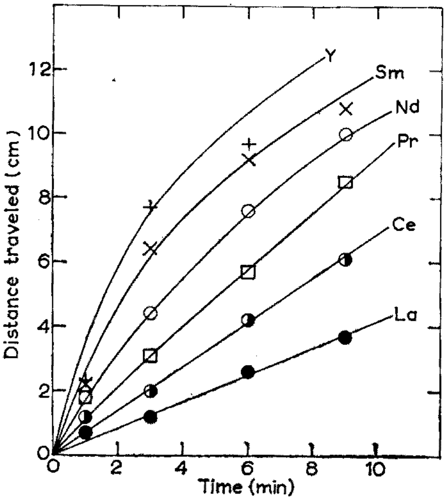

Fig. 1. Distance traveled by the elements La, Ce, Pr, Nd, Sm and Y as a function of time of centrifugal elution. The solution was 0.40 *M* in glycolic acid and had a pH of 3.75. At 9 min, Y had washed off the paper.

For a given running time, a plot of distance traveled as a function of pH will suggest optimum conditions for a particular separation. Fig. 2 is a typical representation. Suggested conditions for each separation are given in Table II.

With the glycolic acid eluant, we were able to separate any adjacent pair of the elements considered with the exception of Nd–Pr and Sm–Y. A partial separation of Nd–Pr was achieved. Sm and Y can be separated with 0.4 *M* lactic acid at a pH of about 4.5.

A good example of the appearance of a chromatogram after elution is shown in Fig. 3.

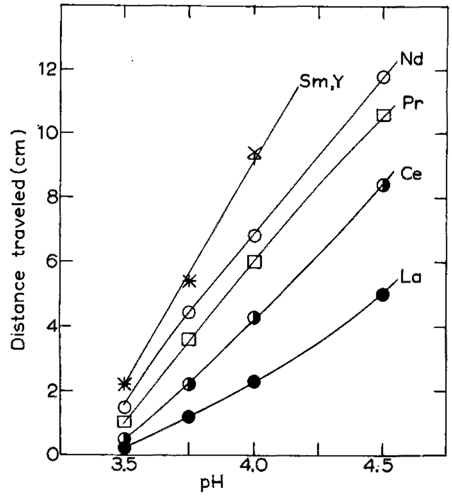

Fig. 2. Distance traveled by the elements La, Ce, Pr, Nd, Sm and Y as a function of eluant pH. The solution was 0.30 *M* in glycolic acid. The running time was 6 min. The Sm(×) and Y(+) did not separate.

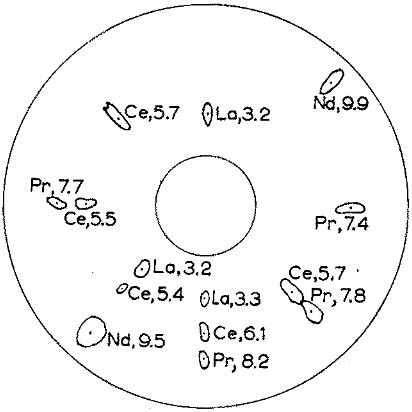

Fig. 3. A typical developed chromatogram after the color has faded showing only the penciled outlines of the spots and the center points to which distance measurements were made. The numbers are the measured distances in cm. The outer circle is the edge of the 32-cm diameter disk. The inner circle describes the 4-cm radius on which the samples were originally placed.

TABLE II

SPECIFIC CONDITIONS FOR SEPARATING PARTICULAR ELEMENTS

Elements	*Time (min)*	*Glycolic acid concentration (M)*	*pH*
La–Ce–Nd La–Ce–Pr partial Nd–Pr	9	0.40	3.75
La–Sm or Y Ce–Sm or Y	3	0.30	3.75
Nd–Sm or Y Pr–Sm or Y	6	0.30	4.00

DISCUSSION

All the distance *vs.* time data were plotted as in Fig. 1 and initial velocities were determined. These are plotted in Fig. 4 as a function of pG, the negative logarithm of the glycolate ion concentration.

In order to interpret the data shown in Fig. 4, we can consider that v, the velocity, is proportional to the amount of rare earth in solution and inversely proportional to the amount in the paper-plus-resin phase:

$$v = K[MG_n^{3-n}]/\{MG_xR_{3-x}\} \qquad (1)$$

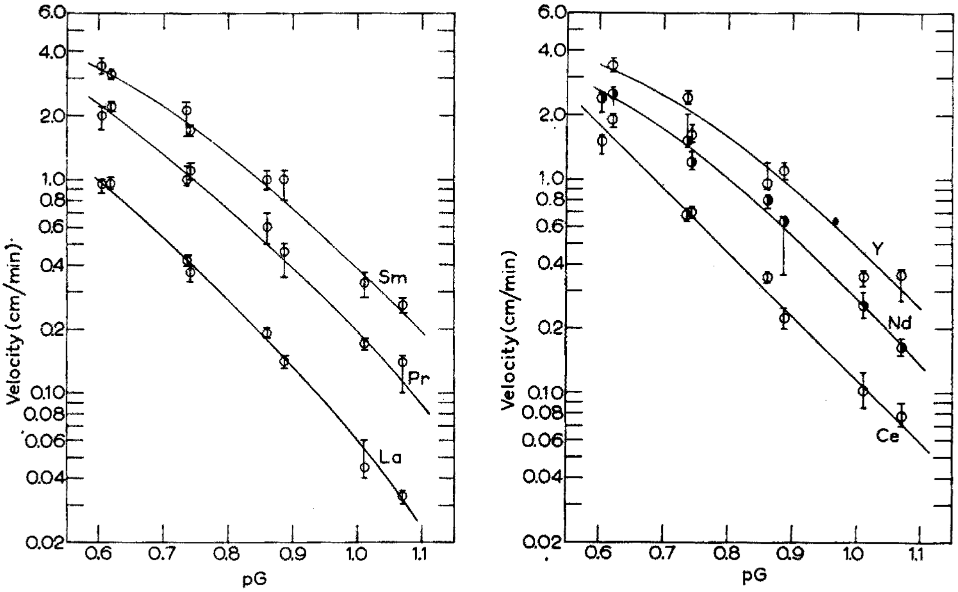

Fig. 4. The logarithm of the initial velocity of the metal species as a function of pG, the negative logarithm of the glycolate anion concentration. The error limits are the experimental uncertainty in reading the slope of the distance *vs.* time plots.

where M is a rare earth ion, G is the glycolate anion, R is a singly charged resin site, K is a proportionality constant dependent on the kinetic forces involved, n is the average number of ligand glycolates in the solution phase per rare earth ion, and x is the average number of ligand glycolate ions in the resin phase per rare earth ion. The [ ] symbolize molarity units; { } symbolize moles.

The expression for v and the subsequent analysis recognizes that the ratio of ligand to metal in the species most probably adsorbed on the resin is not necessarily the ratio predominating in open solution. It is the metal ion species involved in the resin equilibrium whose outward movement is impeded with respect to the solvent flow.

The equilibrium between solvent and resin phase can be written:

$$MG_x^{3-x} + (3-x)\,NH_4R \rightleftarrows MG_xR_{3-x} + (3-x)\,NH_4^+$$

By replacing activity with concentration in the solution phase and activity with mole fraction in the resin phase, we have:

$$K_r = \frac{[NH_4^+]^{3-x}\,\dfrac{\{MG_xR_{3-x}\}}{\{MG_xR_{3-x}\} + \{NH_4R\}}}{[MG_x^{3-x}]\left(\dfrac{\{NH_4R\}}{\{MG_xR_{3-x}\} + \{NH_4R\}}\right)^{3-x}}$$

$$K_r = \frac{[NH_4^+]^{3-x}}{[MG_x^{3-x}]}\,\frac{\{MG_xR_{3-x}\}}{\{NH_4R\}} \quad \text{if} \quad \{NH_4R\} \gg \{MG_xR_{3-x}\} \qquad (2)$$

The equilibrium for the complex formation is: $M^{3+} + n\,G^- \rightleftarrows MG_n^{3-n}$

The appropriate stability constants are

$$K_n = \frac{[MG_n{}^{3-n}]}{[M^{3+}]\,[G^-]^n} \qquad (3)$$

and

$$K_x = \frac{[MG_x{}^{3-x}]}{[M^{3+}]\,[G^-]^x} \qquad (4)$$

Insertion of (2) and (3) in (1) gives:

$$v = K\,\frac{K_n[M^{3+}]\,[G^-]^n\,[NH_4{}^+]^{3-x}}{K_r[MG_x{}^{3-x}]\,\{NH_4R\}} \qquad (5)$$

Insertion of (4) in (5) gives:

$$v = \frac{KK_n[G^-]^{n-x}\,[NH_4{}^+]^{3-x}}{K_rK_x\,\{NH_4R\}}$$

Because of the manner in which the eluant was prepared and because the total rare earth concentration is about one per cent of $[G^-]$,

$$[NH_4{}^+] \approx [G^-]$$

Therefore

$$v = \frac{KK_n[G^-]^{3+n-2x}}{K_rK_x\{NH_4R\}}$$

A log plot of v *vs.* pG should have a negative slope equal to $-(3+n-2x)$. Because both n and x will vary with pG, the line will probably not be straight (Fig. 4).

SONESSON[4] has studied the rare earth–glycolate system and has determined the stability constants for the species $MG_1{}^{2+}$, $MG_2{}^+$, MG_3, $MG_4{}^-$, and $MG_5{}^{2-}$. His data, which unfortunately omit Y, can be used to calculate values of n in the pG range studied here. From these, values of x can be calculated. The results are given in Table III.

Both the values of n and of x decrease with increasing pG, as is to be expected. Similarly, there is a general increase in n and x from La to Sm. But it is interesting to note that Nd and Pr tend to have essentially the same values of n and x in this pG region. SONESSON's data show that n for Nd is less than n for Pr at pG values less than 1.00 and is greater at higher pG values. From the behavior of the other rare earths studied, only the latter behavior would be expected. Thus a crossover in relative stabilities of the glycolate complexes of Nd and Pr occurs just in the pG region most applicable to use of the high speed chromatograph with strong acid ion-exchange paper. This essential indistinguishability of Pr and Nd is also seen in the comparison of x values. The fact that the x values generally lie between 1 and 2 shows that the species undergoing ion exchange are usually singly or doubly charged. This is true even though the n values are close to 3, and there is therefore a large fraction of uncharged metal species in solution.

Although it seems possible to separate Nd and Pr by a properly chosen glycolic acid eluant, it would probably be easier to do this by using an eluant that forms Nd and Pr complexes which differ more in their stabilities.

TABLE III

AVERAGE NUMBER OF GLYCOLATE IONS PER RARE EARTH ION IN THE SOLUTION PHASE (n) AND IN THE RESIN PHASE (x)

Element	pG	$3+n-2x$	n[4]	x
La	0.7	2.74	2.92	1.59
	0.8	2.90	2.77	1.44
	0.9	3.10	2.61	1.26
	1.0	3.40	2.47	1.04
Ce	0.7	2.99	3.10	1.56
	0.8	2.99	2.93	1.47
	0.9	2.99	2.77	1.39
	1.0	2.99	2.61	1.31
Pr	0.7	2.40	3.22	1.91
	0.8	2.79	3.08	1.64
	0.9	2.79	2.93	1.57
	1.0	3.09	2.80	1.36
Nd	0.7	2.06	3.16	2.05
	0.8	2.74	3.03	1.64
	0.9	2.79	2.92	1.56
	1.0	2.96	2.80	1.42
Sm	0.7	1.97	3.30	2.16
	0.8	2.49	3.17	1.84
	0.9	2.69	3.04	1.68
	1.0	2.82	2.92	1.55

SUMMARY

The separation of the rare earths, La, Ce, Pr, Nd, Sm and Y on centrifugally accelerated Amberlite SA-2 cation-exchange paper was studied. All combinations of the elements can be completely separated except the Pr–Nd pair by using as eluant glycolic acid of a properly-chosen concentration (0.30 or 0.40 *M*) and pH (3.0 to 4.5). The Pr–Nd pair can be partially separated. The average number of ligand glycolate ions per rare earth ion in the resin phase was determined for each rare earth over the pG range 0.7 to 1.0.

RÉSUMÉ

Une étude a été effectuée sur la séparation des terres rares, La, Ce, Pr, Nd, Sm et Y, sur papier échangeur de cations, Amberlite SA-2, accélérée par centrifugation. Chacun de ces éléments peut être séparé quantitativement des autres (à l'exception de la paire Pr–Nd) en utilisant comme éluant l'acide glycolique. Pr–Nd peuvent être séparés partiellement. Le nombre moyen d'ions glycolates par ion métallique, dans la résine, a été déterminé pour chaque terre rare.

ZUSAMMENFASSUNG

Die Trennung der Seltenen Erden La, Ce, Pr, Nd, Sm und Y auf zentrifugal beschleunigtem Kationenaustauscherpapier (Amberlite SA-2) wurde untersucht. Alle Kombinationen dieser Elemente (ausser Pr–Nd) können völlig getrennt werden bei Anwendung von 0.3 oder 0.4 *M* Glykolsäure und einem pH-Wert von 3.0–4.5. Im pG-Bereich von 0.7–1.0 wurde in der Harzphase für jedes Element die durchschnittliche Zahl der Liganden bestimmt.

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USE OF PYRIDINIUM BROMIDE PERBROMIDE AS AN ANALYTICAL REAGENT

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For several years, pyridinium bromide perbromide, henceforth called PBPB, has been used as a brominating agent in synthetic organic chemistry. Compounds such as ketones, amines and unsaturates have been brominated with this reagent[1,2]. The ease of handling of the crystalline PBPB, rate of reaction, and the absence of side reactions suggest the desirability of using this reagent in quantitative analytical work.

The present investigation was designed to test the scope of this reagent by attempting the direct titration of phenols, unsaturates, and aromatic ethers. Several methods have been suggested for the bromination of these compounds. The most widely used procedure involves the addition of an excess of bromate–bromide solution, followed by a back-titration with standard thiosulfate solution. This method has been modified by using glacial acetic acid as a solvent and pyridine to catalyze the reaction of bromine with the phenol[3]. Recently HUBER AND GILBERT[4] have reported a direct titration of phenols using bromine in glacial acetic acid as a titrant. The end-point was detected using constant-current potentiometry. In most of the earlier work, little attention was given to slow bromination reactions or those which frequently give several products. BRICKER AND SWEETSER[5] have suggested the photometric technique for the determination of unsaturates and phenols. The ultraviolet absorbance of the tribromide ion (at wavelengths below 360 mμ), when excess reagent had been added, was utilized to detect the end-point. Since the PBPB is highly colored and is reported to yield single reaction products[6], the possibility of applying this reagent to the direct photometric determination of several functional groups is suggested.

EXPERIMENTAL

Apparatus

A Bausch and Lomb Spectrophotometer, Model Spectronic 20, equipped with a Pyrex titration cell, was used for all volumetric work. In the earlier work an overhead stirrer was employed, but later the magnetic stirring pump cell suggested by REHM AND HIGUCHI[7] was found to be much more satisfactory. The spectrum of PBPB was determined using a Beckman DU Spectrophotometer and silica cells.

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Reagents

Three samples of PBPB were used. The first was prepared by the method of DJERASSI AND SCHOLZ[1] which involves the reaction of 48% hydrobromic acid with pyridine dissolved in acetic acid, followed by treatment with liquid bromine. The product from this reaction was recrystallized from hot glacial acetic acid. A second sample was obtained by reacting one mole of pyridine-hydrobromide with a mole of bromine. The product obtained was purified in the absence of acetic acid by drying in a vacuum desiccator. The slow decomposition of PBPB has been reported when this material was recrystallized from hot acetic acid[8]. Solutions of PBPB were then prepared by dissolving this material in reagent-grade acetic acid containing 5–10% methanol to enhance the solubility of the reagent. The solutions were found to decompose 3–5% per week. The stability of the reagent was increased by storing the PBPB solution away from light and in a cool place. The instability may be due, in part, to the possible bromination of methanol and the loss of any excess bromine present.

A sample of PBPB was also obtained from the Arapahoe Chemicals Company and used without further purification. This reagent was more stable than the previously prepared samples and decomposed at a rate of 2% or less per week. If care was taken to prevent evaporation of the solvent, the normality of the PBPB solution changed only 0.5% per week.

Chemicals

Phenols. Most of the phenols were "white label" from Eastman Kodak, and were used without further purification. The samples of *m*-aminophenol, *β*-naphthol, *p*-nitrophenol and salicylic acid were recrystallized.

Unsaturated compounds and ethers. All of the unsaturates and ethers were commercial samples which were purified by distillation or recrystallization. The purity of the volatile materials was checked using gas chromatographic analysis. All samples except resorcinol diethylether were 99% pure or better.

Catalyst. 1,1,3,3-Tetramethylguanidine (American Cyanamid Company) was used as a catalyst in the titration of the phenols. This reagent was purified by distillation. Mercuric chloride (Fisher certified reagent) was used to catalyze the reactions between unsaturates and PBPB.

A 0.05 *M* methanol solution was used in the titration of the unsaturates.

The glacial acetic acid and methanol were Fisher certified reagents. The glacial acetic acid was used without further purification; the methanol was dried over Drierite before use.

Preliminary investigation

A study of the spectrum of PBPB revealed absorbance maxima at 278 and 380 mμ as shown in Fig. 1. In contrast to the bromate–bromide spectrum (dotted line), the PBPB absorbance in the visible region of the spectra permits the use of this reagent for the photometric titration with visible-range spectrophotometers. In order to use bromate–bromide at 350 mμ, the lowest wavelength at which the Spectronic 20 may be used, one must employ an 0.250 *N* solution of this titrant. The PBPB, however, may be used to titrate diluted samples with 0.001 *N* titrant.

Plots of molarity of PBPB *vs.* absorbance were linear at wavelengths from 350 to 525 mμ. This study was performed by successively diluting the PBPB solution over a wide concentration range at each wavelength. Table I shows the useful concentration range of the titrant at various wavelengths.

In general, if the titrant concentration exceeds the value listed in the Table, one may titrate a functional group and find that Beer's law holds for small 0.25-ml increments of excess titrant. If the titrant concentrtaion is lower than the recommended value, Beer's law does not hold for small additions to PBPB past the end-point, and the analysis will be unsuccessful. When the titrant concentration is exceedingly higher than that listed in Table I, very small increments (0.05 ml) of titrant must be added past the end-point since the absorbance is quite high.

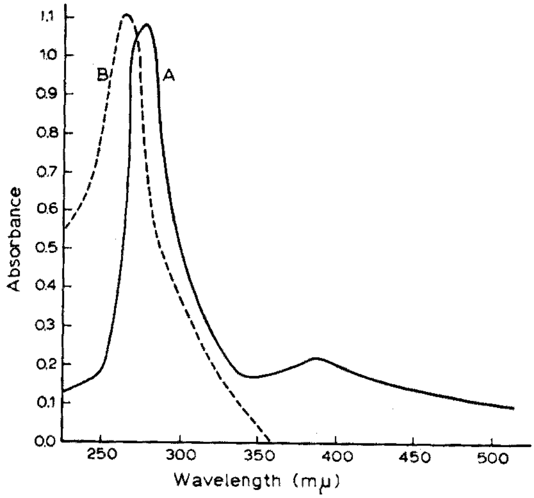


Fig. 1. Absorption spectrum of PBPB. (A) $1.8 \cdot 10^{-3}$ *M* PBPB in glacial acetic acid; (B) $1 \cdot 10^{-4}$ *M* bromate–bromide.

TABLE I

REAGENT CONCENTRATION LIMITS

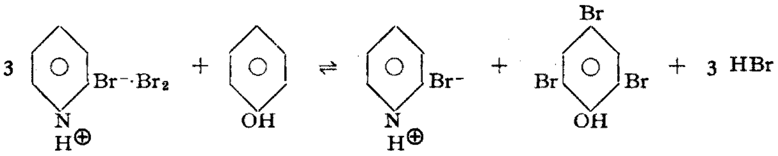
Minimum titrant concentration (N)	*Useful wavelength range (mμ)*
0.0010	325–400
0.0025	350–475
0.0050	400–525
0.0075	475–525

Standardization of PBPB

The PBPB solution was standardized photometrically against primary standard arsenic trioxide. To 10 ml of 0.1 *N* arsenic trioxide was added 40 ml of methanol. The wavelength was set in the region of 400 to 425 mμ. Since the arsenic solution was colorless, the spectrophotometer was adjusted to zero absorbance against a blank solution. The titrant was added from a 10-ml burette, using 1-ml increments before and 0.25-ml increments after the end-point, The absorbance readings, resulting from the addition of excess titrant, were stable 30 sec after each addition of titrant. For the titration 5–10 min were required; the end-point was determined graphically.

Titration of phenols

The bromination of phenols may be illustrated by the following equation:



The phenol solutions were prepared by adding 0.1 to 0.6 mmoles of the phenol to 25 ml of acetic acid followed by 1 ml of tetramethylguanidine. The titration procedure was identical to that in the standardization except for the selection of the wavelength. All of the phenols titrated, except 8-hydroxyquinoline, were colorless and the wavelength was set in the region of 400 to 450 mμ. In all of these cases, L-shaped titration curves were obtained (see Fig. 2). The 8-hydroxyquinoline absorbs from 320 to 525 mμ, thus leading to absorbance before and after the end-point. The wavelength chosen for the titration was 500 mμ since the absorbance of the 8-hydroxyquinoline is small in this region in comparison with that of the PBPB. The titration procedure has the precision of 0.5% recovery or better at phenol concentrations from $2 \cdot 10^{-2}$ to $3 \cdot 10^{-3}$ moles/l, with an accuracy of 1%. Titrations were attempted in the 10^{-4} M region with a precision of only 10%.

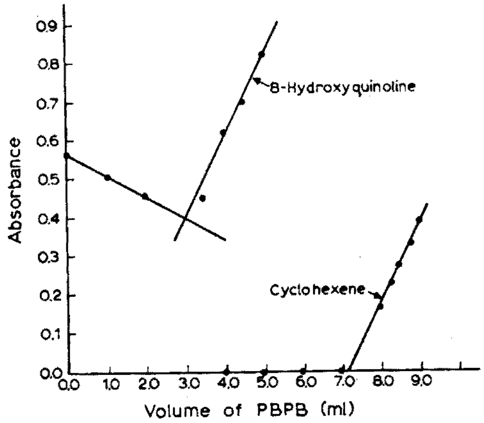
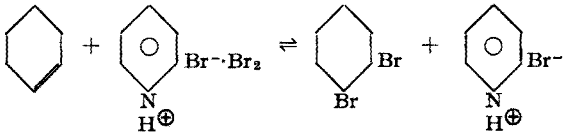


Fig. 2. Titration curves. (A) 8-Hydroxyquinoline; (B) Cyclohexene.

Titration of unsaturates and aromatic ethers

The bromination of unsaturates may be illustrated by the following equation:



The titration media consisted of 10 ml of 0.05 M mercuric chloride dissolved in methanol, 40 ml of methanol, and 10 ml of an 0.05 *M* methanol solution of the compound to be titrated. These substances were placed in the titration cell and the titration procedure was the same as that employed in the standardization. The end-point from the L-shaped titration curve was determined graphically.

RESULTS AND DISCUSSION

Phenols

Phenols of a wide variety of activity were chosen for this study. FRANCIS AND HILL[9] have grouped the errors in phenol brominations into 3 types. The errors may be due to (*1*) oxidation of reactive species such as aminophenols; (*2*) precipitation of brominated products; and (*3*) replacement of certain functional groups such as the carboxylic acid group by bromine. Compounds subject to these errors were chosen for the present study. Table II shows the results of the analysis of a series of phenols. (These results were checked using a non-aqueous acid–base titration.) Results from aminophenol indicate no tendency to form oxidation products in this reaction. In the solvent system employed, precipitation of substituted products did not occur; nor was the carboxylic acid group replaced in the titration of salicylic acid.

TABLE II

RESULTS FROM BROMINATION OF PHENOLS

Phenol	*Number of determinations*	*Moles of PBPB per mole of phenol*	*% Recovery using PBPB*	*% Recovery using non-aqueous acid–base titrations*
Phenol	5	3	99.23 ±0.35	98.6
p-Bromophenol	4	2	100.86 ±0.23	101.2
2,4-Dibromophenol	3	1	99.05 ±0.08	98.7
Salicylic acid	4	2	101.01 ±0.67	100.7
m-Aminophenol	3	3	97.89 ±0.45	
o-Cresol	4	2	95.81 ±0.28	
Resorcinol	6	3	102.84 ±0.26	
8-Hydroxyquinoline	5	2	102.46 ±0.87	
o-tert.-Butylphenol	5	2	100.15 ±0.72	
p-tert.-Butylphenol	5	2	100.42 ±0.27	
2,6-Di-*tert.*-butylphenol	5	1	96.82 ±4.40	

The titrations required 5 to 10 min and were, in general, free from side reactions. Poor results were obtained with three compounds. The analysis of *p*-nitrophenol was unsuccessful due to the slow rate of reaction of this material with PBPB. *β*-Naphthol could not be analyzed due to some unknown side reactions and the formation of a colored product limited the precision of the determination of 2,6-di-*tert.*-butylphenol. BRICKER AND SWEETSER[5] have stated that some compounds are higly sensitive to excess bromination reagent. With these compounds, such as *m*-aminophenol and resorcinol, small increments of titrant must be added beyond the end-point. One can expect a precision of 0.5% or better for colorless phenols and 1% for the colored materials. The precision of this method is not as great as that reported by BRICKER

AND SWEETSER[5] but the reactions are much faster and titrations may be performed using a simple photometric apparatus instead of the Beckman DU Spectrophotometer.

Unsaturates and aromatic ethers

A concentration study was done to determine the upper and lower limits of the procedure for unsaturates and ethers. The wavelengths at which the titrations were done were chosen on the basis of the wavelength study previously mentioned (see Table I). Table III shows the results of this study. The upper limits of concentration of compounds that may be titrated are determined by the low solubility of the PBPB in glacial acetic acid–methanol solution. In general, unsaturates can be titrated with 1% recovery at concentrations of $6 \cdot 10^{-4}$ to $1 \cdot 10^{-1}$ *M*. Aromatic ethers can be titrated to within one per cent in the concentration range $2 \cdot 10^{-2}$ to $3 \cdot 10^{-3}$ *M*.

TABLE III

CONCENTRATION STUDY

Compound	*Concentration (M)*	*Wavelength (mμ)*	*Results*
Cyclohexene	1.0	425	No end-point
Cyclohexene	0.5	350	No end-point
Cyclohexene	0.1	425	100.11% recovery
Cyclohexene	0.01	425	100.42% recovery
Cyclohexene	0.001	330	99.13% recovery
Cyclohexene	0.0006	340	100.67% recovery
Cyclohexene	0.0004	335	105.36% recovery
Cyclohexene	0.0002	330	105.36% recovery
Anisole	0.02	425	99.77% recovery
Anisole	0.01	425	100.26% recovery
Anisole	0.003	400	100.47% recovery
Anisole	0.002	400	105.10% recovery
Anisole	0.001	335	No end-point

TABLE IV

RESULTS FROM THE BROMINATION OF UNSATURATES AND ETHERS

Compound	*Moles of PBPB per mole of compound*	*% Recovery*	*Number of determinations*
Unsaturates			
Allyl alcohol	1	98.41 ±0.50%	7
Cyclohexene	1	99.01 ±0.52%	7
Oleic acid	1	97.95 ±0.77%	3
Cinnamyl alcohol	1	99.83 ±0.64%	3
Cinnamaldehyde	1	95.97 ±0.32%	4
Cinnamic acid	1	99.94 ±0.60%	7
Ethyl cinnamate	1	100.58 ±0.60%	3
Ethers			
Anisole	1	100.26 ±0.38%	7
p-Ethoxydiphenyl	1	102.51 ±0.60%	4
Resorcinol dimethyl ether	2	99.78 ±0.22%	6
Resorcinol diethyl ether	2	94.82 ±3.25%	8

Usually, when the substance being titrated brominated rapidly and clearly, PBPB gave excellent results with a minimum amount of difficulty. When the reactions were slow, quantitative bromination with PBPB was not quite so successful (refer to Table IV).

Concerning the unsaturates, the bromination of allyl alcohol, cyclohexene, oleic acid and cinnamyl alcohol, with the aid of the mercuric chloride catalyst, was quite rapid. The titrations took 10 min or less; the end-points were sharp. The bromination of cinnamaldehyde required approximately 15 min. The region near the end-point was poorly defined in spite of the addition of catalyst. The titration of cinnamic acid required 40 min, even with a catalyst. Ethyl cinnamate, the slowest reacting of all the compounds in this series, required 1 h or more for each titration. The apparent rate of reaction decreased in the order cinnamyl alcohol, cinnamaldehyde, cinnamic acid, and ethyl cinnamate.

The use of PBPB for the titration of ethers is somewhat limited. Anisole and resorcinol dimethyl ether brominated rapidly when mercuric chloride catalyst was added. *p*-Ethoxydiphenyl reacted so slowly with PBPB that the titration required at least 1 h. Resorcinol diethyl ether could be titrated but only one-fourth as much mercuric chloride catalyst was needed and this quantity had to be added near the end-point. Too much mercuric chloride appeared to change the stoichiometry. The ether seemed to substitute one bromine rapidly and another one at a slightly slower rate, thus making the end-point hard to determine. Other ethers, *p*-methoxydiphenyl, *p*-bromoanisole, and diphenyl ether did not brominate at a rate fast enough to titrate.

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SUMMARY

Pyridinium bromide perbromide has been shown to be a satisfactory reagent for the bromination of phenols, unsaturates and aromatic ethers. The color of the reagent permits the spectrophotometric detection of the end-point. Most phenols and unsaturates react fast enough, in the presence of a catalyst, to permit titration within 10 min. The aromatic ethers, in general, react very slowly but yield accurate results. The reagent has the advantage over the conventional bromate–bromide that the titrations are fast and the stoichiometry exact. The speed of reaction of PBPB with many functional groups may permit the use of automatic titration procedures with this reagent.

RÉSUMÉ

L'emploi du bromure perbromure de pyridinium a été appliqué à la bromuration de phénols, de composés non-saturés et d'éthers aromatiques. La couleur de ce réactif permet une détection spectrophotométrique du point final. La plupart des phénols et des composés non-saturés réagissent suffisamment rapidement, en présence d'un catalyseur, pour permettre un titrage en 10 min. Les éthers aromatiques, en général, réagissent très lentement, mais donnent des résultats précis. Les titrages à l'aide de ce réactif, présentant l'avantage d'être plus rapides que ceux au bromate-bromure, peuvent être effectués avec des appareils automatiques.

ZUSAMMENFASSUNG

Es wird gezeigt, dass Pyridinbromidperbromid ein befriedigendes Reagens zur Bromierung von Phenolen, ungesättigten Verbindungen und aromatischen Äthern ist. Die Farbe des Reagenzes erlaubt den spektralphotometrischen Nachweis des Endpunktes. Die meisten Phenole und ungesättigten Verbindungen reagieren in Gegenwart eines Katalysators schnell genug, um eine

Titration in 10 Min. durchführen zu können. Die aromatischen Äther reagieren im allgemeinen sehr langsam, ergeben aber sehr gute Ergebnisse. Das Reagens hat gegenüber dem konventionellen Bromat–Bromid den Vorteil, dass die Titrationen schnell und stöchiometrisch exakt sind. Die Schnelligkeit der Reaktion des PBPB mit vielen funktionellen Gruppen könnte die Anwendung einer automatischen Titration mit diesem Reagens erlauben.

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HALBQUANTITATIVE ANALYSE DURCH MESSUNG DER ENTFÄRBUNGSZEIT VON TÜPFELFLECKEN

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Tüpfelreaktionen werden in verschiedenster Weise zur Durchführung halbquantitativer Analysen herangezogen: Tüpfelkolorimetrie[1], Tüpfelnephelometrie, Tüpfelfluorometrie, Ringofentüpfelkolorimetrie[2], Ausmessung der Fleckengrösse, Retentionsanalyse[3] sind häufig angewendete Methoden der halbquantitativen Analyse.

Wir haben eine neue Methode zur halbquantitativen Schnellanalyse ausgearbeitet, welche auf der Messung der Entfärbungszeit von Tüpfelflecken auf Filterpapierstreifen beruht; darüber wurde bereits vor einiger Zeit berichtet[4]. Das Prinzip der Methode ist folgendes: EinTropfen der zu bestimmenden Lösung wird auf einen Filterpapierstreifen aufgetragen, eine geeignete Tüpfelreaktion ausgeführt, welche ein deutlich gefärbtes, ausreichend stabiles Reaktionsprodukt liefert. Sodann wird der Filterpapierstreifen in der Lösung eines Reagenzes gebadet, welches mit dem Reaktionsprodukt im Tüpfelfleck in der Weise reagiert, dass der Tüpfelfleck entweder weggelöst oder in eine farblose, zumindest aber in eine nur sehr schwach gefärbte Verbindung übergeführt wird. Die zu dieser Entfärbung des Tüpfelfleckes benötigte Zeit wird gemessen. Diese Entfärbungszeit hängt offenbar von mehreren Faktoren ab:

(*1*) von der entsprechenden chemischen Reaktion,
(*2*) vom verwendeten Filterpapier,
(*3*) von der Temperatur,
(*4*) von der Konzentration der „Entfärbelösung",
(*5*) von der Menge an zu Entfärbendem pro Flächeneinheit und damit natürlich von der Konzentration des zu bestimmenden Ions.

Da nun die ersten drei Faktoren konstant gehalten werden und die Konzentration der Entfärbelösung bekannt ist, ist es möglich auf diese Weise die Konzentration der unbekannten Lösung zu bestimmen, vorausgesetzt, dass die Entfärbezeiten ausreichend gut reproduzierbar sind.

Von dem entsprechenden Ion werden jeweils einige Standardlösungen genau bekannter Konzentration bereitet.

Jeweils 3 Tropfen einer Lösung werden auf einen Filterpapierstreifen (Schleicher und Schüll Nr. 589^1-Schwarzband) mit Hilfe einer selbstfüllenden Kapillarpipette (etwa 1 μl) getüpfelt (*vgl.* Fig. 1); hernach wird in einer geeigneten Reagenzlösung gebadet, welche mit dem jeweiligen Ion einen deutlich gefärbten Niederschlag liefert. Der Filterstreifen wird gründlich gespült und auf Filterpapier zur Entfernung des überschüssigen Wassers abgepresst. Die Entfärbungszeiten der aus den verschiedenen Standardlösungen hergestellten Tüpfelflecken werden in einer Reihe (zumeist 4–5) von Lösungen des Entfärbereagenzes verschiedener Konzentration bestimmt. Dies erfolgt durch Einhängen der Filterpapierstreifen mit Hilfe einer geeigneten Plastikklammer in eine 250-ml Weithalsflasche, in welcher sich das Entfärbereagens befindet. Die Lösungen müssen ständig gründlich durchmischt werden (Magnetrührer, *vgl.* Fig. 1); besondere Vorsichtsmassnahmen bezüglich der Temperaturkonstanthaltung (Thermostat) sind nicht erforderlich, da im Temperaturbereich von 18–25° keine sichtbare Abhängigkeit der Entfärbezeit von der Badtemperatur festgestellt wurde. Die Konzentrationen der Standardlösungen und der Entfärbelösungen sind so zu wählen, dass die Entfärbezeiten alle etwa im Bereich von 6–80 Sek liegen. Entfärbezeiten von 10–40 Sek sind am besten messbar, doch hängt dies wohl sehr stark von der Augentüchtigkeit des einzelnen Beobachters ab.

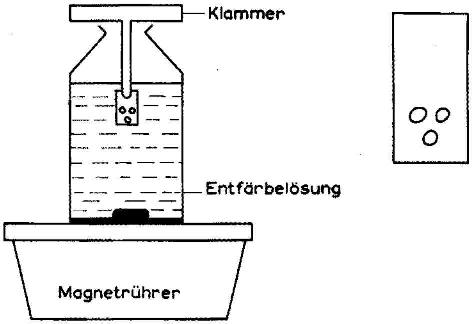

Fig. 1.

Werden die so gefundenen Ergebnisse graphisch dargestellt, indem man für jede Entfärbelösungskonzentration die Entfärbezeiten gegen die Standardlösungskonzentrationen aufträgt, so erhält man eine Schar von Eichkurven; diese sind zumeist gerade.

Wenn nun eine Lösung des entsprechenden Ions unbekannter Konzentration zu bestimmen ist, so werden in gleicher Weise drei Tüpfelflecken erzeugt und die Entfärbungszeiten in einer der Entfärbelösungen gemessen, mit Vorteil eben in derjenigen, in welcher die Entfärbungszeit in einem gut messbaren Bereich liegt. Sollte die Probelösung zu konzentriert sein, so muss sie entsprechend verdünnt werden. Der Mittelwert aus drei Messungen wird berechnet und aus der entsprechenden Eichkurve die Konzentration der Probelösung ermittelt.

Man kann auch so vorgehen, dass man die Entfärbungszeiten der Flecken in drei verschiedenen Entfärbelösungen bestimmt und die Konzentration der Probelösung graphisch extrapoliert.

Auf diese Weise wurden einige Metallionen halbquantitativ bestimmt, so zum Beispiel:

Nickel(II): (*a*) + Dimethylglyoxim, entfärbt mit KCN; (*b*) + Dimethylglyoxim, entfärbt mit HCl.

Eisen(III): + $[Fe(CN)_6]^{4-}$, entfärbt mit $AgNO_3$.

Quecksilber(II): + KJ zur Anfärbung und Entfärbung.

Blei(II): + KJ, entfärbt mit NaOH.

Bezüglich näherer Details zu diesen Bestimmungen sei auf die erste Publikation verwiesen[4].

Hier sollen nun einige weitere Beispiele beschrieben werden.

Halbquantitative Bestimmung von Silber

Der Bestimmung liegt die Entfärbung von Silberchromat mit Natriumchloridlösung zugrunde. Hier beruht also die Entfärbung nicht auf der Auflösung der gefärbten Substanz (Ag_2CrO_4), sondern auf deren Umwandlung in eine farblose Verbindung ($AgCl$).

Die auf Filterpapierstreifen aufgebrachten Tropfen werden in einer 1%-igen K_2CrO_4-Lösung entwickelt; dann wird zur Entfernung des überschüssigen Reagenzes gründlich in Wasser gespült. Die Entfärbungszeit der Tüpfelflecken in NaCl-Lösungen wird gemessen. Folgende Konzentrationen an NaCl-Lösungen wurden zur Entfärbung verwendet: 0.5, 0.75, 1 und 2 g/1000 ml.

Zur Aufstellung der Eichkurven dienten 4 Lösungen von $AgNO_3$, welche 2.5, 5.0, 7.5 und 10.0 mg Ag/ml enthielten.

Halbquantitative Bestimmung von Blei

Die Tüpfelflecken auf Filterpapier werden in 1%iger K_2CrO_4-Lösung entwickelt. Die Entfärbung erfolgt durch Baden in NaOH-Lösung; hier beruht die Entfärbung (im Gegensatz zu der des Silberchromats) auf der Weglösung der gefärbten Substanz (als Plumbit).

Als Entfärbelösung wurden verwendet: 0.01, 0.03, 0.05 und 0.08 *N* NaOH.

Zur Aufstellung der Eichkurven dienten folgende Lösungen: 1.0, 2.5, 5.0 und 7.5 mg Pb/ml.

Halbquantitative Bestimmung von Jodat

Die Bestimmung von Jodat beruht darauf, dass die Lösung mit überschüssigem KJ versetzt und auf Filterpapier getüpfelt wird, welches zuvor mit Stärkelösung imprägniert und getrocknet wurde. Beim Räuchern über HCl wird eine äquivalente Menge an Jod in Freiheit gesetzt. Dieses reagiert mit Stärke unter Bildung der blau gefärbten Jod-Stärke-Verbindung. Deren Entfärbungszeit in verschiedenen Lösungen von Natriumthiosulfat wird gemessen.

Es erwies sich als notwendig, auf Stärke-imprägniertes Filterpapier zu tüpfeln. Bei Verwendung von unbehandeltem Filterpapier waren nur schlecht reproduzierbare Entfärbungszeiten zu messen, da offenbar Jodverluste auftraten.

Entfärbelösungen: 2, 2.8, 4 und 6 g $Na_2S_2O_3 \cdot 5\,H_2O$/1000 ml.

Zur Aufstellung der Eichkurven dienten folgende KJO_3-Lösungen: 1.0, 2.0, 3.0 und 4.0 mg/ml.

Halbquantitative Bestimmung von Chromat und Kupfer(II)

Da die Entfärbungszeiten von Jod-Stärke-Flecken in Natriumthiosulfatlösungen gut reproduzierbar sind, ist est naheliegend, einige andere Ionen auf gleichsam jodometrischem Wege zu bestimmen: Werden angesäuerte Lösungen von Kupfer(II) oder Chromat auf Filterpapier getüpfelt, welches vorher mit Stärkelösung und Kaliumjodidlösung imprägniert wurde, so wird wiederum eine äquivalente Menge Jod freigesetzt. Die zu dessen Entfärbung in $Na_2S_2O_3$-Lösungen benötigte Zeit ist ein Mass für die Konzentration der Kupfer- *bzw.* Chromatlösung.

Als Entfärbelösungen wurden die gleichen wie bei der Jodatbestimmung verwendet.

Zur Aufstellung der Eichkurven dienten folgende Lösungen: 0.5, 1.0, 1.5 und 2.0 mg Cu/ml; 0.15, 0.25, 0.30, 0.40, 0.50, 0.75 und 1.00 mg Cr/ml.

Die Reproduzierbarkeit bei allen diesen halbquantitativen Bestimmungen war zumeist besser als ±10% relativ, erscheint also durchaus zufriedenstellend für eine so einfache Schnellmethode.

Auf die Abhängigkeit der Entfärbungszeiten vom „Altern" der Tüpfelflecken wurde schon in der ersten Mitteilung über diese Methode hingewiesen, ebenso auf die Möglichkeit durch geeignete Zwischenfällungen störende Ionen zu entfernen[4].

Da die Entfärbungszeiten auch sehr deutlich von der Art des Filterpapieres abhängen, bietet sich diese Schnellmethode zur Charakterisierung und Unterscheidung von verschiedenen Filtrierpapierqualitäten an (*vgl.* Tabelle II der ersten Mitteilung).

Diese wenigen Beispiele mögen zeigen, dass mit dieser Methodik wohl noch zahlreiche andere Substanzen halbquantitativ bestimmt werden können.

ZUSAMMENFASSUNG

Es wird ein Verfahren zur halbquantitativen Schnellanalyse beschrieben, welches auf der Messung der zur Entfärbung von Tüpfelflecken auf Filterpapierstreifen in geeigneten Reagenzien benötigten Zeit beruht. Das sehr einfache Verfahren liefert Ergebnisse mit einer für halbquantitative Zwecke wohl ausreichenden Genauigkeit von ± 10%. An einigen Beispielen (Ag^+, Pb^{2+}, JO_3^-, Cu^{2+}, CrO_4^{2-}) wird die Methode erläutert. Auf die Möglichkeit der Verwendung dieser Methode zur Charakterisierung und Unterscheidung von Filtrierpapieren wird hingewiesen.

SUMMARY

A rapid semiquantitative method is described based on measurement of the time required for decolorization of spot reactions on filter paper strips by suitable reagents. This very simple method yields results which are accurate to ± 10%. The method has been verified for several ions (Ag^+, Pb^{2+}, IO_3^-, Cu^{2+}, CrO_4^{2-}). The utility of this method for the characterization and differentiation of filter papers is indicated.

RÉSUMÉ

Une méthode d'analyse semiquantitative est décrite. Elle est basée sur la mesure du temps nécessaire à la décoloration de réactions sur papier filtre, par des réactifs appropriés. Cette méthode, très simple, permettant d'obtenir une précision de ± 10%, a été appliquée à plusieurs ions (Ag^+, Pb^{2+}, IO_3^-, Cu^{2+}, CrO_4^{2-}).

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DETERMINATION OF MANGANESE IN URANIUM BY ION EXCHANGE AND SQUARE-WAVE POLAROGRAPHY

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The determination of trace impurities in uranium and its compounds has required the development of sensitive analytical procedures, and several instrumental methods have been employed. Square-wave polarography provides a sensitive method for the determination of some metallic elements at low levels. GOODE AND CAMPBELL[1] applied square-wave polarography for the simultaneous determination of microgram quantities of copper, lead, cadmium, and zinc in uranium metal. The present author[2] previously developed the most sensitive method for cadmium, in which cadmium was separated from uranium by a column of anion-exchange resin and was determined by square-wave polarography.

In the present work, the determination of manganese was studied. Spectrophotometric[3,4] and emission spectrographic[5] methods have been usually employed for the determination of manganese in uranium, but square-wave polarography presents a more sensitive approach.

EXPERIMENTAL

Apparatus

Polarograph. A Mervyn-Harwell square-wave polarograph, Mark III, was used. All measurements were performed in a water thermostat controlled at 25 ±0.2° and the drop time of the dropping mercury electrode was maintained at 4 sec. Investigations of the supporting electrolytes for manganese were carried out with an agar-bridge saturated calomel electrode; for the routine determination, the mercury pool anode was applied. Dissolved oxygen was removed with a stream of purified nitrogen just before recording of the polarogram. The polarograms were recorded at 0.1 V per min of the rate of change of D.C. applied voltage.

Ion-exchange column. A bank of columns was constructed from glass tubes, of 12 mm internal diameter and 180 mm long, each having a sintered glass disc at the bottom and fitted with a removable 60-ml funnel at the top. The resin bed was supported on the sintered glass disc. The outlet tube was a capillary of 2 mm internal diameter with a stopcock which allowed regulation of the flow rate. The liquid layer in the column was always maintained above the resin by keeping the outlet above the top of the resin bed.

Reagents

Resin bed. Dowex 1X8, 50–100 mesh, analytical grade, chloride form, was thoroughly washed with water and slurried in a beaker, and 13 ml were transferred to the ion-exchange column, allowing the resin particles to settle to form the bed. The height of the resin bed was about 15 cm. For the removal of impurities originally adsorbed in the resin, the resin column was washed with 40 ml each of concentrated, 9 M, 6 M, and 3 M hydrochloric acid, water, and 0.5 M nitric acid successively. The free nitric acid in the column was removed by passing through 50 ml of water and the column was treated with 40 ml of 9 M hydrochloric acid to convert the resin to chloride form and to be ready for use. After use, the resin column was regenerated by removing the adsorbed uranium with water and the impurities with 0.5 M nitric acid and by passing through 40 ml of 9 M hydrochloric acid.

Uranium solution. A solution containing 1 g of uranium in 10 ml of 9 M hydrochloric acid was prepared by dissolving the appropriate amount of uranyl chloride (UO_2Cl_2, Yokosawa Chemicals Co., Tokyo, Japan) and removing manganese by the following procedure. The solution was introduced into the ion-exchange column, and manganese and some other impurities were eluted with 9 M hydrochloric acid. The uranium adsorbed on the resin bed was then eluted with water and the eluate was evaporated nearly to dryness. The residue, *i.e.* the purified uranyl salt, was dissolved in 10 ml of 9 M hydrochloric acid.

Manganese solutions. A $1.00 \cdot 10^{-2}$ M stock solution was prepared by dissolving reagent-grade manganese sulfate ($MnSO_4 \cdot 4H_2O$) and standardized by the ammonium persulfate method. Standard working solutions of $1.00 \cdot 10^{-3}$ M and $1.00 \cdot 10^{-4}$ M were obtained by suitable dilution.

Alkaline triethanolamine solution. The purified reagent (Dotite TEA, Dojindo & Co., Ltd., Kumamoto, Japan) was used as received. A 1 M potassium hydroxide–0.4 M triethanolamine solution was prepared and stored in a glass bottle with a soda-lime tube to prevent absorption of carbon dioxide.

All other reagents were prepared from reagent-grade chemicals, and all solutions were prepared in distilled water purified by passing over a mixed cation–anion exchange resin bed.

Recommended procedure

Weigh 1 g of the sample into a 100-ml conical flask and add 10 ml of 6 M hydrochloric acid. Add drop by drop about 10 ml of 30% hydrogen peroxide while heating the solution to boiling. Hold at this temperature until dissolution is complete, the excess hydrogen peroxide decomposes, and the volume of the solution is reduced to about 5 ml by evaporation. Cool to room temperature and add 5 ml of concentrated hydrochloric acid to make the final solution 9 M in hydrochloric acid.

Transfer the resulting solution into the funnel of the ion-exchange column. Open the stopcock to obtain a flow rate of about 1.5 ml per min, and pass the solution through the resin column into a 100-ml beaker. When the level of the sample solution nears the top of the resin bed, use three 5-ml portions of the 9 M hydrochloric acid to wash out the funnel. Continue passing 9 M hydrochloric acid to elute manganese until a total effluent volume of 60 ml has been collected in the 100-ml beaker. Evaporate the eluate to dryness and add 5 ml of the supporting electrolyte, *i.e.* the 1 M potassium hydroxide–0.4 M triethanolamine solution, to dissolve the residue.

Transfer this solution to the polarograph cell, deaerate for 10 min with nitrogen and record the polarogram at an applied D.C. potential between −0.2 and −0.7 V *vs.* the mercury pool anode. Measure the peak height of the manganese wave in divisions of the recorder scale and obtain the concentration with reference to calibration curves.

In order to determine the blank, carry 10 ml of 9 *M* hydrochloric acid through the entire procedure. The manganese content of the sample is obtained by subtracting the blank.

Preparation of the calibration curves

Use the standard working solution and transfer known quantities of manganese to a series of 100-ml beakers. Evaporate each solution to dryness and add 5 ml of the supporting electrolyte solution. Record the polarograms at several instrument sensitivities and plot the peak height against the manganese quantities.

RESULTS AND DISCUSSION

Separation of manganese from uranium

According to the work of KRAUS AND NELSON[6] on the anion-exchange behavior of uranium(VI) and manganese(II) in hydrochloric acid solution, the differences in adsorbability between them are very large so that their separation in solutions of comparatively high concentration in hydrochloric acid is feasible.

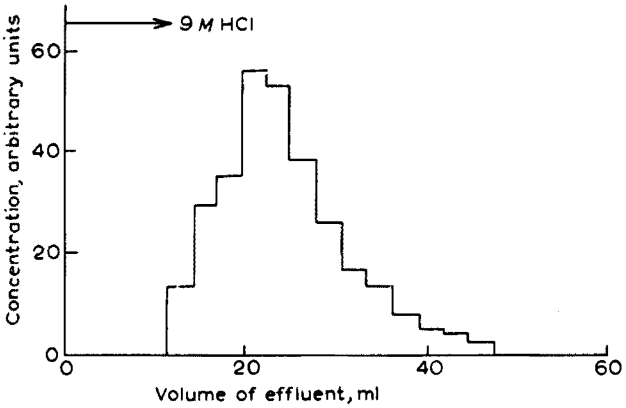

Fig. 1. Elution curve for manganese(II) with 9 *M* hydrochloric acid.

A typical elution curve of manganese(II) is illustrated in Fig. 1. A 9 *M* hydrochloric acid solution containing 1 g of uranium and 27.5 µg of manganese was prepared and introduced into the ion-exchange column. When 9 *M* hydrochloric acid was passed at a flow rate of 1.5 ml per min, manganese(II) was eluted easily because of its slight adsorbability to the anion-exchange resin of strongly basic type, and uranium(VI) was retained in the resin bed. The yellow color of uranium(VI) in the resin bed developed downward very slowly as the eluant was passed through. The effluent fractions were collected every 2 min in small crucibles. After each fraction was evaporated to dryness and 3 ml of the supporting electrolyte solution was added, the manganese concentration was measured by square-wave polarography. As shown in Fig. 1, about 10 ml of eluant was needed to start elution of the manganese-(II) and 50 ml was required to elute it completely. Uranium(VI) was retained in the resin without any leakage.

On elution with 6 *M* hydrochloric acid instead of 9 *M* acid, manganese(II) was eluted more quickly, but the 6 *M* acid was not feasible, because uranium(VI) also began to come through in the eluate fraction of manganese(II).

Supporting electrolyte

The sensitivity of square-wave polarography depends upon the degree of reversibility of the electrode reaction. Although several supporting electrolytes have been proposed for the D.C. polarographic determination of manganese, most of them are not useful for the square-wave polarographic determination, for the electro-reduction of manganese(II) at the mercury electrode is irreversible. To achieve a sensitive determination, a study of supporting electrolytes was carried out.

FERRETT AND MILNER[7] suggested an alkaline cyanide solution which provided a very sensitive determination of manganese in water by square-wave polarography. But manganese(II) is liable to be oxidized to manganese dioxide by air and then its measurement is erratic; also, the polarographic peak of manganese(II) is more or less affected by nickel(II). ISSA *et al.*[8] studied alkaline triethanolamine solution in which manganese(II) was complexed with triethanolamine and oxidized to manganese-(III); these authors used the reduction wave of manganese(III) to manganese(II) for D.C. polarographic determination. Recently, FUJINAGA AND HAGIWARA[9] applied this supporting electrolyte to the square-wave polarographic determination of manganese.

TABLE I

SQUARE-WAVE POLAROGRAPHIC DATA FOR MANGANESE IN SEVERAL SUPPORTING ELECTROLYTES

(Peak height for $1 \cdot 10^{-4}$ *M* Mn(II) at 1/32 of maximum sensitivity)

Supporting electrolyte[a]	*Peak potential (V vs. S. C. E.)*	*Peak height*	*Coloration or precipitation*
1 *M* KOH–0.5 *M* glycerol	−0.2	Overlapped	Faint pink
	−1.72	16	
1 *M* KOH–0.5 *M* diglycerol	No peak		Precipitate
1 *M* KOH–0.3 *M* mannitol	−0.33	30	Faint brown
	−1.72	11	
1 *M* KOH–1 *M* MEA	No peak		Precipitate
1 *M* KOH–1 *M* DEA	−0.48	20	Faint brown
1 *M* KOH–0.4 *M* TEA	−0.49	58	Green
1 *M* KOH–0.1 *M* DHEG	−0.42	55	Clear
1 *M* KOH–0.1 *M* EDDHA	No peak		Precipitate
1 *M* KOH–0.1 *M* NTA	No peak		Precipitate
1 *M* KOH–0.1 *M* EDTA	No peak		Precipitate

[a] MEA = monoethanolamine; DEA = diethanolamine; TEA = triethanolamine; DHEG = dihydroxyethylglycine; EDDHA = ethylenediamine-di(*o*-hydroxyphenylacetic acid); NTA = nitrilotriacetic acid; EDTA = ethylenediaminetetraacetic acid.

In the present investigation, alkaline solutions of several chelating agents, such as alcoholamines, polyalcohols, and aminopolycarboxylic acids, were examined. The polarographic data for manganese in the supporting electrolytes studied are shown in Table I with the remarks on coloration and precipitation.

Among the supporting electrolytes studied, the alkaline aminopolycarboxylic acid solutions, in which the precipitation occurs, failed to give any polarographic peak. In the alkaline glycerol or mannitol solutions, manganese(II) gave two peaks. It has been confirmed by D.C. polarography that the first peak at -0.2 or -0.33 V *vs.* S. C. E. corresponds to the anodic oxidation of manganese(II) to manganese(III), whereas the second peak at -1.72 V *vs.* S. C. E. corresponds to the irreversible reduction of manganese(II) to the metal. The application of the peaks to the determination of manganese, however, is not recommended, because the first peak is partly overlapped by the wave of the anodic dissolution of mercury and the second one is not sufficiently high.

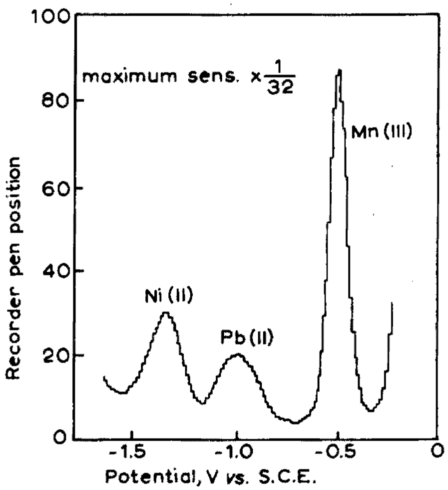

Fig. 2. Square-wave polarogram for $1 \cdot 10^{-4}$ *M* Mn(III), $1 \cdot 10^{-4}$ *M* Pb(II) and $2 \cdot 10^{-4}$ *M* Ni(II) in 1 *M* KOH–0.4 *M* triethanolamine.

The most satisfactory results were obtained in alkaline solutions of alcoholamines, such as diethanolamine, triethanolamine, and dihydroxyethylglycine. In these solutions, manganese(II)– alcoholamine complexes are formed and, at the same time, oxidized to the manganese(III) complexes with air. A well-defined peak, corresponding to the reduction of manganese (III), was obtained from such solutions. The peak height from the 1 *M* alkaline–1 *M* diethanolamine solution was smaller than that from the other two solutions. This is due to the incomplete oxidation of manganese(II) in the former solution. Both the triethanolamine and the dihydroxyethylglycine solutions were quite satisfactory for the determination of manganese. In the present work, triethanolamine, which is easily obtainable, was preferred. Figure 2 shows the polarogram of manganese(III) in the presence of lead(II) and nickel(II), which is obtained from the 1 *M* potassium hydroxide–0.4 *M* triethanolamine solution.

In this supporting electrolyte solution, calibration curves were prepared at several instrument sensitivities. A linear relation was obtained between the concentration and the peak height in the range of 0.5–30 μg of manganese in 5 ml of the supporting electrolyte.

Oxidation of manganese(II)

For the determination of manganese by means of the reduction peak of manganese(III), the preliminary oxidation of manganese(II) must be quantitative. Manganese(II) in alkaline triethanolamine is oxidized by air but complete air-oxidation is not achieved with even moderate concentrations of manganese(II)[8]. Even when small concentrations are encountered as in the square-wave polarographic determination, heating and air-bubbling are necessary to complete the oxidation of manganese(II) in the 0.5 M potassium hydroxide–0.2 M triethanolamine[9].

TABLE II

EFFECT OF AERATION AND HEATING ON THE OXIDATION OF MANGANESE(II)

(Sample solution: $1 \cdot 10^{-5}$ M Mn(III) in 1 M KOH–0.4 M triethanolamine. Peak height: at 1/4 of maximum sensitivity)

Aeration time (min)	*0*	*5*	*10*	*20*
Peak height for aeration at 25°	46	47	46	45
Peak height for aeration at 80°	—	46	45	47

A $1 \cdot 10^{-5}$ M manganese solution in 1 M potassium hydroxide–0.4 M triethanolamine was aerated by passing a stream of air while holding the temperature of the solution at 25 and 80°, and then the polarographic peak height at a potential of −0.48 V *vs.* S. C. E. was measured. As shown in Table II, the results indicate that aeration and heating have no effect on the peak height. Manganese(II) is, therefore, readily oxidized by dissolved oxygen. The disagreement of the present result with the observation by FUJINAGA AND HAGIWARA[9] might be due to the differences in the concentration of the supporting electrolyte.

Effect of foreign ions

Since lead(II), nickel(II), aluminum(III), thorium(IV), titanium(III), chromium(III), vanadium(IV), silver(I), and rare earth ions have no or slight adsorbability on anion-exchange resins of the strongly basic type, they are accompanied by manganese(II) on elution with 9 M hydrochloric acid. As these ions, with the exception of lead(II) and nickel(II), are not readily reduced in polarography, they do not interfere with the determination of manganese.

When the amount of lead is larger than manganese, it may interfere since lead(II) gives a reduction peak near the manganese(III) peak which overlaps at the bottom of the peak. To determine the optimum conditions for the resolution of the peaks of manganese(III) and lead(II), the alkaline triethanolamine solutions were studied with different alkaline–triethanolamine ratios; the results obtained are illustrated in Fig. 3. The peak height of manganese(III) shows a maximum at 0.05 *M* in triethanolamine and the peak potential does not change with the electrolyte concentrations. On the other hand, the lead(II) peak shifts to more negative potentials and the height is suppressed with increase of triethanolamine. In order to obtain a perfect resolution, the concentration of triethanolamine should be above 0.2 *M*. From the 1 *M* potassium hydroxide–0.4 *M* triethanolamine solution, a good resolution can be obtained as was shown in Fig. 2.

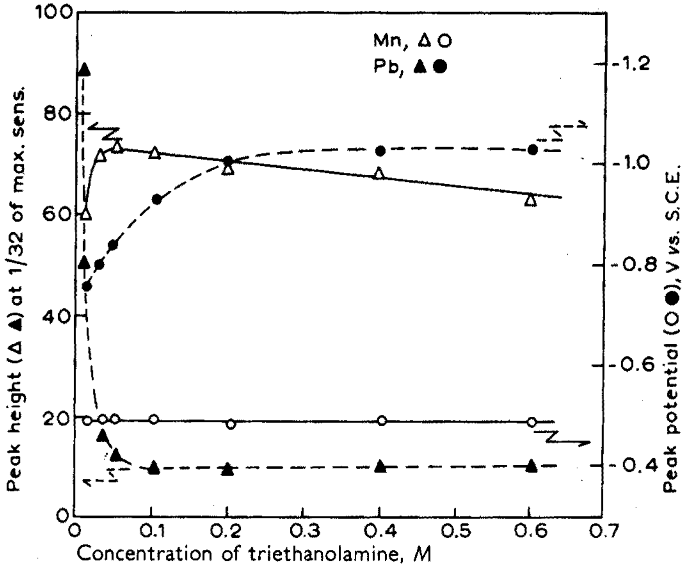

Fig. 3. Variations of peak height and potential with the concentration of triethanolamine for $1 \cdot 10^{-4}$ *M* Mn(III) (solid line) and for $1 \cdot 10^{-4}$ *M* Pb(II) (dotted line).

TABLE III

SQUARE-WAVE POLAROGRAPHIC DATA FOR THE METAL IONS IN THE 1 *M* KOH–0.4 *M* TRIETHANOLAMINE SOLUTION

Ion[a]	*Peak height*[b]	*Reversibility*	*Peak potential (V vs. S. C. E.)*
Mn^{3+}	45	Reversible	−0.49
Fe^{3+}	62	Reversible	−1.05
Pb^{2+}	8	Irreversible	−1.02
Ni^{2+}	4	Irreversible	−1.4
Cu^{2+}	8	Irreversible	−0.55
Cd^{2+}	7	Irreversible	−0.91, −1.02[c]
Zn^{2+}	1	Irreversible	−1.6
CrO_4^{2-}	6	Irreversible	−1.11
UO_2^{2+}	3 (ppt.)	Irreversible	−0.94

[a] Concentration of the ions: $1 \cdot 10^{-5}$ *M*.
[b] Peak height: measured at 1/4 of maximum sensitivity.
[c] Doublet wave.

The square-wave polarographic data for several ions in the 1 M potassium hydroxide–0.4 M triethanolamine solution are shown in Table III. For ease of comparison, a concentration of $1 \cdot 10^{-5}$ M was used for each element and the measurements were carried out at one-fourth of the maximum sensitivity of the instrument. Not only manganese(III) but also iron(III) gives a well-defined sharp peak. An irreversible copper peak, which appears close to the manganese peak, interferes. Copper(II), however, does not accompany manganese(II) during the ion-exchange separation, being strongly absorbed on the anion-exchange resin on elution with 9 M hydrochloric acid. The determination of manganese in uranium by the present method is therefore performed without any interference from other impurities usually contained in the sample.

Accuracy and precision

The described method was evaluated by analysing synthetic samples which were prepared by adding known amounts of manganese to pure uranium solutions. The

TABLE IV

DETERMINATION OF MANGANESE IN SYNTHETIC SAMPLES

Mn added (p.p.m.)	*Mn found (p.p.m.)*	*Mean of Mn found (p.p.m.)*	*Deviation (p.p.m.)*
2.8	3.4 3.5 3.4 3.1	3.4	+0.6
4.4	4.9 5.2 5.4 5.2	5.2	+0.8
5.5	6.0 5.9 6.0 5.6	5.9	+0.4
Blank	0.7 0.5 0.6 0.6	0.6	

TABLE V

DETERMINATION OF MANGANESE IN URANIUM DIOXIDE SAMPLES

Sample	*Mn found by the present method*[a] *(p.p.m.)*	*Mn found by spectroscopy method*[b] *(p.p.m.)*
A	3.8	4
B	5.0	4
C	<0.5	<2

[a] Mean value of 4 determinations.
[b] Carrier distillation method.

results are shown in Table IV. If the blank value, 0.6 p.p.m., is subtracted, the values found coincide with the added ones. These results indicate that manganese is separated by the ion-exchange procedure with 100% efficiency and that the present technique offers an accurate method for determining manganese in uranium.

The reproducibility of the procedure was studied by analyzing 14 separate sample solutions, each containing 5.5 μg of manganese and 1 g of uranium in 9 *M* hydrochloric acid. The average value found was 5.4 μg and the calculated standard deviation was ±0.26 μg.

Analytical results

The method was applied to uranium dioxide samples of reactor-grade. The results are given in Table V with the data obtained by the carrier distillation technique of emission spectrography. The values obtained by the two methods are in a fairly good agreement, and indicate that the present method is more sensitive than the spectrographic method. Once the calibration curves have been established and a bank of the ion-exchange columns has been prepared, many determinations can be performed simultaneously within 4 h.

The author wishes to express his sincere thanks to Dr. K. SAKAI for his helpful discussions, and to Dr. T. NAKATOGAWA and Dr. N. KAWASHIMA for their kind guidance throughout the experiments.

SUMMARY

Traces of manganese in uranium and its compounds can be determined by ion-exchange separation and square-wave polarography. When a 9 *M* hydrochloric acid solution of the sample is introduced into a column of strongly basic anion-exchange resin, manganese can be quantitatively separated from uranium by eluting with 9 *M* hydrochloric acid. The determination of the separated manganese by square-wave polarography is performed in 1 *M* potassium hydroxide–0.4 *M* triethanolamine solution with an excellent sensitivity. The lower limit of the method is 0.5 p.p.m. of manganese.

RÉSUMÉ

Une méthode est décrite pour le dosage de traces de manganèse dans l'uranium et ses composés. La séparation se fait sur résine échangeur d'ions et le dosage par polarographie à ondes carrées. Il est possible de déterminer ainsi des teneurs en manganèse de 0.5 p.p.m.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren von Mangan in Uran beschrieben. Sie beruht auf der Trennung mit Hilfe eines Ionenaustauscherharzes und anschliessender Square wave-Polarographie in einer Grundlösung aus 1 *M* Kaliumhydroxid–0.4 *M* Triethanolamin. Mit dieser Methode können noch 0.5 p.p.m. Mangan in Uran bestimmt werden.

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DETERMINATION OF THORIUM IN ROCKS

THE ARSENAZO III REACTION IN PERCHLORATE MEDIUM

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Many reagents have been used for the photometric determination of small amounts of thorium, the most favoured being "thorin"[1], also known as "thoron", "APANS", and by several other names. The reaction of thorium with thorin, as with other reagents, is not selective, and rather complete separation of thorium from most other elements is required. FLETCHER, GRIMALDI AND JENKINS[2] improved the selectivity of the reaction by introducing mesotartaric acid as a masking agent for zirconium. However, the concentration of mesotartaric acid is critical and rather elaborate separations are still required[3].

KUZNETSOV[4,5] and SAVVIN[6] introduced a series of reagents similar in structure to thorin, and identified by the general name "arsenazo" (Fig. 1). The reactions of arsenazo I and arsenazo II with thorium are similar to that of thorin, that is, they form stable coloured complexes in mildly acid solutions, but increased acidity causes decomposition of the complexes. The arsenazo I and II reactions are somewhat more sensitive than that of thorin, while arsenazo II has a slightly higher tolerance to excess

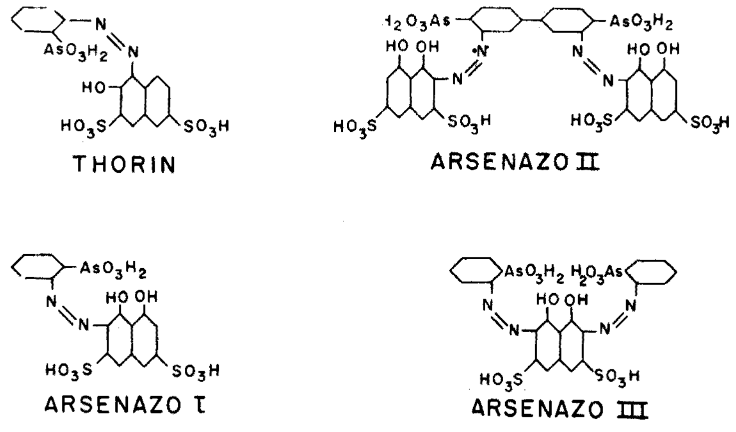

Fig. 1. Reagents for thorium.

acid than has arsenazo I[6]. Arsenazo III, however, has the unusual ability to form stable coloured complexes with thorium at acidities as high as 8 *N*. Zirconium, hafnium and uranium(IV) are the only other elements which enter into similar reactions with this reagent in strongly acid solution. Within limits, zirconium and hafnium can be masked with oxalic acid, while uranium can be oxidized to the hexavalent state.

Increased sensitivity is another advantage in the use of arsenazo III over other reagents. The extent of increase in sensitivity depends on a variety of factors. Thus variations in the concentration of oxalic acid used for masking zirconium and hafnium have a significant effect on the thorium reaction, necessitating the use of a fixed concentration in sample, blank and standard solutions. NEMODRUK AND KOCHETKOVA[7], in a study of the thorium–arsenazo III reaction, deduced that several series of complexes are formed at varying acidities, but that the most sensitive has a thorium–reagent molar ratio of 1 : 3, and is stable in the acidity range of 4 *N* to 6 *N*, either in hydrochloric acid, or in nitric acid (in the presence of inhibitors to prevent oxidation of the reagent).

THE REAGENT

Considerable difficulty was encountered in obtaining a supply of arsenazo III. SAVVIN gives two procedures for synthesizing the reagent[6,8], but warns that a mixture of arsenazo I and arsenazo III may be obtained if operating parameters are not correct. No attempt was therefore made to synthesize the reagent in this work. Most dealers were unable to supply arsenazo III, one of them actually offering arsenazo I on the assumption that they are the same compound. Another provided a substance labelled "arsenazo III", but it failed to give a colour reaction with thorium in 3 *N* acid solution. Infrared analysis revealed[9] that the material was nearly 50% arsenazo I, and that the remainder was not arsenazo III.

Still another supplier provided a substance labelled "arsenazo III". This material gave a qualitative colour reaction with thorium in strongly acid solution, but the sensitivity was lower than expected, and aqueous solutions of the material appeared to be unstable. It was suspected, on the basis of SAVVIN's work[8] that some arsenazo I was present. This was confirmed by infrared analysis, which indicated the presence of over 25% arsenazo I[9].

A purification procedure was then attempted. The impure material was leached with successive portions of water, in which arsenazo I is more soluble than is arsenazo III. The residue was dissolved in dilute sodium carbonate solution and reprecipitated by the addition of hydrochloric acid and ethanol. This procedure gave a 20% yield of a product which reacted with thorium very much as reported by SAVVIN. Infrared analysis indicated that the "purified" product was largely arsenazo III, but that it also contained appreciable impurities[9].

A supply of pure arsenazo III was finally obtained through the kindness of SAVVIN himself, who presented some of it to R. W. BOYLE, of the Geological Survey of Canada when the latter visited the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, in November, 1962. Practically all of the original development work on the analytical properties of arsenazo III and its analogues[10,11] was done at that Institute.

Subsequently, information was received that the suppliers of the impure material were planning to make available a purer product sometime in 1963.

APPLICATION TO ROCKS

SAVVIN[8,12] gives a procedure in which silicate rock samples are decomposed with hydrofluoric acid alone. The insoluble fluorides, which include that of thorium, are separated and dissolved by repeated fuming with perchloric acid. A final photometric determination (covering the range 0 to 25 μg of thorium) is made in 2.8 *N* hydrochloric acid, in the presence of ascorbic acid to reduce iron(III) and of oxalic acid to mask zirconium.

However, some components of some rocks are not decomposed by hydrofluoric acid. Notable among those is zircon, which may contain a significant portion of the thorium in a rock. The acidity in the final solution also appears to be lower than the optimum recommended by NEMODRUK AND KOCHETKOVA[7].

In a method designed for use with ultrabasic rocks, POLYAKOV AND VOLYNETS[13] fuse the sample with sodium peroxide, leach the melt with water, and dissolve the residue in acid. An ammonium hydroxide precipitation is then made, and the precipitate filtered and redissolved in acid. Thorium is separated from the resulting solution by ion exchange and finally determined as in SAVVIN's method, except that the final acidity is 5 *N*.

No attempt was made to apply this procedure in this work because difficulties were foreseen in obtaining a resin with the properties of the KU-2 used by POLYAKOV AND VOLYNETS, who state further that their procedure "should be rigidly adhered to".

In an effort at combining the complete decomposition procedure suggested by POLYAKOV AND VOLYNETS and the simple fluoride separation used by SAVVIN, an attempt was made to decompose "whole rock" samples with potassium bifluoride. This technique proved entirely unsatisfactory. Somewhat better results were obtained by decomposing the sample by sodium peroxide sinter[14], leaching with water, dissolving the residue in acid, adding hydrofluoric acid to precipitate fluorides and finishing as in SAVVIN's method. In general, however, results by this procedure tended to be low and erratic.

OXALATE SEPARATION

In a procedure for use on ferruginous and siliceous lowgrade thorium ores and on fluorapatite and phosphorite (all of which contain at least 10 times as much thorium as there is in most rocks), LUKYANOV, NIKOLSKAYA AND KOZLOVA[15] decompose the sample by peroxide fusion, and then leach with water. The resulting residue is dissolved in acid, calcium is added, and the latter precipitated with oxalic acid to concentrate the thorium. The oxalates are ignited to oxides at 700°, the oxides are dissolved in hydrochloric acid, and thorium is determined in the resulting solution. The final acidity is 4 *N*, and the concentration of oxalic acid in the coloured solution is about one-tenth of that recommended by SAVVIN[6].

The oxalate separation procedure was applied to rocks in this work, with slight modification to allow for the lower concentrations of thorium involved. It was found, however, that the ignited oxides were contaminated with particles of carbon from the filter paper. Although this difficulty could have been eliminated by longer ignition or by use of a filtering crucible, a wet oxidation with nitric and perchloric acids was introduced for the purpose of destroying the filter paper and oxalic acid. A higher ignition temperature could also have been used to burn off the carbon, but such treatment might have yielded a form of thorium oxide which would not dissolve in hydrochloric acid. Although oxalic acid is present in the final coloured solution, it is essential that the oxalate ion in the precipitate be destroyed, so that the oxalate concentration in the final solution may be precisely controlled.

THE COLOUR REACTION IN PERCHLORIC MEDIUM

Since the wet oxidation yielded a perchloric acid solution, it was decided to do the final determination in that medium. Three unexpected differences from the hydrochloric medium were observed, all of them indicating a superiority in the perchloric medium (Fig. 2): (*a*) the reaction is more sensitive, (*b*) the system follows Beer's law over a wide range, and (*c*) the colour appears to be more stable.

These properties of the perchloric system are surprising, since NEMODRUK AND

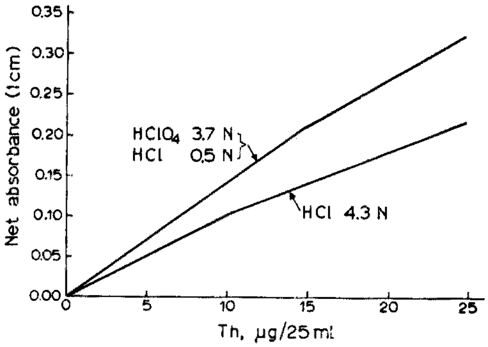

Fig. 2. Effect of perchloric acid.

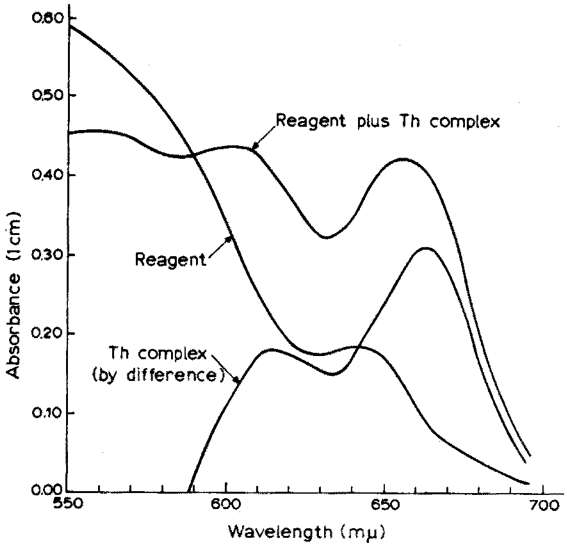

Fig. 3. Absorption spectra.

Kochetkova[7] reported identical operating parameters in hydrochloric and nitric media. Chung and Riley[16] report that the thorium complex with thorin is stable at higher acidities in perchlorate medium than in chloride medium, but they do not suggest that sensitivity is enhanced in perchlorate medium.

The curve for the hydrochloric system in Fig. 2 checks with one given by Savvin[6] who gives no explanation for the break in the curve. Nemodruk and Kochetkova[7] report that the 1 : 3 complex slowly changes, after several hours, to the 1 : 4 complex, which has a lower extinction coefficient. It was observed in our work that coloured solutions in hydrochloric medium show noticeable fading if left overnight, but that those in perchloric medium retain their colour, to the naked eye at least. In the absence of thorium, the reagent is rose-coloured in acid solution. The thorium complex itself is green, but appears purple in the presence of excess reagent (Fig. 3).

DECOMPOSITION OF THE SAMPLE

Rafter's low-temperature sodium peroxide sinter method[14] has many advantages ove- the classical peroxide fusion. Thus the controlled temperature permits more reprodur cible treatment, and attack on the crucible is minimized. Platinum crucibles may be used, a procedure which would not be possible at fusion temperatures. As modified by Grimaldi *et al.*[3] the sinter involves heating at a lower temperature but for a longer time than in Rafter's original technique.

Our initial work involved sintering in platinum, but this resulted in occasional high blank readings. No explanation was found for this effect, although it does suggest interference from platinum. The effect was eliminated by using iron crucibles. The small amounts of hydrous ferric oxide derived from the crucibles actually proved beneficial as a carrier for microgram quantities of thorium in the water leaching of the sinter cake of blanks, standards and samples which are low in iron and magnesium content.

Some silicate samples left a gelatinous residue after acid treatment of the residue from the water leach of the sinter cake. Since all such samples contained relatively large amounts of silica and either calcium or magnesium, it was assumed that calcium or magnesium silicates had been formed in the ignition of the samples before the sintering, and that these silicates had not been decomposed in the water leach. Ignition of the residue, followed by treatment with hydrofluoric acid, confirmed that the residue was silica. Separate thorium determinations on such residues showed that as much as 1 μg of thorium may be held by this silica — corresponding to 2 p.p.m. of thorium on a 0.5-g sample. Unfortunately, all of the samples which showed this effect contained less than 10 p.p.m. of thorium, so it is not known whether the effect is more pronounced with higher thorium contents.

For carbonate samples, direct attack with hydrochloric or nitric acid is used, any insoluble residue being brought into solution by treatment with hydrofluoric and perchloric acids, or by sodium peroxide sinter, where required.

EFFECT OF TITANIUM

In the wet oxidation of the oxalate precipitate, some samples produced an insoluble residue, which failed to redissolve on treatment with hydrochloric and/or perchloric acids. The resulting suspension was entirely unsuitable for photometric analysis.

Some other samples, which gave a clear solution after fuming with perchloric acid, produced unstable colours with arsenazo III, the absorbance showing a steady decline. "Complete analysis", which had been done on these samples before the thorium work, revealed that all of the samples showing these effects had relatively high titanium contents. Although the precipitation of thorium on the calcium oxalate carrier would presumably eliminate most of the titanium, apparently some titanium was carried down with the oxalates, and produced the familiar intractable residue on fuming with perchloric acid.

Since it was known that oxalic acid produces a masking effect on zirconium (and to a lesser extent on thorium) in the final solution for photometry, it was postulated that a similar effect existed with titanium, but that the reaction between titanium and oxalic acid was slow. Assuming some reaction between titanium and arsenazo III in the presence of thorium, one would expect initial readings to be high, but that fading would proceed towards a correct value. To test these assumptions, three solutions were carried through the procedure, beginning with the oxalate precipitation. The first solution was a blank, the second contained 20 μg of thorium, and the third, 20 μg of thorium and 5 mg of titanium.

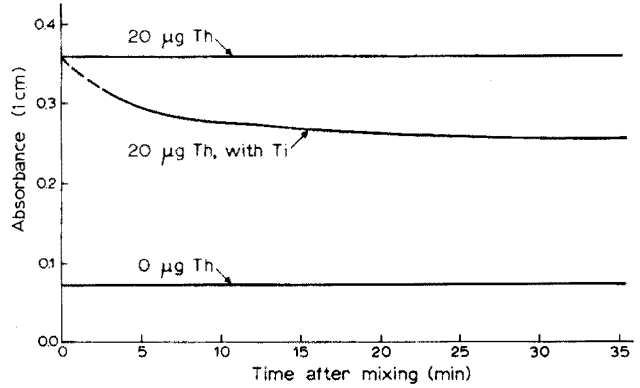

Fig. 4. Effect of titanium.

Results (Fig. 4) were unexpected. Apparently, titanium produces a negative effect, which becomes progressively more pronounced with passage of time. It will be noted that extrapolation of the absorbance *vs.* time curve for the solution containing titanium, to zero time, gives an apparently correct absorbance reading. The actual amount of titanium carried down with the oxalates was not determined, but could be assumed to be a fraction of a milligram. SAVVIN[8] reports that no interference may be expected from titanium where its concentration does not exceed that of thorium by more than a factor of 10. However, he does not state the nature of the titanium interference.

The oxalate precipitation used was that of LUKYANOV, NIKOLSKAYA AND KOZLOVA[15], in which solid oxalic acid is added to a 0.2 *N* hydrochloric acid solution of the sample. In an effort to reduce the co-precipitation of titanium, the procedure was changed to the homogeneous precipitation of CARRON *et al.*[17]. Methanolic methyl oxalate solution is added to the hot nitrate solution of the sample at pH 3.8. After digestion, the pH is adjusted to 2.0 and further calcium is added subsequently. The precipitates thus procured are more nearly white, suggesting reduced co-precipitation of iron and presumably of titanium. Both titanium effects are minimized, but not entirely eliminated. For samples containing more than 1% titanium oxide (corresponding to 3 mg of titanium on a 0.5-g sample), double precipitation of the oxalates is recommended.

EFFECT OF CALCIUM

In the course of the development work on this method, it was observed that the magnitude of the blank reading varied considerably, and that the same was true, although to a lesser extent, of the slope of the calibration curve. The source of this variability was found to lie in the calcium content of the final solution, as shown in Fig. 5. It will be noted that the calcium concentration also affects the range of thorium concentrations over which Beer's law is effective.

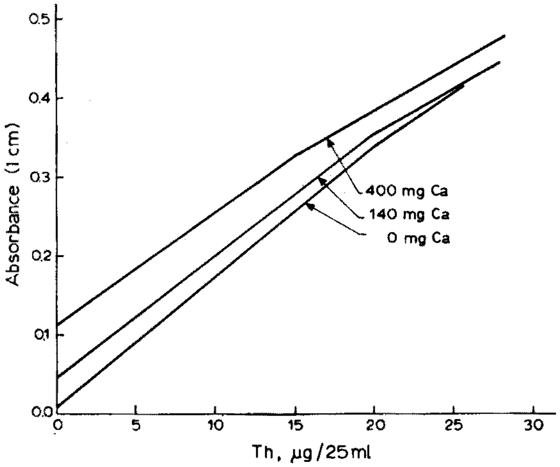

Fig. 5. Effect of calcium.

In actual analysis, it is important that the calcium content of sample, standard and blank be as close together as possible. Generally, the magnitude of the calcium effect is such that an approximate knowledge of the calcium content is adequate.

RECOVERY OF THORIUM AS THE OXALATE

Failure to achieve quantitative recovery of thorium in oxalate precipitations is an all-too-familiar phenomenon. As a check on recovery, solutions containing known variable amounts of thorium and fixed quantities of calcium were taken through the oxalate precipitation and analyzed photometrically for thorium. The calibration curve was based on standard solutions containing the same quantities of thorium and calcium as were in the test solutions, but no oxalate precipitation was done on the standards. Results (Table I) show that recoveries were satisfactory.

RESULTS

To check the reproducibility and accuracy of the results obtained by the proposed method, 3 standard samples and 4 unknowns were analyzed, the latter repeatedly, on

TABLE I

RECOVERY OF THORIUM IN OXALATE PRECIPITATION

Thorium (μg)	
Taken	*Found*
0.0	0.0
5.0	5.2
10.0	9.9
15.0	15.3
20.0	20.0
25.0	24.8

TABLE II

RESULTS ON ACTUAL SAMPLES

Sample no.	*Thorium (p.p.m.)*	
	Present	*Found*
G-1	52[a]	54
W-1	2[a]	4
Syenite 1	1270[b]	1240
B-317	—	36
		33
		37
B-318	—	29
		30
B-319	—	48
		43
B-320	—	10
		12
		11

[a] Recommended values, U.S.G.S. Bulletin 1113.
[b] Recommended value, Canadian Association for Applied Spectroscopy.

different days. Results (Table II) suggest adequate precision and accuracy. Some of the determinations on the unknown samples were done on samples which were sintered in platinum crucibles, others in iron crucibles, but such changes in procedure appear to have little effect on the results. In the analysis of the syenite, the sample solution was aliquoted after decomposition.

EXPERIMENTAL

Apparatus

Most of the photometric readings were made with a Beckman Model DU spectrophotometer, a few on a Beckman Model B. Absorption spectra were recorded on a Bausch and Lomb Model 505 spectrophotometer. Infrared spectra[9] were recorded for us on a Perkin-Elmer Model 21 infrared spectrophotometer, using potassium bromide pellets.

Recommended procedure

In the procedure finally adopted, 0.5-g samples of rock are first ignited at a high temperature. After cooling, the samples are mixed with sodium peroxide and sintered at 460° for 1 h. The cooled cake is allowed to react with water. Two blanks are normally carried to this point. A known quantity of thorium is then added to one blank, to serve as a standard. The hydroxide suspension is filtered and brought into solution by means of diluted nitric and hydrochloric acids. (Carbonate samples are taken to this point as outlined above.)

Calcium is added and oxalates precipitated homogeneously by CARRON's procedure[17]. The filtered oxalates, together with the filter papers, are returned to solution by digestion with nitric acid, followed by fuming with perchloric acid. Where the titanium dioxide content of the sample is known or suspected to be over 1%, the oxalate precipitation is repeated. After removal of excess perchloric acid, a small, controlled quantity of hydrochloric acid is added, and the residue taken up in a small volume of water. Iron(III) is reduced by the addition of a little ascorbic acid. Controlled quantities of perchloric and oxalic acids are then added, followed by arsenazo III. The solutions are photometered at 660 mμ.

Special reagents

Sodium hydroxide (500 g/l). Dissolve 250 g in about 325 ml of water. Allow to stand overnight. Decant and dilute to 500 ml. Store in polyethylene. For the *alkaline wash solution* dilute 5 ml of this solution to 500 ml.

Methyl oxalate solution. Heat oxalic acid crystals at 100° overnight. Cool in a desiccator. Break up the crust and heat at the same temperature one hour longer. Cool in a desiccator. Dissolve 100 g of the anhydrous oxalic acid in 250 ml of methanol. Allow to stand at least 3 days and filter immediately before using.

Calcium nitrate solution (10 mg CaO per ml). Weigh 9 g of calcium carbonate into a large beaker. Cover with water and dissolve by adding a slight excess of nitric acid. Evaporate to dryness. Take up with a small volume of water and again evaporate to dryness. Dissolve in about 450 ml of water and adjust the pH to the green colour of bromophenol blue indicator. Dilute to 500 ml.

Oxalic acid complexing solution. Dissolve 40 g of oxalic acid crystals in about 400 ml of hot water. Filter and dilute to 500 ml. For the *oxalic acid wash solution,* dilute 60 ml of this solution to 480 ml.

Perchloric acid (4 : 1). Mix 400 ml of perchloric acid (70%) with 100 ml of water.

Arsenazo III solution. Dissolve 50 mg of arsenazo III in about 90 ml of water and dilute to 100 ml.

Standard thorium solution (5 μg Th per ml). Prepare a concentrated solution, containing about 100 μg of thorium per ml, by dissolving thorium nitrate in water, adding sufficient nitric acid to give a final normality of 1 *N*. Standardize gravimetrically by evaporating aliquots to dryness and carefully igniting to oxide. Dilute an aliquot to give a working solution of 5 μg of thorium per ml. in 1 *N* nitric acid.

Method

Samples should be finely ground, preferably below 200 mesh. Up to 4 samples can be conveniently handled in one batch.

For silicate samples, weigh 0.5 g of sample into a porcelain crucible. Ignite over a Meker burner for 15 min. Allow to cool. Break up lumps with a small spatula and ignite again for 10 min. Allow to cool.

Set up 2 blanks by weighing 5 g of sodium peroxide into each of two 50-ml iron crucibles. Mix each sample with 4 g of sodium peroxide in the porcelain crucible. Line the bottom of a 50-ml iron crucible with about 0.5 g of sodium peroxide. Add the sample–peroxide mixture. "Rinse" the porcelain crucible with about 0.5 g of sodium peroxide, and use the "rinsings" to cover the charge in the iron crucible. Cover all of the iron crucibles and heat in a muffle furnace at 460° for 1 h. Remove from the heat and allow to cool to room temperature.

Remove the crucible covers, wipe off the outside of each crucible with clean tissue, and place in a 250-ml beaker. Add 50 ml of water to the crucible and cover the beaker immediately with a watch glass. When the reaction subsides, rinse down the material spattered on the watch glass and the walls of the beaker. Rinse off and remove the crucible. Pipette 5 ml of standard thorium solution into one of the blanks, which then serves as a check standard. Dilute all of the suspensions to about 125 ml and boil for 15 min.

Filter on Whatman No. 42, 9-cm filter paper and wash with hot alkaline wash solution. Discard the filtrate. Place the original beaker under the filtering funnel, and dissolve the residue through the paper with 4 5-ml portions of hot 2 *N* nitric acid, followed by 3 similar portions of hot 2 *N* hydrochloric acid, and two more of hot 2 *N* nitric acid. Finally, wash the paper 3 or 4 times with water.

If any silica remains on the paper, ignite it in a small platinum crucible, treat with a few drops of perchloric acid and a few ml of hydrofluoric acid and evaporate 3 times to perchloric fumes. Take up with a little water and combine with the main solution in the 250-ml beaker. (If any insoluble residue remains at this point, it should be separated and sintered with sodium peroxide.) The solution is now ready for the oxalate precipitation.

If the sample is a carbonate, raise the temperature slowly in the initial ignition. After the second ignition, rinse the cooled sample into a 150-ml beaker with a little water. Add 5 ml of hydrochloric acid, cover and warm to dissolve, adding a little nitric acid if necessary. Evaporate to dryness and bake to separate silica as usual. Take up the dry residue with hot hydrochloric acid (1 : 1), warm to dissolve soluble matter, and filter into a 250-ml beaker. Wash with hot hydrochloric acid (1 : 10). Ignite the silica and treat with perchloric and hydrofluoric acids as described above. While the silica is being treated separately, evaporate the filtrate to dryness. Add 10 ml of nitric acid, boil, and again take to dryness. Add 5 ml of nitric acid and a little water, and warm to dissolve. The solution is now ready for oxalate precipitation.

Add sufficient calcium nitrate solution to bring the CaO content of the solution to about 150 mg, 10 ml of hydrogen peroxide (30%) and sufficient water to bring the volume to 125 ml. Cover the beaker and heat on a hot plate set at low heat. Remove the cover and add sodium hydroxide solution (500 g/l) dropwise from a polypropylene pipette, with stirring, until the pH is just over 3.8. (This pH can be checked with short-range pH paper. It comes quite close to the point where hydrous ferric oxide begins to precipitate.) Add 15 ml of freshly filtered methyl oxalate solution, stir and allow to digest uncovered on the low-temperature hot plate for 30 min. Remove from the heat, add a little paper pulp, and again add the concentrated sodium hydroxide solution, to pH 2. Allow to stand one hour longer. Add 5 ml of the calcium nitrate solution, dropwise, with stirring, and allow the solution to stand for another hour.

Filter on a Whatman No. 42, 9-cm filter paper, covered with a thin layer of filter paper pulp. Wash with cold oxalic acid wash solution.

Place the filter and precipitate in the original beaker and add 25 ml of nitric acid. Break up the paper, rinse down the walls of the beaker, and rinse off and remove the stirring rod. Cover the beaker with a watch glass and digest on a hot plate set at low heat until a clear solution is obtained (preferably overnight).

(If there is any reason to suspect the presence of more than 1% titanium oxide in the original sample, the solution must be evaporated to dryness and taken up with dilute nitric acid. The entire oxalate precipitation procedure is then repeated, but no calcium is added.)

Rinse off and remove the watch glass, add 5 ml of perchloric acid, cover with a "Speedyvap" watch glass and heat on a sand bath until perchloric fumes are evolved. Allow to cool, rinse down the watch glass and the walls of the beaker, and again heat on the sand bath, this time until all perchloric fumes are expelled. Allow to cool, add 1 ml of hydrochloric acid, rinse down the watch glass and the walls of the beaker, and evaporate to dryness on the sand bath. Allow to cool, add 1 ml of hydrochloric acid and 5 ml of water. Swirl to dissolve. Add a few crystals of ascorbic acid and swirl to decolorize. Pour into a dry 25-ml volumetric flask. Rinse the beaker with 10 ml of perchloric acid (4 : 1) and pour the rinsings into the volumetric flask. Add 5 ml of oxalic acid complexing solution directly to the flask, and swirl to mix. Rinse the beaker with 2 ml of water and add the rinsings to the flask. Add 1 ml of arsenazo III solution and dilute to volume. Mix well before measuring the absorbance in a 1-cm absorption cell at 660 mμ.

Calibration

Into 6 150-ml beakers, measure 0, 1, 2, 3, 4, 5 ml of standard thorium solution (*i.e.*, 0 to 25 μg of thorium). Add 20 ml of calcium nitrate solution and 5 ml of perchloric acid to each. Cover with "Speedyvap" watch glasses and continue as in the last paragraph above. Plot absorbance *vs.* μg of thorium.

CONCLUSION

A method has been developed for determining traces of thorium, with acceptable results for the samples studied thus far. Further studies could be made on the nature of the effects of platinum, titanium and calcium, and of how and why these effects and the sensitivity of the method vary in different anionic media. Some preliminary experiments were tried in a possible application of the method to the determination of small amounts of thorium in zircon. LUKYANOV, SAVVIN AND NIKOLSKAYA[18] reported a procedure for thorium in zircon, but it involved heating a zirconium sulfate residue to a point where sufficient sulfate had been decomposed to prevent masking of the thorium reaction, without heating to the point where the residue would not redissolve in hydrochloric acid. There is room for much further work.

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SUMMARY

Savvin's reagent, arsenazo III, has been examined for the determination of traces of thorium in rocks. The superior sensitivity and selectivity of the arsenazo III reaction over the thorin reaction have been confirmed. Sensitivity and stability have been improved by working in a perchlorate medium. Anomalous effects were observed in the presence of relatively large amounts of titanium. Silicate samples are decomposed by Rafter's peroxide sinter, the sinter cake leached with water, and the residue dissolved in acid. Thorium is collected on a calcium oxalate precipitate and determined photometrically in perchlorate medium at 660 mμ. The normal working range is 0 to 25 μg of thorium on a 0.5-g sample.

RÉSUMÉ

L'auteur propose l'utilisation de l'arsenazo III (réactif de Savvin) pour le dosage de traces de thorium dans les minerais (0–25 μg Th/0.5 g d'échantillon). Ce réactif présente une sensibilité et une sélectivité supérieures à celles du thorin. On procède par désagrégation du silicate à analyser, puis on recueille le thorium sur un précipité d'oxalate de calcium et on le dose photométriquement, en milieu perchlorique, à 660 mμ.

ZUSAMMENFASSUNG

Zur Bestimmung von Spuren Thorium in Gesteinen wurde Arsenazo III geprüft und die hohe Empfindlichkeit und Selektivität des Reagenzes bestätigt. Der Arbeitsbereich lag bei 0–25 μg Thorium für eine Probe von 0.5 g. Das Thorium wurde nach dem Aufschluss zusammen mit Calciumoxalat ausgefällt und spektralphotometrisch in einem Perchlorat-Medium bei 660 mμ bestimmt. Anomale Effekte wurden in Gegenwart von relativ grossen Mengen Titan beobachtet.

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DETERMINATION OF CALCIUM, STRONTIUM AND BARIUM IN SINGLE CRYSTALS OF ALKALI HALIDES BY NEUTRON ACTIVATION

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Ionic crystals can include in their crystal lattice during crystallization from solutions or melts small quantities of impurities in either interstitial or substitutional positions. The presence of these impurities has a strong influence on many of the physical properties of single crystals, such as ionic conductivity, light absorption, dielectric loss, etc. The effect is particularly strong if the impurity has a valence different from the valences of the main constituents of the crystal. In spite of the importance of the influence of impurities on the mentioned properties, very little experimental work has been done with the systematic application of trace analysis, even although many of the trace analysis techniques have sensitivities well below one part per million.

We have studied the determination of alkaline earth metals in single crystals of alkali halides in support of the research programs on solid state physics carried on by Euratom and by the University of Milan.

TABLE I

SENSITIVITIES OF A FEW OF THE TRACE ANALYSIS TECHNIQUES FOR THE DETERMINATION OF ALKALINE EARTH METALS (in μg/ml)

	Activation analysis (neutron flux = $2 \cdot 10^{13}$ neutrons/cm^2 · sec)	*Copper spark*	*Flame spectrophotometry*	*Amperometric titration*
Ca	0.1	0.1	0.03	100
Sr	0.015	0.5	0.1	
Ba	0.0012	0.1	3	25

Table I shows the sensitivities of the trace analysis techniques frequently employed for the analysis of alkaline earths, compared on a common basis[1]. It may be seen that activation analysis compares favourably with the other techniques for the determination of strontium and barium, while it is somewhat less sensitive than flame photometry for the determination of calcium. The matrix effect has not been taken into account in this comparison. The sensitivity of emission spectrography and flame photometry, for example, is in this case lower than the one reported, due to the diminution of the excitation of the alkaline earth metals in presence of high quantities

TABLE II

MOST IMPORTANT RADIOISOTOPES FORMED BY NEUTRON ACTIVATION OF ALKALI HALIDES CONTAINING IMPURITIES OF CALCIUM, STRONTIUM AND BARIUM

	Reaction	*Isotope formed*	*Decay*			*Saturation activity*[a] *(dpm/μg)*
			Half-life	*β-Energy (MeV)*	*γ-Energy (MeV)*	
Lithium	(n,α)	^{3}H	12.26 y	0.018	None	$8.5 \cdot 10^{11}$
Sodium	(n,γ)	^{24}Na	15 h	1.39	1.37; 2.76	$1.6 \cdot 10^{7}$
Potassium	(n,γ)	^{42}K	12.5 h	1.98; 3.54	1.53	$1.28 \cdot 10^{6}$
Rubidium	(n,γ)	^{86}Rb	18.7 d	0.68; 1.76	1.08	$4.40 \cdot 10^{6}$
	(n,γ)	^{88}Rb	17.8 m	2.5; 3.6; 5.3	0.9; 1.86	$2.80 \cdot 10^{6}$
Cesium	(n,γ)	^{134m}Cs ↓	3.2 h	None	0.127; 0.137	$1.62 \cdot 10^{7}$
	(n,γ)	^{134}Cs	2.3 y	0.65	0.60; 0.79	$1.40 \cdot 10^{8}$
Calcium	(n,γ)	^{45}Ca	164 d	0.25	None	$2.34 \cdot 10^{5}$
	(n,γ)	^{49}Ca ↓	8.8 m	0.95; 2.00	3.10; 4.05	$3.56 \cdot 10^{4}$
		^{49}Sc	57 m	2.00	None	
Strontium	(n,γ)	^{85m}Sr ↓ ↘	70 m	None	0.15; 0.225; 0.513 (^{85}Rb)	σ unknown
	(n,γ)	^{85}Sr → ^{85}Rb	65 d	None	0.513 (^{85}Rb)	$4.60 \cdot 10^{4}$
	(n,γ)	^{87m}Sr	2.8 h	None	0.39	$1.06 \cdot 10^{6}$
	(n,γ)	^{89}Sr	53 d	1.46	None	$3.40 \cdot 10^{3}$
Barium	(n,γ)	^{131}Ba ↓	11.5 d	None	0.124; 0.216; 0.372; 0.496	$5.40 \cdot 10^{4}$
		^{131}Cs	10 d	None	None	
	(n,γ)	^{139}Ba → ^{139}La	85 m	0.82; 2.22; 2.38	0.143; 0.166 (^{139}La)	$1.98 \cdot 10^{6}$

[a] Calculated for a thermal flux of $2 \cdot 10^{13}$ neutrons/cm^{2}·sec.

of sodium and potassium. Activation analysis has been used for the determination of alkaline earths in water[2-4], high purity metals[5,6], sodium–potassium alloys[7], silicon[8], phosphorus[9], tellurium and selenium[10,11]. Much work has also been done on biological specimens and meteorites (see ref. 12 for general bibliography).

Although the presence of the alkaline halide matrix does not decrease the sensitivity of the determination of alkaline earths to a great extent, the irradiation of high quantities of halogens and alkali metals is nevertheless disturbing. Table II shows the most important radioisotopes formed during irradiation of alkaline halides containing impurities of alkaline earths. The amount of activity formed if the irradiation time is sufficiently long to obtain equilibrium between formation and decay of the radioisotopes formed (saturation activity) is also reported. Sodium, potassium and the halides only form rather short-lived activities (shorter than 36 h). Rubidium and cesium form both short-lived and long-lived activities. Lithium only forms (by the (n, γ) reaction) ^{7}Li, a radioisotope with a half-life of 0.86 sec, but important quantities of tritium are formed by the (n, α) reaction. Tritium is a pure β-emitter with a maximum energy of only 18 KeV, weak enough to be neglected if the chemical separations are carried on in a gloved-box. The alkaline earths form both long-lived and short-lived activities. ^{49}Sc is formed by β^--decay of ^{49}Ca. Its activity is proportional to the concentration of calcium, with some limitations that will be discussed later.

It may be seen from the saturation activities in Table II that if the alkaline earths are present in p.p.m. their activities are many orders of magnitude lower than the activity of the matrix. Chemical separations should in this case be done in a prohibitively high radiation field and very high decontamination factors should be obtained. A proper choice of irradiation and decay times might permit the analysis of sodium and potassium halides, if the long-lived isotopes of the alkaline earths were measured. The time required to complete the analysis would be in this case rather long, and the sensitivity would also be much lower than when the short-lived alkaline earths are measured.

The presence of the matrix could also induce a systematic source of error by the self-shielding of neutrons within the matrix, owing to the high neutron capture cross-section of the alkaline halides, which is particularly important in the case of chlorides.

To avoid these difficulties in the present work the matrix was eliminated before the irradiation by dissolving the crystal in high purity water and passing the solution through a cation exchanger, that was then irradiated. The adsorption and elution conditions were chosen after a study of the distribution coefficients of the alkaline earths on the resin. A blank correction must be made for the presence of traces of alkaline earths in the reagents.

Calcium, strontium and barium are determined in the same sample with a single irradiation of 90 min by measuring, after a suitable chemical separation, the activity of ^{49}Sc, ^{87m}Sr and ^{139}Ba formed during irradiation. The chemical separations are carried on after the addition of carriers containing traces of the long-lived isotopes ^{46}Sc, ^{85}Sr and ^{133}Ba. The chemical yield is then rapidly measured by comparing their activity before and after the separation. The detection limits for our routine operating conditions were 0.5 μg for calcium, 0.1 μg for barium and 0.01 μg for strontium. Lower detection limits could be obtained if necessary.

EXPERIMENTAL

Procedure

Removal of the matrix. A sample of 0.2–0.5 g of the single crystal to be analysed is dissolved in 30 ml of water and passed through a cation-exchange resin contained in a silica column (4 mm diameter and 50 mm long) at a flow rate of 0.1 ml per min or less. The resin (BioRad AG 50 W, X-8, 100–200 mesh) is purified before the adsorption by passing through the column 5 ml of high-purity 4 *M* hydrochloric acid and 5 ml of hot water. The high-purity acid is prepared by adsorbing gaseous hydrogen chloride into water twice-distilled from a quartz still. Both acid and water are stored in polyethylene to minimize the impurity uptake. After the adsorption step the resin is washed with 2 ml of water, dried under an infrared lamp and transferred to an irradiation capsule.

Irradiation. Solid calcium carbonate and dilute solutions of strontium and barium nitrates sealed in thin silica vials are used as comparators. The capsule with the resin and the comparators are packed as close as possible to minimize flux inhomogeneity and irradiated in the pneumatic facility of the Ispra 1 reactor. The thermal neutron flux in this position is $2 \cdot 10^{13}$ neutrons/cm^2·sec.

Separation of scandium and alkaline earth metals. The irradiated resin is transferred to a sintered glass filter and the adsorbed cations are eluted with 15 ml of hot 4 *M* hydrochloric acid, containing carriers of Sc, Sr and Ba (10 mg each). Known amounts of the long-lived isotopes ^{46}Sc, ^{85}Sr and ^{133}Ba are added for the radiochemical measurement of the separation yields. The solution is made basic with ammonia and the alkaline earths are precipitated with 50% potassium carbonate. A few milligrams of aluminium(III) are used to coprecipitate scandium. The precipitate is digested for a few minutes on a hot plate and then separated by centrifugation, washed and dissolved in hydrochloric acid.

Purification of scandium. Scandium is precipitated with ammonia, and centrifuged. The supernate is left for the determination of strontium and barium. The precipitate is dissolved in hydrochloric acid and brought to pH 1. Scandium is extracted with a 5% solution of thenoyltrifluoroacetone (TTA) in benzene, and then back-extracted into 1 *M* hydrochloric acid. The procedure is repeated twice, then scandium is precipitated as hydroxide, filtered and mounted for β-counting.

Purification of strontium and barium. The solution from the separation of scandium is adjusted to pH 8. Strontium and barium are then precipitated as phosphates. The precipitate is dissolved in concentrated nitric acid and cooled in an ice-water bath. The nitrates of strontium and barium are precipitated with fuming nitric acid, dissolved in water and reprecipitated. The decontamination obtained by the precipitation of strontium and barium as nitrates is very good[13] and the precipitate may generally be analysed directly by γ-ray spectroscopy. If necessary, strontium and barium are separated by precipitating barium as chromate and strontium as oxalate.

Determination of the chemical yields. The chemical yields are determined by comparing the activity of ^{46}Sc, ^{85}Sr and ^{133}Ba introduced with the carrier solution and the final activity of the separated fractions. The measurements are made by γ-ray spectroscopy after the decay of the short-lived isotopes.

Activity measurements. A 3″ × 3″ NaI(Tl) integral line by Harshaw was used as detector for the determination of strontium and barium. The output pulses were analysed with a Laben 200-channel pulse-height analyser.

The activity of ^{49}Sc was measured with a plastic scintillation β-counter with a programming unit for the automatic measurement of the activity at prefixed intervals. Pulse-height discrimination curves of the sample and of the standard were made to check the purity of ^{49}Sc. In case of presence of other β-emitting impurities of different energy, the discriminator was set at a suitable level to minimize the impurity effect. The decay was then followed for the time necessary to resolve the composite decay curve.

STUDY OF ADSORPTION AND ELUTION OF ALKALINE EARTH METALS ON CATION-EXCHANGE RESINS

The conditions for adsorption of the alkaline earth metals on the resin to eliminate the matrix before irradiation, and for elution of the irradiated cations, were chosen after a study of the variation of the distribution coefficients of alkaline earth metals with the molarity of the alkali halide solution. They were determined by batch equilibration[14]. Radioactive tracers and gross β- or γ-counting were used to determine the concentration of the ions. The resin was stored dry and weighed at the ambient humidity. The moisture content was determined by heating a sample to constant weight at 100°.

RESULTS

Table III gives a set of results obtained in the analysis of single crystals of different origin. It may be seen that if the crystals are grown with very pure reagents and with carefully cleaned equipment such as in the cases of samples 4, 5 and 9, the concentration of alkaline earth impurities may be lowered almost to negligible levels. It may also be seen that if the crystals are grown from melts to which small amounts of alkaline earth halides have been added, only the analysis of the final crystal can measure the actual concentration of alkaline earths in the crystal.

TABLE III

CONCENTRATION OF ALKALINE EARTH METALS IN SINGLE CRYSTALS OF DIFFERENT ORIGIN (in p.p.m.)

No.	*Matrix*	*Origin*	*Ca*	*Sr*	*Ba*
1	KCl	Harshaw Chemical Co., lot 1	12.8	23.8	4.8
2	KCl	University of Milan, Physics of Solid State	1	3.0	0.53
3	KCl	Korth Chem. Co.	N.D.[a]	0.03	0.96
4	KCl	University of Milan, Physics of Solid State, ~ 1160 p.p.m. of Sr as $SrCl_2$ added to the melt	N.D.	167	0.27
5	KCl	Korth Chem. Co., ~7000 p.p.m. of Sr as $SrCl_2$ added to the melt	N.D.	82	0.55
6	KCl	Harshaw Chem. Co., lot 2	12.3	N.D.	0.90
7	KCl	Harshaw Chem. Co., lot 3	32.4	2.1	N.D.
8	KBr	Harshaw Chem. Co.	N.D.	2.0	3.5
9	KI	University of Milan, Physics of Solid State	N.D.	<0.01	<0.1
10	KI	Johnson-Matthey Specpure reagent crystals (analytical report 1 p.p.m. of Ca, not detected Sr and Ba)	1.3	0.25	1.23

[a] N.D. = not determined.

The precision and accuracy obtained with our technique were rather difficult to evaluate, because of the lack of single crystals with accurately known amounts of alkaline earths. The procedure adopted was to choose the purest alkaline halide available (Johnson-Matthey Specpure potassium iodide), measure its alkaline earth content, dissolve 0.5 g of it in high purity water and add known amounts of standardized solutions of calcium, strontium and barium iodides. The resulting solution was then analysed and the alkaline earth content of the Johnson-Matthey Specpure potassium iodide subtracted together with the reagent blank. The results are shown in Table IV with the calculated accuracy and precision. The accuracy is rather good, while the precision, although not ideal, is still rather good for trace analysis.

TABLE IV

ACCURACY AND PRECISION OF ALKALINE EARTH DETERMINATION

	Ca			*Sr*			*Ba*		
Analysis	*Added*[a]	*Found*	*Found*/*Added*	*Added*	*Found*	*Found*/*Added*	*Added*	*Found*	*Found*/*Added*
A	21	26.5	1.26	5.9	6.1	1.03	1.6	1.4	0.88
B	21	18.5	0.88	12	10.4	0.87	3.3	3.3	1.00
C	32	29.1	0.91	19.6	20.6	1.05	15.2	13.1	0.86
D	129	114	0.88	37.3	37.3	1.00	10.3	12.7	1.23
Average accuracy			0.98			0.99			0.99
Relative standard deviation			16%			8%			15%

[a] Amounts added and found are given in μg.

DISCUSSION

Elimination of the matrix

The first step in neutron activation analysis is generally the irradiation step. Chemical separation, if necessary, follows. Contaminations from the chemical reagents used are thus avoided. When chemical separations are made before the irradiation step, one should be sure:

(*1*) that the amount of the trace element to be determined which is introduced through the reagents is negligible. If this is not the case a blank correction must be done, with a corresponding diminution of sensitivity and precision;

(*2*) that the chemical separations to remove the undesirable elements have no influence on the concentration of the elements to be determined even if present in trace quantities.

Cation exchange has been used by us to remove the halogen and the alkaline metal. The halide ion is obviously not retained by the cation exchanger, while both the alkali and alkaline earth metals exchange with the resin in the hydrogen form. The higher specific charges of the alkaline earths make their adsorbability into the exchanger phase much greater than that of the alkali metals, as shown by the distribution coefficients known from the literature. The greatest part of these data are referred to acidic media (hydrochloric acid in particular) of different molarity. An extensive study for many cations has been made by STRELOW[15] and some of his results are reported in Table V. In order to keep the blank correction at a minimum, it was necessary for us to use the lowest amount of resin and then study the adsorption process in these rather critical conditions. In particular, it was necessary to investigate whether the difference in the anion and the presence of large amounts of alkali ions would affect the separation significantly. In Table IV the distribution coefficients measured for the alkaline earths from different media and molarities are reported. Some of the literature data are also reported for comparison. It may be seen that the agreement of the distribution coefficients of strontium in hydrochloric acid is fairly good at high molarity. Some discrepancies exist at low molarity, where small variations of molarity have a significant effect on K_d. It should also be pointed out that some non-uniformity between different batches of a particular exchanger type always exists due to the nature of the polymerization process itself during synthesis of ion exchangers[16]. The presence of the alkali ions instead of the hydrogen ions during adsorption decreases the adsorbability of the alkaline earths. It is still nevertheless sufficiently high for practical separations on small columns of 0.1–0.2 ml of resin. The presence of iodide instead of chloride ions makes the K_d lower at low molarities and higher at high molarities. While this effect is certainly interesting from a theoretical point of view, its magnitude is not such as to have a practical effect on the separations.

TABLE V

DISTRIBUTION COEFFICIENTS OF ALKALINE EARTH METALS ON CATION-EXCHANGE RESIN
(Adsorption from different media)

Ion media (M)	*Na*	*K*	*Ca*			*Sr*			*Ba*		
	HCl[a]	*HCl*[a]	*HCl*[a]	*KCl*	*KI*	*HCl*	*KCl*	*KI*	*HCl*[a]	*KCl*	*KI*
0.1	52	106	3200		382	6380 4700[a]	2890	1710	> 10,000		2220
0.2	28.3	64	790		305	1870 1070[a]	730	665	2930		1310
0.5	12	29	151		90	239 217[a]	135	182	590		525
1.0	5.6	13.9	42.3		28	79 60[a]	40	64.6	126.9		148
2.0	3.6	7.4	12.2		11	18 18[a]	11.7	18.3	36		50.7
4.0			7.3			6 7[a]	4.8	9.8	11.9		25.2

[a] Reference 15.

From the data of Table V the advantage of running the adsorption step from as dilute solutions as possible is evident. On the other hand the well-known effect of the flow rate on the performance of column separations makes it desirable to run the adsorption at the lowest practical flow rate when small columns are used.

In practice the samples to be analysed were diluted to 0.1 molar solutions. The adsorption step was run overnight at a flow rate lower than 0.1 ml per min, on columns of 0.1 g of resin. This procedure was tested with the use of ^{45}Ca, ^{85}Sr and ^{133}Ba as radioactive tracers and the losses of activity were found to be negligible. The resin may retain up to a few thousand p.p.m. of alkaline earths before any leakage of activity is found.

Trace analysis by neutron activation of the resin as received from the manufacturer showed that the impurity content was too high for trace work. The resin was then purified by the method already described. The determination of the blank correction was made by running through the procedure a pure water sample for each lot of analyses requested. The blank correction was rather low for strontium and barium (about 0.01 and 0.1 μg respectively). It was higher for calcium (about 1 μg), but this was still much lower than the calcium content of single crystals of alkali halides analysed so far. The error due to the blank subtraction was thus sufficiently low.

Determination of calcium

Calcium is generally determined by activation analysis through the formation of the long-lived ^{45}Ca (half-life 164 days). The determination of ^{49}Sc formed by decay of ^{49}Ca was preferred in this work. The reactions are:

$$^{48}\text{Ca} \xrightarrow{\text{n},\gamma} {}^{49}\text{Ca}$$

$$^{49}\text{Ca} \xrightarrow[t\frac{1}{2}\,=\,8.8\text{ m}]{\beta^-} {}^{49}\text{Sc}$$

The growth and decay of ^{49}Sc during and after the irradiation may be calculated from the laws of decay and growth of radioactive isotopes, and are summarized by the following relationships:

$$\text{A}_{49_{\text{Sc(T)}}} = \text{N}_{48_{\text{Ca}}}\sigma_{48_{\text{Ca}}}\phi\lambda_{49_{\text{Sc}}}\left(\frac{\text{e}^{-\lambda_{49_{\text{ScT}}}} - \text{e}^{-\lambda_{49_{\text{CaT}}}}}{\lambda_{49_{\text{Sc}}} - \lambda_{49_{\text{Ca}}}} + \frac{1 - \text{e}^{-\lambda_{49_{\text{ScT}}}}}{\lambda_{49_{\text{Sc}}}}\right)$$

$$\text{A}_{49_{\text{Sc(t)}}} = \frac{\lambda_{49_{\text{Sc}}}}{\lambda_{49_{\text{Sc}}} - \lambda_{49_{\text{Ca}}}}\text{A}_{49_{\text{Ca(T)}}}(\text{e}^{-\lambda_{49_{\text{Cat}}}} - \text{e}^{-\lambda_{49_{\text{Sct}}}}) + \text{A}_{49_{\text{Sc(T)}}} \cdot \text{e}^{-\lambda_{49_{\text{Sct}}}}$$

where $\text{A}_{49_{\text{Sc(T)}}}$ and $\text{A}_{49_{\text{Ca(T)}}}$ are the activities of ^{49}Sc and ^{49}Ca at the end of the irradiation time T, and $\text{A}_{49_{\text{Sc(t)}}}$ is the activity of ^{49}Sc after the decay time t. $\text{N}_{48_{\text{Ca}}}$ is the number of atoms of ^{48}Ca, $\sigma_{48_{\text{Ca}}}$ its neutron activation cross-section, ϕ the neutron flux and λ the decay constant. The results are graphically shown in Fig. 1 as per cent saturation activity *vs.* time for 4 different irradiation times. The growth and decay of a hypothetical isotope with the same half-life as ^{49}Sc directly formed by neutron irradiation are shown for comparison. It may be seen that at the end of the irradiation and during a few of the parent's half-lives ^{49}Sc is still being formed by the decay of the parent. If chemical separations are made in this first period, particular care must be taken to avoid any separation of parent and daughter, that would introduce a serious error in the determination. In the first hour of our procedure the opening of the irradiation capsule, the elution from the resin and the precipitation of the carbonate are made. After one hour over 99% of the ^{49}Ca formed has decayed to ^{49}Sc and the chemical separation can be carried out thoroughly. Approximately 2 h are necessary for the chemical separation of scandium, including the preliminary waiting time.

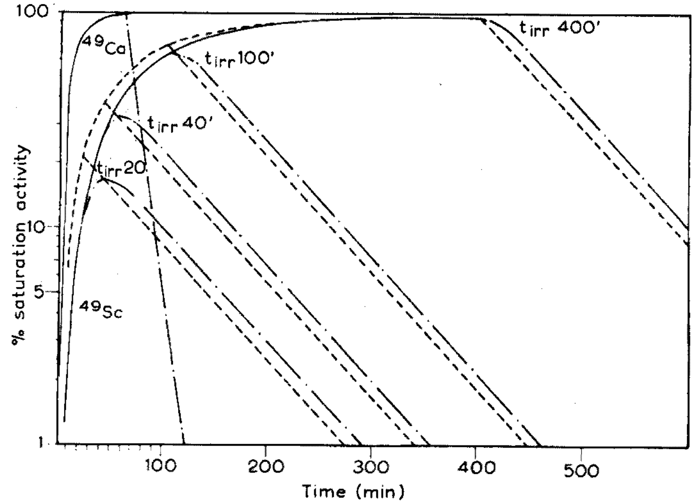

Fig. 1. Build-up of ^{49}Ca and ^{49}Sc from irradiation of Ca and decay after the irradiation: —build-up of ^{49}Ca and ^{49}Sc during irradiation; —·—decay of ^{49}Ca and ^{49}Sc after the irradiation; - - - -build-up and decay of a hypothetical isotope of the same half-life as ^{49}Sc, directly formed by (n, γ) reaction.

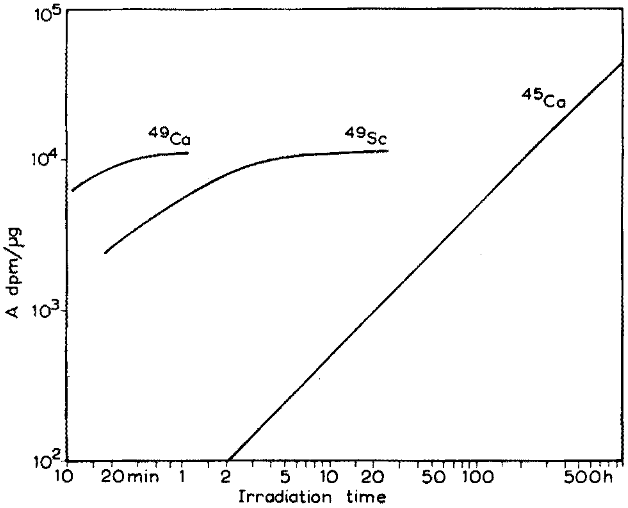

Fig. 2. Growth during neutron irradiation of the activity of isotopes that can be used for trace analysis of calcium.

In Fig. 2 the specific activity of ^{49}Sc following neutron activation is compared with that of the long-lived isotope ^{45}Ca, generally used for determining calcium. A 2-h decay has been taken into account in the curve of ^{49}Sc. It may be seen that the disintegration rate attained by ^{49}Sc in 90 min is only attained by ^{45}Ca after 150 h. It should also be noted that while 90-min irradiations may generally be done in high flux positions, very long irradiations can generally be done only in lower flux positions. Both ^{45}Ca and ^{49}Sc are pure β-emitters. The maximum energy of their β-particles is respectively 0.25 and 2.00 MeV. The higher energy of the β-particles of ^{49}Sc makes the measurement of the activity easier, as the self-shielding of β-particles within the source is negligible. The possibility of following the decay of ^{49}Sc is also a good check of its radiochemical purity. The addition of ^{46}Sc for the measurement of the separation yield does not interfere in the determination as the weak β-energy particles of ^{46}Sc (maximum energy 0.36 MeV) are stopped by a β-absorber of 100 mg/cm^2 without a significant decrease of the counting rate of ^{49}Sc.

Determination of strontium and barium

Strontium and barium are determined by measuring the 0.39 MeV photopeak of ^{87m}Sr and the 0.16 MeV photopeak of ^{139}Ba. Figure 3a shows a γ-spectrum of the strontium and barium nitrates precipitated together with fuming nitric acid. The

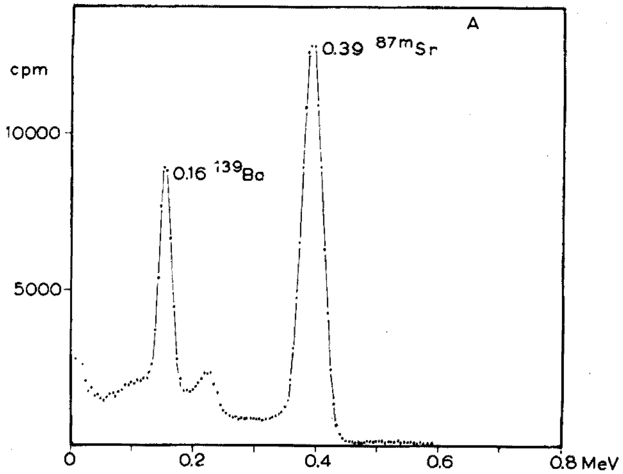

Fig. 3a. Gamma spectrum of the strontium and barium fraction 2 h after the end of the irradiation.

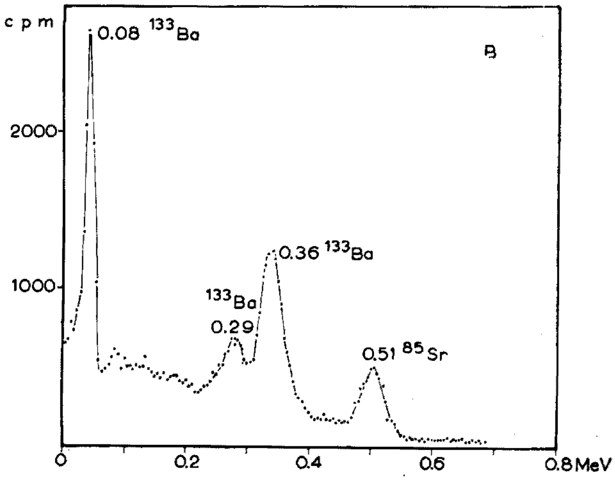

Fig. 3b. Gamma spectrum of the strontium and barium fraction 36 h later.

decontamination from other foreign activities is excellent. The chemical yields are determined by measuring the 0.51 MeV photopeak of ^{85}Sr and the 0.36 MeV photopeak of ^{133}Ba after the decay of the short-lived isotopes. Figure 3b shows the same precipitate of strontium and barium nitrates one day later. The activity of ^{133}Ba added for the chemical yield determination must be kept rather low to avoid interferences when the 0.39 MeV photopeak of ^{87m}Sr is measured.

CONCLUSIONS

The possibility of using activation analysis for the determination of trace quantities of alkaline earths in single crystals of alkali halides has been investigated in connection with research on the effect of impurities on the physical properties of ionic crystals.

The matrix is eliminated before the irradiation by an ion-exchange procedure that ensures a quantitative recovery of trace quantities of alkaline earths. The problems of handling a highly activated matrix and obtaining high decontamination factors in the chemical separations were thus avoided. A reagent blank correction must be made, thus decreasing the sensitivity and precision of the determinations compared with those obtained on non-activated matrices. A more careful purification of the reagents used for the removal of the matrix would probably lower the detection limit and increase the precision, if necessary. The short-lived isotopes ^{87m}Sr and ^{139}Ba formed by (n, γ) capture on the stable elements are used for the determination of strontium and barium. Calcium is determined by measuring the ^{49}Sc formed by β^--decay of the short-lived ^{49}Ca. The nuclear properties of ^{49}Sc make the measurement of calcium concentration easier and more sensitive than if the long-lived ^{45}Ca were measured. Radiochemical separation is used to separate the isotopes to be measured. The chemical yields of the separations are measured radiochemically by tracing the carrier solution with the long-lived isotopes ^{46}Sc, ^{85}Sr and ^{133}Ba and measuring their activity before and after the separations.

Both the accuracy and the precision of the method were found satisfactory for the present applications, but a higher precision would be desirable in the study of high purity single crystals.

We thank Dr. FIESCHI of the University of Milan and Dr. CAMAGNI of Euratom for helpful discussions on the role of impurities in single crystals. The suggestions and criticisms of Prof. G. BERTOLINI, director of the Nuclear Chemistry Service, are also gratefully acknowledged.

SUMMARY

The determination by neutron activation of trace quantities of calcium, strontium and barium in single crystals of alkali halides has been studied. The matrix is eliminated before the irradiation by an ion-exchange procedure. Gamma spectroscopy after radiochemical separation is used to determine strontium and barium. Calcium is determined by measuring the β-activity of ^{49}Sc formed by the decay of ^{49}Ca. Long-lived radioactive tracers are used to determine the chemical yields.

RÉSUMÉ

Une étude a été effectuée sur l'analyse par activation, au moyen de neutrons, de traces de calcium strontium et baryum dans des halogénures alcalins. Après séparation radiochimique, la spectroscopie gamma est utilisée pour déterminer strontium et baryum. Le calcium est dosé en mesurant l'activité β de ^{49}Sc, formé par désintégration de ^{49}Ca. Des traceurs radioactifs de longues périodes sont utilisés pour déterminer les rendements chimiques.

ZUSAMMENFASSUNG

Es wurde die Bestimmung von Spuren Calcium, Strontium und Barium in Alkalihalogenid-Einkristallen mit Hilfe der Neutronaktivierungsanalyse untersucht. Die Matrix wurde vor der Bestrahlung mit einem Ionenaustauscher abgetrennt. Das Strontium und Barium wurden nach radiochemischer Abtrennung γ-spektroskopisch bestimmt, das Calcium durch Messung der β-Aktivität des durch Zerfall des ^{49}Ca entstandenen ^{49}Sc. Zur Bestimmung der chemischen Ausbeute wurden langlebige radioaktive Tracer benutzt.

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THEORY OF TITRATION CURVES

IV. POINTS OF MINIMUM SLOPE ON POTENTIOMETRIC STRONG ACID–STRONG BASE AND PRECIPITATION TITRATION CURVES

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In two preceding papers[1,2] we discussed the locations of the inflection points of maximum slope on potentiometric acid–base and precipitation titration curves. By taking dilution into account, we obtained results that differed considerably from those obtained by neglecting it.

It is generally believed that there are two classes of potentiometric titration curves. One includes titrations of strong acids and bases and precipitation titrations, and is believed to be characterized by a continuous increase of slope up to an inflection point that more or less coincides with the equivalence point. The other includes titrations of weak acids and bases and redox titrations, and is believed to differ from the first in that its members have two inflection points: one of minimum slope more or less halfway to the equivalence point, the other of maximum slope more or less coincident with the equivalence point.

It is the purpose of this paper to demonstrate the incorrectness of this general belief by showing that titration curves of the first class may also possess two inflection points, and by describing the conditions under which the point of minimum slope can be observed.

First, however, it may be remarked that titration curves of the second class will exhibit only the inflection point of maximum slope under certain conditions. The titration curve for the titration of iron(II) with a strong oxidizing agent has a point of minimum slope when the titration is performed in the ordinary way. But if an excess of iron(III) is present in the original solution only the point of maximum slope is observed. The same effect is produced by adding an excess of acetate ion to a solution of acetic acid before titrating it with a strong base, or by sufficiently diluting a solution of a weak acid before titrating it* (ref. 3).

Of course these are special conditions. What is important is that a titration curve inherently possessing two inflection points may exhibit only the one of maximum slope when the titration is performed under special conditions. In this light it can be

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* This increases the extent of dissociation in the original solution; if K_a is much larger than $K_w^{\frac{1}{2}}$ the increase will be so extensive that the titration curve will assume the form of that for a "strong" (*i.e.*, essentially completely dissociated) acid. If K_a is comparable to or smaller than $K_w^{\frac{1}{2}}$ the degree of dissociation approaches a limiting value much lower than 1 as the dilution increases.

said that strong acid–strong base and precipitation titration curves, like other kinds of titration curves, inherently possess two inflection points, but are commonly believed to possess only one because they are usually discussed under special conditions that serve to mask the existence of the inflection point of minimum slope.

STRONG ACID–STRONG BASE TITRATIONS

Equation (11) of ref. 1 gives a rigorous description of an inflection point in any titration of a monobasic strong acid with a monoacidic strong base. It is

$$f = \frac{(3r-1)C_b^2 - 16K_w \pm (r+1)C_b\sqrt{C_b^2 - 32K_w}}{4r\,(C_b^2 + 4K_w)} \qquad (1)$$

where f, the fraction of the equivalent volume of base added, is given by the equation

$$f = V_bC_b/V_a^0C_a^0 \qquad (2)$$

and r is the dilution parameter defined by the equation

$$r = C_b/C_a^0 \qquad (3)$$

while V_a^0 and C_a^0 are the initial volume (ml) and the initial concentration (moles/l) of the acid titrated, and V_b and C_b are the volume (ml) of base added at the point under consideration and the concentration (moles/l) of the base.

Equation (1) possesses two roots. The one at which f has the higher value, obtained by taking the positive sign before the last term in the numerator of the right-hand side, corresponds to the point at which the slope of the curve is a maximum; its location and the manner in which this is dependent on the values of r and C_b were discussed in ref. 1. The other root, obtained by taking the negative sign, corresponds to the point of minimum slope, and is the one of interest here.

In order for the titration curve to have *two* inflection points, both of which are physically significant, there are two conditions that must be satisfied. One is that the values of f at both inflection points must be real and unequal; this is equivalent to

$$C_b > \sqrt{32K_w} \quad (= 5.657 \cdot 10^{-7} \text{ at } 25^\circ) \qquad (4)$$

The other is that the values of f at both inflection points must be positive; this is equivalent to

$$(3r-1)C_b^2 - 16K_w - (r+1)C_b\sqrt{C_b^2 - 32K_w} \geq 0 \qquad (5)$$

For each value of C_b there is a minimum value of r that just satisfies eqn. (5). Some of these values are given in Table I. Comparing them with those given in Table II of ref. 1 for the minimum values of r and C_a^0 required to yield a single physically meaningful inflection point, it is evident that three apparently different kinds of titration curves may be obtained at any given value of C_b. If C_a^0 exceeds the value given in Table I, two inflection points will be obtained; if it is smaller than the value given in Table I but larger than that given in Table II of ref. 1, only one inflection point will be obtained, and that will be the one where the slope is a maximum; if

TABLE I

MINIMUM CONCENTRATIONS OF STRONG ACID YIELDING TWO PHYSICALLY MEANINGFUL INFLECTION POINTS ON TITRATION WITH STRONG BASE

(The values in this Table pertain to the titration of C_a^0 *F* monobasic strong acid with C_b $(=C_a^0/r)$ *F* monoacidic strong base. The first column gives the value of C_b. The second gives the smallest value of r, and the third gives the smallest value of C_a^0, at which two inflection points having physical significance (*i.e.*, occurring at real positive values of f) exist. The value of K_w is taken as $1.00 \cdot 10^{-14}$; if K_w differs from this value, both C_b and C_a^0 should be multiplied by $10^7 K_w^{\frac{1}{2}}$)

$10^7 \cdot C_b$	r	$10^7 \cdot C_a^0$
5.657	0.500	2.828
6	0.667	4.00
8	0.853	6.82
10	0.912	9.12
12	0.941	11.29
16	0.968	15.49
20	0.980	19.60
30	0.991	29.7
40	0.995	39.8
100	0.9992	99.9
1000	0.999992	1000.0

it is smaller than the value given in Table II of ref. 1, the curve will exhibit no inflection point, but will have a slope that decreases continuously from the start of the titration. Of course a continuously decreasing slope will also be obtained if C_b is smaller than the value demanded by eqn. (4), regardless of the value of C_a^0.

It is obvious from Table I that the minimum value of r that is required to yield an inflection point of minimum slope approaches 1 as C_b increases. From eqn. (1) the condition for the existence of two inflection points when $C_b \gg \sqrt{32K_w}$ is evidently

$$(3r - 1)C_b^2 - (r + 1)C_b^2 \geq 0 \tag{6}$$

whence $r \geq 1$. An inflection point of minimum slope is therefore always possible in titrations of strong acids with strong bases when both solutions are moderately concentrated provided only that the base is less concentrated than the acid (or, conversely, in titrations of strong bases with strong acids when both solutions are moderately concentrated provided that the acid is less concentrated than the base). It is because such titrations have been considered only under the special condition that dilution is negligible ($r = 0$) or insufficient to demonstrate the existence of both inflection points* on calculated titration curves that they have been believed to possess only one inflection point.

Values of f at the first inflection point are given in Table II for various values of C_b and r. With r constant, the value of f is seen to decrease as C_b increases; for very large C_b (and correspondingly large C_a^0), the value of f approaches a limit that is given by

$$f = \frac{(3r - 1)C_b^2 - (r + 1)C_b^2}{4rC_b^2} = \frac{1}{2} - \frac{1}{2r} \tag{7}$$

which has been used in computing the values given in the last line of Table II. For

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* As will presently appear, if $r = 1$ the first inflection point occurs at $f \approx 0$ when the solutions are moderately concentrated.

TABLE II

LOCATIONS OF INFLECTION POINTS OF MINIMUM SLOPE ON POTENTIOMETRIC STRONG ACID–STRONG BASE TITRATION CURVES

(Each number in the body of this Table gives the value of f at the inflection point of minimum slope when C_b and r $(= C_a^0/C_b)$ have the values given in the first column and across the top of the Table, respectively. The value of K_w is taken as $1.00 \cdot 10^{-14}$; if K_w differs from this value, C_b should be multiplied by $10^7 K_w^{\frac{1}{2}}$)

$10^7 \cdot C_b$	*Value of f at the first inflection point for r =*		
	1	*3*	*10*
5.657	0.333	0.556	0.633
6	0.175	0.467	0.560
7	0.114	0.410	0.513
8	0.0790	0.386	0.493
10	0.0459	0.364	0.475
12	0.0304	0.354	0.467
15	0.0188	0.345	0.460
20	0.0103	0.340	0.456
30	0.00450	0.336	0.452
∞	0	0.333	0.450

large values of r the inflection point of minimum slope therefore approaches $f = 1/2$, and the titration curve then has the shape classically ascribed to that representing the titration of a weak acid with a strong base (except, of course, at and near the equivalence point). This may perhaps be more readily seen from Fig. 1 than from any more extended argument. In view of our earlier comments[2] about the ambiguity of the notion of "maximum buffer capacity", it is interesting to note that the inflec-

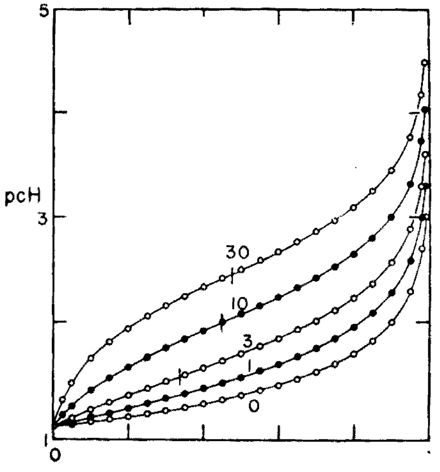

Fig. 1. Calculated titration curves for titrations of 0.1 F monobasic strong acid with various concentrations of monoacidic strong base. The number beside each curve gives the corresponding value of r $(= C_a^0/C_b)$, and the short vertical lines intersecting the curves for which $r > 1$ correspond to the positions of the points of minimum slope calculated from eqns. (1) and (7), which yield virtually identical results under these conditions. For $r = 1$ there is an inflection point of minimum slope at $f = 0$.

tion points of minimum slope in this Fig. represent points of maximum buffer capacity under the conditions to which the curves refer.

When C_a^0 is sufficiently large and f is not too close to 1, the titration curve may be described by the equation[4]

$$[\mathrm{H}^+] = (1 - f)\,\varrho C_a^0 \tag{8}$$

where the volume parameter ϱ is defined by the equation

$$\varrho = \frac{V_a^0}{V_a^0 + V_b} = \frac{C_b}{C_b + fC_a^0} \tag{9}$$

(*cf.* eqn. (15) of ref. 1). Transforming eqn. (8) into logarithmic form and differentiating twice yields

$$\frac{\mathrm{d}^2(\mathrm{pc}_\mathrm{H})}{\mathrm{d}f^2} = \frac{0.4343\,(C_b + fC_a^0)\,[C_b + (2f - 1)C_a^0]}{(1 - f)^2(C_b + fC_a^0)^2} \tag{10}$$

which can equal zero (since the assumptions made in its derivation are not valid at or near the equivalence point) only if

$$C_b + (2f - 1)C_a^0 = 0$$

or

$$f = \frac{1}{2} - \frac{C_b}{2C_a^0} = \frac{1}{2} - \frac{1}{2r} \tag{11}$$

which is identical with eqn. (7) but which may more clearly indicate the nature of the limitations involved.

ISOVALENT PRECIPITATIONS

The titration curve for the titration of V_B^0 ml of C_B^0 F B^{m+} with C_A F A^{m-} to give the isovalent precipitate BA is described by eqns. (1)–(11) with appropriate changes of the symbols, as follows:

$V_a^0 \rightarrow V_\mathrm{B}^0$ $\quad [\mathrm{H}^+] \rightarrow [\mathrm{B}^{m+}]$
$V_b \rightarrow V_\mathrm{A}$ $\quad \mathrm{pc}_\mathrm{H} \rightarrow \mathrm{pc}_\mathrm{B}$
$C_a^0 \rightarrow C_\mathrm{B}^0$ $\quad K_w \rightarrow K_\mathrm{BA}$
$C_b \rightarrow C_\mathrm{A}$

To avoid the discontinuity that would otherwise occur at the point where precipitation of BA just begins, it is necessary to assume that the original solution is saturated with BA. But this is a trivial assumption, and repetition of the above arguments for this essentially identical case seems unwarranted.

HETEROVALENT PRECIPITATIONS

When a C_B^0 F solution of B^{m+} in equilibrium with the solid heterovalent precipitate $\mathrm{B}_n\mathrm{A}_m$ is titrated with a C_T F solution of A^{n-}, any inflection point on the titration curve (which, as in the isovalent case, is essentially a plot of pc_B *vs.* f) must conform to eqn. (16) of ref. 2, which is

$$2\{(z + 1)[\mathrm{B}^{m+}] - \alpha z\}^2 \frac{r(z + rf)}{zC_\mathrm{B}^0(z + r)} = (1 - z^2)[\mathrm{B}^{m+}] + \alpha z^2 \tag{12}$$

where r is the dilution parameter defined by the equation

$$r = C_B^0/C_T \tag{13}$$

which is analogous to eqn. (3); z is the charge ratio given by

$$z = n/m \tag{14}$$

while α and f are given by

$$\alpha = \frac{zC_B^0(1 - f)}{z + rf} \tag{15}$$

and

$$f = \frac{zV_TC_T}{V_B^0C_B^0} \tag{16}$$

In ref. 2 the conditions for the existence of an inflection point were discussed at length. This discussion will not be repeated here; it will merely be noted that (as in the case of the strong acid–strong base titration) the conditions required for the existence of two inflection points subsume those required for the existence of one.

Clearly eqn. (12) is quadratic in $[B^{m+}]$; at the same time it is of some higher order (which depends on the value of z) in f. Explicit general equations for the values of f at the inflection points are therefore too complicated to be useful. A preferable approach is to observe that the two roots of eqn. (12), which are given explicitly by

$$[B^{m+}] = \frac{q \pm \sqrt{q^2 - 4ps}}{2p} \tag{17}$$

where

$$p = 2(z + 1)^2 \tag{17a}$$

$$q = 4\alpha z(z + 1) + \frac{zC_T\,(z + r)(1 - z^2)}{z + rf} \tag{17b}$$

$$s = 2\alpha^2z^2 - \frac{\alpha z^3C_T\,(z + r)}{z + rf} \tag{17c}$$

correspond to two inflection points. The one corresponding to the negative sign in the numerator of the right-hand side of eqn. (17) occurs at a lower concentration of B^{m+} than that corresponding to the positive sign. Hence the former represents the point of maximum slope, while the latter represents the point of minimum slope. For both to appear on the titration curve, it is necessary that

$$\frac{q + \sqrt{q^2 - 4ps}}{2p} \leq [B^{m+}]^0 \tag{18}$$

where $[B^{m+}]^0$, the concentration of B^{m+} in the solution being titrated, is given by the equation

$$[B^{m+}]^0 = C_B^0 + \frac{zK^{1/m}}{([B^{m+}]^0)^z} \tag{19}$$

and may be equated to $C_B{}^0$ if the solution is not too dilute and if the solubility product of the precipitate is not too large.

Substituting eqns. (17a–c) into eqn. (17) and simplifying yields the following equation for the value of $[B^{m+}]$ at the first inflection point:

$$[B^{m+}] = \frac{zC_T}{4(z+1)(z+rf)}[4r(1-f)+(z+r)(1-z) + \sqrt{8zr(z+r)(1-f)+(z+r)^2(1-z)^2}] \qquad (20)$$

Of course this is applicable to the isovalent as well as to the heterovalent case; in the former one simply has $z = 1$, so that

$$[B^{m+}] = \frac{C_T}{8(1+rf)}[4r(1-f)+\sqrt{8r(1+r)(1-f)}] \qquad (21)$$

at the first inflection point.

Although in principle it is possible to use eqn. (20) together with the equation for the titration curve (eqn. (6) of ref. 2) to evaluate $[B^{m+}]$ and f at the point of minimum slope in any titration in which eqn. (18) is satisfied (and in which the other conditions laid down in ref. 2 are also satisfied), the calculations are tedious and appear unlikely to serve any substantial purpose. It is much more useful, both because it is simpler and because it is more relevant to the practical execution of such titrations, to describe the conditions under which a point of minimum slope will appear when the solution being titrated is moderately concentrated and when the solubility product of the precipitate is very small. Under these conditions the solubility of the precipitate will be negligible as long as f is not too close to 1. Accordingly one may describe the titration curve by an equation that is analogous to eqn. (8):

$$[B^{m+}] = (1-f)\,\varrho C_B{}^0 \qquad (22)$$

where the volume parameter ϱ is defined by the equation

$$\varrho = \frac{V_B{}^0}{V_B{}^0+V_T} = \frac{nC_T}{nC_T+fmC_B{}^0} = \frac{z}{z+rf} \qquad (23)$$

Substituting eqn. (23) into eqn. (22), differentiating twice, and combining the resulting expressions for the derivatives with the equation (eqn. (13) of ref. 2) that defines the inflection point,

$$[B^{m+}]\frac{d^2[B^{m+}]}{df^2} = \left(\frac{d[B^{m+}]}{df}\right)^2 \qquad (24)$$

one obtains

$$[B^{m+}] = \frac{z(z+r)C_B{}^0}{2r(z+rf)} \qquad (25)$$

If the inflection point occurs at $f = 0$, where $[B^{m+}] = C_B{}^0$ (since the solubility of the precipitate is assumed negligible), one must have $z = r$. All other factors being equal, it is evident from eqn. (25) that increasing r decreases the value of $[B^{m+}]$ — that is, increases the value of f — at the inflection point. We may therefore write

$$r \geq z \tag{26}$$

as the criterion for the existence of an inflection point of minimum slope under these conditions. This is in accord, as of course it should be, with the conclusion regarding the isovalent case ($z = 1$) drawn from eqn. (6).

Combining eqns. (22) and (23) yields the following equation for the titration curve:

$$[\mathrm{B}^{m+}] = \frac{zC_{\mathrm{B}}^{0}(1 - f)}{z + rf} \tag{27}$$

Since the inflection point must satisfy both eqn. (25) and eqn. (27), one may combine these to give

$$f = \frac{1}{2} - \frac{z}{2r} \tag{28}$$

at the inflection point. For the isovalent case ($z = 1$) this becomes identical with eqns. (7) and (11).

From Table II it may be seen that the value of f described by eqns. (7) and (11) is approached within 1% for values of r between 1 and 10 when a strong acid is titrated with strong base that is even as dilute as $3 \cdot 10^{-6}$ F. It therefore seems entirely safe to conclude that the difference between the actual location of the point of minimum slope and the location predicted by eqn. (28) will be too small to detect in any practical titration.

SUMMARY

Strong acid–strong base and precipitation titration curves, like other kinds of potentiometric titration curves, inherently possess an inflection point where the slope is a minimum as well as one where it is a maximum. In any kind of titration the first of the inflection points can be caused to occur earlier, and can eventually be made to disappear altogether, by adopting certain expedients. For a weak acid–strong base titration, for example, these include decreasing the concentration of the acid titrated and titrating in the presence of an excess of its conjugate base. For strong acid–strong base and precipitation titrations they include decreasing the concentration of the substance titrated and increasing the concentration of the titrant. The conditions under which a physically significant inflection point of minimum slope can exist are defined, and explicit equations are given from which its position can be calculated under various experimental conditions, for strong acid–strong base and for both isovalent and heterovalent precipitation titrations.

RÉSUMÉ

Les courbes de titrage acide fort/base forte et de précipitation, de même que d'autres courbes de titrage potentiométrique, présentent un point d'inflexion où la pente est minimum et un autre où la pente est maximum. Le premier de ces points d'inflexion peut être provoqué plus tôt ou peut éventuellement être supprimé, dans certaines conditions. Des équations sont données permettant de calculer leur position dans diverses conditions expérimentales, pour des titrages acide fort/base forte, et pour des titrages par précipitation, soit isovalente, soit hétérovalente.

ZUSAMMENFASSUNG

Titrationskurven, die man bei der Titration von starken Säuren mit starken Basen und bei Fällungstitrationen erhält, besitzen ebenso wie andere potentiometrische Titrationskurven einen Wendepunkt, wo die Neigung ein Minimum ist, als auch einen, so sie ein Maximum ist. Bei einer beliebigen Titration kann der erste Wendepunkt vor dem Äquivalenzpunkt auftreten oder unter gewissen Bedingungen ganz verschwinden. Die Bedingungen, bei denen ein Wendepunkt mit minimaler Neigung auftritt, werden definiert und Gleichungen zur Berechnung seiner Lage unter verschiedenen experimentellen Bedingungen abgeleitet.

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Short Communications

The polarographic behaviour of diazoacetophenone

We have investigated the polarographic behaviour of diazoacetophenone in aqueous phosphate buffer solutions in the pH range 6 to 8.

The buffer solutions used were prepared according to the method of CLARK AND LUBS[1]. Solutions for polarography were made by dissolving the required amount of diazoacetophenone, prepared by the method of BRADLEY AND ROBINSON[2], in 1 ml of alcohol and diluting to 100 ml with the buffer solution. All solutions exhibited 3 polarographic reduction waves in the potential range 0 to −2.0 V *vs.* S.C.E., the best defined polarograms being obtained at pH 6. The first and second waves showed pronounced maxima which were suppressed by the addition of 0.002% Triton X-100. The half-wave potentials (V *vs.* S.C.E.) of the first, second and third waves obtained with millimolar solutions of diazoacetophenone were as follows: pH 6.0 (−0.86, −1.33, −1.68), pH 6.8 (−0.84, −1.29, −1.64), pH 7.8 (−0.84, −1.46, −1.71). Variation of the concentration of diazoacetophenone did not markedly influence the half-wave potentials. The first wave was shown to be diffusion-controlled whereas the second and third waves were not.

Controlled potential coulometric reduction at pH 6 gave n-values of 6, 2 and 2 for the first, second and third waves respectively. In these experiments, solid potassium chloride was added to the buffer solution to give a concentration of 0.05 *M* potassium chloride, in order that a silver anode could be used in conjunction with a mercury pool cathode. Addition of potassium chloride did not affect the shape of the polarogram and had only a slight effect upon the half-wave potentials. The formation of a pinkish-brown precipitate was observed during the electrolysis at a potential corresponding to the plateau of the first wave and the residual solution was shown to contain ammonium ion. No precipitation was observed during electrolyses at potentials corresponding to the plateaux of the second and third waves.

Our results suggest that the polarographic reduction of diazoacetophenone proceeds via "ω"-aminoacetophenone and acetophenone to give phenylmethylcarbinol, according to the following scheme:

First step: $C_6H_5COCHN_2 + 7\ H^+ + 6\ e \rightarrow C_6H_5COCH_2NH_2 + NH_4^+$

Second step: $C_6H_5COCH_2NH_2 + 3\ H^+ + 2\ e \rightarrow C_6H_5COCH_3 + NH_4^+$

Third step: $C_6H_5COCH_3 + 2\ H^+ + 2\ e \rightarrow C_6H_5CH(OH)CH_3$

In order to obtain further support for this mechanism we investigated the reduction of acetophenone alone in the same buffer solution. Two barely separated waves of equal height were obtained, the mid-point between the waves being at −1.67 V *vs.* S.C.E. This suggests a total two-electron reduction to the carbinol[3]. Addition of acetophenone to the solution of diazoacetophenone did not affect the first and second waves but resulted in an increase in the height of the third wave (see Fig. 1).

The precipitate observed during controlled potential reduction at the potential of the plateau of the first wave may result from the further reaction of aminoacetophenone; it is known that aminoacetophenone readily condenses to 2,5-diphenyl-3,6-dihydropyrazine which, in turn, is readily oxidized to the pyrazine. The nature of

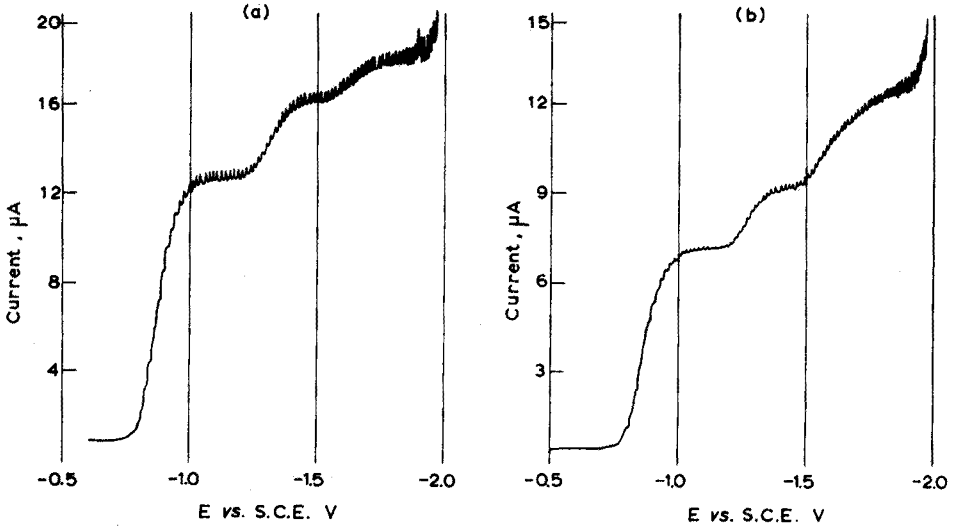

Fig. 1. Polarograms of (a) 10^{-3} M diazoacetophenone in aqueous phosphate buffer solution, pH 5.8; (b) a mixture of equal volumes of 10^{-3} M diazoacetophenone and 10^{-3} M acetophenone in aqueous phosphate buffer solution, pH 5.8.

this precipitate and of the other products of the controlled potential electrolyses is being investigated.

It is interesting to compare these results with those of FOFFANI *et al.*[4] and of ZUMAN AND HORÁK[5]. The first-named workers studied the polarographic behaviour of diazoacetophenone in a solvent consisting of 10% ethanol–90% water containing various buffer systems. They reported two reduction waves, with an ill-defined third wave observable in weakly acidic or weakly alkaline solution. At pH values greater than 5, the first wave was attributed to a 6-electron reduction to give the aminoketone, the second wave was attributed to the reduction of the carbonyl group, and the third wave was supposed to be due to secondary electrode effects. ZUMAN AND HORÁK studied the reduction of α-aminoketones in Britton–Robinson buffers. In the case of substituted "ω"-aminoacetophenones they obtained two reduction waves, the first of which was shown to be due to reduction of the C–N bond and the second to reduction of acetophenone. The waves obtained by ZUMAN AND HORÁK were similar to the second and third waves obtained by us. These facts, taken in conjunction with the enhancement of the third wave by acetophenone addition, are more consistent with the mechanism outlined above than with that suggested by FOFFANI *et al.*

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Paper chromatographic separation of some less familiar transition metals using a solvent containing chloroform

The use of solvents containing chloroform for the separation of inorganic ions was suggested previously by the authors[1]. Several solvent systems containing alcohols, ketones, esters and phenol with chloroform, were studied and it was shown that mixed solvents can be used for separating copper, cobalt, nickel and iron. One of these systems, containing 47.6% chloroform, 23.8% acetone, 23.8% amyl alcohol and 4.5% concentrated hydrochloric acid was very successful for the above separation. In the present work the use of this solvent system was extended for the separation of ions of many less familiar elements including some of the noble metals.

Reagents

All the solutions for migration studies were prepared from E. Merck or B.D.H. samples of high purity to give 5 μg of the ion concerned in 100 ml of the solution. For separation studies, solutions containing 50 μg of the ion concerned per 100 ml were used. The salts used were the nitrates of uranium, zirconium, thorium, iron, silver, copper and cadmium, and the chlorides of gold, platinum and palladium; vanadium sulphate, sodium tungstate and sodium molybdate were also used.

Whatman No. 1 paper (discs of 12.5 cm diameter) was used for all studies.

Procedure

RUTTER'S[2] technique of radial development was used throughout. The paper discs with cut-out wicks about 2–3 cm long (width 2–3 mm at the connecting end and 1 mm at the free end) were used instead of capillaries. All spotting was done with a micropipette (0.02 ml drop). After the spots had been dried, the solvent was allowed to run for 3–4 h in cases of individual ions for R_F studies. An aqueous 5% solution of potassium ferrocyanide was used for spraying molybdate, uranyl, vanadyl and iron(III) ions; tin(II) chloride–hydrochloric acid was used for tungstate, gold(III), platinum(IV) and palladium(II) ions. Silver and cadmium were detected by spraying with hydrogen sulphide solutions. Copper was detected with a rubeanic acid (0.5% in 90% alcohol) spray in the copper–cadmium separation and with a potassium ferrocyanide spray in the copper–silver and copper–gold separations. Chromatograms were finally dried at room temperature (*ca.* 25°).

All R_F values were calculated with respect to the outer fronts of the rings concerned.

For separations, mixtures were prepared from equal volumes of the component solutions, and a drop of the mixture was applied. In the case of zirconium or molybdate ions, any turbidities or precipitates obtained on mixing were dissolved by adding 1–2 drops of concentrated hydrochloric acid. Chromatograms were prepared as usual. When two or more sprays were used, the rings developed by the first spray were covered with a thick paper stencil before the next spray was used, in order to avoid unwanted interactions.

Results

The R_F values for the ions studied were as follows:
WO_4^{2-} (0.00); MoO_4^{2-} (0.69); UO_2^{2+} (0.28); Zr^{4+} (0.00); Th^{4+} (0.11); VO^{2+} (0.13); Au^{3+} (1.00); Pt^{4+} (0.77); Pd^{2+} (0.57); Fe^{3+} (0.92); Cu^{2+} (0.74); Cd^{2+} (1.00); Ag^+ (0.10).

The separations that were successfully carried out, are listed below:

(*1*) Zr^{4+}, Th^{4+}, UO_2^{2+}, MoO_4^{2-} and Fe^{3+};
(*2*) WO_4^{2-}, MoO_4^{2-}, UO_2^{2+}, VO^{2+} and Fe^{3+};
(*3*) Pd^{2+}, Pt^{4+} and Au^{3+};
(*4*) Ag^+ and Cu^{2+};
(*5*) Cu^{2+} and Au^{3+};
(*6*) Cu^{2+} and Cd^{2+}.

The time required to effect the above separations was 4 and 6 h for sets 1 and 2, 2 h for set 3 and 1 h for sets 4–6.

Discussion

The R_F values reported indicate the possibilities for separation of the ions under study in various combinations. The separations reported above confirm these possibilities, and prove that chloroform-containing solvents can be used for the separation of many less familiar elements including the noble metals. As suggested previously[1], it is mainly the presence of alcohols and ketones in the solvent systems that allows the ions to move on the paper; hydrochloric acid helps in obtaining better rings and more reproducible results.

Many separations have been reported for Mo, V, W, Fe, U, Th and Zr in binary or multiple combinations[3]. But chloroform-containing solvents have been applied only for the UO_2^{2+}–Th^{4+} separation by SUCHY[4], who used pyridine–chloroform–toluene (7:2:1). In the present work, clear separations were obtained for two sets of five metals out of the above seven transition metals.

The noble metals have been separated previously with solvents containing butanol and 1 *N* hydrochloric acid[5,6] and also in ketonic solvents[7]. The separation of platinum, palladium and gold by means of a chloroform-containing solvent is a new and successful attempt in extending the range of possible solvents. The separations of copper–silver, copper–gold and copper–cadmium are also noteworthy.

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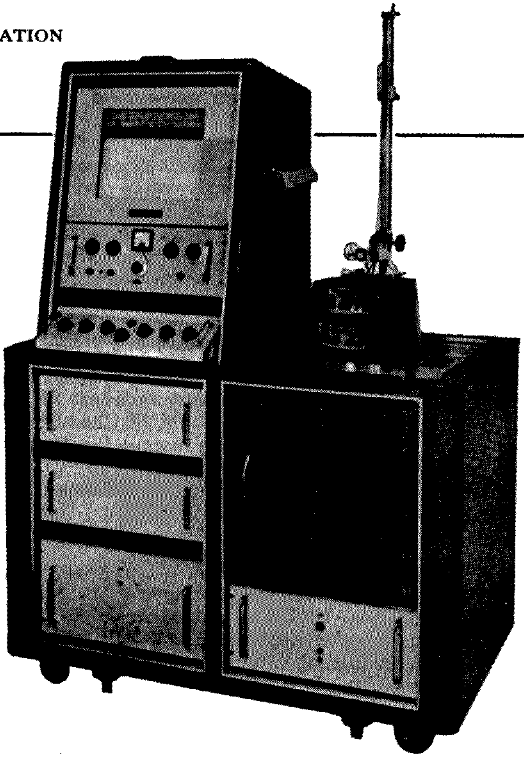

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