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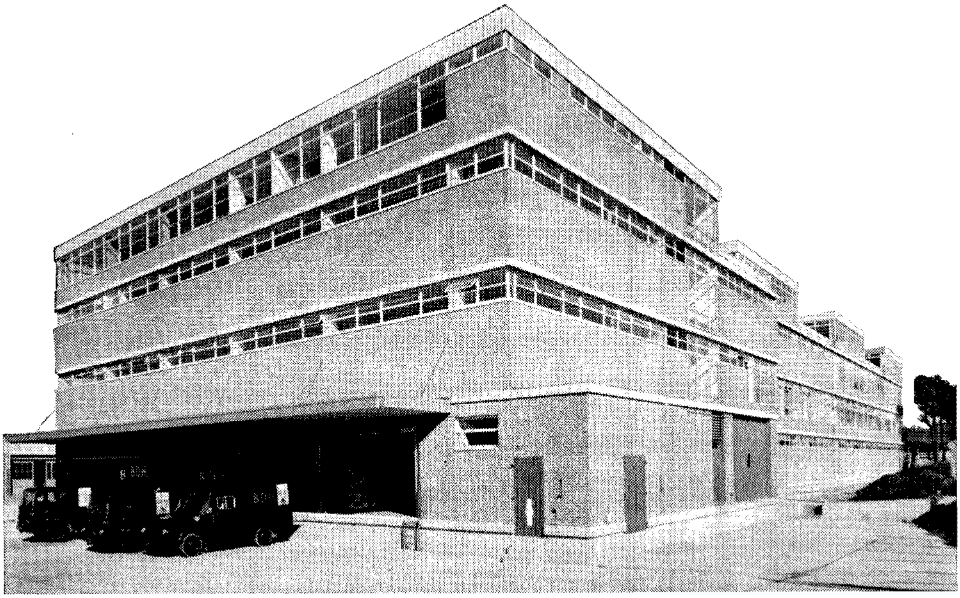

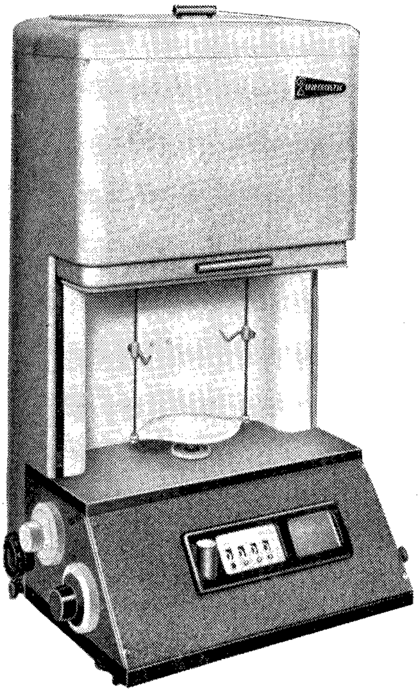

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SUMMARIES FOR CARD INDEXES

Amperometric determination of metals with thioacetamide—IV: The rate of formation of thallium sulphide in ammoniacal thallium^{I} solution using thioacetamide: Maria Pryszczewska, *Talanta*, 1963, **10**, 135.

Summary—By quantitative polarographic investigation of the rate of precipitation of thallium^{I} sulphide with thioacetamide (TAA), the following expression for the rate of reaction between Tl^{I} and TAA in ammoniacal solution has been established:

$$-\frac{d[Tl^{I}]}{dt} = k \, . \, \frac{[Tl^{I}][CH_3CSNH_2][NH_3H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Tl^+}}{f_{H^+}{}^{\frac{1}{2}}}$$

(f = activity coefficient). The value of the rate constant, k, is given by $9{\cdot}63 \times 10^{-6} \pm 0{\cdot}60 \times 10^{-6}$ mole$^{-\frac{3}{2}}$ litre$^{\frac{3}{2}}$ min^{-1} at 25°. The equation has been tested over the pH range 11·4 – 12·7, and at ammonia concentrations of 2·25 – 9·0 moles per litre. The rate of precipitation of thallium sulphide in concentrated ammonia at 25° reaches a value suitable for the amperometric determination of thallium^{I}.

Studies of the absorptiometric determination of soluble phosphorus in textiles: J. T. McAloren and G. F. Reynolds, *Talanta* 1963, **10**, 145.

Summary—A study is reported of a standard procedure for the absorptiometric determination of phosphorus in textiles by the molybdenum blue method. This method has been shown to lack reproducibility when the phosphorus concentration exceeds 0·5 μg/ml in the final solution, and an investigation of possible causes of failure is reported. The development of a modified procedure covering the range 0–3% of phosphorus in the sample is described. An alternative method for the determination of higher concentrations of phosphorus is suggested.

Cation-exchange separation of scandium: Hiroshi Hamaguchi, Rokuro Kuroda, Korekazu Aoki, Ryuitiro Sugisita and Naoki Onuma, *Talanta*, 1963, **10**, 153.

Summary—A cation-exchange study of scandium is described. The distribution coefficients of scandium and other common metals have been determined by a batch method. The empirical formula of the scandium complex existing in the thiocyanate-hydrochloric acid system is suggested as being $Sc(SCN)_2Cl$. Scandium can be separated from thorium, zirconium, iron, titanium, aluminium and calcium using an ammonium thiocyanate-hydrochloric acid mixture as eluent. Some separation of scandium from the rare earths is also achieved, but the heavier rare earths cannot be separated cleanly.

***N,N,N′,N′*-Tetramethyl-*o*-tolidine (Tetron) as a reagent for the determination of small amounts of oxidising agents:** N. Jordanov and Ch. Daiev, *Talanta*, 1963, **10**, 163.

Summary—*N,N,N′,N′*-Tetramethyl-*o*-tolidine is proposed as a very sensitive reagent for the determination of small amounts of oxidising agents (Au^{III}, Ce^{IV}, BrO_3^-, *etc.*) The following have been determined; the normal redox potential of the organic compound over a range of pH values; the number of electrons involved in the oxidation; the composition of the products of oxidation; the extinction coefficients of the various coloured products produced by different oxidants. The compound has a higher normal redox potential than *o*-tolidine ($\Delta E_o = 140$ mv) and is therefore more selective. Its reactions have sensitivities about double those of *o*-tolidine.

A new reductimetric reagent: Iron^{II} in a strong phosphoric acid medium—II: Titration of molybdenum^{VI} with iron^{II} at room temperature: G. Gopala Rao and Seetarama Raju Sagi, *Talanta*, 1963, **10**, 169.

Summary—The results are presented of investigations leading to the development of a procedure for the titrimetric determination of molybdenum^{VI} with iron^{II} sulphate in a strong phosphoric acid medium (11·5—13·0*M*) at room temperature, using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Advantages of the procedure are similar to those previously described for the titration of uranium^{VI} with iron^{II}.

Photometric determination of boron in aqueous medium using phthalein violet: Věnceslav Patrovský, *Talanta*, 1963, **10**, 175.

Summary—A selective and sensitive photometric determination of boron in aqueous medium, using phthalein violet, is described. After ion-exchange or phosphate separation of various cations, the method permits the determination of as little as 0·1 mg of boron in 50 ml.

The analysis of beryllium and beryllium oxide—VII: Determination of nickel: James O. Hibbits and Silve Kallmann, *Talanta*, 1963, **10**, 181.

Summary—A method is described for the determination of nickel in beryllium or beryllium oxide. Nickel is precipitated with benzotriazole using cadmium as a carrier. A further separation from other elements is made by passing a hydrochloric acid-isopropyl alcohol solution through Dowex-1 anion-exchange resin. If necessary, separation of nickel from manganese is made by chloroform extraction of the nickel dimethylglyoxime complex. Nickel is finally determined as the dimethylglyoxime complex in an aqueous medium. The method is accurate to ±3% relative or 3 μg of nickel, whichever is greater, and is essentially specific for the determination of nickel.

Summaries for card indexes

Precipitation from mixed solvents—II: Nickel 8-hydroxyquinolate: Lester C. Howick and Jerry L. Jones, *Talanta*, 1963, **10**, 189.

Summary—Preferential volatilisation of the organic components of a water-acetone-ethanol mixture has been shown to lead to the formation of large, dense, easily-filtered crystals of nickel 8-hydroxyquinolate. Specific directions are given for the analysis of solutions containing 3–30 mg of nickel. The separation of 30 mg of nickel from 540 mg of magnesium or 1400 mg of calcium can be accomplished with less than 1 mg of co-precipitation.

Precipitation from mixed solvents—III: Magnesium 8-hydroxyquinolate: Lester C. Howick, Nora L. Ford and Jerry L. Jones, *Talanta*, 1963, **10**, 193.

Summary—Preferential volatilisation of the organic solvent from a water-acetone mixture leads to the formation of large, grainy, easily-filtered crystals of magnesium 8-hydroxyquinolate. Using this method, magnesium can be separated satisfactorily from sodium, potassium and barium.

Precipitation from mixed solvents—IV: Copper 8-hydroxyquinolate: Lester C. Howick and Jerry L. Jones, *Talanta*, 1963, **10**, 197.

Summary—The technique of precipitation from mixed solvents has been applied to the case of copper 8-hydroxyquinolate. Although the time before observing the first visible precipitate was less than 5 min, the final crystals were large, well-formed, and very regular. The method has been shown to be applicable to the analysis of samples containing between 3 and 30 mg of copper, and to result in good separations from calcium, magnesium and lead.

Separation of Silver, lead and mercury^{II} by ion-exchange chromatography: Anil K. De and Santosh K. Majumdar, *Talanta*, 1963, **10**, 201.

Summary—A method has been developed for the ready separation of silver, lead and mercury^{II} from each other by ion exchange chromatography. Lead is eluted with $0.25M$ ammonium acetate, then silver, and finally mercury^{II} with $0.5M$ and $4M$ ammonium acetate, respectively.

Liquid scintillation counting of plutonium-239 from biological samples: Taft Y. Toribara, Donald A. Morken and Carol Predmore, *Talanta* 1963, **10**, 205.

Summary—The conditions for the measurement of plutonium-239 activity from biological samples by liquid scintillation counting have been determined. It has been found that considerable quantities of iron may be tolerated in the final counting solution if phosphoric acid is added to form a colourless complex. Appreciable quantities of plutonium are adsorbed on the counting bottle when perchloric acid is used, and again the addition of phosphoric acid eliminates the difficulty by complexing the plutonium.

The separation and determination of plutonium in diverse biological samples: TAFT Y. TORIBARA, CAROL PREDMORE and PAUL A. HARGRAVE *Talanta*, 1963, **10**, 209.

Summary—A greatly simplified separation scheme for plutonium in biological samples has been devised. It is based on the absorption of an anionic form of quadrivalent plutonium in a strong hydrochloric acid solution by a strong base anion-exchange resin. The greatest difficulty in obtaining complete recovery from some samples was in getting the sample completely dissolved. For the acid-insoluble portion of samples such as faecal ash, it was necessary to resort to carbonate and bisulphate fusions. Elution from the ion-exchange column was accomplished with sulphurous acid, and the final determination was made by liquid scintillation counting.

The determination of microgram quantities of zirconium in iron, cobalt and nickel alloys by X-ray fluorescence: OWEN H. KRIEGE and JOSEPH S. RUDOLPH, *Talanta*, 1963, **10**, 215.

Summary—Microgram amounts of zirconium are separated from iron cobalt and nickel alloys by precipitation with *p*-bromomandelic acid, following which the zirconium is determined by X-ray fluorescence. Replicate results are reported for metal samples containing 0·003–0·5% of zirconium. An evaluation of the accuracy of this procedure was made using National Bureau of Standards certified samples.

A nomogram for acid-base titrations: E. WÄNNINEN, *Talanta*, 1963, **10**, 221.

Summary—A mathematical treatment of acid-base titrations, based on the concept of conditional constants which is analogous to the treatment of complexometric titrations, is presented. Equations are derived for calculating the pH at the equivalence point, and the titration error when the end-point deviates from the equivalence point. The values of these quantities can be determined without complicated calculations from a nomogram included in the paper.

The determination of thiomalic acid: G. ARAVAMUNDAN and C. RAMA RAO, *Talanta*, 1962, **10**, 231.

Summary—The extent of oxidation of thiomalic acid by iodine, potassium iodate, potassium bromate, potassium periodate and chloramine-T depends on alkalinity, temperature and duration of reaction. Therefore these oxidants do not provide a satisfactory method for the determination of thiomalic acid.

Separation of titanium from iron and aluminium: RUDOLF PŘIBIL and VLADIMIR VESELY, *Talanta*, 1963, **10**, 233.

Summary—Titanium can be separated easily from iron and aluminium by precipitation with sodium hydroxide in the presence of triethanolamine. The precipitated titanium hydroxide is filtered off, dissolved in nitric acid, and determined complexometrically. Certain other elements are masked with EDTA. The proposed method is suitable for all types of material containing a considerable amount of titanium, such as Fe-Ti alloys, titanium ores or concentrates, or artificial titanates.

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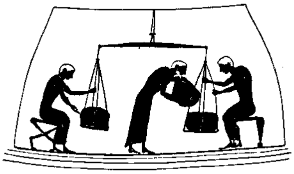

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[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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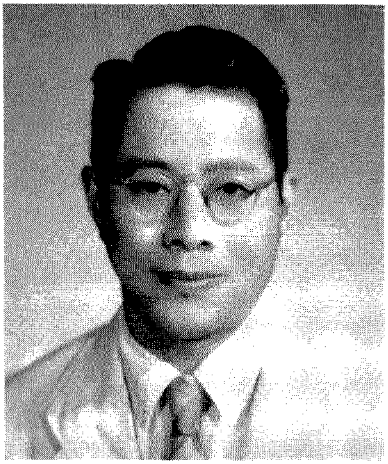

Shu-Chuan Liang (China) was born in 1912 in Chefoo. He obtained his B.Sc. from Yenching University, Peking, in 1933, then studied for his Dr. phil. nat. (1937) at the University of Munich, Germany. After a short stay in the laboratory of Professor (at that time Dozent) F. Hecht in Vienna, Dr. Liang returned to China to teach analytical chemistry at Chungking University. In 1947 he joined Academia Sinica. He is particularly interested in the analytical chemistry of the rarer elements.

Talanta, 1963, Vol. 10, pp. 135 to 143. Pergamon Press Ltd. Printed in Northern Ireland

AMPEROMETRISCHE BESTIMMUNG DER METALLE UNTER DER ANWENDUNG VON THIOACETAMID—IV*

UNTERSUCHUNGEN ÜBER Tl_2S-BILDUNGSGESCHWINDIGKEIT IN AMMONIAKALISCHEN Tl^+-IONENLÖSUNGEN MITTELS THIOACETAMID†

Maria Pryszczewska
Institut für Allgemeine Chemie, Technische Hochschule Szczecin, Polen

(*Eingegangen am* 30 *Mai* 1962. *Angenommen am* 28 *September* 1962)

Zusammenfassung—Auf Grund der quantitativen-polarographisch durchgeführten-Untersuchungen über Tl_2S-Fällungsgeschwindigkeit mittels TAA wurde folgende Gleichung für Reaktionsgeschwindigkeit zwischen Tl^+-Ionen und TAA in ammoniakalischen Lösungen abgeleitet

$$-\frac{d[Tl(I)]}{dt} = k \,.\, \frac{[Tl(I)][CH_3CSNH_2][NH_3H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Tl^+}}{f_{H^+}^{\frac{1}{2}}}$$

(f = Aktivitätskoeffizient)

Der Zahlenwert von Geschwindigkeitskonstante (k) beträgt: $9{,}63 \,.\, 10^{-6} \pm 0{,}60 \,.\, 10^{-6}$ $Mol^{-\frac{3}{2}}$ $L^{\frac{3}{2}}$ $Min.^{-1}$ für Temp. 25°C. Die Geltung dieser Gleichung wurde im pH-Intervall vom 11,4 bis 12,7 und im NH_3H_2O-Konzentrationsgebiet von 2,25 Mol/L bis 9,0 Mol/L überprüft. Die Tl_2S-Fällungsgeschwindigkeit erreicht in Temp. ca 25°C erst in konzentrierten Ammoniaklösungen die für amperometrische Bestimmungen der Tl^+-Ionen entsprechende Werte.

EINLEITUNG

Obwohl wir TAA schon ziemlich lang in unserer analytischen Praxis anwenden, doch anfangs wurde er von uns als bequemer H_2S-Vertreter ausschliesslich in der qualitativen Analyse gebraucht.

Die von uns angegebene Methode der systematischen qualitativen Analyse der Kationen mit Gebrauch von TAA[1] weicht von der klassischen Methode (unter Anwendung von H_2S) nur so weit ab, wie es Rücksicht auf den spezifischen chemischen Charakter des TAA notwendig machte.

Diese Untersuchung über Tl_2S-Fällungsgeschwindigkeit mittels TAA aus ammoniakalishcen Tl^+-Ionenlösungen bildet nur einen Teil des allgemeinen Problems der Anwendung des TAA zu amperometrischen Bestimmung der Metalle der H_2S-und der $(NH_4)_2S$-Gruppe. Die Arbeit über dieses Problem wird in unserem Institut durchgeführt. Bis nun wurde die Methode der amperometrischen Bestimmung der Ag^+-Ionen,[2] der Cd^{2+}-Ionen[3] und der Pb^{2+}-Ionen[4] mittels TAA angegeben. Es geht eben zu Ende die Arbeit über die Methode der amperometrischen Bestimmung der Tl^+-Ionen mittels TAA.

Charakteristisch für diese Methoden ist die Anwendung des TAA—nicht wie sonst in der erhöhten Temperatur ca 100°C sondern in der gewöhnlichen Temperatur ca 25°C. Die für amperometrische Bestimmungen entsprechende Sulfidfällungs-

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* Part III

† Thioacetamid wird von nun an kurz als TAA beeichnet.

geschwindigkeit wird—in der Temperatur ca 25°C—meistens erst in alkalischen Lösungen der Metallionen erreicht. Die Untersuchungen über die Reaktionsgeschwindigkeit der Metallionen mit TAA in eben diesen Bedingungen (d.h. in alkalischem pH-Gebiet und in der gewöhnlichen Temperatur) sind für das Problem der Anwendung des TAA als Reagens zur elektrometrischen Bestimmung der Metalle von spezieller Wichtigkeit.

Solche Untersuchungen in Bezug auf Cadmiumionen wurden schon durchgeführt.[5]

Die jetzige Arbeit über die Reaktionsgeschwindigkeit der Tl^+-Ionen mit TAA bildet die Fortführung dieser Untersuchungen. Im Laufe sind analoge Untersuchungen in Bezug auf manche andere Metalle.

Die Sulfidfällungsgeschwindigkeit der Metalle mittels TAA wurde schon früher durch Swift und Mitarbeiter in saurem pH-Gebiet und in erhöhter Temperatur ca 90°C untersucht.[6–10] Diese Autoren haben auch den Prozess der Hydrolyse des TAA in saurem und alkalischem pH-Gebiet und die Eigenschaften des TAA in amoniakalischen Puffern[6,11,12] untersucht. Die Hydrolyse des TAA wurde auch von Rosenfeld und Taylor gründlich untersucht.[13]

Alle diese Untersuchungen lieferten wertvolles experimentales Material, welches unter anderem schon zur teilweisen Lösung des Problems des Mechanismus der Reaktion der Metallionen mit TAA ausgenützt wurde.[6–10]

Unsere Untersuchungen über Sulfidbildung der Metalle mittels TAA in alkalischem pH-Gebiet und in gewöhlicher Temperatur werden hoffentlich—abgesehen von ihrer Bedeutung für amperometrische Zwecke—neues experimentales Material (eventuell auch für das Problem des Mechanismus der Reaktion des TAA mit Metallionen) liefern, da in solchen pH-und Temperatur-Bedingungen derartige Untersuchungen eher nicht geführt waren.

Die Reaktion der Tl^+-Ionen mit TAA, die überhaupt bis nun nicht untersucht wurde, ist—unter anderem—auch darum interessant weil ihr Verlauf von dem der anderen, untersuchten Metalle abweicht.

DER EXPERIMENTALE TEIL

Apparatur

Polarograph "Radiometr PO3m" (Dänemark). Tropfende, Quecksilberelektrode als Kathode und gesättigte Kalomelektrode als Anode.

Termostat nach Wobser.

Generator zur elektrolytischen Gewinnung des Wasserstoffs. (Die Luft wurde aus jeder Lösung durch Wasserstoffstrom eliminiert).

Automatische 1-ml Mikrobürette (zur Dosierung des TAA).

Lösungen

$TlNO_3$-Standardlösung wurde aus dem "reinen" Handelspräparat nach Reinigung und dreimaliger Kristallisation vorbereitet. Thioacetamidlösung aus dem "reinen" Handelspräparat nach dreimaliger Kristallisation vorbereitet und amperometrisch mittels $AgNO_3$-Standardlösung bestimmt.[2]

$AgNO_3$, $NaNO_3$, NH_4NO_3 wurden aus "analytisch reinen" Handelspräparaten nach zweimaliger Kristallisation angewandt. $NaNO_3$ wurde als Grundelektrolyt und zugleich als Ionenstärke-Stabilisator angewandt.

Der pH-Wert der Lösungen wurde mittels Ammoniakpuffer ($NH_3H_2O + NH_4NO_3$) konstant gehalten.

Prozedur. Die experimentale Bestimmung der Sulfidbildungsgeschwindigkeit, wurde so wie früher[3,5] polarographisch durchgeführt. Jede untersuchte Lösung wurde amperometrisch—mittels TAA—nach der Entfernung der Luft bestimmt.

Während dieser Bestimmung nach der Einführung in die Lösung der ersten Dose des TAA rejestrierte man den Reduktionsstrom der Tl^+-Ionen (und zugleich die $TlNO_3$-Konzentration) in gleichen Zeitabständen. Die Abhängigkeit des Reduktionsstroms und der zu ihm proportionalen Tl^+-Ionenkonzentration von der Zeit war—in genügendem Zeitintervall—linear (Abb. 1 u. 2). Auf Grund der so erhaltenen Daten wurde die Reaktionsgeschwindigkeit zwischen TAA und Tl^+-Ionen in jedem untersuchten Fall bestimmt.

ERGEBNISSE UND DISKUSSION

Zuerst wurde die Abhängigkeit der Reaktionsgeschwindigkeit der Tl_2S-Fällung von der Konzentration des TAA untersucht. Die dazu angewandten Lösungen einer Serie haben ausser der gleichen Ionenstärke (die bei allen untersuchten Lösungen dieselbe war) die gleiche NH_3H_2O-, NH_4NO_3- und $TlNO_3$-Konzentration. Nur die CH_3CSNH_2-Konzentration war—bei dieser Untersuchung—in jeder Lösung der Serie die andere.

Aus diesen Untersuchungen folgte, dass die Reaktionsgeschwindikeit der TAA-Konzentration proportional ist. Aber bei ziemlich grossen Werten der Reaktionsgeschwindigkeit wurden Abweichungen von der Proportionalität beobachtet.

Infolge weiterer analoger Untersuchungen wurde die proportionale Abhängigkeit der Reaktionsgeschwindigkeit von der Tl^+-Ionen Konzentration festgestellt. Aber auch hier wurden Abweichungen von der Proportionalität bei ziemlich grossen Werten der Reaktionsgeschwindigkeit beobachtet.

Der Reihe nach wurde der Einfluss der H^+-Ionenkonzentration auf die Reaktionsgeschwindigkeit der Sulfidfällung untersucht. Die Geschwindigkeit der Tl_2S-Fällung wurde experimental in Serien von Lösungen von derselben NH_3H_2O-Konzentration und verschiedenem pH Wert bestimmt.

Aus Ergebnissen dieser Untersuchungen folgt, dass die Tl_2S-Fällungsgeschwindigkeit eine absteigende Funktion der H^+-Ionenaktivität ist (Abb. 1).

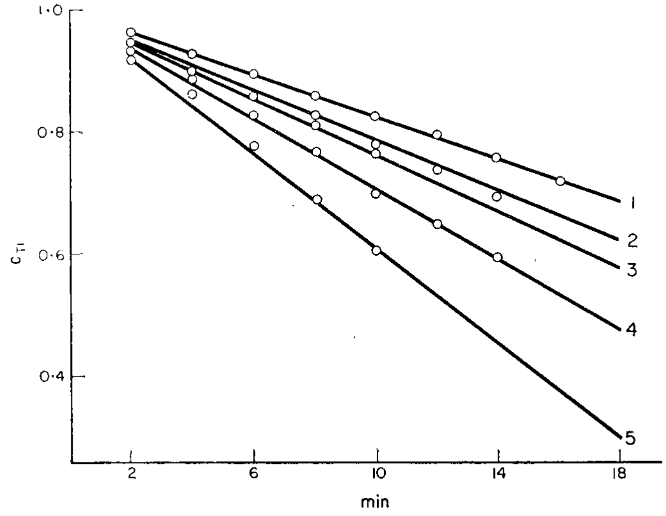

Abb. 1.—Reaktionsgeschwindigkeit der Tl_2S-Fällung als a_{H^+}-Funktion.

Temp. = 25°C 1. $a_{H^+} = 2,42 . 10^{-12}$
Pot. = −0,9v 2. $a_{H^+} = 1,46 . 10^{-12}$
$[TlNO_3] = C_{Tl} = 1,60 . 10^{-3}$ Mol/L 3. $a_{H^+} = 1,11 . 10^{-12}$
$[CH_3CSNH_2] = 6,05 . 10^{-4}$ Mol/L 4. $a_{H^+} = 7,30 . 10^{-13}$
$[NH_3H_2O] = 6,75$ Mol/L 5. $a_{H^+} = 3,67 . 10^{-13}$

Um diese Funktion exakt, ausdrücken zu können, hat man drei Gleichungen—als im untersuchten Fall zulässig—berücksichtigt.

Es sind folgende* Gleichungen:

$$-\frac{dc_{Tl}}{dt} = k' \frac{c_{Tl} \cdot c_T}{c_H} \cdot \frac{f_{Tl}}{f_H} \tag{1}$$

$$-\frac{dc_{Tl}}{dt} = k'' \frac{c_{Tl} \cdot c_T}{c_H{}^2} \cdot \frac{f_{Tl}}{f_H{}^2} \tag{2}$$

$$-\frac{dc_{Tl}}{dt} = k''' \frac{c_{Tl} \cdot c_T}{c_H{}^{\frac{1}{2}}} \cdot \frac{f_{Tl}}{f_H{}^{\frac{1}{2}}} \tag{3}$$

Nach Einsetzen in diese Gleichungen entsprechender Werte für c_T, c_{Tl}, c_H, f_{Tl}, f_H und experimental erhaltener Werte für die Reaktionsgeschwindigkeit ($-dc_{Tl}/dt$) wurden die Werte von k', k'', k''' aus den obigen Gleichungen für jeden untersuchten Fall berechnet.

Die H^+-Ionen-Konzentration jeder (ammoniakalisch gepufferten) Lösung wurde rechungsweise bestimmt.

Der Wert des Aktivitätskoeffizienten f_{H^+} wurde nach Angaben von Kolthof[14] berechnet und f_{Tl^+} nach der Gleichung (IV) von Debye u. Hückel.[14]

Die Ergebnisse dieser Untersuchungen geben die Tabellen 1 bis 3 an.

Wie aus den Daten der Tabellen folgt, ist in jeder untersuchten Serie nur der Wert von k''' aus der Gleichung 3 für verschiedene a_{H^+}-Werte annähernd konstant.

In Übereinstimmung damit wäre nur die Gleichung 3 für die Tl_2S-Fällungsgeschwindigkeit die richtige. Folglich ist die Reaktionsgeschwindigkeit umgekehrt dem zweiten Wurzel aus dem a_{H^+}Wert proportional.

Obwohl der Wert von k''' für alle Lösungen einer und derselben Serie (d.h. für Lösungen von gleicher NH_3H_2O-Konzentration) konstant ist, doch ist er verschieden für Serien von verschiedener NH_3H_2O-Konzentration, indem dieser Wert mit der

TABELLE I.—REAKTIONSGESCHWINDIGKEIT DER Tl_2S-FÄLLUNG ALS A_{H^+} FUNKTION

Temp. = 25°C $[TlNO_3] = C_{Tl} = 1{,}60 \,.\, 10^{-3}$ Mol/L
Pot. = −0,9v $[CH_3CSNH_2] = C_T = 6{,}05 \,.\, 10^{-4}$ Mol/L
$\mu = 0{,}5$ $[NH_3H_2O] = C_{Am} = 4{,}5$ Mol/L
$f_{H+} = 0{,}88$
$f_{Tl+} = 0{,}63$

Nr.	a_{H+} $C_H \,.\, f_H$	k' $-\frac{dc_{Tl}}{dt} \cdot \frac{C_H}{C_{Tl} \,.\, C_T} \cdot \frac{f_H}{f_{Tl}}$	k'' $-\frac{dc_{Tl}}{dt} \cdot \frac{C_H{}^2}{C_{Tl} \,.\, C_T} \cdot \frac{f_H{}^2}{f_{Tl}}$	k''' $-\frac{dc_{Tl}}{dt} \cdot \frac{C_H{}^{\frac{1}{2}}}{C_{Tl} \,.\, C_T} \cdot \frac{f_H{}^{\frac{1}{2}}}{f_{Tl}}$	k'''/C_{Am}
1	$3{,}68 \,.\, 10^{-12}$	$8{,}40 \,.\, 10^{-11}$	$3{,}20 \,.\, 10^{-22}$	$4{,}34 \,.\, 10^{-5}$	$9{,}6 \,,\, 10^{-6}$
2	$7{,}30 \,.\, 10^{-13}$	$3{,}77 \,.\, 10^{-11}$	$2{,}80 \,.\, 10^{-23}$	$4{,}43 \,.\, 10^{-5}$	$9{,}8 \,.\, 10^{-6}$
3	$5{,}58 \,.\, 10^{-13}$	$3{,}78 \,.\, 10^{-11}$	$1{,}78 \,.\, 10^{-23}$	$4{,}33 \,.\, 10^{-5}$	$9{,}6 \,.\, 10^{-6}$
4	$3{,}68 \,.\, 10^{-13}$	$2{,}66 \,.\, 10^{-11}$	$9{,}83 \,.\, 10^{-24}$	$4{,}36 \,.\, 10^{-5}$	$9{,}7 \,.\, 10^{-6}$
5	$1{,}84 \,.\, 10^{-13}$	$1{,}74 \,.\, 10^{-11}$	$3{,}19 \,.\, 10^{-24}$	$4{,}05 \,.\, 10^{-5}$	$9{,}0 \,.\, 10^{-6}$

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* Von nun an werden in Gleichungen und Tabellen folgende Abkürzungen gebraucht:
c_T statt TAA-Konzentration
c_{Tl} statt $TlNO_3$-Konzentration
C_H statt H^+-Ionen-Konzentration
f_{Tl} statt $f_{Tl}{}^+$
f_H statt $f_H{}^+$

TABELLE II.—REAKTIONSGESCHWINDIGKEIT DER Tl_2S-FÄLLUNG ALS A_{H^+} FUNKTION

Temp. = 25°C $[TlNO_3] = C_{Tl} = 1{,}60 \,.\, 10^{-3}$ Mol/L
Pot. = −0,9v $[CH_3CSNH_2] = C_T = 6{,}05 \,.\, 10^{-4}$ Mol/
$\mu = 0{,}5$ $[NH_3H_2O] = C_{Am} = 6{,}75$ Mol/L
$f_H{}^+ = 0{,}88$
$f_{Tl}{}^+ = 0{,}63$

Nr.	a_{H^+}	k'	k''	k'''	k'''/C_{Am}
	$C_H \,.\, f_H$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H}{C_{Tl}\,.\,C_T}\cdot\frac{f_H}{f_{Tl}}$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H{}^2}{C_{Tl}\,.\,C_T}\cdot\frac{f_H{}^2}{f_{Tl}}$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H{}^{\frac{1}{2}}}{C_{Tl}\,.\,C_T}\cdot\frac{f_H{}^{\frac{1}{2}}}{f_{Tl}}$	
1	$2{,}42 \,.\, 10^{-12}$	$10{,}20 \,.\, 10^{-11}$	$2{,}48 \,.\, 10^{-22}$	$6{,}60 \,.\, 10^{-5}$	$9{,}7 \,.\, 10^{-6}$
2	$1{,}46. \,.10^{-12}$	$8{,}24 \,.\, 10^{-11}$	$1{,}20 \,.\, 10^{-22}$	$6{,}80 \,.\, 10^{-5}$	$10{,}2 \,.\, 10^{-6}$
3	$1{,}11 \,.\, 10^{-12}$	$6{,}90 \,.\, 10^{-11}$	$7{,}67 \,.\, 10^{-23}$	$6{,}55 \,.\, 10^{-5}$	$9{,}7 \,.\, 10^{-6}$
4	$7{,}30 \,.\, 10^{-13}$	$5{,}33 \,.\, 10^{-11}$	$3{,}93 \,.\, 10^{-23}$	$6{,}50 \,.\, 10^{-5}$	$9{,}6 \,.\, 10^{-6}$
5	$3{,}67 \,.\, 10^{-13}$	$3{,}97 \,.\, 10^{-11}$	$1{,}46 \,.\, 10^{-23}$	$6{,}55 \,.\, 10^{-5}$	$9{,}7 \,.\, 10^{-6}$

TABELLE III.—REAKTIONSGESCHWINDIGKEIT DER Tl_2S-FÄLLUNG ALS A_{H^+} FUNKTION

Temp. = 25°C $[TlNO_3] = C_{Tl} = 1{,}60 \,.\, 10^{-3}$ Mol/L
Pot. = −0,9v $[CH_3CSNH_2] = C_T = 6{,}05 \,.\, 10^{-4}$ Mol./L
$\mu = 0{,}5$ $[NH_3H_2O] = C_{Am} = 9{,}00$ Mol/L
$f_{H^+} = 0{,}88$
$f_{Tl^+} = 0{,}63$

Nr.	a_{H^+}	k'	k''	k'''	k'''/C_{Am}
	$C_H \,.\, f_H$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H}{C_{Tl}\,.\,C_T}\cdot\frac{f_H}{f_{Tl}}$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H{}^2}{C_{Tl}\,.\,C_T}\cdot\frac{f_H{}^2}{f_{Tl}}$	$-\frac{dc_{Tl}}{dt}\cdot\frac{C_H{}^{\frac{1}{2}}}{C_{Tl}\,.\,C_T}\cdot\frac{f_H{}^{\frac{1}{2}}}{f_{Tl}}$	
1	$3{,}68. \ 10^{-12}$	$1{,}68 \,.\, 10^{-10}$	$6{,}25 \,.\, 10^{-22}$	$8{,}82 \,.\, 10^{-5}$	$9{,}80 \,.\, 10^{-6}$
2	$2{,}31 \,.\, 10^{-12}$	$1{,}32 \,.\, 10^{-10}$	$3{,}00 \,.\, 10^{-22}$	$8{,}83 \,.\, 10^{-5}$	$9{,}80 \,.\, 10^{-6}$
3	$9{,}20 \,.\, 10^{-13}$	$8{,}90 \,.\, 10^{-11}$	$8{,}30 \,.\, 10^{-23}$	$9{,}20 \,.\, 10^{-5}$	$10{,}20 \,.\, 10^{-6}$
4	$3{,}68 \,.\, 10^{-13}$	$5{,}36 \,.\, 10^{-11}$	$2{,}02 \,.\, 10^{-23}$	$8{,}92 \,.\, 10^{-5}$	$9{,}90 \,.\, 10^{-6}$
5	$1{,}84 \,.\, 10^{-13}$	$3{,}50 \,.\, 10^{-11}$	$6{,}45 \,.\, 10^{-24}$	$8{,}26 \,.\, 10^{-5}$	$9{,}18 \,.\, 10^{-6}$

NH_3H_2O-Konzentration steigt, d.h., dass der Wert von k''' eine aufsteigende Funktion der NH_3H_2O-Konzentration ist.

Experimentale Bestimmung der Reaktionsgeschwindigkeit für Serien von Lösungen von demselben pH-Wert und veränderlichen NH_3H_2O-Konzentration ermöglichten diese Funktion in der Form einer Gleichung auszudrücken.

Die Untersuchungsergebnisse einer derartigen Serie gibt die Tabelle IV und die Abb. 2 an.

Es ist aus der Tabelle IV ersichtlich, dass der Wert von k''' mit der NH_3H_2O-Konzentration steigt, doch der Ausdruck k'''/C_{Am} behält annähernd konstanten Wert nicht nur für alle Lösungen dieser Serie (d.h. der Serie aus der Tabelle IV) sondern überhaupt für alle untersuchten Serien, also auch für die Serien aus den Tabellen I bis III.

Die Gleichung:

$$k'''/c_{Am} = \text{const.} = k \tag{4}$$

drückt diese Abhängigkeit aus. Der Wert k''' is nach dieser Gleichung der NH_3H_2O-Konzentration proportional.

Nachdem wir in die Gleichung (3) den Wert für k''' aus der Gleichung (4) einsetzen, bekommt die Gleichung (3) die Form:

$$-\frac{dc_{Tl}}{dt} = k.\frac{c_{Tl}\cdot c_T\cdot c_{Am}}{c_H{}^{\frac{1}{2}}}\cdot\frac{f_{Tl}}{f_H{}^{\frac{1}{2}}} \tag{3', IV}$$

TABELLE IV.—REAKTIONSGESCHWINDIGKEIT DER Tl_2S-FÄLLUNG ALS FUNKTION DER NH_3H_2O-KONZENTRATION

Temp. = 25°C [$TlNO_3$] = C_{Tl} = 1,60 . 10^{-3} Mol/L
Pot. = −0,9v [CH_3CSNH_2] = C_T = 6,10 . 10^{-4} Mol/L
μ = 0,5 a_{H^+} = = 3,68 . 10^{-13}
f_{H^+} = 0,88
f_{Tl^+} = 0,63

Nr.	[NH_3H_2O] Mol/L	k''' $-\frac{dc_{Tl}}{dt} \cdot \frac{C_H^{\frac{1}{2}}}{C_{Tl} . C_T} \cdot \frac{f_H^{\frac{1}{2}}}{f_{Tl}}$	$k/'''C_{Am}$
1	2,25	2,08 . 10^{-5}	9,26 . 10^{-6}
2	3,36	3,20 . 10^{-5}	9,40 . 10^{-6}
3	4,50	4,24 . 10^{-5}	9,40 . 10^{-6}
4	6,75	6,20 . 10^{-5}	9,17 . 10^{-6}
5	9,00	8,97 . 10^{-5}	9,95 . 10^{-6}

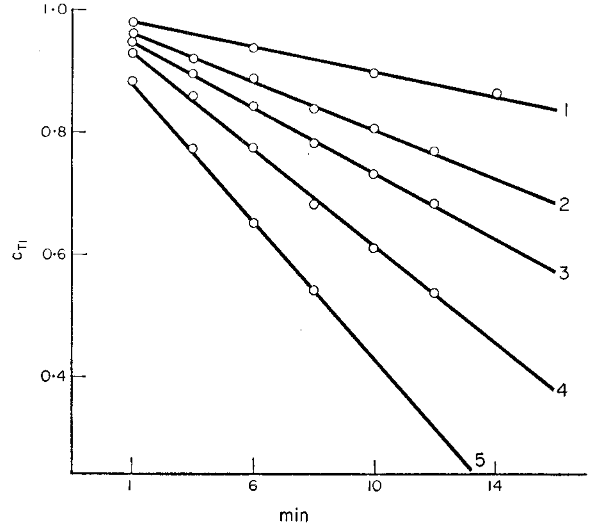

ABB. 2—Reaktionsgeschwindigkeit der Tl_2S-Fällung als Funktion der NH_3H_2O-Konzentration.
Temp. = 25°C 1. [NH_3H_2O] = 2,25 Mol/L
Pot. = −0,9 v 2. [NH_3H_2O] = 3,36 Mol/L
[$TlNO_3$] = C_{Tl} = 1,60 . 10^{-3} Mol/L 3. [NH_3H_2O] = 4,50 Mol/L
[CH_3CSNH_2] = 6,10 . 10^{-4} Mol/L 4. [NH_3H_2O] = 6,75 Mol/L
a_H^+ = 3,68 . 10^{-13} Mol/L 5. [NH_3H_2O] = 9,00 Mol/L

Der Zahlenwert von Geschwindigkeitskonstante (k) aus dieser Gleichung wurde berechnet auf Grund der experimentalen Daten, zwischen anderem auch aus den Daten, welche die Serien aus der Tabellen I–IV betreffen. Der so erhaltene Mittelwert von k beträgt für Temp. 25°C 9,63 . 10^{-6} ± 0,60 . 10^{-6} $Mol^{-\frac{3}{2}}.L^{\frac{3}{2}}.Min.^{-1}$
Die Gleichung (3′, IV) bestimmt die Tl_2S-Fällungsgeschwindikeit in Tl^+-Ionenlösungen von ziemlich grosser NH_3H_2O-Konzentration. Ihre Geltung wurde auf folgende Weise überpriefft: die Reaktionsgeschwindigkeit ($-dc_{Tl}/dt$) wurde auf Grund dieser Gleichung (d.h. der Gleichung 3′, IV), indem man für k den eben angegebenen Wert einsetzte, in jedem konkreten Fall berechnet und mit dem experimental gefundenem Wert verglichen.

In dem NH_3H_2O-Konzentrationsintervall vom 2,25 Mol/L bis 9,00 Mol/L und dem pH-intervall vom 11,4 bis 12,7 ist die Übereinstimmung dieser Werte ziemlich gut, wie es aus der Tabelle V ersichtlich ist.

TABELLE V.—ÜBERPRÜFUNG DER REAKTIONSGESCHWINDIGKEITSGLEICHUNG (3′, IV)

Nr.	a_{Tl}	a_T	a_H	c_{Am}	$-\frac{dc_{Tl}}{dt} . 10^5$Mol/L.Min.	
	$c_{Tl} . f_{Tl}$		$c_H . f_H$		experim. bestimmt	berechnet aus Gleichung (3′, IV)
1.	$1{,}02 . 10^{-3}$	$6{,}10 . 10^{-4}$	$3{,}68 . 10^{-13}$	2,25 Mol/L	2,10	2,22
2.	$1{,}02 . 10^{-3}$	$6{,}10 . 10^{-4}$	$3{,}68 . 10^{-13}$	3,36 Mol/L	3,20	3,32
3.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$3{,}68 . 10^{-12}$	4,50 Mol/L	1,38	1,39
4.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$7{,}30 . 10^{-13}$	4,50 Mol/L	3,15	3,13
5.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$5{,}58 . 10^{-13}$	4,50 Mol/L	3,50	3,58
6.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$3{,}68 . 10^{-13}$	4,50 Mol/L	4,43	4,41
7.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$1{,}84 . 10^{-13}$	4,50 Mol/L	5,76	6,23
8.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$2{,}42 . 10^{-12}$	6,75 Mol/L	2,57	2,58
9.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$1{,}46 . 10^{-12}$	6,75 Mol/L	3,45	3,32
10.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$1{,}11 . 10^{-12}$	6,75 Mol/L	3,80	3,81
11.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$7{,}30 . 10^{-13}$	6,75 Mol/L	4,61	4,69
12.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$3{,}67 . 10^{-13}$	6,75 Mol/L	6,60	6,62
13.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$3{,}68 . 10^{-12}$	9,00 Mol/L	2,84	2,79
14.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$2{,}31 . 10^{-12}$	9,00 Mol/L	3,52	3,52
15.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$9{,}20 . 10^{-13}$	9,00 Mol/L	5,90	5,58
16.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$3{,}68 . 10^{-13}$	9,00 Mol/L	9,10	8,82
17.	$1{,}02 . 10^{-3}$	$6{,}05 . 10^{-4}$	$1{,}84 . 10^{-13}$	9,00 Mol/L	11,60	12,50

Die Reaktionsgeschwindigkeit der Tl_2S-Fällung ist viel geringer als—in analogen Arbeitsbedingungen—im Falle der Ag_2S-Fällung,[2] der CdS-Fällung[3,5] und der PbS-Fällung.[4] Man kan sie gewissermassen regulieren (in Übereinstimmung mit der Gleichung 3′, IV) z.B. durch die Anwendung entsprechender NH_3H_2O-Konzentration.

Aus unsern Untersuchungen über amperometrische Bestimmungsmethode der Tl^+-Ionen mittels TAA folgt, dass die Tl_2S-Bildungsgeschwindigkeit die für amperometrische Zwecke entsprechende Werte erst in Tl^+-Ionenlösungen von ziemlich grosser Ammoniakkonzentration erreicht. (Ausführlicher darüber in der nächsten Mitteilung)

Swift u. Mitarbeiter haben die Sulfidbildung der Metalle mittels TAA, die nicht durch Hydrolyse des TAA kontrolliert ist, als "direkte Reaktion" bezeichnet.[9]

Es ist ersichtlich schon aus der Form der oben angegebenen Reaktionsgeschwindigkeitsgleichung (3′, IV), dass die Tl_2S-Fällung mittels TAA in ammoniakalischem Milieu eben den Charakter der direkt verlaufenden Reaktion hat und nicht durch Hydrolyse des TAA kontrolliert ist.

Dasselbe betrifft auch die CdS-Fällung mittels TAA in ammoniakalischen Cadmiumionenlösungen von ziemlich grosser Ammoniakkonzentration. Für diesen Fall wurde folgende Gleichung abgeleitet:

$$-\frac{dc_{Cd}}{dt} = k\,\frac{c_{Cd} \cdot c_T}{c_{Am} \cdot c_H^{\frac{1}{2}}} \cdot \frac{f_{Cd}}{f_H^{\frac{1}{2}}}$$

Der Wert von k aus der letzten Gleichung beträgt: $7{,}8 . 10^{-4}$ $Mol^{\frac{1}{2}}.L^{-\frac{1}{2}}$ $Min.^{-1}$ für Temperatur 25°C.[5]

Im Falle der Cadmiumionen verläuft die Sulfidbildung auch direkt—wie aus der Form der Geschwindigkeitsgleichung folgt—und nicht durch Hydrolyse des TAA. Aber der Verlauf dieser "direkten Reaktion" ist nicht derselbe wie im Falle der Tl^+-Ionen, was sofort aus Vergleich der Reaktionsgeschwindigkeitsgleichung für Cd^{2+}-Ionen und Tl^+-Ionen ersichtlich ist. Die Sulfidfällungsgeschwindigkeit ist im Fall der Cadmiumionen umgekehrt der Ammoniakkonzentration proportional, bei der Tl^+-Ionen dagegen steigt sie proportional mit dieser Konzentration.

Der Name "direkte Reaktion" kann also—wie aus obigen Zusammenstellung folgt—Reaktionen der Metallionen mit TAA umfassen von nicht gänzlich demselben Mechanismus.

Obwohl für manche Metallionen Geschwindigkeitsgleichung ihrer direkten d.h. nicht mittelbar durch Hydrolyse verlaufenden Reaktion angegeben wurde,[5,6,8–10] doch bis nun ist der Mechanismus derartigen Reaktion, der in Übereinstimmung mit der Reaktionsgeschwindigkeitsgleichung wäre, in keinem Fall angegeben worden.

Das Problem des Mechanismus der "direkten Reaktion" der Metallionen mit TAA ist also offen. Die Untersuchungen, welche experimentales Material für seine Lösung liefern, werden hoffentlich diese Lösung beschleunigen.

Zum Abschluss, noch über die Ursache des—eben angegebenen—Unterschieds zwischen den Tl^+-Ionen und Cadmiumionen in der Sulfidbildungsgeschwindigkeit von der Ammoniakkonzentration. Vielleicht liegt die Ursache dieser Differenz darin, dass NH_3 nur im Falle der Cadmiumionen und nicht der Tl^+-Ionen als Komplexbildner auftritt.

Summary—By quantitative polarographic investigation of the rate of precipitation of thallium^{I} sulphide with thioacetamide (TAA), the following expression for the rate of reaction between Tl^{I} and TAA in ammoniacal solution has been established:

$$\frac{d[Tl^{I}]}{dt} = k \, . \, \frac{[Tl^{I}][CH_3CSNH_2][NH_3H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Tl^+}}{f_{H^+}{}^{\frac{1}{2}}}$$

(f = activity coefficient). The value of the rate constant, k, is given by $9{\cdot}63 \times 10^{-6} \pm 0{\cdot}60 \times 10^{-6}$ mole$^{-\frac{3}{2}}$ litre$^{\frac{3}{2}}$ min^{-1} at 25°. The equation has been tested over the pH range 11·4 – 12·7, and at ammonia concentrations of 2·25 – 9·0 moles per litre. The rate of precipitation of thallium sulphide in concentrated ammonia at 25° reaches a value suitable for the amperometric determination of thallium^{I}.

Résumé—Des recherches quantitatives en polarographie sur le taux de précipitation du sulfure de thallium I par la thiocétamide (T.A.A.) ont permis d'établir la formule suivante concernant la vitesse de réaction entre Tl^{I} et TAA en solution ammoniacale.

$$\frac{d|Tl^{I}|}{dt} = k.\frac{|Tl^{I}||CH_3CSNH_2||NH_3H_2O|}{|H^+|^2}\cdot\frac{f\,Tl^{I}}{f\,H^{+\frac{1}{2}}}$$

(f: coefficient d'activité). La valeur de la constante de réaction, k, est donnée par $9{,}63 \times 10^{-6} \pm 0{,}60 \times 10^{-6}$ mole$^{-3/2}$ litre$^{3/2}$ min. à 25°.

L'équation a été vérifiée pour des valeurs de pH comprises entre 11,4 et 12,7, et pour des concentrations de la solution ammoniacale de l'ordre de 2,25 à 9,0 moles/litre.

Le taux de précipitation du sulfure de thallium en solution ammoniacale concentrée à 25° atteint une valeur correcte pour le dosage ampérométrique du thallium I.

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STUDIES OF THE ABSORPTIOMETRIC DETERMINATION OF SOLUBLE PHOSPHORUS IN TEXTILES

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Summary—A study is reported of a standard procedure for the absorptiometric determination of phosphorus in textiles by the molybdenum blue method. This method has been shown to lack reproducibility when the phosphorus concentration exceeds 0·5 μg/ml in the final solution, and an investigation of possible causes of failure is reported. The development of a modified procedure covering the range 0–3% of phosphorus in the sample is described. An alternative method for the determination of higher concentrations of phosphorus is suggested.

INTRODUCTION

A STANDARD method for the absorptiometric determination of phosphorus in smoulder- or flame-proofed textiles has been in use for a number of years, but results have not been fully satisfactory. This method is based on the water extraction of the soluble phosphate and final absorptiometric determination of the molybdenum blue complex after reduction with tin^{II} chloride. The concentration range covered is 0 to 1% and a number of laboratories have reported poor reproducibility, especially in the upper half (0·5 to 1%) of this range. Inaccuracies in this region were disturbing because the soluble phosphorus content of smoulder-proofed textiles may be up to 1%, while that of flame-proofed materials may be as high as 5%. The work described in this paper was therefore undertaken to study this method, to investigate possible causes of failure and to develop a modified procedure.

The literature relating to the determination of phosphorus is extensive and an exhaustive survey was therefore not attempted. Because, however, the inaccuracies in the method under investigation appeared to occur when phosphorus concentrations greater than 0·5 μg/ml were present, interest was directed to those authors who claimed accuracy for methods dealing with final concentrations above this level. Boltz and Mellon[1] examined the use of the reduced heteropoly blue colour for the determination of phosphorus, as well as for germanium, silicon and arsenic. They found that Beer's law was obeyed up to a concentration of 1·5 μg of phosphorus/ml. Berenblyum and Chain[2] extracted the molybdophosphoric acid with isobutyl alcohol and reduced the complex in this solution with chlorostannic acid. The method was stated to be insensitive to variations in acidity and concentration of reducing agent. Leuck and Boltz[3] similarly extracted with isobutyl alcohol and, after reduction, measured the absorption of the heteropoly blue colour of solutions containing up to 1·3 μg of phosphorus/ml at 725 mμ. Kitson and Mellon[4] determined up to 40 μg/ml of phosphorus as the molybdivanadophosphoric acid complex by measuring the absorption in aqueous

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solution at 460 mμ. Boltz and Mellon[5] measured the absorption of the yellow (unreduced) molybdiphosphorus heteropoly complex at 380, 400 and 420 mμ and determined phosphorus up to a concentration of 25 μg/ml. Elwell and Wilson[6] measured the absorption from phosphorus up to a concentration of 1·3 μg/ml using the molybdivanadophosphate complex extracted into isoamyl alcohol. Wadelin and Mellon[7] measured the absorption at 310 mμ of 50-μg/ml concentrations of phosphorus using the unreduced heteropoly complex extracted into a 1-butanol/chloroform mixture, while Schaffer, Fong and Kirk[8] used liquid-liquid extraction with octyl alcohol to determine millimicrogram quantities of phosphorus. In addition, Fontaine[9] used an absorption peak of a reduced molybdenum blue at 820 mμ and Hague and Bright[10] made the determination at 830 mμ. The wavelength used for the method under investigation is 725 mμ (filter maximum). The difference in the wavelengths employed for these determinations is a strong indication that more than one heteropoly blue compound may be formed in these reactions.

EXPERIMENTAL

Apparatus

A Unicam SP.500 ultraviolet and visible spectrophotometer was used for all determinations described in this paper.

Procedure under investigation

Extract 20 g of the textile sample, cut into small pieces, for 30 min with 400 ml of boiling water. Decant and make two further extractions, each with 200 ml of boiling water for 15 min, combine the extracts in a 1-litre graduated flask and make up to volume with water. Treat 25 ml of the extract with a mixture of nitric and sulphuric acids (223 ml of concentrated sulphuric acid and 100 ml of concentrated nitric acid diluted to 1 litre with water) and evaporate to fumes. Cool, dilute with about 15 ml of water and add 1 ml of 1% potassium permanganate solution. Boil for 1 min, then decolorise excess permanganate by dropwise addition of saturated sulphur dioxide solution. Evaporate to fumes, cool, add 0·5 ml of concentrated hydrobromic acid, again evaporate to fumes, cool, transfer to a 500-ml graduated flask and make up to volume with water. Place two 10-ml aliquots of the prepared solution in 100-ml graduated flasks. To the first aliquot add 10 ml of 7*N* sulphuric acid and dilute to about 60 ml. Add 10 ml of 5% ammonium molybdate solution in 36*N* sulphuric acid, followed by 10 ml of freshly prepared tin^{II} chloride solution (0·5 g of tin^{II} chloride and 0·8 ml of concentrated hydrochloric acid diluted to 1 litre with water) dropwise with continuous agitation. Make up to 100 ml with water. Treat the second aliquot in the same way, except that the addition of ammonium molybdate is omitted, to provide a blank solution. Determine the absorption of the two solutions on a Spekker absorptiometer using the setting water-water 1·00, Ilford red 608 filters and a tungsten lamp.

Obtain the phosphorus content of the original sample by referring the difference reading to a calibration graph prepared from standard potassium dihydrogen phosphate solutions.

Preliminary studies

In order to test the reproducibility of the above procedure a number of determinations were made using standard phosphate solutions. Aliquots of 1, 2, 5 and 10 ml of a solution of potassium dihydrogen phosphate containing 10 μg of phosphorus/ml, were placed in 100-ml graduated flasks and treated with 10-ml portions of 7*N* sulphuric acid. The solutions were diluted to about 60 ml and 10 ml of 5% ammonium molybdate in 3·6*N* sulphuric acid added, followed by 10 ml of freshly prepared tin^{II} chloride solution, added dropwise with continuous agitation.

Each solution was then made up to volume with water and allowed to stand for 15 min. A corresponding series of blanks was prepared as above, but with the addition of ammonium molybdate omitted. The tin^{II} chloride solution was prepared by dissolving 0·5 g of pure tin^{II} chloride in 0·8 ml of 10*N* hydrochloric acid and diluting to 1 litre. This solution was freshly prepared each day and its strength was checked by titration against standard iodide solution.

Transmission curves plotted from these solutions showed a peak with a maximum at 700 mμ for the phosphomolybdate blue complex. This is thus the optimum wavelength for the determination, but because the method as normally used specifies a filter with a maximum at 725 mμ the absorption of each solution was measured at both of these wavelengths.

The absorptions obtained with a number of series of solutions, prepared as above and measured in 1-cm cells against water as zero, are shown plotted against phosphorus concentration in Fig. 1.

The successive dilutions made in the standard method are such that 1 ml of the standard phosphate solution employed is equivalent to 0·1 % of phosphorus in the textile sample. For this reason, except where otherwise stated, all phosphorus concentrations quoted in this paper are given as percentage content of phosphorus in an original sample.

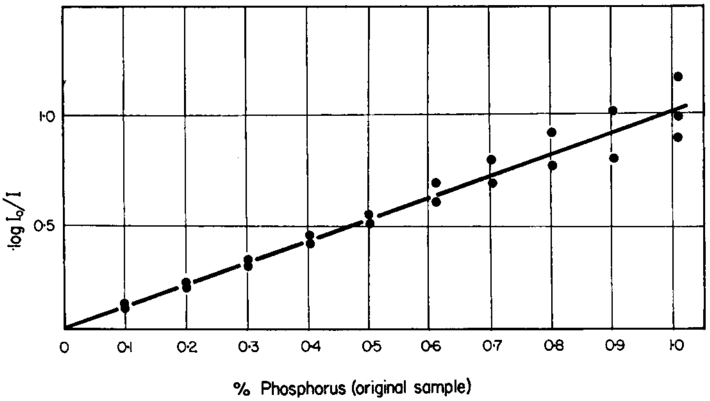

FIG. 1.—Graph of absorption of phosphomolybdate blue against phosphorus concentration (original sample). (Measured at 725 mμ.)

A study of Fig. 1 showed that the method gave reproducible results below 0·5% of phosphorus, but above this concentration a progressive spread of absorption of replicates appeared. This was confirmed by a large number of further determinations, and in addition a number of variations in the procedure were made in an effort to locate possible causes of the lack of repeatability. These included a delay of 1 hr between the addition of ammonium molybdate and that of tin^{II} chloride and a delay of 1 hr after the addition of sulphuric acid followed by a period of 30 min after the addition of ammonium molybdate. The whole procedure was also carried out at 45° before cooling to 25° for measurement. Although variations in phosphorus recoveries were evident after these variations in treatment they were all small and gave no indication of any trend. Solutions which were allowed to stand for 1 hr after development of the molybdenum blue colour, however, showed significant changes in absorption as indicated by the apparent recoveries listed in Table I.

TABLE I

Phosphorus added, %	Phosphorus found, %			
	Measured at 700 mμ		Measured at 725 mμ	
	Immediately	After 1 hr	Immediately	After 1 hr
0·100	0·105	0·100	0·103	0·100
0·200	0·193	—	0·200	—
0·300	0·293	0·257	0·300	0·305
0·400	0·385	—	0·400	—
0·500	0·500	0·455	0·510	0·530

Nature of the phosphomolybdate complex

In view of the lack of reproducibility of results for all solutions of phosphate concentration greater than 0·5 μg/ml it was considered that the conditions employed might only be suitable for the formation of the heteropoly blue in concentrations below this value. The concentration of reagents used in this reaction is known to be critical, although those used in this work are comparable with solutions successfully employed by Boltz and Mellon[1] and by Lueck and Boltz[8] and others.

It has been stated that the heteropoly blue compound formed on reduction is of uncertain composition[11] and it appeared from the tendency for absorption to decrease on standing (Table I) that it might be present in an unstable state. Solutions containing about 0·5 μg of phosphorus/ml were therefore treated as before to develop the blue colour, then allowed to stand for a considerable period of time, during which the extinction was measured at intervals. A typical solution which had 0·526 μg of phosphorus/ml initially gave an extinction equivalent to 0·50 μg of phosphorus/ml after 1 hr and only 0·274 μg/ml after 18 hr. On further prolonged standing it was found that the blue compound settled out completely leaving a clear solution.

These results indicated that the heteropoly blue compound was not in solution but was a suspended solid in a form approaching the colloidal state. Some confirmation of this was obtained by adding agar solution to a freshly reduced phosphomolybdenum blue "solution" when immediate precipitation occurred leaving a clear, colourless solution.

In view of these results it was decided not to attempt to establish conditions for the determination in aqueous solution of concentrations of phosphorus greater than 0·5 μg/ml. Because of the colloidal nature of the phosphomolybdate complex, any such conditions would be unreliable and it would be preferable to attempt to obtain the complex in true molecular solution by liquid-liquid extraction. A number of organic solvents were tried and it was concluded from these experiments that iso-amyl alcohol was the most satisfactory for the present purpose. A solution of the heteropoly blue in this solvent gave an absorption curve with a maximum at 710 mμ.

Modification of the procedure

In order to study the effect of employing a liquid-liquid extraction after the formation of the heteropoly blue complex a series of standard phosphorus solutions was prepared as described under *Preliminary Studies*. These were treated and allowed to stand for 15 min, exactly as previously described. Each solution was then extracted twice with 10-ml portions of isoamyl alcohol. The two extracts were combined and the absorption of the resulting 20-ml solutions was measured at 710 mμ in each case. The results, shown graphically in Fig. 2, indicated that a good linear relationship, with very little spread of results between replicates, was now obtainable throughout the entire range of 0–1 % of phosphorus in the original sample.

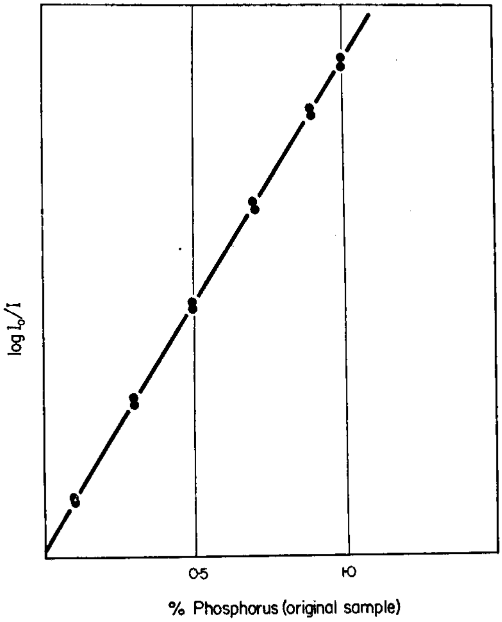

Fig. 2.—Graph of absorption of phosphomolybdate blue after extraction into isoamyl alcohol, against phosphorus concentration (original sample).

Examination of the possible extension of this modified procedure for the determination of higher phosphorus concentrations was next made. A further series of solutions was prepared as before, but extending up to 5% of phosphorus. These were treated as before and extracted with isoamyl alcohol before measurement. Repeatable results were obtained but the graph was no longer linear over the whole concentration range as shown in Fig. 3. It was considered that this might be caused either by the fact that the molybdate concentration was too low for complete formation of the complex, or that the tin^{II} chloride was insufficient to effect complete reduction. Some experiments were therefore performed to see to what extent these two reagents could be increased without producing fictitious results.

Experiments carried out in the absence of phosphorus showed that at low acidity molybdate alone could be reduced by tin^{II} chloride to give a blue compound which could be extracted into isoamyl alcohol and whose absorption peak interfered with that of the phosphomolybdate heteropoly blue complex. It was further shown that the conditions for the satisfactory formation of the phosphomolybdate blue complex (high molybdate concentration and normal acid concentration) were in opposition to those required for the suppression of the interfering "molybdenum blue" (low molybdate concentration and high acidity). The conditions employed in the original method were found to be about optimum. Increase of molybdate or tin^{II} chloride concentrations under the conditions employed was therefore impracticable and to overcome this difficulty it was decided to attempt to separate the phosphomolybdate from excess molybdate by extraction into isoamyl alcohol before reduction with tin^{II} chloride.

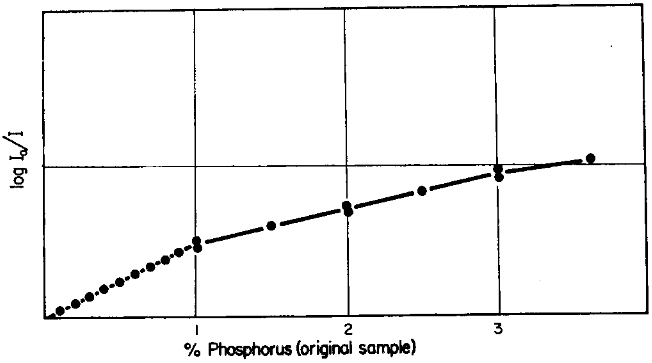

FIG. 3.—Graph of absorption of phosphomolybdate blue after extraction into isoamyl alcohol, against phosphorus concentration (original sample).

A series of standard phosphate solutions was again prepared and each was treated with 17 ml of 20% sulphuric acid. They were then made up to 90 ml and 10 ml of 10% sodium molybdate solution were added. Twenty-ml aliquots of these solutions were extracted with 20-ml portions of isoamyl alcohol. The isoamyl alcohol extracts were washed with distilled water and treated with 20-ml

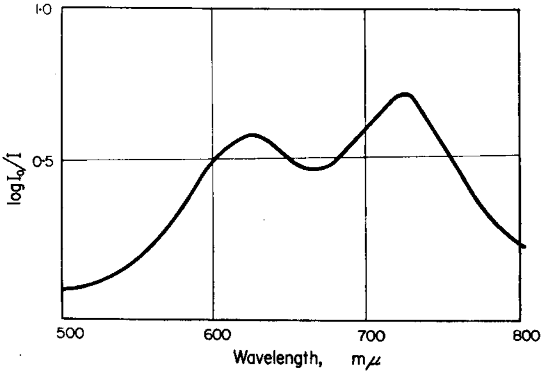

FIG. 4.—Transmission curve of phosphomolybdate heteropoly blue solution after extraction into isoamyl alcohol before reduction with tin^{II} chloride.

aliquots of 0·2% tin^{II} chloride in 1N hydrochloric acid. The absorption of these solutions was measured at 720 mμ. A typical curve is given in Fig. 4. This curve indicated that it is probable that two distinct blue compounds are formed, as might also be inferred from Fig. 3.

The calibration curve obtained in this way was linear and reproducible up to 3 μg of phosphorus per ml but it was not possible to obtain reproducible results for concentrations above this value. It was therefore concluded that, although the modifications made had overcome the previous difficulties encountered with phosphorus concentrations above 0·5% of phosphorus, it was not possible to extend the range of this procedure beyond 3%.

CONCLUSIONS

The experiments described in this paper show that the method for the determination of phosphorus in textiles, as given in *Procedure under Investigation*, provides reproducible results, but only at phosphorus concentrations below 0·5 μg/ml in the final solution. Modifications in procedure did not cause any significant changes, but a sharp decrease in absorption of the phosphomolybdate heteropoly blue complex occurred on prolonged standing. Studies of this phenomenon showed that this is because the complex is not in true molecular solution, but is a suspension under these conditions, probably approaching the colloidal state. There appears to have been no previous report of this in relation to analytical methods, although reference to it has been made in the literature.[12] This difficulty may be overcome by the inclusion of an extraction into isoamyl alcohol, but interference may be encountered from an interfering blue complex, produced in the absence of phosphorus by reduction of molybdate by tin^{II} chloride. To avoid possible errors from this it is recommended that separation of the phosphomolybdate complex from excess molybdate, by extraction into isoamyl alcohol, should be carried out before reduction with tin^{II} chloride. Under these conditions it has been shown that reproducible results may be obtained up to an initial concentration of 3% of phosphorus in the sample. The method is therefore not suitable for the determination of phosphorus in fire-proofed textiles (up to 5% of phosphorus) and the use of a method based on the absorption of the phosphovanadomolybdate complex at 426 mμ, after extraction into isoamyl alcohol is suggested. A procedure based on the method of Elwell and Wilson[6] was shown to be capable of determining concentrations of phosphorus well above the 5% required and to give reproducible results in the 1–5% of phosphorus range. A detailed investigation of the suitability of this procedure was outside the scope of the work reported in the present paper, but the procedure should present no difficulty for routine determinations of phosphorus in textiles.

Zusammenfassung—Es wird über eine Studie berichtet Phosphor in Textilien nach der Molybdänblaumethode absorptiometrisch zu bestimmen. Die Methode zeigte Nachlassen der Reproduzierbarkeit, wenn die Konzentration an Phosphor 0.5 Microgram per ml Endlösung überschritt. Möglichkeiten für die Erklärung dieses Verhaltens werden diskutiert. Die Entwicklung einer abgeänderten Arbeitsweise und das Studium andered Methoden werden präsentiert.

Résumé—Les auteurs étudient la méthode normalisée de dosage du phosphore dans les textiles par le bleu de molybdène. On a montré que cette méthode manquait de reproductibilité lorsque la concentration en phosphate était supérieure à 0,5 μg/ml dans la solution finale et une étude des causes possibles de ce phénomène est donnée. Les auteurs proposent des modifications de la méthode.

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CATION-EXCHANGE SEPARATION OF SCANDIUM

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Summary—A cation-exchange study of scandium is described. The distribution coefficients of scandium and other common metals have been determined by a batch method. The empirical formula of the scandium complex existing in the thiocyanate-hydrochloric acid system is suggested as being $Sc(SCN)_2Cl$. Scandium can be separated from thorium, zirconium, iron, titanium, aluminium and calcium using an ammonium thiocyanate-hydrochloric acid mixture as eluent. Some separation of scandium from the rare earths is also achieved, but the heavier rare earths cannot be separated cleanly.

THE separation of scandium presents very difficult problems. Specific separation methods for scandium may be limited to the application of solvent-extraction and ion-exchange techniques. A detailed approach to the problem of the separation of scandium from otherwise troublesome elements was made by Fischer and Bock[1] in the extraction of scandium by ethyl ether from a solution containing a high concentration of ammonium thiocyanate. A satisfactory separation of scandium has been obtained from rare earths, thorium and zirconium, as well as from manganese, magnesium and calcium was achieved. A tributylphosphate extraction method[2] is also effective in separating scandium from rare earths, beryllium, aluminium, chromium^{III} and, if hydrogen peroxide is added, from titanium. Iron^{III}, thorium and uranium cannot be separated by this extraction method. Methods using 8-hydroxyquinoline[3] and thenoyltrifluoroacetone[4] are also available, but are not specific for scandium.

A few investigations of the ion-exchange separation of scandium have been described. Separation of scandium from yttrium and lanthanum has been effected by the use of Amberlite IR-100H with citric acid elution.[5] Scandium can be almost completely separated from the rare earths by EDTA or NTA elution.[6] Hydrazine diacetic acid has also been found to be efficient for separating scandium from the rare earths.[7] Attention appears largely to have been directed to the use of organic complexing agents as eluents. Addition of organic complexing agents to the analytical system, however, causes serious interference in the subsequent steps designed for the determination of scandium. It would be preferable to isolate scandium by elution with an inorganic eluent, thus causing no complications in the effluent analysis. Recently, describing the adsorption of some metal ions on anion-exchangers from thiocyanate solution, Turner *et al.* reported[8] that scandium can be cleanly separated from chromium using potassium thiocyanate solution as eluent.

A method is described in this paper for separating scandium from thorium, zirconium, iron^{III}, titanium, aluminium and calcium, as well as from the rare earths by a cation-exchange method. Scandium can be chromatographically eluted with hydrochloric acid containing ammonium thiocyanate. The probable composition of the scandium thiocyanate complex formed appears to be $Sc(SCN)_2Cl$ or a similar compound as indicated below.

EXPERIMENTAL

Apparatus and reagents

Ion-exchange resin: Diaion SK 1 (Mitsubishi Kasei Chem. and Ind. Co. Ltd.), a styrene-base strong acid type of resin, equivalent to Dowex 50-X8, 100–200 mesh. Before use the resin must be purified. The resin, free from fine particles, is placed in a large column and washed with a solution 2*M* in NH_4SCN and 0·5*M* in HCl, and then with water. Then the resin is converted to the hydrogen form with 3*M* HCl, and is washed with water until a negative chloride test is obtained with silver nitrate. In equilibrium studies the resin in the hydrogen form was first dried for 2 hr at 80° and was then stored in a desiccator over a saturated solution of potassium bromide. In column studies, coventional resin columns of internal diameter 1·1 cm, packed at the bottom with glass wool, were used. To prepare the column, a slurry of 10 g of resin with water is poured into the column. The bed has a height of 16 cm.

Stock solutions of metals

Scandium: Dissolve *ca.* 120 mg of 99·9% scandium oxide in small amounts of 3*M* hydrochloric acid, evaporate to dryness and dilute to 100 ml with 1·0*M* hydrochloric acid. The strength of this solution was determined by titration with (ethylenedinitrilo)-tetra-acetate solution (0·01*M*) previously standardised against analytical-reagent primary-standard zinc metal. The stock solution contains 0·758 mg of scandium per ml.

All chemicals used for other stock solutions were of reagent quality, unless otherwise mentioned.

Measurement of distribution coefficient, K_d.

Portions (1·0 g) of Diaion SK 1 resin were weighed out accurately and transferred into 100-ml Erlenmeyer flasks. One ml of a standard solution of cation in 0·5*M* hydrochloric acid was added, followed by 39 ml of 0·5*M* hydrochloric acid containing sufficient ammonium thiocyanate to give a final volume of 40 ml of ammonium thiocyanate solution of the desired concentration. The flasks were stoppered and shaken in a mechanical shaking device at 25 ± 1° until the exchange equilibrium was attained. Shaking for 1 hr was usually sufficient for the purpose. The resin was then separated from the aqueous phase by filtration, and an aliquot of the filtrate (35 ml) was analysed for the cation by titration with 0·01*M* EDTA standard solution. The value of the distribution coefficient, K_d, was calculated by the following formula.

$$K_d = \frac{\text{original amount of cation—amount of cation per ml of aqueous phase}}{\text{amount of cation per ml of aqueous phase}}\ .$$

The amount of the cation was added to the system so that equilibrium was reached at less than 3% loading of the cation with respect to resin capacity. The result of K_d measurements is illustrated in Fig. 1.

Ion-exchange separation

Load the metal ions (including the scandium ion) on the column, and rinse the column with small amounts of water. During the experiment keep the flow rate at 1·0 ± 0·2 ml per min for columns containing 10 g of dry resin. Conditions for elution can be predicted approximately from a distribution coefficient plot such as that shown in Fig. 1. The distribution coefficient curve for scandium falls below thorium and rare earths and above aluminium, zirconium, titanium and iron.

Elution curves are plotted in Fig. 2 for the two- or three-component systems with scandium as one component. For separating scandium from rare earths and thorium it is preferable to elute scandium with an eluent 1*M* in NH_4SCN and 0·5*M* in HCl. Rare earths and thorium remain on the column, being stripped effectively by eluting with an eluent, 2*M* in NH_4SCN and 0·5*M* in HCl. Aluminium, titanium, iron and zirconium can be desorbed from the column before eluting scandium with the thiocyanate-hydrochloric acid system. Suitable concentrations of eluents are : 1*M* NH_4SCN–0·5*M* HCl for aluminium; 0·5*M* NH_4SCN–0·5*M* HCl for titanium; and 1*M* NH_4SCN–0·5*M* HCl or 1*M* NH_4SCN–1*M* HCl for zirconium. Because of highly anionic character of the iron-thiocyanate complex, the choice of eluent concentration for iron is rather arbitrary. An eluent with 0·5*M* NH_4 SCN–0·5*M* HCl is sufficient to separate iron before eluting scandium. Complete separation of calcium

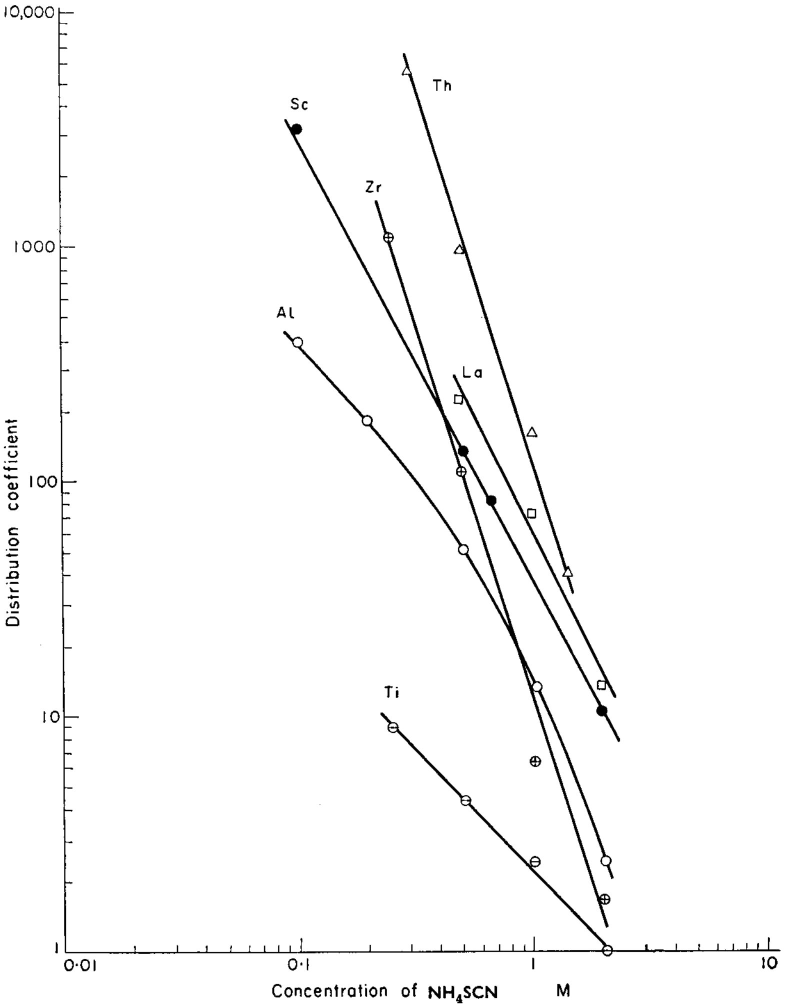
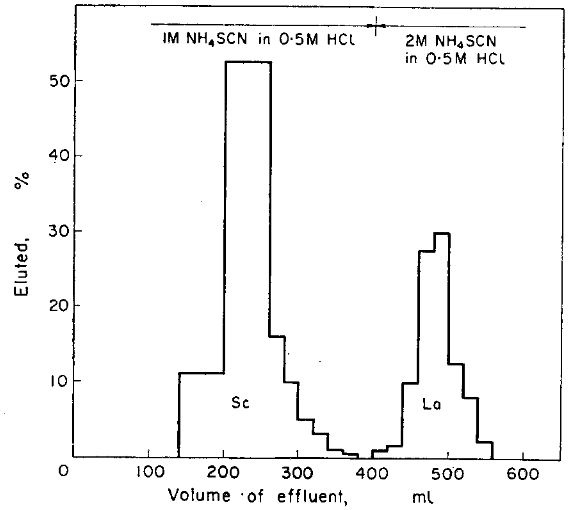
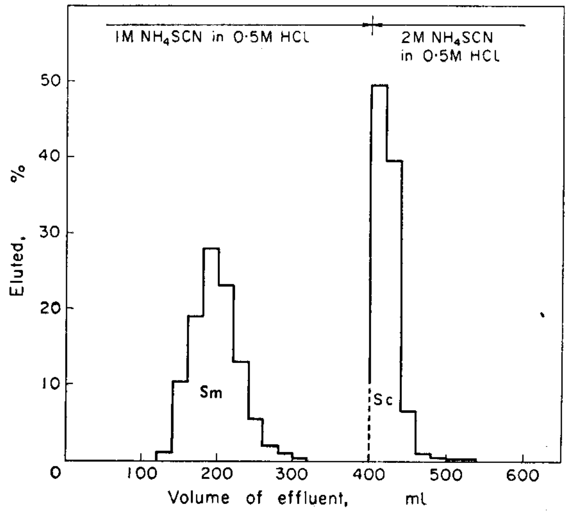


FIG. 1.—Distribution coefficients with Diaion SK 1 at different concentrations of ammonium thiocyanate.
(Concentration of hydrochloric acid 0·5M.)

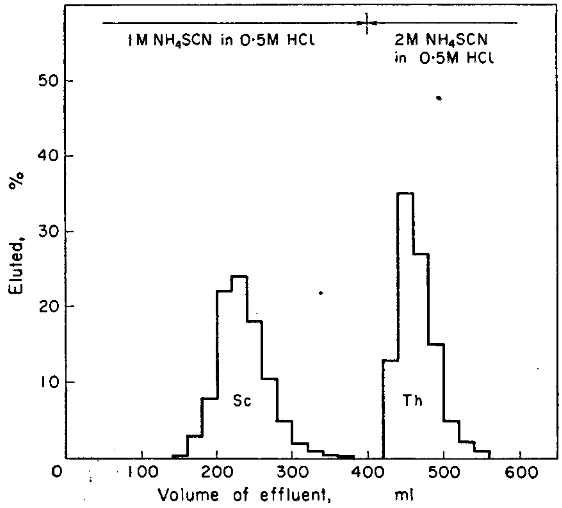
FIG. 2.—Elution curves for scandium.



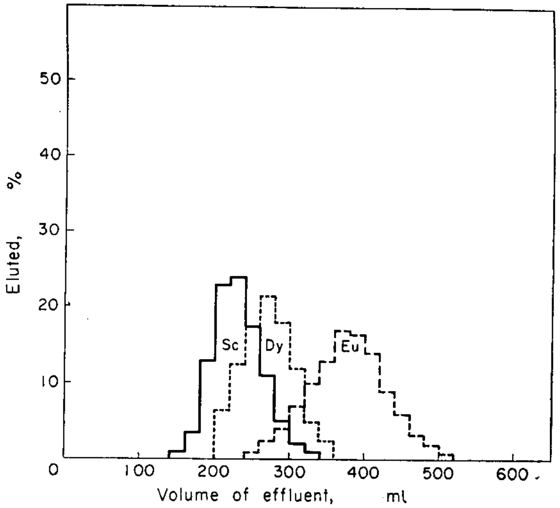
(*a*) Elution of scandium and lanthanum.



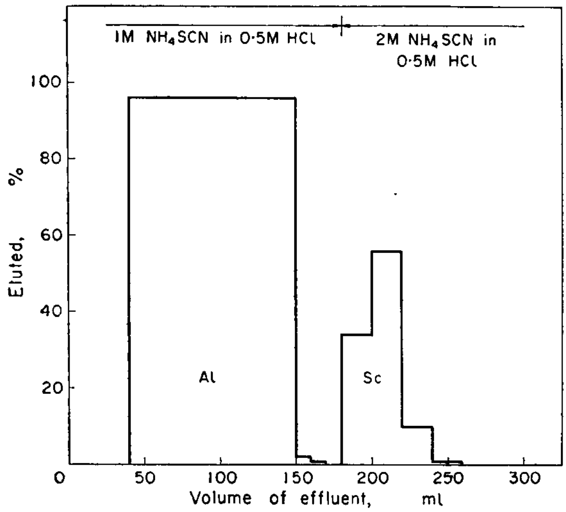
(*b*) Elution of scandium and samarium.



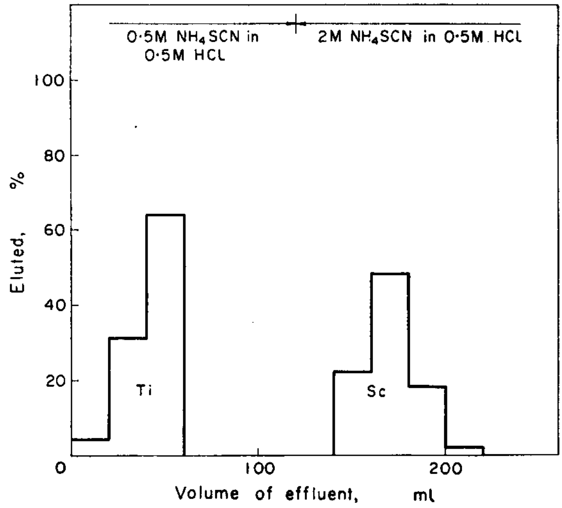
(*c*) Elution of scandium and thorium.



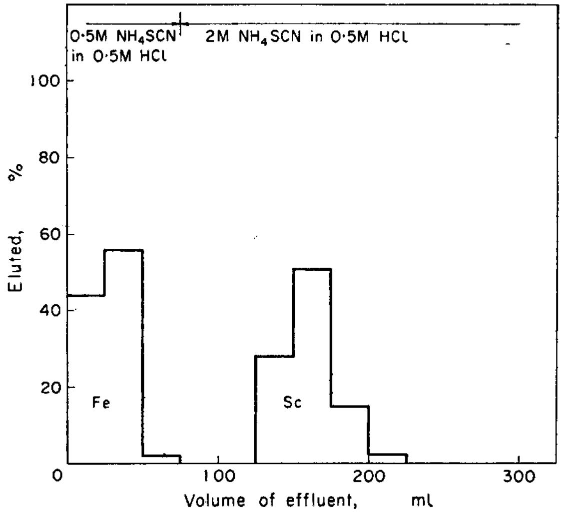
(*d*) Elution of scandium, dysprosium and europium.



(*e*) Elution of aluminium and scandium.

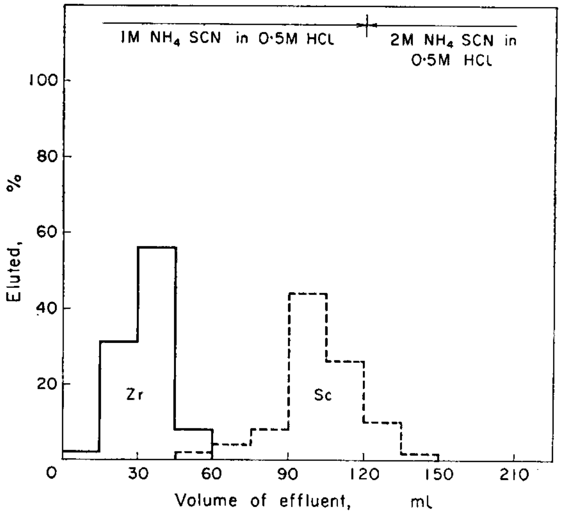


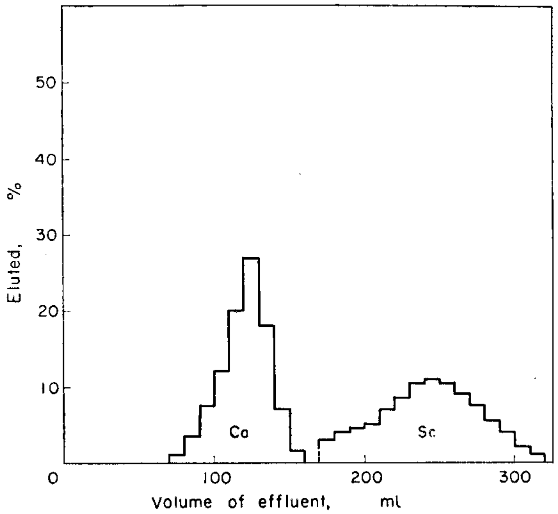
(*f*) Elution of titanium and scandium.



(*g*) Elution of iron and scandium.

(*h*) Elution of zirconium and scandium.





(*i*) Elution of calcium and scandium.

and scandium could not be achieved in any conditions. Elution with 0·5*M* NH_4SCN–1*M* HCl as eluent gave the most satisfactory result, but the elution curves of the two components over-lapped to a considerable extent. In the present work it was assumed that the elution of the scandium component began at the 170-ml portion. As indicated in Table I, a lower yield of scandium from a scandium–calcium mixture is obtained by assuming this. To separate calcium from scandium by elution with 0·5*M* NH_4SCN–1*M* HCl a somewhat longer resin bed is necessary. As indicated in Fig. 2, quantitative separation of scandium from rare earths (up to samarium) is obtained with the condition described above, whereas rare earths heavier than dysprosium show practically the same behaviour as scandium. The elution curve for scandium, dysprosium and europium (Fig. 2*d*) was obtained by synthesising the three elution curves for the separate components through a single column. Europium separation may be achieved with a longer column.

TABLE I.—SEPARATION OF SCANDIUM ON 1·1 × 16 CM DIAION SK 1 CATION-EXCHANGE COLUMNS

Mixture of ions	Added, *mg*	Recovered *mg*	*ml*	Eluent
Sc and Al	Sc 2·37	2·43	80	2*M* NH_4SCN, 0·5*M* HCl
	Al 5·60	5·62	170	1*M* NH_4SCN, 0.5*M* HCl
Sc and Ti	Sc 2·27	2·29	100	2*M* NH_4SCN, 0·5*M* HCl
	Ti 1·50	1·44	80	0·5*M* NH_4SCN, 0·5*M* HCl
Sc and Fe	Sc 2·27	2·24	100	2*M* NH_4SCN, 0·5*M* HCl
	Fe 14·14	14·38	60	0·5*M* NH_4SCN, 0·5*M* HCl
Sc and Zr	Sc 2·27	2·21	110	1*M* HN_4SCN, 1*M* HCl
	Zr 2·70	2·70	60	1*M* HN_4SCN, 1*M* HCl
Sc and La	Sc 2·40	2·42	380	1*M* NH_4SCN, 0·5*M* HCl
	La 15·12	15·15	160	2*M* NH_4SCN, 0·5*M* HCl
Sc and Sm	Sc 2·27	2·27	320	1*M* NH_4SCN, 0·5*M* HCl
	Sm 4·73	4·63	140	2*M* NH_4SCN, 0·5*M* HCl
Sc and Th	Sc 2·37	2·37	380	1*M* NH_4SCN, 0·5*M* HCl
	Th 4·76	4·74	140	2*M* NH_4SCN, 0·5*M* HCl
Sc and Ca	Sc 2·27	2·10	190	0·5*M* NH_4SCN, 1*M* HCl
	Ca 3·17	3·08	160	
Sc, La and Th				
	Sc 2·27	2·27	360	1*M* NH_4SCN, 0·5*M* HCl
	La 15·12	—	180	2*M* NH_4SCN, 0·5*M* HCl
	Th 8·52	8·45		

Determination of separated metals

All the metals examined except titanium were determined by titration with (ethylene-dinitilro)-tetra-acetate (EDTA) standard solution (0·01*M*) at the appropriate pH values, using metal indicators. Ammonium thiocyanate does not interfere except in the iron determination. It is recommended, however, that the test solution is diluted with water to less than 0·3*M* in NH_4SCN before the EDTA titration.

Rare earths and thorium were titrated with Xylenol Orange (XO) as the metal indicator at pH 4·5–6 (hexamine buffer) and pH 2·5 to 3·5 (sodium acetate buffer) respectively.

Zirconium was determined by back-titration with standard thorium solution, using XO as indicator, after adding a known excess of standard EDTA solution to the cooled test solution, and adjusting to pH 2–3. Aluminium was determined in the presence of small amounts of Cu-EDTA by titration with standard EDTA in boiling solution at pH 3 (ammonium acetate buffer), using 1-(2-pyridylazo)-2-naphthol as an indicator. Iron was determined by titration with EDTA at pH 1·7–3 (sodium acetate buffer) with Variamine Blue B base as an indicator, after destroying thiocyanate with nitric acid. Titanium was determined spectrophotometrically by the Tiron method[9] after destroying thiocyanate with nitric acid.

RESULT AND DISCUSSION

In Table I results are given for the separation of scandium from the other elements on the cation-exchange column. These results indicate a satisfactory separation of scandium from metals that cause serious interferences in routine analysis methods for scandium. Because of the simplicity of effluent analysis, the present method seems to facilitate the rather complicated separation of scandium. Thiocyanic acid was selected for eluting metal ions chromatographically from a cation-exchange column because metal-thiocyanate complexes are more stable than the corresponding chloride complexes. For instance, thorium can hardly be eluted with $2M$ hydrochloric acid from a cation-exchange column; elution with $8M$ hydrochloric acid is usually necessary. However, thorium can be easily eluted from the column with an eluent $2M$ in NH_4SCN and $0{\cdot}5M$ in HCl, and there is essentially no tailing of bands. This is also the case for the other elements.

To determine the composition of the thiocyanate complex species of scandium existing in the experimental condition, a plot of log $(\lambda_0/\lambda - 1)$ *vs.* log concentration of thiocyanate or hydrochloric acid was made, according to the procedure described by Schubert.[10] λ and λ_0 denote the distribution coefficients for scandium in the presence of and absence of complexing agent respectively. If the concentration of hydrochloric acid is kept constant at $0{\cdot}5M$, and the concentration of ammonium thiocyanate is varied, the plot of $(\lambda_0/\lambda - 1)$ *vs.* log concentration of ammonium thiocyanate (where λ_0 denotes the distribution coefficient for scandium in $0{\cdot}5M$ hydrochloric acid) gives a straight line with a slope equal to 2·01, which is sufficiently close to indicate that the scandium:thiocyanate ratio is 1:2 (Fig. 3).

A similar plot $(\lambda_0'/\lambda - 1)$ *vs.* log concentration of hydrochloric acid, (where λ_0' is the distribution coefficient for scandium in $1M$ ammonium thiocyanate solution containing no hydrochloric acid) also gives a straight line, with a slope equal to 1·25, which suggests a 1:1 ratio (Fig. 4). Thus the scandium thiocyanate in hydrochloric acid medium is likely to be $Sc(SCN)_2Cl$ or a similar compound. From Figs. 3 and 4 it is also possible to estimate the approximate dissociation constants for the following equations.

$$ScCl^{++} + 2SCN^- \rightarrow ScCl(SCN)_2 \tag{1}$$

$$K_1 = \frac{[ScCl^{++}][SCN^-]^2}{[ScCl(SCN)_2]} \tag{1'}$$

$$Sc(SCN)_2{}^+ + Cl^- \rightarrow ScCl(SCN)_2 \tag{2}$$

$$K_2 = \frac{[Sc(SCN)_2{}^+][Cl^-]}{[ScCl(SCN)_2]} \tag{2'}$$

At log $[SCN^-] = 0$, log $(\lambda_0/\lambda - 1)$ is equal to $-\log K_1$, *i.e.*, pK_1. Thus, from Fig. 3, pK_1 is estimated to be 2·57. In a similar way pK_2 is equal to 0·79 from Fig. 4. From the values of pK_1 and pK_2 the equilibrium constant K_3 for the following equation can easily be obtained.

$$Sc(SCN)_2{}^+ + Cl^- \rightarrow ScCl^{++} + 2SCN^- \tag{3}$$

$$K_3 = \frac{K_1}{K_2} = \frac{[ScCl^{++}][SCN^-]^2}{[Sc(SCN)_2{}^+][Cl^-]} \tag{3'}$$

Thus, K_3 is estimated to be $1{\cdot}65 \times 10^{-2}$, and pK_3 1·78. It suggests that the affinity of thiocyanate ions for scandium is greater than that of chloride ions for scandium. This would cause scandium to be eluted from the cation-exchange columns with greater facility by thiocyanate elution.

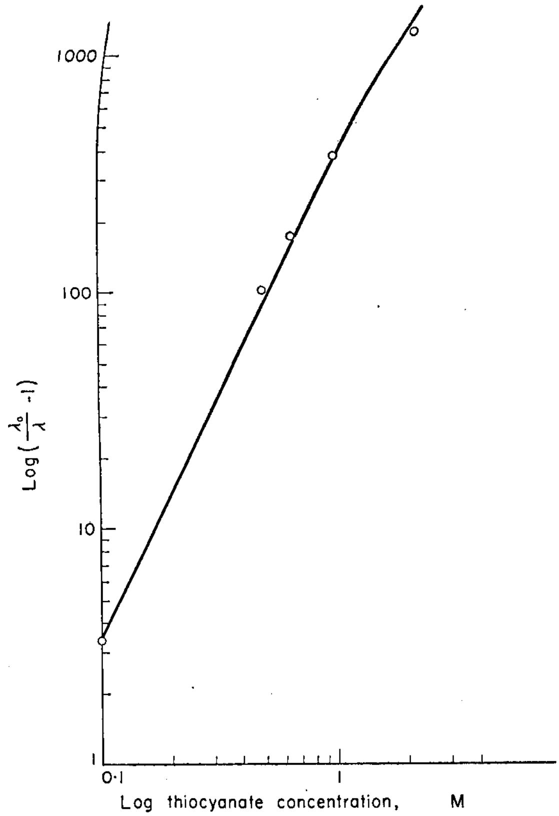


FIG. 3.—Variation in (λ_0/λ − 1) as a function of ammonium thiocyanate concentration.
λ_0: Distribution coefficient for scandium in 0·5*M* hydrochloric acid.
λ: Distribution coefficient for scandium in the presence of ammonium thiocyanate and 0·5*M* hydrochloric acid.

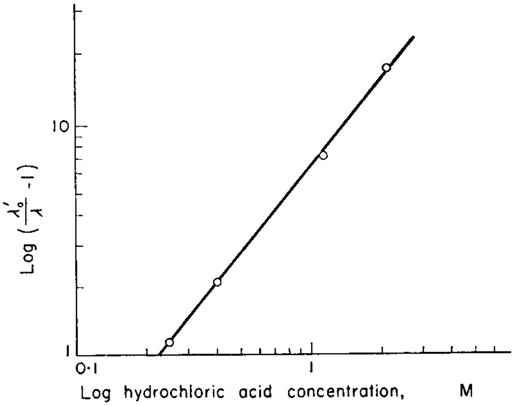


FIG. 4.—Variation in (λ_0'/λ − 1) as a function of hydrochloric acid concentration.
λ': Distribution coefficient for scandium in 1*M* ammonium thiocyanate solution.
λ: Distribution coefficient for scandium in the presence of hydrochloric acid and 1*M* ammonium thiocyanate.

Zusammenfassung—Eine Studie über Ionenaustausch mit Scandium wird beschrieben. Der Verteilungskoeffizient für Scandium und einige andere gewöhnliche Metalle wurde nach der "batch"-Methode bestimmt. Als empirische Formel des Scandiumkomplexes in einem Thiocyanate-HCl-Medium wird $Sc(SCN)_2Cl$ vorgeschlagen. Scandium kann von Th, Zr, Fe, Ti, Al und Ca getrennt werden indem man mit einem Ammoniumthiocyanate-HCl-Gemisch eluiert. Trennung von seltenen Erden ist ebenfalls möglich doch ist die Separierung von den schwereren Erden nicht ganz rein.

Résumé—Le comportement du scandium sur résine échangeur de cations a été étudié. Les coefficients de partage entre le scandium et d'autres ions métalliques courants ont été mesurés par la méthode de simple équilibre. La formule $Sc(SCN)_2Cl$ est proposée pour le complexe formé par le scandium en milieu acide chlorhydrique-thiocyanate. Le scandium peut être séparé du thorium, du zirconium, du fer, du titane et du calcium par élution au moyen d'un mélange d'acide chlorhydrique et de thiocyanate d'ammonium. La séparation du scandium des terres rares a été réalisée mais les terres rares les plus lourdes ne peuvent être completement séparées.

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N,N,N',N'-TETRAMETHYL-*o*-TOLIDIN (TETRON) ALS REAGENZ ZUR BESTIMMUNG GERINGER MENGEN VON OXYDATIONSMITTELN

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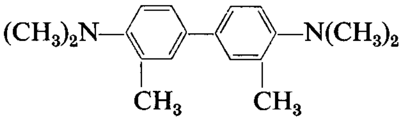
Zusammenfassung—*N,N,N',N'*-Tetramethyl-*o*-Tolidin wird als sehr empfindliches Reagenz zur Bestimmung geringer Mengen von Oxydationsmitteln [Au(III), Ce(IV), BrO_3^- u.a.] vorgeschlagen. Bestimmt wurden: sein normales Redoxpotential bei unterschiedlichen pH-Werten, die Zahl der bei der Oxydation ausgetauschten Elektronen, die Zusammensetzung des oxydierten Produkts und die Extinktionskoeffizienten seiner Farbumsetzungen mit unterschiedlichen Oxydationsmitteln. Im Vergleich mit dem *o*-Tolidin bestitzt das vorgeschlagene Reagenz ein höheres normales Redoxpotential ($\Delta E_0 = 140$ mV) und ist infolgedessen auch selektiver als jenes. Zugleich sind seine Reaktionen etwa zweimal empfindlicher.

DIE Farbreaktionen des *o*-Tolidins (3,3'-Dimethylbenzidins) mit Oxydationsmitteln sind bekanntlich bedeutend empfindlicher als die des Benzidins.[1] Andererseits zeigen die Untersuchungen von R. Belcher, A. Nutten und W. Stephen,[2] daß die an *N* substituierten Benzidine gleichfalls das Benzidin an Empfindlichkeit übertreffen. Es ist daher anzunehmen, daß ein Benzidinderivat, das mittels Methylgruppen sowohl an *o*-Stelle als auch an Aminogruppen substituiert ist, die Vorzüge der beiden erwähnten Verbindungsarten in sich vereinen würde. Eine derartige Verbindung ist das *N,N,-N',N'*-Tetramethyl-*o*-tolidin (Tetron)



Die Untersuchungen an diesem Reagenz können Auskunft geben nicht nur über die Empfindlichkeit seiner Umsetzungen mit Oxydationsmitteln, sondern auch über den Einflüß der CH_3- und $-N(CH_3)_2$-Gruppen auf das normale Redoxpotential der substituierten Benzidine sowie die Farbe ihrer Oxydationsprodukte und den Mechanismus ihrer Entstehung.

Die Synthese des Tetrons ist zwar längst gelungen,[3,4] doch ist diese Verbindung in der analytischen Chemie lediglich als Fällungsmittel für $ReCl_6^{2-}$ [5] verwendet worden. Ihre reduzierendoxydierenden Eigenschaften sind unerforscht.

EXPERIMENTELLER TEIL

Um die Charakteristik des Tetramethyl-*o*-tolidins als Reagenz zur quantitativen Bestimmung von Oxydationsmitteln vervollständigen sowie die Zusammensetzung seines Oxydationsprodukts klären zu können, wurden potentiometrische und spektrophotometrische Untersuchungen sowie solche mit Ionenaustauschern durchgeführt.

Man untersuchten den Verlauf des Redoxprozesses durch potentiometrische Titrierung einer 0,002*M* Tetronlösung bei bestimmtem durch geeigneten Puffer aufrechterhaltenen pH-Wert. Titration bei pH > 1 mit 0,1 n Br_2-Lösung und bei pH $\leqslant 1{,}5$ mit Ce^{IV} in der Zelle bei bestimmter Temperatur und in nach dem Verfahren von Mirev und Šopov[6] vom Sauerstoff gereinigter Stickstoffatmosphäre. Wir bedienten uns einer Platinelektrode (als Indikatorelektrode) und einer gesättigten Kalomelelektrode (als Bezugselektrode). Die elektromotorische Kraft hat man mit dem Röhren-pH-Messer GV-52 der Firma L. Seibold bestimmt.

Es stellte sich heraus, daß in ausgesprochen sauren Medien das Potential des Systems im Gang der Titration recht stabil bleibt, sich bei pH > 2 hingegen mit der Zeit wesentlich ändert.

Der Potentialsprung ist im Äquivalentpunkt (s. Abb. 1) deutlich ausgeprägt und beträgt etwa 150 MV. Daß der Redoxprozess reversibel verläuft, stellte man durch Rücktitrierung mit Fe^{2+} fest.

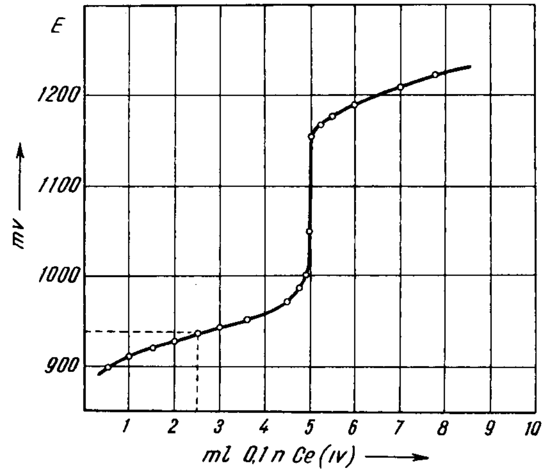


ABB. 1.—Potentiometrische Titrierung des Tetramethyl-*o*-tolidins mit Ce(IV) bei pH = 1,45. $E_0 = 948$ mV.

Aus der Menge des verbrauchten Oxydationsmittels wurde das Äquivalentgewicht des Tetrons als $\frac{M}{2}$ berechnet, d.h. die Zahl der ausgetauschten Elektronen beträgt 2. Dann

$$E = E_0' + \frac{0{,}059}{2} \lg \frac{[\text{oxy}]}{[\text{red}]}, \tag{1}$$

wo E_0' das normale Redoxpotential ist.

Das normale Redoxpotential E_0' ist bei [oxy] = [red] gleich E und ergibt sich durch Titration mit der halben Äquivalentmenge des Oxydationsmittels. Seine Angaben für Tetron und *o*-Tolidin sind je nach dem pH-Wert des Mediums aus Abb. 2 zu entnehmen. Sie liegen, wie man sieht, in einer Geraden mit Neigung 0,059. Es gilt für gegebenes E_0' die Gleichung

$$E_0' = E_0 - 0{,}059\,\text{pH} \tag{2}$$

Nach Ersetzen in (1) erhält man

$$\begin{aligned} E &= E_0 + 0{,}059 \lg \left[H^+\right] + \frac{0{,}059}{2} \lg \frac{[\text{oxy}]}{[\text{red}]} \\ &= E_0 + \frac{0{,}059}{2} \lg \frac{[\text{oxy}]\,.\,[H^+]^2}{[\text{red}]}\,. \end{aligned} \tag{3}$$

Bei der Oxydation des Tetrons werden demnach 2e und $2H^+$ ausgetauscht. Dies war auch zu erwarten, wenn man berücksichtigt, daß bei der Abgabe der beiden Elektronen eine Doppelbindung geschaffen wird.

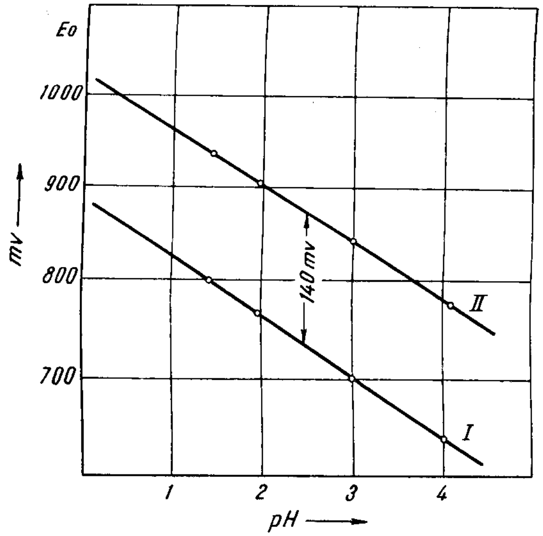
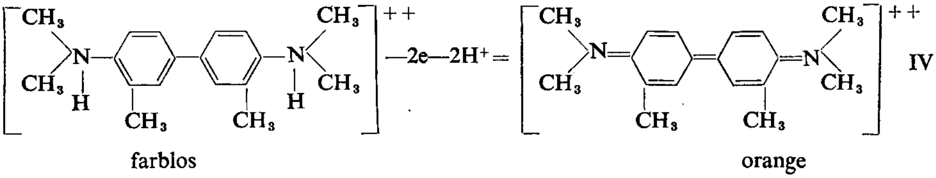


ABB. 2.—Abhängigkeit des Normalredoxpotentials vom pH-Wert.
I—*o*-Tolidin, II—Tetramethyl-*o*-tolidin.



Die Annahme dieses Oxydationsmechanismus wird von den Angaben unterstützt, die mit Hilfe von Ionenaustauschern ermittelt wurden. Sowohl die reduzierte als auch die oxydierte Form des Reagenzes bleiben am Kationit haften, werden jedoch vom Anionit durchgelassen. Aus der Menge der vom Kationit äquivalent ausgeschiedenen Wasserstoffionen lassen sich Rückschlüße auf die Ladung des zurückgehaltenen Ions ziehen. Zu diesem Zweck muß die Lösung in Bezug auf das zu bestimmende Ion und die Wasserstoffionen isonormal sein und darf keine anderen Kationen enthalten.

Das Tetron sei in 10^{-3} n Lösung, die zugleich einen pH-Wert von 3 haben möge. Sobald die Lösung durch die Säule geht, wird die Konzentration ihrer Wasserstoffionen um 10^{-3} Gramm-Ionen zunehmen. Dann ist

$$\mathrm{pH} = -\lg(10^{-3} + 10^{-3}) = -\lg 2 \,.\, 10^{-3} = 3 - \lg 2 = 3 - 0{,}30 = 2{,}70$$

Arbeitet man bei pH = 4, so muß die Lösung eine 10^{-4} n sein

$$\mathrm{pH} = -\lg(10^{-4} + 10^{-4}) = -\lg 2 \,.\, 10^{-4} = 4 - \lg 2 = 4 - 0{,}30 = 3{,}70$$

Bei isonormalen Lösungen beträgt demgemäß die Änderung des pH-Wertes 0,30. Diese Differenz ist groß genug um den Versuch quantitativ durchführen zu können. Es ist ohneweiteres einzusehen, daß die Änderung des pH-Wertes bei $2 \,.\, 10^{-3}$ n Lösung des zu bestimmenden Ions gleich lg 3, bei $3 \,.\, 10^{-3}$ n Lösung gleich lg 4 usw. sein wird. Im allgemeinen: liegt eine Lösung $a \,.\, 10^{-x}$ n vor und ist die Konzentration von $\mathrm{H}^+ - 1 \,.\, 10^{-x}$ n, so muß $\Delta\,\mathrm{pH} = \lg(a + 1)$ sein.

Der beschriebene Arbeitsgang erbrachte den Nachweis, daß sowohl das oxydierte als auch das reduzierte Ion des Reagenzes zwei positive Ladungen besitzen.

Das Oxydationsprodukt des Tetrons ist von intensiv orangegelber Farbe. Seine bei unterschiedlichen pH-Werten aufgenommene Absorptionskurve weist stets ein Absorptionsmaximum auf, das gegenüber dem des *o*-Tolidins in genügend sauerem Medium um etwa 500 Å verschoben ist (s. Abb. 3). Diese spektrophotometrischen Aussagen zeugen eindeutig davon, daß die Oxydation des Tetrons in allen Fällen zu ein und derselben Verbindung führt. In dieser Hinsicht unterscheidet es sich wesentlich vom *o*-Tolidin, das bei der Oxydierung in schwach sauerem Medium ein merichinoides Produkt von blauer Farbe ergibt.[7]

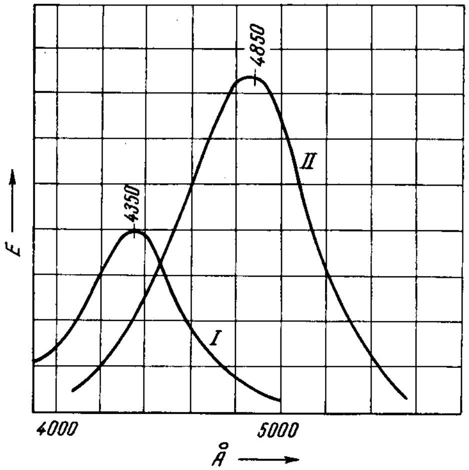


ABB. 3.—Absorptionskurven
I—*o*-Tolidin, II—Tetramethyl-*o*-tolidin.

Die Möglichkeit, manche Oxydationsmittel mit Tetron photometrisch zu bestimmen, wurde unter reinen Bedingungen in der Weise geprüft, daß man zum Oxydationsmittel 1 ml einer 0,1%-igen Tetronlösung in 5%-iger H_2SO_4 hinzusetzte. Die Zeitdauer bis zur vollständigen Entwicklung und Vertiefung der Färbung hängt in hohem Maße von der Art und Konzentration des Oxydationsmittels, dem pH-Wert und der Temperatur ab; sie beträgt etwa ½ bis 10 Minuten.

Die durch die normalen dezimalen Extinktionskoeffizienten angegebene Empfindlichkeit der Farbumsetzungen mit manchen Oxydationsmitteln ist aus der Tabelle I zu ersehen.

TABELLE I

Oxydationsmittel	ε	Oxydationsmittel	ε
$Au^{(III)}$	50 000	$Cr_2O_7^{2-}$	4 500
$Ce^{(IV)}$	17 500	ClO_3^-	100
MnO_4^-	17 500	BrO_3^-	33 000
VO_4^-	8 000	JO_3^-	4 000

Die Färbung ist zeitbeständiger als die des *o*-Tolidins. Diese Tatsache steht in Einklang mit der von R. Belcher, A. Nutten und W. Stephen[2] festgestellten Stabilität der Oxydationsprodukte des an *N*-substituierten Benzidins.

DISKUSSION

Die gegenüber den Aminogruppen an *o*-Stelle lagernden Methylgruppen wirken bekanntlich herabsetzend auf das Potential des Amins [(E_0 (Benzidin) — E_0 (*o*-Tolidin) = 50 mv]. Unsere Befunde (s. Abb. 2) zeigen, daß die in die Aminogruppen eingeführten Methylgruppen einen umgekehrten Effekt im Sinne der Potentialerhöhung hervorrufen. Der unterschiedliche Einfluß der CH_3-Gruppen je nach ihrer Stellung ließe sich erklären, wenn man von Gleichung (4) ausgehen würde. Hieraus folgt, daß die reduzierte Form bei ihrer Oxydation 2e und $2H^+$ abgibt. Die Abgabe von Elektronen wird um so leichter vor sich gehen, je größer die Elektronendichte des aromatischen Systems, die von H^+-Ionen hingegen, je schwächer die Basizität der Verbindung ist. Die Methylgruppen weisen einen positiven Induktions- und Konjugations-effekt auf. Führt man sie unmittelbar in den Benzolkern ein, so würden sie die Elektronen zu diesem hinüberziehen und somit seine Elektronendichte vergrößern, sein Redoxpotential hingegen verringern. Lagert man aber die Methyl- an die Aminogruppen, dann erhöhen die erstgenannten die Basizität der Verbindung; diese würde dann schwieriger H^+ abgeben, daher auch schwerer oxydierbar sein, und ein höheres normales Redoxpotential besitzen.

CH_3-Gruppen an *o*-Stellung bedingen keine Farbänderung des Oxydationsprodukts (die Oxydationsformen von Benzidin und Tolidin sind in saurem Medium von gelber Farbe). Eine Farbänderung bewirken hingegen an Aminogruppen gelagerte Methylgruppen. Vermutlich lockern diese die Stabilität der Elektronen im chromophoren System auf und führen daher zur Verschiebung des Absorptionsmaximums in Richtung der grösseren Wellenlänge.

Aus den vorangehenden Darlegungen ist ersichtlich, daß die Einführung von Methylgruppen in die Aminogruppen zwei für die analytische Praxis wichtige Effekte hervorbringt: es wird nämlich das normale Redoxpotential des Systems erhöht, was die Umsetzungen mit manchen starken Oxydationsmitteln spezifischer werden läßt, und es findet eine Vertiefung der Färbung sowie Erhöhung der Empfindlichkeit statt.

Wir nehmen die Gelegenheit wahr, dem wissenschaftlichen Mitarbeiter, Herrn N. Marekov, für seine wertvollen Anregungen unseren herzlichsten Dank auszusprechen.

Summary—*N,N,N',N'*-Tetramethyl-*o*-tolidine is proposed as a very sensitive reagent for the determination of small amounts of oxidising agents. The following have been determined; the normal redox potential of the organic compound over a range of pH values; the number of electrons involved in the oxidation; the composition of the products of oxidation; the extinction coefficients of the various coloured products produced by different oxidants. The compound has a higher normal redox potential than *o*-tolidine ($\Delta E_0 = 140$ mv) and is therefore more selective. Its reactions have sensitivities about double those of *o*-tolidine.

Résumé—*N,N,N',N'*-Tetramethyl-*o*-tolidine est proposée comme réactif très sensible pour la détermination de petites quantités d'oxydants. On a determiné: le redoxpotentiel normal de ce composé organique pour différentes valeurs de pH, le nombre des electrons, échangés au cours de la réaction oxydante, la composition des produits oxydés et leurs coefficients d'extinction des ses formes colorées, developpées par des oxydants différents. En comparaison de l'*o*-tolidine le réactif proposé possède un redoxpotentiel normal plus élevé ($\Delta E_0 = 140$ meV) et c'est pourquoi il est plus selectif que l'*o*-tolidine. Cependant ses réactions sont à peu près deux fois plus sensibles.

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A NEW REDUCTIMETRIC REAGENT: IRON^{II} IN A STRONG PHOSPHORIC ACID MEDIUM—II*

TITRATION OF MOLYBDENUM^{VI} WITH IRON^{II} AT ROOM TEMPERATURE

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Summary—The results are presented of investigations leading to the development of a procedure for the titrimetric determination of molybdenum^{VI} with iron^{II} sulphate in a strong phosphoric acid medium (11.5—13.0*M*) at room temperature, using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Advantages of the procedure are similar to those previously described for the titration of uranium^{VI} with iron^{II}.

The procedure now reported is of considerable theoretical significance, because it involves a reaction which is the reversal of the normal redox reaction. An explanation of this reversal is afforded by a consideration of the formal redox potentials of the Mo^{VI}/Mo^{V} and Fe^{III}/Fe^{II} couples in a strong phosphoric acid medium. The authors are the first to determine the formal redox potential of the Mo^{VI}/Mo^{V} couple in media of varying phosphoric acid concentration. A comparison of the formal potentials of the two couples shows that the Fe^{III}/Fe^{II} couple has a potential higher than that of the Mo^{VI}/Mo^{V} couple up to a concentration of 5.8*M* phosphoric acid, beyond which it is less. When the concentration of phosphoric acid is greater than 11.0*M*, the difference between the formal potentials of the Mo^{VI}/Mo^{V} and Fe^{III}/Fe^{II} couples becomes sufficiently great to enable iron^{II} to reduce Mo^{VI} rapidly even at room temperature.

The literature on the determination of molybdenum^{VI} by titration with reductimetric reagents is rather scanty. Willard and Fenwick[2] stated that it is possible to titrate sodium molybdate at 80° with titanium^{III} sulphate solution in a medium which contains 5–10% (by volume) of concentrated hydrochloric acid. The equivalence point of the titration was detected potentiometrically using a polarised bimetallic electrode system with platinum electrodes. Titrations in a sulphuric acid medium were reported to be unsatisfactory. Even in a hydrochloric acid medium a correction was found to be necessary, because the potentiometric end-point corresponds to a finite excess of titanium^{III} sulphate solution over that theoretically necessary for the reduction of molybdenum^{VI} to molybdenum^{V}.

Fisher and Lyubimtsev[3] used tin^{II} chloride for the potentiometric titration of molybdenum^{VI}. In this titration, they recommended the addition of a little Mohr's salt because it helps rapid establishment of the equilibrium potentials and a sharp jump of the potential at the equivalence point. They found that, in the presence of Mohr's salt, titrations could be carried out at room temperature. It is reported that

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* Part I—see reference 1.

the presence of chloride also helps a more rapid establishment of the equilibrium potentials. Brintzinger and Rost[4] employed chromium^{II} for the potentiometric titration of molybdenum^{VI} and iron^{III} in mixtures. When the titration was carried out with chromium^{II} sulphate in a sulphuric acid medium, the first break in potential was found to correspond to the reduction of iron^{III} to iron^{II} and the second break to the reduction of molybdenum^{VI} to molybdenum^{V}. However, when the titration was carried out with chromium^{II} chloride in a hydrochloric acid medium, the first break in the curve was found to correspond to the reduction of both iron^{III} and molybdenum^{VI} (iron^{III} to iron^{II} and molybdenum^{VI} to molybdenum^{V}); the second break was found to correspond to the further reduction of molybdenum^{V} to the tervalent state. Flatt and Sommer[5] obtained results in substantial agreement with those of Brintzinger and Rost, although Nikolaeva[6] obtained discordant results concerning the reduction of molybdenum^{V} to molybdenum^{III}. Acosta[7] preferred to add an excess of chromium^{II} sulphate to molybdenum^{VI} and titrate the mixture potentiometrically with potassium dichromate in an atmosphere of nitrogen. The first break in the titration curve was found to correspond to the oxidation of unreacted chromium^{II} and the second to that of molybdenum^{V}. Tungsten^{VI} was also found to be reduced by chromium^{II}.

EXPERIMENTAL

Determination of Formal Redox Potential of Mo^{VI}/Mo^{V} *Couple in a Concentrated Phosphoric Acid Medium*

The procedure adopted is almost the same as that detailed previously.[1] A solution containing 0·144 mole of molybdenum is reduced in a mercury reductor in 3*M* hydrochloric acid and later diluted to give a solution containing 0·048 mole of molybdenum and 1·0*M* hydrochloric acid per litre. Five ml of this solution are mixed with 5 ml of a solution containing an equivalent quantity of molybdenum^{VI} in 1·0*M* hydrochloric acid; this mixture is then treated with the required quantity of phosphoric acid and made up to 50 ml. Several such mixtures are made with varying phosphoric acid concentration but with the concentrations of molybdenum^{V}, molybdenum^{VI} and hydrochloric acid remaining constant. In each solution the potential of the Mo^{VI}/Mo^{V} couple is measured against a saturated calomel electrode at 30°, using a platinum gauze electrode as indicator electrode. During such measurements it has been observed that the potentials are unsteady in the beginning but become fairly stable after about 30 min. The drift in potential has been observed to increase with increasing concentration of phosphoric acid. During the measurement of potential the mixture is kept in a carbon dioxide atmosphere and stirred well with a magnetic stirrer. The results are given in Table I.

TABLE I. FORMAL POTENTIAL OF THE Mo^{VI}/Mo^{V} COUPLE IN PHOSPHORIC ACID MEDIA

Concentration of phosphoric acid, *M*	Potential (N.H.E) of Mo^{VI}/Mo^{V} couple, *V*	Colour of the mixture
0·00	0·406*	
1·16	0·415	Blue
2·32	0·424	Orange-red
3·48	0·437	Orange-red
4·64	0·446	Orange-red
5·80	0·464	Dirty green
6·96	0·498	Dirty green
8·12	0·536	Dirty green
9·28	0·568	Green
10·44	0·606	Green
11·60	0·645	Green
13.00	0·685*	Green

* Values obtained by extrapolation.

When the potential values are plotted against the overall phosphoric acid concentration, the resulting curve is as shown in Fig. 1. This figure also incorporates the curve showing the variation of the formal potential of the Fe^{III}/Fe^{II} couple with increasing phosphoric acid concentration.[1] From the curves, it will be observed that the redox potential of the Fe^{III}/Fe^{II} couple is greater than that of the Mo^{VI}/Mo^{V} couple below 5.8*M* phosphoric acid. Above this concentration of phosphoric acid, the potentials are reversed and the redox potential of the Fe^{III}/Fe^{II} couple falls below that of the Mo^{VI}/Mo^{V} couple. It is interesting to note that the redox potential of the Mo^{VI}/Mo^{V} couple increases with increasing phosphoric acid concentration while that of the Fe^{III}/Fe^{II} couple decreases.

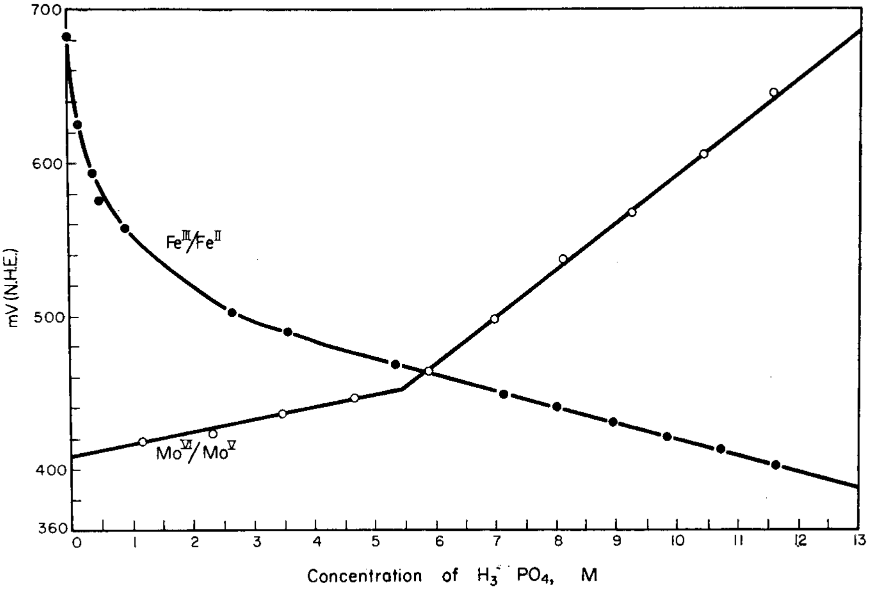

FIG. 1.—Influence of phosphoric acid concentration on the formal potentials of the Fe^{III}/Fe^{II} and Mo^{VI}/Mo^{V} couples.

When the concentration of phosphoric acid is 13.0*M*, the difference in potentials of the two couples is about 300 mV. It is obvious, therefore, that molybdenum^{VI} can very speedily oxidise iron^{II} in a medium of 13.0*M* phosphoric acid. The increase in the Mo^{VI}/Mo^{V} potential with increasing phosphoric acid concentration is most likely caused by the phosphoric acid forming a stronger complex with molybdenum^{V} than with molybdenum^{VI}.

Potentiometric Titration of Molybdenum^{VI} with Iron^{II} in a Concentrated Phosphoric Acid Medium

Reagents

Mohr's salt solution: A 0·5*M* solution of iron^{II} sulphate was prepared from a sample of AnalaR iron^{II} ammonium sulphate supplied by British Drug Houses Ltd. (London, England). The overall concentration of sulphuric acid in this solution was maintained at 0·5*M*. The solution, after suitable dilution, was standardised against a standard solution of potassium dichromate before each series of experiments. The concentration of iron is kept high to maintain the titre low so that the concentration of phosphoric acid in the titration mixture does not fall appreciably.

Molybdenum^{VI} solution: A solution containing about 0·1 mole of molybdenum (0·1*M*) was prepared from AnalaR ammonium molybdate supplied by British Drug Houses Ltd. This solution was standardised after reduction to molybdenum^{V} in a mercury reductor in 3M hydrochloric acid with a standard solution of cerium^{IV} sulphate according to the method of Furman and Murray[8] as improved by Gopala Rao and Suryanarayana.[9]

Syrupy phosphoric acid: As described previously.[1] In Fig. 2 are given the curves showing the relation between $\frac{\Delta E}{\Delta V}$ and V. It will be noted from these curves that the potential break at the equivalence point increases with increasing phosphoric acid concentration. We have observed that an increase in phosphoric acid concentration increases the difficulty in rapid attainment of the equilibrium potential.

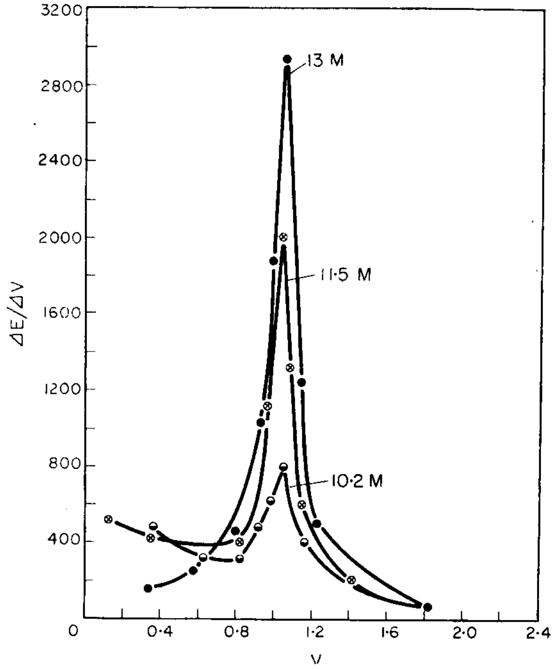

Fig. 2.—Influence of phosphoric acid concentration on the potentiometric titration curve.

Procedure

A medium of 13M phosphoric acid is recommended. About 2 to 4 ml of 0·1M molybdenum^{VI} solution are taken in a titration vessel fitted with a five-holed stopper. These holes accommodate the inlet and outlet tubes for carbon dioxide, the micro-burette containing the iron^{II} solution, the platinum wire electrode and one limb of the saturated potassium chloride bridge. Enough phosphoric acid is then added to make the total volume up to 30–60 ml, so as to increase the overall concentration of phosphoric acid to about 13M. The mixture is stirred by means of a magnetic stirrer while it is titrated with a 0·5M iron^{II} sulphate solution. The iron^{II} sulphate solution must be at least five times as concentrated as the molybdenum^{VI} solution in order to have a sufficient potential break. With 0·5M iron^{II} sulphate solution it has been observed that the potential break at the equivalence point is about 60 mV per drop of iron^{II} sulphate solution when the total volume of the titration mixture is about 30 ml, and about 30 mV when the total volume of the titration mixture is about 60 ml. With more dilute solutions of iron^{II} sulphate the potential break per drop of the reductant is lower. The volume of the titration mixture should also be kept within 30–60 ml in order to provide for effective stirring. On account of the highly viscous nature of the phosphoric acid medium, effective stirring is rendered more and more difficult as the volume of the titration mixture is increased.

Potentiometric titrations have been carried out using both a platinum wire as well as a platinum gauze as indicator electrodes. We have, however, observed that relatively stable potentials are obtained more easily with a wire electrode than with a gauze electrode. For this reason a wire electrode is to be preferred in the electrometric titration, although the potentials obtained with its aid may not be the true potentials. In titrations with a wire electrode, potential readings are taken 3 min after the addition of each portion of the titrant; while using a gauze electrode potential readings are taken 5 min after addition of the titrant. A curve is drawn showing the relation between $\frac{\Delta E}{\Delta V}$ and V and the equivalence point read from this curve.

Some typical results are presented in Table II, where the amount of molybdenum present has been calculated on the basis that molybdenum^{VI} is reduced quantitatively to molybdenum^{V} by iron^{II} in a phosphoric acid medium. The close agreement between the amounts of molybdenum^{VI} taken and the molybdenum^{VI} found provides sufficient proof for the assumed stoicheiometry. Further proof in favour of this stoicheiometry is afforded by the overlapping of the absorption curves of molybdenum^{VI} reduced in two different ways: (1) in a mercury reductor, and (2) by the present method and containing the same concentration of molybdenum and phosphoric acid (11·5*M*).

TABLE II. POTENTIOMETRIC TITRATION OF MOLYBDENUM^{VI} WITH IRON^{II} IN 13·0*M* PHOSPHORIC ACID

Molybdenum taken, *mmoles*	Molybdenum found, *mmoles*
0·2000	0·1968
0·2500	0·2460
0·3000	0·3030
0·3500	0·3465
0·3750	0·3765
0·4000	0·4004

Visual Indicator Titration of Molybdenum^{VI} with Iron^{II} in a Strong Phosphoric Acid Medium

The formal redox potential of the Mo^{VI}/Mo^{V} couple is 0·685 V in 13·0*M* phosphoric acid, while that of the Fe^{III}/Fe^{II} couple is 0·386 V. Therefore the transition potential of methylene blue (0·55 V) and of thionine (0·56 V) lies intermediate between the potentials of the two redox systems involved in the titration of molybdenum^{VI} with iron^{II} and it is likely that these dyes can function satisfactorily as reversible oxidation reduction indicators in the titration. Separate experiments have shown that the reduction of methylene blue (or thionine) by iron^{II} and the re-oxidation of the leuco dye by molybdenum^{VI} are quite fast when the concentration of phosphoric acid is above 11·5*M*. Titrations have been carried out using 1·0 ml of a 0·10% solution of the dye for 60 ml of the titration mixture. The titration apparatus is similar to the one used for the potentiometric titration. The indicator correction has been found to be negligible. The end-point of the titration is marked by a sharp colour change from blue to light green, but the colour transition is not sharp if the concentration of phosphoric acid falls below 11·5*M* at the equivalence point. It has also been observed that the amount of molybdenum assayed should not exceed 0·6 mmoles, otherwise the green colour of molybdenum^{V} makes detection of the end-point difficult. Some typical results are presented in Table III and these show that the method gives an accuracy of ±0·5%. The visual indicator method has been found to be more convenient than the potentiometric method. Visual titrations can be carried out using even 0·1*M* solutions of iron^{II}, keeping in mind the precautions already mentioned. Two–six ml of 0·1*M* molybdenum^{VI} solution are mixed with 50 ml of syrupy phosphoric acid, 1·0 ml of indicator solution added and titration carried out with 0·1*M* iron solution.

TABLE III

Molybdenum^{VI} taken, *mmoles*	Molybdenum^{VI} found, *mmoles*	
	Methylene blue	Thionine
0·2000	0·2000	0·2005
0·2500	0·2510	0·2505
0·2700	0·2700	0·2700
0·3000	0·2985	0·2995
0·3500	0·3500	0·3505
0·4000	0·4012	0·4000
0·4500	0·4480	0·4505

Interferences

Uranium^{VI} interferes because it is also quantitatively reduced by iron^{II} under the experimental conditions prescribed here. Tungsten^{VI} does not interfere. On the other hand, the addition of tungsten is beneficial because it reduces the tendency for potential drift and enables the early attainment of stable potentials. Chromium^{VI} and vanadium^{V} interfere because they are also reduced by iron^{II}.

Zusammenfassung—Eine Methode zur titrimetrischen Bestimmung von Molybdän(VI) mit Eisen(II) in stark phosphorsaurem Medium (11.5–13 m) bei Raumtemperatur wird beschrieben. Endpunktsanzeige erfolgt potentiometrisch oder visuall mit Methylenblau oder Thionin als interne Redoxindicatoren. Die Vorteile der Methode sind gleich den schon fürher für die Titration von Uran(VI) beschriebenen.

Résumé—Les auteurs ont mis au point le dosage du molybdène(VI) par le sulfate de fer(II) en milieu acide phosphorique concentré (11,5 à 13,0 M) à la température ordinaire, le point équivalent étant déterminé par potentiométrie ou visuellement au moyen du bleu de méthylène ou de la thionine comme indicateur d'oxydo-réduction. Les avantages de la méthode sont analogues à ceux décrits précèdemment pour le titrage de l'uranium(VI) par le fer(II).

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PHOTOMETRIC DETERMINATION OF BORON IN AQUEOUS MEDIUM USING PHTHALEIN VIOLET

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Summary—A selective and sensitive photometric determination of boron in aqueous medium, using phthalein violet, is described. After ion-exchange or phosphate separation of various cations, the method permits the determination of as little as 0·1 mg of boron in 50 ml.

INTRODUCTION

IT is well known that most fluorescence or colorimetric reactions of boric acid take place in concentrated sulphuric acid or in ethanol. To the first class of reagents belong the anthraquinone[1] or azochromotropic dyes,[2] for example quinalizarin,[3] carminic acid[4] or dianthrimide.[5] The second class is represented by curcumin[6] or related substances.[7] Other types of reactions of boric acid are based on the formation of ion-association compounds of fluoroboric acid with basic dyes.[8-10] The disadvantages of these methods are evident. In the last few years some reactions of boric acid in aqueous medium[11] have been described, for example with chromotropic acid,[12] Victoria violet,[13] derivatives of H-acids[14-16] or pyrocatechol violet,[17,18] but analytical use of these reactions is unlikely.

In a systematic study of the analytical properties of hydroxyphthaleins and related compounds it has been found that pyrocatechol phthalein, called because of the characteristic colour of its ammoniacal solution "phthalein violet", has its absorption maximum at 595 mμ decreased by boric acid in the pH range 9–9·5. This reaction is very suitable for the photometric determination of boron.

EXPERIMENTAL

Apparatus

The absorption curves were obtained with a Uvispek spectrophotometer (Hilger, London). Photometric measurements were carried out with a Spekker photometer (Hilger, London). pH measurements were made with an electronic pH meter ("K" Laboratorni potřeby).

Column preparation

The ion-exchange column employed was 250 mm long, with an internal diameter of 18 mm. The column was made of polyvinyl chloride and filled with Dowex 50-X8. The column was prepared in the usual way in the H^+-form with 100–150 ml of 4–6*M* HCl, and then washed with 200 ml of water.

All chemical operations were carried out in silica or polyvinyl vessels.

Reagents

Synthesis of phthalein violet: Melt 22 g of pyrocatechol, 15 g of phthalic anhydride and 2 ml of concentrated sulphuric acid. After 5–10 min pour in about 200 ml of water, mix well, and boil. Cool, and separate the black oily product from the aqueous phase. Then add about 100 ml of water and 1 g of $NaHCO_3$, boil gently, mix well and cool. Approximately neutralise with dilute hydrochloric acid, cool in an ice-box, and decant the aqueous layer. Recrystallise the black product from ethanol.

Phthalein violet is a black powder, which dissolves in acetone, methanol or ethanol to give a brown solution, and in dilute ammonia to give a violet solution. In the last medium it behaves also as a metallochromic indicator similar to pyrocatechol violet.

For the determination of boron use a 0·25% solution in ethanol.

Stock solution of boron: Dissolve 0·881 g of $Na_2B_4O_7.10\ H_2O$ or 0·572 g of H_3BO_3 in about 100 ml of water and dilute to 1000 ml. 1 ml of this solution contains 0·1 mg of boron.

All chemicals were obtained from Lachema, Brno, and were of analytical purity.

RESULTS

The determination of boron is based on the observation that the absorption maximum of phthalein violet at 595 mμ in the pH range 9–9·5 is decreased by boric acid. Some bivalent metals can be screened by ethylenediaminetetra-acetic acid or by cyanide. Tervalent and quadrivalent ions are retained (and also bivalent ions) on an ion-exchange resin, or are precipitated by phosphate at pH 6–7.

Maximum absorption

The maximum of the absorption curve of the phthalein violet at pH 9–9·5 is at 595 mμ. In the presence of excess boric acid the violet hue changes to a yellowish-brown one. The curves of Fig. 1 were obtained by measurement against a "blank" with water.

Influence of pH

The difference of the absorbance of a "blank" solution of phthalein violet and the solution after reaction with 0·5 mg of boron is constant in the pH range 9–9·5 (Table I).

TABLE I.—EFFECT OF pH ON THE FORMATION OF THE BORON COMPLEXES WITH PHTHALEIN VIOLET
(0·5 mg of boron)

pH	8·5	8·8	9·0	9·2	9·5	9·7	10·0
ΔA 600 mμ	0·47	0·58	0·63	0·62	0·62	0·60	0·54

Influence of concentration of dye and calibration curve

If the ratio of reagent to boric acid is assumed to be 1 : 1, the molecular weight of reagent is taken as 350, and the optical length of the cells is 10 mm, then the optimal concentration of the dye is 5 ml of 0·25% ethanolic solution of phthalein violet in a final volume of 50 ml. This concentration is sufficient for the determination of 0·1–0·7 mg of boron in 50 ml. To increase the sensitivity (0·01–0·1 mg of boron) 40-mm cells and 2 ml of 0·1% ethanolic solution of phthalein violet in a final volume of 25 ml may be used, taking into account a "blank" determination.

Influence of time

The absorbance reaches a constant value between 20 and 30 min after preparing the solution. If the solution is slightly warmed, and then cooled, the absorbance can be measured immediately after mixing the reagents (Table II).

Effect of foreign ions

The influence of foreign ions is indicated in Table III. Most of the ions interfere, but they can be removed by a cation-exchange resin or by phosphate precipitation.

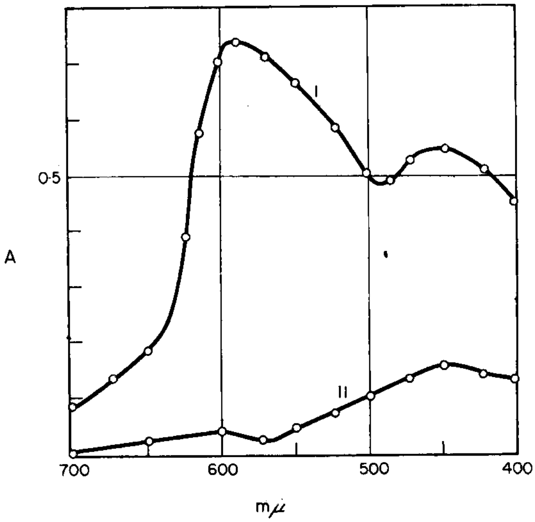

FIG. 1.—Absorbance curves of phthalein violet (I) and its boron complex (II).

TABLE II.—EFFECT OF TIME
(0·5 mg of boron)

Time, *min*	5*	5	10	15	20	30	40	60
ΔA 600 mμ	0·54	0·42	0·48	0·51	0·55	0·54	0·56	0·57

* measured after heating and cooling.

TABLE III.—DETERMINATION OF 0·5 mg OF BORON IN THE PRESENCE OF FOREIGN IONS

Boron found, *mg*	Difference, %	Added ions, *mg*	Screening
0·52	+4·0	Ca 10	EDTA
0·51	+2·0	Mg 15	EDTA
0·52	+4·0	Mn 5	EDTA
0·83	+66·0	Zn 6	EDTA
0·53	+6·0	Zn 10	KCN
0·48	−4·0	Cu 10	KCN
0·55	+10·0	Ni 6	KCN
0·51	+2·0	LiCl 500	—
0·46	−8·0	NaCl 250	—
0·50	0·0	NaCl 100	—
0·21	−58·0	KCl 1000	—
0·50	0·0	NH_4Cl 1000	—
0·50	0·0	Al 25	separated by cation exchange
0·49	−2·0	Al 25	separated by phosphate
0·50	0·0	NH_4F 80	—
0·51	+2·0	P_2O_5 10	—

It should be noted that more than 0·1 g of sodium or potassium chloride in 50 ml diminishes the absorbance. This fact must be borne in mind when the sample is decomposed by fusing with sodium carbonate. Lithium and ammonium chloride, phosphate, fluoride or sulphate do not interfere. Most of the alkali metals are also retained on the cation-exchange resin.

Analytical procedure

Transfer 5–25 ml of solution freed from other ions, and containing 0·1–0·7 mg of boron, to a 50-ml volumetric flask, add 1–2 ml of 0·1*M* NH_4-EDTA (ammonium salt of ethylenediamine-tetra-acetic acid), about 0·1 g of hydrazinium chloride or 0·2 ml of a saturated solution of Na_2SO_3, 5 ml of 0·25% ethanolic solution of phthalein violet and finally 5–10 ml of ammonia–ammonium chloride buffer, pH 9·5. Add water to 50 ml, mix and after 20 min measure absorbance against a "blank" at 595–600 mμ (orange filter).

Determination of boron in tourmaline concentrates and in glasses

Fuse 1 g of finely powdered sample in a platinum crucible with 0·3 g of sodium carbonate (or better, with lithium carbonate, if the content of boron is low). Decompose the melt with about 10 ml of hot water, and after 10–30 min add 1 ml of concentrated hydrochloric acid. Leave to stand till the solution is almost clear. Warm gently if necessary, and then dilute with 10–25 ml of water.

Separation of foreign ions by cation exchange

Dilute the weakly acidic solution with approximately 100 ml of water and neutralise with 10% NaOH till the red colour of methyl orange changes to orange and a precipitate of silica and basic salt appears. Filter, and wash the precipitate with 100 ml of water. Transfer the filtrate to the ion-exchange column, passing it through at a rate of 3–4 ml/min. Wash the column with 50 ml of water, evaporate the eluate if necessary (the loss of boron during evaporation is negligible from a weakly acidic solution), transfer to a volumetric flask and dilute to 100–250 ml with water. Pipette an aliquot, and determine the boron as described above.

Separation of foreign ions as phosphates

To a small volume of the solution add about 0·5 ml of concentrated phosphoric acid and neutralise drop by drop with dilute ammonia till the orange or yellow colour of methyl red appears. Mix well, dilute in a volumetric flask to 50 or 100 ml and allow to stand for about 1 hr. Filter through dry paper into a dry vessel (discard the first part of the filtrate), pipette an aliquot, and determine the boron as described above.

In the presence of fluoride the precipitation of aluminium phosphate is not quantitative and this method cannot be used. The foreign ions can be separated by 8-hydroxyquinoline.[19]

Some results are shown in Table IV.

TABLE IV.—DETERMINATION OF BORON IN TOURMALINES AND GLASS

Sample	Foreign ions separated by cation exchange Boron determined by volumetric analysis, %	 phthalein violet, %	Foreign ions separated by phosphate Boron determined by phthalein violet, %
Tourmaline I	3·03	3·03	
	2·98		
Tourmaline II	3·50	3·58	3·31*
	3·40		
Tourmaline III	3·88	3·82	3·34*
Tourmaline IV	2·96	3·10	2·70*
Glass, "Sial"	2·51		2·50
	2·51		2·47

* Low results in the presence of fluoride. These are caused by the formation of the aluminium chelate. In the presence of fluoride the formation of $AlPO_4$ is not quantitative.

DISCUSSION

Pyrocatechol phthalein also forms stable blue-green chelates with many metals. Complexes with bivalent metals can be destroyed by ethylenediaminetetra-acetic acid, but the ter- and quadrivalent ones must be separated by cation exchange. Pyrocatechol phthalein forms a more stable complex with boric acid than does pyrocatechol sulphophthalein. A comparison of these two reagents and the properties of their complexes with boric acid will be published in a future paper.

Zusammenfassung—Eine selektive und empfindliche Methode zur Bestimmung von Bor wird beschrieben. Nach Entfernung verschiedener Kationen mittels Ionenaustausch oder Phosphatfällung wird Bor mit Brenzkatechinphthalein photometriert. 0.1 mg B in 50 ml Lösung kann noch bestimmt werden.

Résumé—L'auteur décrit une méthode de dosage spectrophotométrique sélective et sensible du bore à l'aide de la phtaléine de pyrocatéchol. Après séparation de divers cations par échange d'ions ou par le phosphate, la méthode permet le dosage de 0,1 mg de bore dans 50 ml.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—VII*

DETERMINATION OF NICKEL†

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Summary—A method is described for the determination of nickel in beryllium or beryllium oxide. Nickel is precipitated with benzotriazole using cadmium as a carrier. A further separation from other elements is made by passing a hydrochloric acid-isopropyl alcohol solution through Dowex-1 anion-exchange resin. If necessary, separation of nickel from manganese is made by chloroform extraction of the nickel dimethylglyoxime complex. Nickel is finally determined as the dimethylglyoxime complex in an aqueous medium. The method is accurate to ±3% relative or 3 μg of nickel, whichever is greater, and is essentially specific for the determination of nickel.

INTRODUCTION

ON the basis of previous experience,[1] it was judged that a specific method for the determination of nickel would result from the precipitation of nickel with benzotriazole from a basic medium containing citric acid, using cadmium (or perhaps copper, cobalt or zinc) as a carrier. After destruction of the precipitate with nitric acid and perchloric acids, the nickel would be isolated by an anion-exchange separation using $9M$ hydrochloric acid, and determined by means of the dimethylglyoxime complex. Experience with cadmium[1] had shown that the benzotriazole precipitate obtained from a medium containing citric acid was essentially free of those elements which would interfere with the measurement of the nickel dimethylglyoxime complex, with the exception of cobalt and copper. An anion-exchange separation should then provide a solution containing only nickel and non-interfering elements.

The following discussion presents the results as they were obtained, and indicates where and how the initially selected procedure failed, and what steps were taken to overcome its inadequacies.

EXPERIMENTAL

Apparatus

Cary Model 14 spectrophotometer with 5-cm cells.

Ion-exchange columns: One cm i.d. containing 15 cm of Dowex-1 X 8 resin, 100–200 mesh, with a 50-ml reservoir (Fig. 1). Prepare the columns (using suction at all times) by washing with 150 ml of $3M$ nitric acid, 100 ml of water, and 150 ml of hydrochloric acid-isopropyl alcohol mixture. The columns should be regenerated by washing (with suction) with 100 ml of water, 150 ml of $3M$ nitric

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* Part VI: *Talanta*, 1961, **8**, 209.

† This work was carried out under the auspices of the Atomic Energy Commission.

acid, and 100 ml of water. With the suction off, stir the resin well and (with suction on) allow it to settle. Wash with 100 ml of water, and 150 ml of hydrochloric acid-isopropyl alcohol mixture.

Reagents

Standard nickel solutions: Prepare two standard solutions containing 10 μg and 8 μg of nickel per ml respectively.

Cadmium solution: 4 mg per ml.

Sulphuric acid: $36M$ and $6M$.

Hydrochloric acid: $12M$, $1{\cdot}2M$, $0{\cdot}5M$, and $0{\cdot}12M$.

Tartaric acid solution: 50% (w/v); filter if necessary.

Ammonium hydroxide: $15M$ and $0{\cdot}3M$.

Benzotriazole solution: 4% (w/v). Dissolve the reagent in hot water, and filter if necessary. Prepare just before use.

Filter paper: Munktell's 00 or equivalent.

Filter paper pulp: Cut up about 12 pieces of filter paper, and shake vigorously in a stoppered Erlenmeyer flask with about 200 ml of hot water until a pulp is obtained.

Wash solution: 0·4% benzotriazole-1% tartaric acid. Prepare fresh as needed, and chill in an ice bath.

Nitric acid: $15M$ and $3M$.

Perchloric acid: $11{\cdot}6M$.

Hydrochloric acid-isopropyl alcohol solution: Mix 2 litres of hydrochloric acid, 3·3 litres of isopropyl alcohol and 700 ml of water. Allow to cool to room temperature before using.

Citric acid solution: 5% (w/v). Prepare this solution fresh by appropriate dilution of a stock 50% (w/v) solution. (The 5% solution tends to form a mould on standing.)

Potassium persulphate solution: 5% (w/v). Prepare fresh as needed.

Sodium hydroxide: 40% (w/v); filter if necessary.

Dimethylglyoxime disodium salt solution: 3% (w/v).

Citrate buffer solution: Dissolve 170 g of citric acid in about 300 ml of water. Add 240 ml of ammonium hydroxide. Adjust the pH to 9·0–9·5 with ammonium hydroxide, and transfer to a 1-litre separatory funnel. Add 10 ml of dimethylglyoxime solution and extract three times with 10-ml portions of chloroform. Filter and dilute to 1 litre.

Hydroxylamine hydrochloride solution: 10% (w/v). Store in a refrigerator.

Chloroform.

Procedure

By appropriate preliminary treatment, obtain the sample in 350 ml of solution (in a 600-ml beaker) containing 100 μg of nickel, 10 ml of hydrochloric acid, 20 ml of $6M$ sulphuric acid, 40 ml of 50% tartaric acid, and 100 mg of cadmium. Add 50 ml of ammonium hydroxide and immediately adjust the pH to about 8·2. Allow to cool and adjust the pH (with ammonium hydroxide) to 8·5 ± 0·1. Add 50 ml of 4% benzotriazole solution and a small amount of filter paper pulp. Cover with a watch glass and heat on a steam bath at 60–70° for 1 hr, stirring the solution every 20 min to increase coagulation of the precipitate. Remove from the steam bath and set aside overnight. Filter through Munktell's 00 paper and wash the beaker and stirring rod several times with the wash solution.

Transfer the paper and precipitate to the original beaker and add 50 ml of nitric acid and 10 ml of perchloric acid. Cover with a Speedyvap watch glass. Heat on a hot plate and evaporate to perchloric acid fumes. Wash the beaker wall and watch glass with water and evaporate the solution to dryness.

Dissolve the residue in the hydrochloric acid-isopropyl alcohol mixture (warming gently if necessary). Transfer the solution to the ion-exchange column. (A total of 50–60 ml of this mixture should be sufficient for dissolution of the residue and quantitative transfer to the column reservoir.) Perform the ion-exchange separation, using suction, rinsing the reservoir twice with small portions of the hydrochloric acid-isopropyl alcohol mixture and finally, wash the columns with 2 to 50-ml portions of this mixture.

Transfer the eluate, containing nickel, to a clean 600-ml beaker, add 5 ml of sulphuric acid, and evaporate to sulphur trioxide fumes. Destroy the organic material by the slow addition of nitric acid to the fuming sample. Remove the sample from the hot plate, and wash the cover glass and beaker wall with water. Evaporate to sulphur trioxide fumes and destroy the remainder of the organic material with nitric acid as before. Evaporate the solution to dryness (do not bake).

Dissolve the residue in $1{\cdot}2M$ hydrochloric acid (boil if necessary) and transfer to a 50-ml volumetric flask, diluting to the mark with water.

Transfer a 20-ml aliquot to a 150-ml beaker and add 3 ml of 5% citric acid. Adjust the pH to 8·5 with ammonium hydroxide and then to 10·5 ± 0·1 with 40% sodium hydroxide. Add 3 ml of 5% potassium persulphate. (If the sample is not clear and colourless after the persulphate addition,

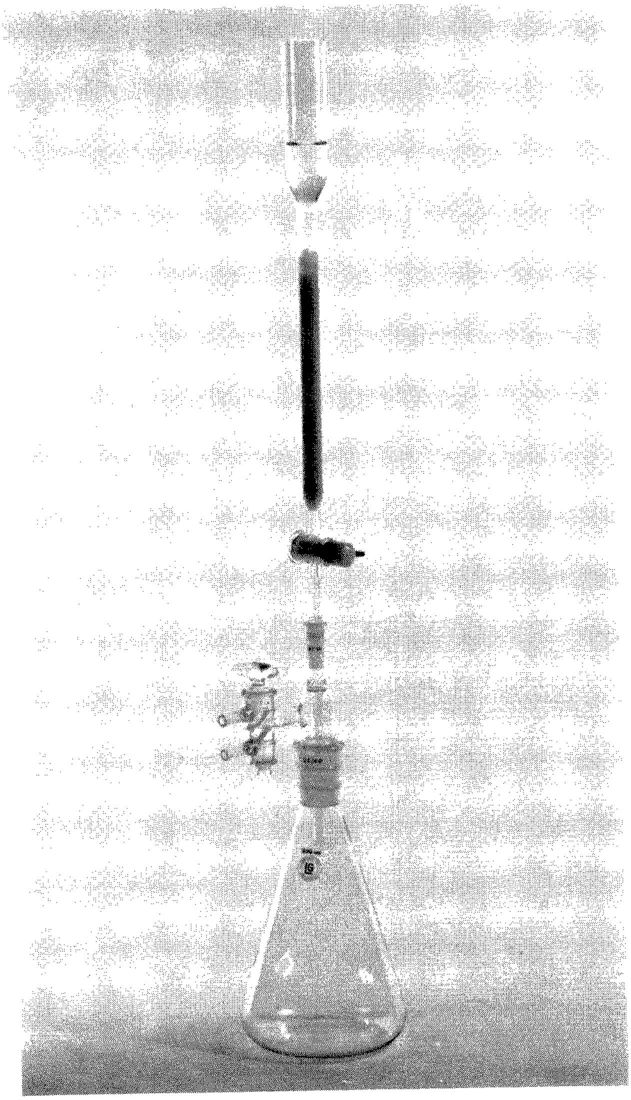

FIG. 1.—Ion-exchange apparatus.

discard the sample, and treat another aliquot as described below.) Add 1 ml of 3% dimethylglyoxime, and transfer the solution to a 50-ml volumetric flask. Dilute to the mark and allow 1 hr for colour development. Measure the absorbance of the solution in 5-cm cells at 465 mμ, using water in the reference cell. Determine the amount of nickel by reference to a calibration curve obtained using the colour-development step only.

If the solution was not clear and colourless before the addition of dimethylglyoxime, transfer another 20-ml aliquot to a 150-ml beaker. Add 2 ml of 50% citric acid, 10 ml of citrate buffer, and 5 ml of 10% hydroxylamine hydrochloride. Adjust the pH to 8·75 ± 0·1 with ammonium hydroxide, and transfer to a 125-ml separatory funnel. Add 1 ml of dimethylglyoxime solution, and set aside for 15 min. Add 10 ml of chloroform, stopper tightly and shake vigorously for 1 min. Transfer the chloroform extract to another 125-ml separatory funnel containing 25 ml of 0·3*M* ammonium hydroxide. Add 1 ml of dimethylglyoxime solution to the first funnel, and again extract for 1 min with 5 ml of chloroform. Transfer the chloroform extract to the second funnel. Add 3 ml of chloroform to the first funnel, and complete the extraction of nickel, adding the extract to the second funnel, and discarding the aqueous phase. Stopper the funnel containing the chloroform extracts and shake for 1 min. Allow the phases to separate completely (about 30 min is required), and remove most of the aqueous phase by means of a pipette attached to a vacuum line. Wash the stopper and the funnel walls with about 25 ml of water, swirl gently, and again remove the aqueous phase by suction. Add 50 ml of 0·5*M* hydrochloric acid, stopper tightly and shake for 1 min. Allow the phases to separate, remove and discard the chloroform layer, and transfer the aqueous phase to a 250-ml beaker, washing the funnel with water to ensure quantitative transfer. Add 3 ml of sulphuric acid, evaporate to sulphur trioxide fumes, and destroy the organic material with nitric acid as described previously. Evaporate the solution to dryness (do not bake).

Dissolve the residue in 20 ml of 0·12*M* hydrochloric acid (heating gently if necessary) and develop the nickel dimethylglyoxime colour as described above.

A blank and standard should be carried through the entire procedure in order to correct for the amount of nickel in the reagents used, and to ensure that quantitative recovery of the nickel has been obtained.

Comments regarding procedure

Fifteen g of tartaric acid will ensure that 1 g of beryllium oxide will not precipitate.

The pH of the filtrates from the benzotriazole precipitation was usually about 8·2.

Blanks obtained using the procedure were usually equivalent to about 5–10 μg of nickel, but were consistent for a group of samples run simultaneously. Because of the rather large number and amounts of reagents used, it is essential that the reagents be nearly nickel-free, or that the amounts added to all samples are maintained reasonably constant. The only problem the authors had in maintaining constant blanks, was in securing filter paper pulp of constant (or low) nickel content. It was for this reason that the pulp was prepared from Munktell's filter paper.

The time necessary to analyse a sample will, of course, depend on the difficulty of dissolution. After the precipitate has been allowed to stand overnight, one can destroy the organic matter in 12–16 samples with nitric and perchloric acids, and complete the ion-exchange separation in one day. The next day, the eluates can be evaporated, diluted, aliquoted and analysed, provided of course, that the extraction step for separation from manganese is unnecessary.

Poor results will be obtained if (*a*) reasonable control of reagents is disregarded, (*b*) reasonable care in the extraction step is not exercised, and, most important of all, (*c*) the residue after evaporation of the eluate is not completely dissolved (by boiling with 1·2*M* hydrochloric acid, if necessary).

DISCUSSION AND RESULTS

Measurement of the nickel dimethylglyoxime complex

Sandell[2] has summarised the information available with regard to the nickel dimethylglyoxime complex. Briefly, it appears that two coloured compounds can be formed when dimethylglyoxime is added to a basic solution of a nickel salt which has been treated with an oxidising agent. Many workers have had difficulty in obtaining both rapid colour development and colour stability. The following comments are applicable to the procedure described:

1. Only one coloured complex is formed, having its maximum absorbance at 465 mμ. This was ascertained by immediately and repeatedly obtaining the absorbance

spectrum of a solution of the complex. No peak at 445 $m\mu$, an absorption peak of the other coloured complex, was detected.

2. The absorbance reaches a maximum value in about 20 min and is stable for at least 24 hr. Some solutions have been stable for as long as a month.

3. Beer's law is obeyed for the concentration range 0–1 μg of nickel per ml.

4. The absorbance is remarkedly reproducible, as indicated by the fact that, for several hundred measurements of a solution containing 0·78 μg of nickel per ml, the absorbance was found to vary over the narrow range of 0·893–0·900. These values were obtained during a 1-yr period, and are, of course, dependent on the instrument used for measurement.

5. No significant difference occurs when the amount of citric acid is varied from 1 to 5 ml, the amount of potassium persulphate from 2 to 5 ml, the amount of dimethylglyoxime from 0·5 to 1·5 ml, and the pH from 10·0 to 11·0.

6. Ten mg of the following elements *do not* interfere (within ±3%) with the determination of 40 μg of nickel when present during the colour development step: Al, Sb^{III}, As^{III}, Ba, Be, B, $Br(Br^-)$, Cd, Ca, Cs, $Cl(Cl^-)$, Dy, Er, Eu, $F(F^-)$, Gd, Ga, Ge, Hf, Ho, In, $I(I^-)$, La, Pb, Li, Lu, Mg, Mo, Nd, Nb, $P(PO_4^{3-})$, K, Pr, Rb, Sm, Sc, Se, Si, Na, Sr, Ta, Te, Tb, Th, Tm, Sn^{II}, W, V, Yb, Y, Zn, or Zr.

7. Table I indicates the effect of elements which would interfere with the determination of 40 μg of nickel if present in 10-mg amounts during the colour development step.

TABLE I.—EFFECT OF ELEMENTS WHICH INTERFERE (IN 10-MG AMOUNTS) WITH THE DETERMINATION OF 40 μg OF NICKEL (COLOUR DEVELOPMENT STEP ONLY)

Element	Amount added, *mg*	Error, %	Element	Amount added, μg	Error, %
Tl[a]	5	+1·3	Ir[f]	1000	+1·3
U(VI)[f]	1·25	+2·4	Pd	1000	+3·5
Hg[a]	1	0·0	Cr(III)[a,e]	500	+1·2
Ag[a]	1	+2·0	Cr(VI)[f]	200	+1·5
In[a,d]	1	+1·3	Ce(IV)[a,e,f]	200	+0·3
Bi[a]	1	+0·6	Fe(III)[a,f]	100	+3·0
Au[a]	1	+1·4	Co	70	+1·5
Ti[a]	1	+0·8	Cu	50	+1·9
Pt[e]	1	−1·2	Rh[d,e]	50	+1·9
Re[e]	1	−1·6	Mn(II)[a,g]	50	+1·5

[a] Precipitates when present in 10-mg amounts.
[b] Precipitates when present in 5-mg amounts.
[c] Precipitates when present in 1-mg amounts.
[d] Precipitates when present in 0·1-mg amounts.
[e] Retards colour development.
[f] Coloured at pH 10·5.
[g] The presence of Mn^{II} in amounts of 50 μg or greater is apparent by the faint yellow colour of the solution when neutralised with NH_4OH and NaOH.

Anion-exchange separation of nickel

As mentioned in the introduction, it was anticipated that nickel would be precipitated with benzotriazole using cadmium, copper, cobalt or zinc as a carrier. Regardless of which element proved satisfactory, both copper and cobalt would also be carried, at least partially, and would interfere with the measurement of nickel (see Table I). Preliminary attempts to use a 9*M* hydrochloric acid medium for the separation of

40 µg of nickel from 50 mg of copper or cobalt were unsatisfactory for two reasons. First, it was quite difficult to get a clean separation and secondly, it was necessary to perform the separation in a hood because of the annoying fumes. Consequently, it was decided to use the 4*M* hydrochloric acid-55% isopropyl alcohol medium investigated by Fritz and Pietrzyk.[3] It was immediately found that the flow-rate through the column described was only about 4 ml/hr. Although all reports known to the authors advise against using suction to augment the flow-rate during ion-exchange, this possibility was investigated. It was found that despite visual observation of channeling and voids, the separation was quite efficient. Table II indicates some of the results obtained using the separation described.

TABLE II.—SEPARATION OF 40 µg OF NICKEL BY ANION-EXCHANGE (4*M* HCl-55% ISOPROPYL ALCOHOL)

Ni, added, µg	Added, *mg* Cd	Zn	Cu	Co	Ni recovery[a], %
40	—	—	—	50	100·5, 100·8, 100·3, 101·0, 99·5, 99·3
40	10	10	10	50	100·0, 101·3, 101·0
40	10	10	50	10	98·5, 100·0, 100·3
40	50	10	10	10	100·3, 99·3, 99·8

[a] Corrected for blanks caused by residual nickel in the Cd, Zn, Cu and Co. Confirmation of the fact that the absorbance values were caused by nickel was obtained spectrographically.

When 10 mg of nickel were carried through the ion-exchange separation, blanks from the next run using the same columns showed no column memory.

Precipitation of nickel with benzotriazole using cadmium as a carrier

It was mentioned in the introduction that we hoped to be able to precipitate nickel with benzotriazole from a basic medium containing citric acid, using copper, cobalt, cadmium or zinc as a collector. A great deal of work was done to collect nickel quantitatively in this manner, using 50 mg of cobalt, copper and cadmium, and varying the precipitation conditions, temperature, *etc.* At best, the recovery of nickel varied from 90 to 100%. Consequently, the precipitation of nickel was studied using tartaric acid rather than citric acid. The procedure used was identical to that described, with the following exceptions. The precipitation was made using 400 µg of nickel. After filtration and destruction of the precipitate, the residue was dissolved and diluted to 200 ml. Nickel was determined directly on a 20-ml aliquot without an ion-exchange separation. The results of this study are shown in Table III.

TABLE III.—PRECIPITATION OF 400 µg OF NICKEL WITH BENZOTRIAZOLE

pH	BeO added, *g*	Ni recovery, %	pH	BeO added, *g*	Ni recovery[a], %
7·5	—	99·8	7·5	1·0	98·7
8·0	—	98·9	8·0	1·0	99·1
8·5	—	99·9	8·5	1·0	99·0
8·75	—	99·8	8·75	1·0	99·3
9·0	—	99·5	9·0	1·0	98·9

[a] Corrected for the residual amount of nickel in the BeO used (see Table IV and Discussion for method of correction).

A pH of 8·5 was selected for further investigation and a more thorough study was made of the recovery of nickel after precipitation, anion-exchange separation and colour development. These results are shown in Table IV.

TABLE IV.—PRECIPITATION OF NICKEL WITH BENZOTRIAZOLE AT pH 8·5

Ni added, μg	BeO added, *g*	Ni found[a], μg	Ni recovery[a], %
—	—	4·5, 4·5, 4·5, 4·3, 4·7[b]	—
10	—	14·3, 15·5, 14·8, 15·5	—
		14·3, 14·8, 14·5, 15·3	—
—	1	9·7, 10·3[b]	—
10	1	18·5, 20·0, 20·3	—
100	—	—	103, 99, 100, 99, 101, 99, 99[c]
100	1	—	100, 100, 100, 101, 102, 103

[a] All results above are from individual determinations.

[b] These results were confirmed by spectrographic analysis of the coloured solutions.

[c] Other results obtained during further work: 99, 100, 99, 98, 102, 99, 98, 100, and 98% recovery.

TABLE V.—THE EFFECT OF OTHER ELEMENTS (10 mg OF EACH) ON THE DETERMINATION OF 100 μg OF NICKEL

Element added	Recovery %	Element added	Recovery %	Element added	Recovery %	Element added	Recovery %
Al	98	$F(F^-)$	100	Hg^{II}	98	Sr	101
Sb^{III}	98	Gd	99[b]	Mo	99	Ta	98
As^{III}	98	Ga	101[e]	Nd	99[b]	Te	98
Ba	99*	Ge	98	Nb	97	Tb	99
Bi	100	Au	100	Pd	98	Tl^{I}	97
B	100	Hf	98	$P(PO_4^{3-})$	100	Th	98
$Br(Br^-)$	99	Ho	100	Pt	103	Tm	102
Cd	102[f]	In	97	K	99[d]	Sn^{II}	99
Ca	99	$I(I^-)$	99	Pr	98[c]	Ti^{III}	101
Ce^{IV}	100	Ir	99, 100, **98†**	Re	99	Ti^{IV}	98
Cs	99[d]	Fe^{II}	102	Rh	97, 97 **97†**	W	97
Cr^{III}	97	Fe^{III}	103	Rb	99[d]	U^{VI}	101
Cr^{VI}	98	La	97[a]	Sm	97[a]	V	101[e]
Co	99	Pb	100	Sc	100	Yb	100
Cu	99	Li	99[d]	Se	98	Y	98
Dy	100	Lu	98	Si	100	Zn	102[f]
Er	100	Mg	98	Ag	99	Zr	98
Eu	98[c]	Mn^{II}	**100†**	Na	99[d]	NO^{3-}	97[g]
						ClO_4^-	98[h]

[a,b,c,d,e,f] These elements tested in groups as indicated.

[g] 5 ml of 14*M* nitric acid.

[h] 5 ml of 72% perchloric acid.

* $BaSO_4$ precipitated. Effect of Ba tested by filtering the solution before spiking with nickel.

† Indicates modified procedure (extraction step) used.

Effect of other elements

The elements which were known to interfere with the measurement of the nickel dimethylglyoxime complex (see Table I) were tested first. It was found that several were partially carried during the precipitation, but only manganese was present during the colour development step at a sufficiently high concentration to interfere. Its presence in interfering quantities is readily apparent by the yellow colour of the solution after neutralisation with ammonium hydroxide and sodium hydroxide. A modification of the procedure was therefore necessary if manganese were to be tolerated in the samples to be analysed. The modification chosen was the extraction of the nickel dimethylglyoxime complex with chloroform as described in *Procedure*. This was found to give excellent results for the separation and recovery of 40 μg of nickel in the presence of 10 mg of manganese^{II}, rhodium or iridium.

Table V summarises the results obtained when the entire procedure was tested in the presence of other elements.

The solutions containing erbium, lutetium, yttrium, holmium, ytterbium, thulium and scandium were turbid after neutralisation, and before the addition of benzotriazole. The colours of the precipitate and solution indicated that most or all of the copper and gold was precipitated with benzotriazole, and that cobalt, chromium, manganese, platinum, palladium, iridium, rhodium and vanadium were partially precipitated. Gold, and part of the iridium and palladium remain on the columns during the ion-exchange separation, and are not removed during their regeneration. The resin must therefore be discarded.

Application of the method

Results obtained when the method was applied to New Brunswick Laboratory standard samples are shown in Table VI.

TABLE VI.—ANALYSIS OF NBL STANDARDS

Sample	Ni found, *ppm*	Ni content, nominal *ppm*
BeO 72-2	69, 71	72
Be 86	224, 227, 226	200[a]

[a] Value assigned was compromised to fit spectrographic curves.[4]

Zusammenfassung—Eine Methode zur Bestimmung von Nickel in Beryllium und Berylliumoxyd wird beschrieben. Nickel wird unter Zusatz von Cadmium als Spurenfänger mit Benzotriazol gefällt. Weitere Trennungen werden erzielt, indem eine Salzsäure-Isopropanol-Lösung durch einen Dowex-1 Anionenaustauscher geschickt wird. Wenn nötig, wird Nickel von Mangan durch Extraktion des Dimethylglyoximes in Chloroform erzielt. Nickel wird schliesslich mit Dimethylglyoxim in wässriger Lösung bestimmt. Der relative Fehler der Methode ist $\pm 3\%$ oder 3 μg, was immer der grössere Wert ist. Die Bestimmung ist praktisch spezifisch für Nickel.

Résumé—L'auteur décrit une méthode de dosage du nickel dans le béryllium ou l'oxyde de béryllium. Le nickel est précipité par le benzotriazole en présence de cadmium comme entraîneur. Une séparation ultérieure des autres éléments est effectuée par passage d'une solution d'acide chlorhydrique dans l'alcool isopropylique sur la résine

échangeur d'anion Dowex-1. Si cela s'avère nécessaire, la séparation du nickel du manganèse est effectuée par extraction dans le chloroforme de la diméthylglyoxime de nickel. Finalement le nickel est dosé par la diméthylglyoxime en milieu aqueux. La précision de cette méthode qui est essentiellement spécifique pour le dosage du nickel est de 3% ou 3 μg de nickel selon la concentration.

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PRECIPITATION FROM MIXED SOLVENTS—II*

NICKEL 8-HYDROXYQUINOLATE

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Summary—Preferential volatilisation of the organic components of a water-acetone-ethanol mixture has been shown to lead to the formation of large, dense, easily-filtered crystals of nickel 8-hydroxyquinolate. Specific directions are given for the analysis of solutions containing 3–30 mg of nickel. The separation of 30 mg of nickel from 540 mg of magnesium or 1400 mg of calcium can be accomplished with less than 1 mg of co-precipitation.

IT has been reported earlier[1,2] that aluminium 8-hydroxyquinolate had been precipitated as well-defined, highly pure crystals by a technique which involved the addition of considerable amounts of acetone to a buffered aqueous solution. Addition of the precipitating agent was followed by a period of heating which caused the preferential volatilisation of the acetone and resulted in the gradual formation of the precipitate. This method of controlled precipitation possesses the advantages of the more common techniques for accomplishing precipitation from homogeneous solution. In addition, it also possesses the definite advantages of requiring only commonly available precipitants and of permitting the close control of pH throughout the course of the precipitation.

The work reported in this paper represents some of the experiments which have been performed to test the response of other precipitates to this type of treatment. For this purpose the same precipitant was chosen but a cation in a different oxidation state and with a different configuration was employed. It was found that a three-component system yielded better results than the two-component system previously used, and that the improvement in the handling characteristics of the precipitate were sufficient to make this a practical method of removing nickel from a solution quantitatively.

EXPERIMENTAL

Reagents

Nickel: A nickel solution was prepared from reagent-grade $NiSO_4 \cdot 6H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey). The solution was standardised by precipitation with dimethyl glyoxime[3] and was found to contain 29·75 ± 0·07 mg of nickel per 10 ml of solution. For the study of the co-precipitation of calcium a nickel solution which contained 3 mg of nickel per ml of solution was prepared by weighing reagent-grade $NiCl_2 \cdot 6H_2O$.

Magnesium: Reagent-grade $MgSO_4 \cdot 7H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey) was used to prepare a solution which contained 300 mg of magnesium per 25 ml of solution.

Calcium: Reagent-grade $Ca(NO_3)_2 \cdot 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was used to prepare a solution which contained 1000 mg of calcium per 25 ml of solution.

8-*Hydroxyquinoline:* A 5% solution in 2*N* acetic acid was prepared by adding 5·7 ml of glacial acetic acid to 2·50 g of the reagent-grade material (Fisher Scientific Company, Fair Lawn, New Jersey); after a gentle warming and agitation to dissolve the reagent, the solution was diluted to 50 ml with distilled water.

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* Part I: See ref. 2.

All other chemicals were reagent-grade. It was noted that certain lots of reagent-grade acetone required distillation in order to remove an unidentified water-insoluble residue.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes and standardised with E. H. Sargent and Co. buffer solution was used for all pH measurements.

Procedure for nickel

From 1 to 10 ml of the nickel solution were mixed with 60 ml of distilled water in a 250-ml beaker. To this mixture were then added 60 ml of acetone, 20 ml of ethanol, 4 ml of the 8-hydroxyquinoline solution, and 20 ml of 4*M* ammonium acetate. The reaction mixture was placed on a water bath at 70–75° and left uncovered for 3 hr. Visible precipitation began after approximately 5–30 min. At the end of the evaporation period the solutions were cooled to room temperature and filtered through medium-porosity sintered-glass crucibles. The precipitates were washed three times with distilled water and were dried overnight at 135–140°. The pale yellow-green product was weighed as anhydrous $Ni(C_9H_6ON)_2$. The gravimetric factor is 0·16913. Filtrate pH's were 5·2–5·3.

Magnesium co-precipitation

Ten-ml samples of the nickel sulphate solution were treated as described above, with the exception that 120–540 mg of magnesium were added.

Calcium co-precipitation

Ten-ml samples of the prepared nickel chloride solution were treated as described above with the exception that 600–1400 mg of calcium were added.

RESULTS AND DISCUSSION

Formation of the precipitate under the conditions described was found to result in a vast improvement in the handling characteristics. When the precipitate was formed by the direct addition method described for aluminium by Olson, Koch and Pimentel,[4] a fluffy, voluminous material was obtained which required approximately 1 hr to filter using a medium-porosity filtering crucible and vacuum supplied by an aspirator. Using the same filtering conditions, the material produced by the evaporation process was easily filtered in less than 10 min. This great increase in filterability is probably related to the increase in crystalline size that is shown in Figs. 1 and 2.

A series of seven 10-ml samples of nickel sulphate was analysed by this procedure and they were found to contain 29.82 ± 0.04 mg of nickel. In addition, a number of samples containing various amounts of nickel were analysed, with the results presented in Table I.

Substitution of acetone for the 20 ml of ethanol called for in the procedure gave desirable precipitates but the rate of precipitation appeared to be more rapid when no ethanol was present, a situation which could conceivably lead to poorer separations

TABLE I.—NICKEL PRECIPITATED FROM AN ACETONE-ETHANOL-WATER MIXTURE

Nickel added, *mg*	Nickel found, *mg*	Error, *mg*
2·98	2·99	0·01
5·95	6·05	0·10
11·90	11·99	0·09
14·88	14·92	0·04
17·85	17·84	0·01
23·80	23·88	0·08
29·75	29·78	0·03

Average error: 0·05 mg

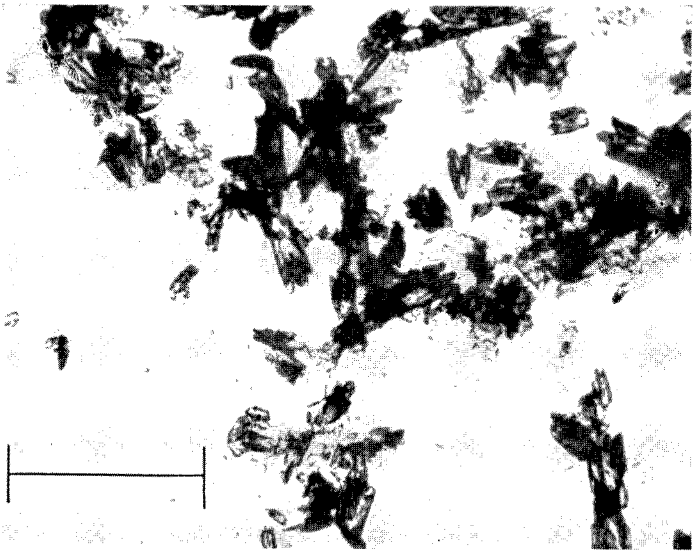

FIG. 1.—Nickel 8-hydroxyquinolate produced by direct addition. (Distance shown is 0·1 mm.)

FIG. 2.—Nickel 8-hydroxyquinolate produced by solvent evaporation. (Distance shown is 0·1 mm.)

from diverse ions. Times required for the first visible precipitate to form can be altered somewhat by changing the relative volumes of water and organic constituents. Those mentioned herein appeared to yield precipitates of maximum crystallinity and were convenient for the particular size of vessel employed.

Tables II and III show the low degree of co-precipitation that occurs even in the presence of large amounts of diverse ions. It was noted that when more than 240 mg of magnesium were present in the solution a turbidity developed upon the addition of the ammonium acetate buffer. This was probably caused by the insolubility of high salt concentrations in the less polar mixed solvent medium. The problem was circumvented by heating the samples to 70° on the water bath before the addition of the buffer. No deleterious effects upon the precipitate were noted, and no such behaviour was observed in the samples containing calcium nitrate.

TABLE II.—MAGNESIUM PRECIPITATED PER 30 mg OF NICKEL

Magnesium added, *mg*	Magnesium precipitated, *mg*	
	Trial A	Trial B
120	0·3	—
180	0·3	0·4
240	0·5	0·5
300	0·4	0·6
360	0·4	0·5
420	0·6	0·6
480	0·6	0·6
540	—	0·6

TABLE III.—CALCIUM PRECIPITATED PER 30 mg OF NICKEL

Calcium added, *mg*	Calcium precipitated, *mg*
600	0·4
800	0·5
1000	0·6
1200	0·9
1400	0·7

Attempts were made to precipitate samples by the direct addition method under similar conditions. The extreme difficulty in filtering these samples eventually lead to the discontinuation of such attempts.

These results show that the precipitation of nickel 8-hydroxyquinolate from a solution of mixed solvents is a practical and convenient method for determining nickel or for quantitatively removing this ion from solution. Certainly one would not expect this reagent to display the selectivity of dimethylglyoxime for nickel. It would, however, be useful when interfering ions were not present or for separating those metal ions which form insoluble 8-hydroxyquinolates at this pH from those which do not.

Acknowledgement—The authors gratefully acknowledge the financial support of the Research Corporation of the Atomic Energy Commission under contract AT(40-1)-2954 and of the American Oil Company who sponsored the fellowship held by one of the authors (J.L.J.).

Zusammenfassung—Bevorzugte Verdampfung der organischen Komponente in Wasser-Aceton-Äthanol Mischungen führt zur Bildung von grossen, kompakten und leicht filtrierbaren Kristallen von Nickeloxinat. Genaue Vorschriften zur Bestimmung von 3–30 mg Nickel werden gegeben. Die Trennung von 30 mg Nickel von mindestens 540 mg Magnesium oder 1400 mg Calcium ist möglich.

Résumé—La volatilisation préférentielle des constituants organiques d'un mélange eau-acétone-éthanol a conduit à la formation de gros cristaux denses et aisément filtrables d'oxinate de nickel. Une mode opératoire est donné pour le dosage de solution contenant 3 à 30 mg de nickel. La séparation de 30 mg de nickel d'au moins 540 mg de magnésium ou de 1400 mg de calcium a été effectuée.

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PRECIPITATION FROM MIXED SOLVENTS-III*

MAGNESIUM 8-HYDROXYQUINOLATE

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Summary—Preferential volatilisation of the organic solvent from a water-acetone mixture leads to the formation of large, grainy, easily-filtered crystals of magnesium 8-hydroxyquinolate. Using this method, magnesium can be separated satisfactorily from sodium, potassium and barium.

EARLIER reports[1-3] have shown that aluminium and nickel 8-hydroxyquinolates may be precipitated as well-defined, highly pure crystals by volatilisation of the organic component of a water-organic solvent mixture. This technique has now been applied to the determination of magnesium as its 8-hydroxyquinolate with excellent results.

The conventional, direct-addition method of precipitating magnesium 8-hydroxyquinolate yields a more crystalline and granular material than is obtained with most cations. Heyn and Finston[4] have shown improvement in crystal size when the precipitate was formed from homogeneous solution by the hydrolysis of urea. Recently, Gordon *et al.*,[5] have reported the use of the hydrolysis of 8-acetoxyquinoline. The results presented herein compare favorably with those obtained by the other methods.

EXPERIMENTAL

Reagents

Magnesium: A standard magnesium solution was prepared from reagent-grade $MgSO_4 \cdot 7H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey) which had been dried for 3 hr at 450° to give anhydrous $MgSO_4$.[6] The solution was prepared to have 14·39 mg of magnesium per 10 ml of solution. For the study of coprecipitation of barium, a solution of $MgCl_2 \cdot 6H_2O$ (reagent-grade, Mallinckrodt Chemical Works, St. Louis, Missouri) was prepared and standardised by the method of this report. In a series of 5 samples, the $MgCl_2$ solution was found to contain 13·35 ± 0·02 mg of magnesium per 10 ml of solution.

Sodium: Reagent-grade NaCl (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was used to prepare a solution which contained 1000 mg of sodium per 10 ml of solution.

Potassium: Reagent-grade KCl (Merck and Co., Inc., Rahway, New Jersey) was used to prepare a solution containing 1000 mg of potassium per 20 ml of solution.

Barium: Reagent-grade $BaCl_2 \cdot 2H_2O$ (Mallinckrodt Chemical Works, St. Louis, Missouri) was used to prepare a solution containing 10 mg of barium per ml of solution.

8-*Hydroxyquinoline:* A 2% solution of 8-hydroxyquinoline (reagent-grade, J. T. Baker Chemical Company, Phillipsburg, New Jersey) in acetone was prepared by adding 98 ml of acetone to 2·00 g of 8-hydroxyquinoline. A fresh solution was prepared for each determination.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreaux column using all-glass apparatus. This precaution was necessary to remove an unidentified water-insoluble material.

Ethanolamine: Ethanolamine (Matheson Coleman and Bell, East Rutherford, New Jersey) was used without further purification.

All other chemicals were reagent-grade.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes was used for all pH measurements.

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* Part II: See ref. 3.

Procedure

Magnesium: Preliminary experiments have shown that the following procedure will give best results for the precipitation of magnesium 8-hydroxyquinolate.

Add to a 10-ml sample containing from 7 to 16 mg of magnesium, in a 250-ml beaker, 9 ml of 2*M* acetic acid, 10 ml of 0·5*M* ammonium chloride, 20 ml of distilled water and 30 ml of 1·66*M* ethanolamine. Eighty ml of acetone are then added, followed by 10 ml of 2% 8-hydroxyquinoline in acetone. The reaction mixture is placed on a water bath at 65–70° and left uncovered for 3 hr. Visible precipitation occurs within 2 min after the addition of the 8-hydroxyquinoline. The precipitate is filtered hot through a medium-porosity sintered-glass crucible. The precipitates are washed with a 1% ammonia solution and dried at 102° for 2 hr. The yellow product is weighed as $Mg(C_9H_6ON)_2{\cdot}2H_2O$. The gravimetric factor for conversion to magnesium is 0·06975. Filtrate pH's were 9·5 to 9·7.

Coprecipitation: In the coprecipitation studies the magnesium solutions (containing 12–13 mg of magnesium) were treated as described above, except that the diverse ions were added with enough distilled water to make 20 ml of solution. This replaced the 20 ml of distilled water in the general procedure.

RESULTS AND DISCUSSION

The conditions described herein lead to the formation of a coarse, grainy precipitate which can be easily filtered in 10 min using a vacuum supplied by an aspirator. Quantitative results are obtained in the determination of 7–16 mg of magnesium, as shown in Table I.

TABLE I.—PRECIPITATION OF MAGNESIUM 8-HYDROXYQUINOLATE

Magnesium added, *mg*	Magnesium recovered, *mg*	Diverse ion	Amount of diverse ion, *mg*	Error, *mg*
5·75	6·51	None		+0·76
7·19	7·06	None		−0·13
8·63	8·58	None		−0·05
10·07	10·10	None		+0·03
11·51	11·52	None		+0·01
14·39	14·33*	None		−0·06*
15·83	15·80	None		−0·03
12·95	12·98*	Na^+	1000	+0·03*
12·95	12·95†	K^+	1000	0·00†
13·35	13·30	Ba^{2+}	1	−0·05
13·35	13·30	Ba^{2+}	5	−0·05
13·35	13·31	Ba^{2+}	10	−0·04
13·35	13·32	Ba^{2+}	15	−0·03
13·35	13·33	Ba^{2+}	20	−0·02
13·35	13·41	Ba^{2+}	35	+0·06
13·35	13·39	Ba^{2+}	40	+0·04
13·35	13·41	Ba^{2+}	50	+0·06
13·35	15·48	Ba^{2+}	200	+2·13

* average of 5 determinations
† average of 6 determinations

In previous work with aluminium and nickel 8-hydroxyquinolates, the time required for the formation of the first visible precipitates was from 5 to 30 min. In this study none of the solvent compositions investigated were successful in extending this time beyond 3 min. Despite this rapid initial precipitation, the final material had an average particle size comparable to that obtained by other authors. The crystals are larger than those obtained by the conventional method described by Moyer and Remington[7] or by the hydrolysis of 8-acetoxyquinoline described by Gordon *et al.*,[5] as can be seen in Fig. 1, 2 and 3. A comparison of the photomicrograph of the

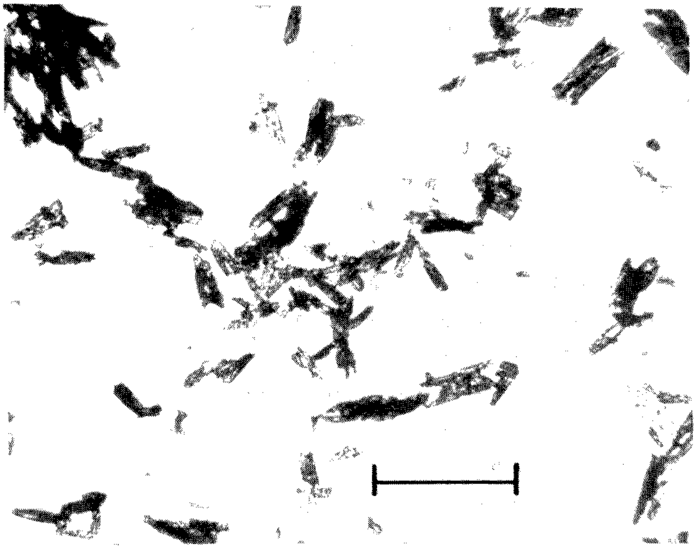

FIG. 1.—Magnesium 8-hydroxyquinolate by direct addition. (Distance shown is 0·1 mm.)

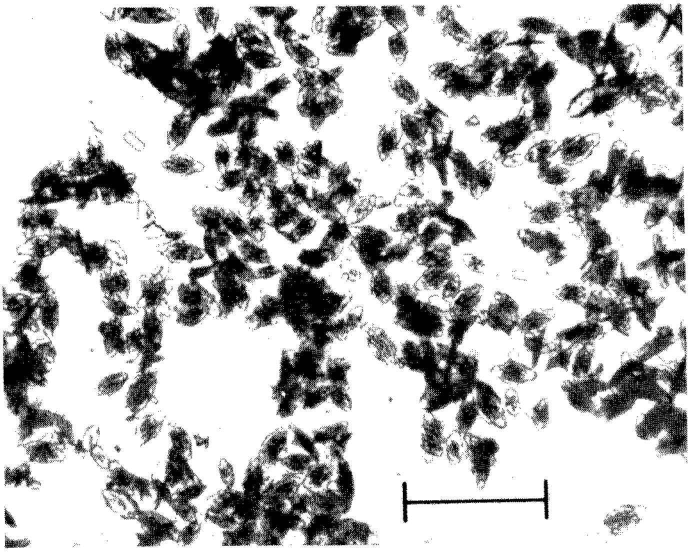

FIG. 2.—Magnesium 8-hydroxyquinolate by hydrolysis of 8-acetoxyquinoline. (Distance shown is 0·1 mm.)

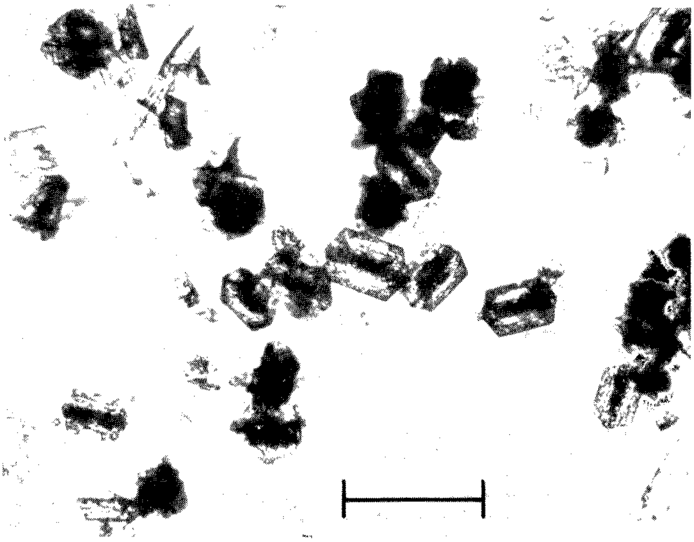

FIG. 3.—Magnesium 8-hydroxyquinolate by solvent evaporation. (Distance shown is 0·1 mm.)

precipitate obtained by this method (Fig. 3) with that of the precipitate obtained by the hydrolysis of urea, reported by Heyn and Finston,[4] shows that the precipitate sizes are approximately the same.

In preliminary experiments, 2*M* ammonium hydroxide was used to maintain the pH at 10. It was found that precipitation was incomplete, and that the pH of the filtrate was lower than expected. In one instance the pH of the initial solution (with no acetone added) was 10·06. After heating on a water bath at 70° for 3 hr, the pH of the solution was 7·30. This large decrease in pH was thought to be caused by the evaporation of ammonia from the solution. For this reason, ethanolamine, which has a basic strength comparable to that of ammonia, but a higher boiling point, was substituted in the procedure. With ethanolamine, experimentation has shown that if the initial pH is 10·00, the pH of the solution after heating at 70° for 3 hr decreases only to 9·45. Because the precipitation of magnesium 8-hydroxyquinolate is complete over a pH range of 9·4 to 12·7,[8] ethanolamine is recommended to maintain the pH of the solution within the accepted limits.

Table I shows that 13 mg of magnesium can be separated easily from 1000 mg of sodium or potassium or 50 mg of barium. The separation of magnesium from sodium and potassium was comparable to that obtained by Gordon *et al.*,[5] and by Heyn and Finston.[4] The separation from barium was slightly better than that obtained by Gordon *et al.*, who was unable to separate successfully 12 mg of magnesium from 50 mg of barium.

CONCLUSIONS

The precipitation of magnesium 8-hydroxyquinolate by the evaporation of a volatile organic solvent yields results which are superior to those obtained by the direct addition of reagents, and comparable to those obtained by other methods of gradual precipitation. In addition, it permits the close control of pH and employs commonly available reagents.

Acknowledgements—The authors gratefully acknowledge the financial support of the Research Corporation of the Atomic Energy Commission under contract AT(40-1)-2954 and of the American Oil Company who sponsored the fellowship held by one of the authors (J.L.J.)

Zusammenfassung—Bevorzugte Verdampfung der organischen Komponente in einer Azeton-Wassermischung führt zu Bildung von grossen, groben und leichtfiltrierbaren Kristallen von Magnesiumoxinat. Mittels dieser Methode kann Magnesium zufriedenstellend von Natrium, Kalium und Barium getrennt werden.

Résumé—La volatilisation préférentielle du solvant organique d'un mélange eau-acétone conduit à la formation de gros cristaux bien formés et aisément filtrables d'oxinate de magnésium. En utilisant cette méthode le magnésium peut être séparé de façon satisfaisante du sodium, du potassium et du baryum.

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PRECIPITATION FROM MIXED SOLVENTS—IV*

COPPER 8-HYDROXYQUINOLATE

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Summary—The technique of precipitation from mixed solvents has been applied to the case of copper 8-hydroxyquinolate. Although the time before observing the first visible precipitate was less than 5 min, the final crystals were large, well-formed, and very regular. The method has been shown to be applicable to the analysis of samples containing between 3 and 30 mg of copper, and to result in good separations from calcium, magnesium and lead.

EARLIER reports[1–4] have shown that some of the 8-hydroxyquinolates may be precipitated with increased purity and crystallinity in the presence of large amounts of organic solvents. The work reported in this paper describes experiments designed to test the applicability of this technique to copper 8-hydroxyquinolate.

EXPERIMENTAL

Reagents

Copper: Reagent-grade copper shot (Fisher Scientific Company, Fair Lawn, New Jersey), 99·98% assay, was washed with dilute nitric acid, distilled water, and finally with acetone. After 15 min of air drying, a carefully weighed sample was dissolved in a minimum of 1:1 nitric acid, the solution was brought to the first permanent turbidity by the addition of ammonia, 5 ml of 6*M* acetic acid were added, and the entire sample was diluted to a final volume of 1 litre. The amount of copper corresponded to 30·01 mg of copper per 10 ml of final solution. This same value was obtained upon electrodeposition of the copper from a measured portion.

Magnesium: Reagent-grade $MgSO_4·7H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey) was used to prepare a solution which contained 120 mg of magnesium per 10 ml of solution.

Calcium: Reagent-grade $Ca(NO_3)_2·4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was used to prepare a solution which contained 400 mg of calcium per 10 ml of solution.

Lead: Reagent-grade $Pb(NO_3)_2$ (Mallinckrodt Chemical Works, St. Louis, Missouri) was used to prepare a solution which contained 120 mg of lead per 10 ml of solution.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreaux column using an all-glass apparatus. This precaution was found to be necessary because some lots of acetone contained appreciable amounts of a water-insoluble material.

8-Hydroxyquinoline: A 5% solution in 2*M* acetic acid was prepared by adding 5·7 ml of glacial acetic acid to 2·50 g of the reagent-grade material (Fisher Scientific Company, Fair Lawn, New Jersey); after gentle warming and agitation to dissolve the reagent, the solution was diluted to 50 ml with distilled water.

All other chemicals were reagent-grade and were used without further purification.

Apparatus

A Beckman Model G pH meter, equipped with glass and calomel electrodes and standardised with E. H. Sargent and Co. buffer solution, was used for all pH measurements.

Procedure for copper

To a 250-ml beaker are added 10 ml of a solution containing between 3 and 30 mg of copper, 40 ml of water, 100 ml of acetone, and 3–4 ml of chloroform. The mixture is heated to 65° on the water

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* Part III: See ref. 4.

bath and 3·3 ml of 5% 8-hydroxyquinoline solution are added, followed by 20 ml of 4*M* ammonium acetate. After a 4-hr heating period, the samples are removed from the bath, filtered through medium-porosity sintered-glass crucibles, washed with distilled water and dried for at least 1 hr at 135–140°. The gravimetric factor for anhydrous $Cu(C_9H_6ON)_2$ is 0·18059. Filtrate pH's are in the range of 5·5–5·6.

Effect of diverse ions

The above procedure was repeated except that solutions containing calcium, magnesium or lead were substituted for the 40 ml of water.

RESULTS AND DISCUSSION

Eight 10-ml portions of the standard copper solution were analysed by the above method and an average value of 29·95 mg of copper with a standard deviation of 0·03 mg was obtained. This value is in good agreement with the expected value of 30·01 mg, and the low standard deviation indicates the degree of reproducibility of the analysis. In addition, samples containing various amounts of copper were analysed by this method with the results shown in Table I.

TABLE I.—COPPER PRECIPITATED FROM AN ACETONE-CHLOROFORM-WATER SYSTEM

Copper added, *mg*	Copper found, *mg*	Error, *mg*
3·00	3·02	+0·02
6·00	6·07	+0·07
9·00	9·03	+0·03
9·00	9·05	+0·05
9·00	8·96	−0·04
15·01	15·02	+0·01
15·01	14·97	−0·04
21·01	20·93	−0·08
21·01	20·93	−0·08
30·01	29·89	−0·12

Average error: 0·06 mg.

The ability of this method to separate copper from up to 480 mg of magnesium, or 1200 mg of calcium, or 480 mg of lead when combined with approximately 30 mg of copper was tested. In all cases the error induced in the final dried precipitate by the presence of these diverse ions was less than 0·1 mg.

The precipitate formed by the evaporation was a coarse, granular material which showed no tendency to cling to the walls of the beaker, was easily transferred to the filtering crucible, and could be easily filtered and washed in less than 10 min. By contrast, when attempts were made to perform the analysis by a direct addition method, similar to that recommended for aluminium by Olson, Koch and Pimentel,[5] the precipitates formed were extremely light and voluminous. This contrast is most readily seen in the photomicrographs of Figs. 1 and 2, which compare the products of these two methods of preparation.

In the course of some preliminary experiments which were designed to test various solvent systems it was noted that the colour of the precipitate was markedly dependent upon the organic solvents present. When the precipitate was formed with only water and acetone present it was yellow-brown. When chloroform was also added the crystals were not only larger, but tended to be greener. The intensity of the green colour appeared to be roughly proportional to the amount of chloroform added, until green became the predominate colour in the presence of 5 ml of this solvent.

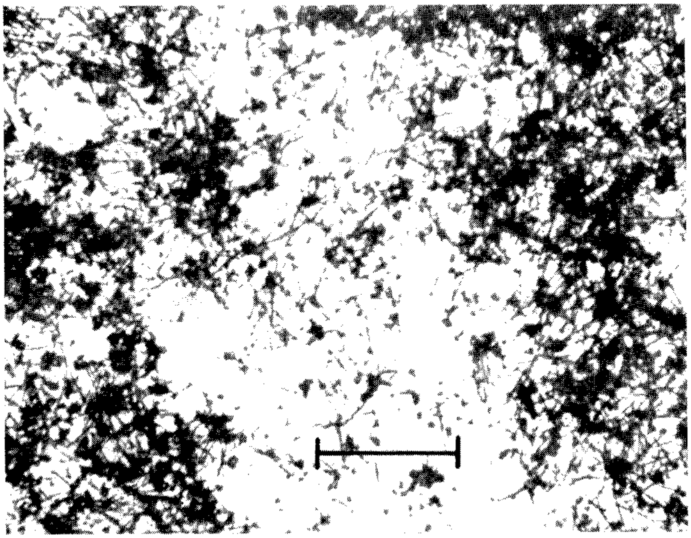

Fig. 1.—Copper 8-hydroxyquinolate produced by direct addition. (Distance shown is 0·1 mm.)

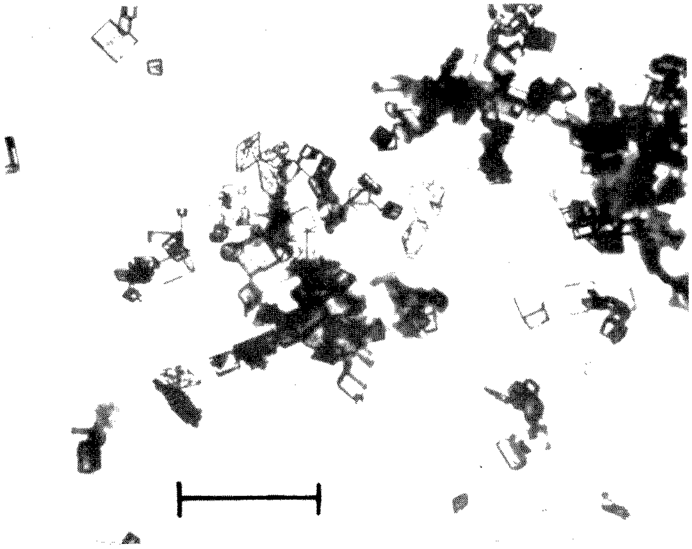

Fig. 2.—Copper 8-hydroxyquinolate produced by solvent evaporation. (Distance shown is 0·1 mm.)

The nature of this colour change has not been investigated further, but it has been shown that under the drying conditions employed all precipitates were yellow-brown after drying and that there was no significant difference in the weights of the dried materials.

As was noted in the case of the magnesium 8-hydroxyquinolate, this great alteration in the final appearance of the precipitate was not accompanied by the appreciable induction period before the first visible precipitate is formed which is usually noted with methods of precipitation from homogeneous solution. In none of the solvent systems investigated was the time required for the formation of the first visible precipitate more than 5 min.

It was also observed that in those solutions which contained a high concentration of added salt a small volume of a separate phase would form during the early portion of the heating period. This second phase always disappeared during the first hour of heating and the precipitates obtained from these samples were not detectably different from others in which the phase separation had not occurred.

CONCLUSIONS

The slow evaporation of acetone and chloroform from an aqueous solution containing copper and 8-hydroxyquinoline is an effective method of producing large crystals of copper 8-hydroxyquinolate. The technique may be employed for the gravimetric determination of copper or for the quantitative separation of this ion from the solution.

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Zusammenfassung—Die Methode der Fällung aus Lösungsmittelgemischen wurde auf Kupferoxinat angewendet. Wenngleich die Zeit bis zum Erscheinen der ersten, sichtbaren Partikel sehr kurz ist, werden doch grosse, wohlausgebildete und sehr regelmässige Kristalle erhalten. Die Methode wurde auf die Bestimmung von 3–30 mg Kupfer angewendet und erbrachte gute Trennung von Calcium, Magnesium und Blei.

Résumé—La technique de précipitation à partir de solvants mixtes a été appliquée à l'oxinate de cuivre. Bien que la formation d'un précipité visible à l'oeil soit très rapide, les cristaux obtenus sont gros, bien formés et très réguliers. La méthode est applicable au dosage d'échantillons renfermant de 3 à 30 mg de cuivre et la séparation de calcium, de magnésium et de plomb est bonne.

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SEPARATION OF SILVER, LEAD AND MERCURY$^{\text{II}}$ BY ION-EXCHANGE CHROMATOGRAPHY

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Summary—A method has been developed for the ready separation of silver, lead and mercury$^{\text{II}}$ from each other by ion exchange chromatography. Lead is eluted with 0·25*M* ammonium acetate, then silver, and finally mercury$^{\text{II}}$ with 0·5*M* and 4*M* ammonium acetate, respectively.

Because of growing interest in the separation of heavy metals, particularly by ion exchange chromatography, the separation of silver, lead and mercury$^{\text{I}}$ has received considerable attention from analytical chemists. Silver, lead and mercury are members of the same group in the classical scheme of qualitative analysis. In analytical mixtures as well as in some ores and industrial products, however, mercury$^{\text{II}}$ is usually encountered so that the separation of silver, lead and mercury$^{\text{II}}$ deserves prior consideration from the point of view of quantitative work. The technique of ion exchange chromatography appeared particularly attractive for a clean-cut separation of mixtures of this type. A method has been developed for ready separation of silver, lead and mercury$^{\text{II}}$ in their mixtures at the milligram level, based on their differences in ion-exchange potential on a cation exchanger, Dowex 50W-X8 (hydrogen form). No such work has been reported so far in the literature.

Kemula and coworkers[1] developed a procedure for the separation of silver from copper based on the adsorption of both ions on the cation exchanger, Wolfatit KPS-200. Copper was eluted as the complex $CuCl_4^{-2}$ by hydrochloric acid while silver was precipitated on the column. Majumdar and De[2] described a method for the separation of strontium from silver on Dowex 50W-X8 (50–100 mesh) by selective elution with 4*M* nitric acid.

EXPERIMENTAL

Apparatus

A burette, 0·8 cm in diameter, with sintered glass at the lower end, was used as the ion exchange column, the rate of flow of the solutions being regulated by adjusting the stopcock. A small funnel was attached to the top of the tube for pouring in resin and the solutions.

Reagents

Silver nitrate solution (*ca.* 5 *mg of silver*/*ml*): 4·5 g of silver nitrate (E. Merck) were dissolved in 500 ml of distilled water and the solution was standardised by thiocyanate titration with iron$^{\text{III}}$ alum as indicator.[3]

Mercury$^{\text{I}}$ *nitrate solution* (*ca.* 5 *mg of mercury*$^{\text{II}}$/*ml*): 5·6 g of mercury$^{\text{II}}$ nitrate (E. Merck) were dissolved in 500 ml of distilled water, 0·5*M* in nitric acid. The mercury content was determined by thiocyanate titration with iron$^{\text{III}}$ alum as indicator.[3]

Lead nitrate solution (*ca.* 5 *mg of lead*/*ml*): 3·99 g of lead nitrate (Merck and Co., Inc., Rahway, N.J., U.S.A.) were dissolved in 500 ml of water. The solution was standardised iodometrically.[4]

Ion exchange resin: Dowex 50W-X8 (Dow Chemical Co., Midland, Mich., U.S.A.), hydrogen form, 100–200 mesh, was used. The resin was conditioned, *etc.*, as described previously.[5]

All other reagents were either chemically pure or reagent grade chemicals.

Basis of separation

Preliminary quantitative studies on the ion exchange behaviour of silver with nitric acid, sulphuric acid and ammonium acetate are summarised in Table I. The elution constants were calculated as before.[2] Two hundred ml of nitric acid (1–2*M*), sulphuric acid (0·5–1·5*M*) or ammonium acetate (1–2*M*) are adequate for the quantitative removal of *ca.* 30 mg of silver from the resin bed. Organic solvent eluants like butyl alcohol, ethyl acetate, and a mixture of ethyl acetate and butyl alcohol failed to give a satisfactory elution of silver.

TABLE I.—ION EXCHANGE BEHAVIOUR OF SILVER
(Dowex 50W-X8, 100–200 mesh, 0·8 × 20·5 cm)

Eluant, *M*		Silver recovery, %	Elution constant
HNO_3:	0·5	82·2	0·05
	1·0	98·5	0·11
	2·0	101·4	0·22
H_2SO_4:	0·5	98·3	0·06
	1·0	101·4	0·11
	1·5	102·8	0·14
CH_3COONH_4:	0·25	72·6*	0·03
	0·5	87·7	0·06
	1·0	102·8	0·11
	2·0	101·3	0·11

* Elution with 400 ml of eluant.

The separation of silver, lead and mercury^{II} is based on the difference in their distribution coefficients or elution constants with respect to ammonium acetate. From the data in Table II it follows that of the two common eluting agents, nitric acid and ammonium acetate,[5,6] the latter is preferable in view of the more favourable separation factors. With 0·25*M* ammonium acetate a good separation factor is provided for silver-lead and also for lead-mercury. It was observed that 300 ml of 0·25*M* ammonium acetate eluted lead alone—the effluent was free from silver and mercury. Further, 0·5*M* ammonium acetate offers a good separation of silver from mercury—150 ml of this eluant removed silver alone and the effluent was free from mercury. Finally, mercury^{II} was removed from the resin bed by 100 ml of 4*M* ammonium acetate.

TABLE II.—SEPARATION FACTORS FOR SILVER-LEAD-MERCURY

Eluent, *M*		Elution constant			Separation factor	
		Ag	Pb	Hg	Pb/Ag	Pb/Hg
CH_3COONH_4:	0·25	0·03	0·11	v.s.^{a}	3·7	Large
	0·5	0·06	0·22	v.s.^{a}	3·6	Large
	1·0	0·11	0·39	v.s.^{a}	3·5	Large
	2·0	0·11	0·39	v.s.^{b}	3·5	Large
HNO_3:	0·5	0·05	v.s.^{a}	v.s.^{a}	Small	Small
	1·0	0·11	v.s.^{c}	0·24	Small	Small
	2·0	0·22	0·39	0·58	1·8	0·7

[a] No elution up to 200 ml.
[b] 26·2% recovery (200 ml elution).
[c] 15% recovery (200 ml elution).
v.s. = very small.

Procedure

The solution containing a synthetic mixture of silver, lead and mercury in different proportions was passed through the resin bed at the rate of 1 ml/min, then the sample container was rinsed with two 10-ml portions of water at the same flow rate. Lead was first eluted with 300 ml of 0·25*M* ammonium acetate and the effluent saved for determination of lead iodometrically. Next silver was removed by elution with 150 ml of 0·5*M* ammonium acetate and finally mercuryII with 100 ml of 4*M* ammonium acetate. Silver and mercury were determined in their respective effluents by direct titration with ammonium thiocyanate using iron^{III} alum as indicator.

The results in Table III are reproducible to within ±2%. Fig. 1 gives further proof that ammonium acetate can be used for the selective elution and ready separation of silver, lead and mercury. The method can be adapted for large-scale separations using larger columns.

TABLE III.—ION EXCHANGE SEPARATIONS OF SILVER, LEAD AND MERCURY^{II}

No.	Taken, *mg*			Recovered, %		
	Ag	Pb	Hg	Ag	Pb	Hg
1	6·1	11·9	29·6	99·5	101	100·8
2	6·1	29·8	59·2	100·5	101	98
3	12·1	11·9	29·6	102·8	98·1	98·5
4	30·2	29·8	59·2	101·3	102	98·7

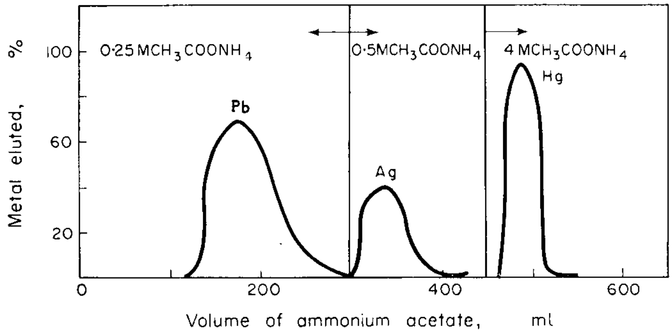

FIG. 1.—Ion exchange separation of silver, lead and mercury^{II}.

Acknowledgements—The authors thank the Council of Scientific and Industrial Research, India, for financial assistance and Dow Chemical Co., Midland, Michigan, U.S.A., for the gift of the resin.

Zusammenfassung—Eine neue Methode zur Trennung von Silber, Blei und Quecksilber(I) mittels Ionenaustauschchromatographie wurde entwickelt. Blei wird zuerst mit 0.25 n Ammoniumazetat, Sodann Silber mit 0.5 n Ammoniak und schliesslich Quecksilber mit 4 n Ammoniak eluiert.

Résumé—Une nouvelle méthode de séparation rapide de l'argent, du plomb et du mercure(II) par échange d'ions a été mise au point. Le plomb, l'argent et le mercure(II) sont successivement élués par des solutions d'acétate d'ammonium 0,25, 0,5 et 4 N respectivement.

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LIQUID SCINTILLATION COUNTING OF PLUTONIUM-239 FROM BIOLOGICAL SAMPLES*

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Summary—The conditions for the measurement of plutonium-239 activity from biological samples by liquid scintillation counting have been determined. It has been found that considerable quantities of iron may be tolerated in the final counting solution if phosphoric acid is added to form a colourless complex. Appreciable quantities of plutonium are adsorbed on the counting bottle when perchloric acidis used, and again the addition of phosphoric acid eliminates the difficulty by complexing the plutonium.

STUDIES which required a knowledge of the plutonium contents of all tissues, organs and excreta from animals exposed to a plutonium aerosol necessitated first the solution of several analytical problems among which was that of the actual measurement of the activity. The usual method for counting plutonium-239 consists of evaporation of a small amount of solution containing the plutonium in a contaminant-free solution on a planchet, firing to remove any organic material and then counting.[3] This method requires a very complete separation of the plutonium, and only a fraction of the final sample is counted. Furthermore, it was found that the firing step often caused some of the plutonium to become air-borne.

The relative ease with which a liquid scintillation counter can be used to count soft β-particles suggested its use for the α-particles. Horrocks and Studier[1] have described the use of liquid scintillation counting to measure the plutonium-241 (a low energy β-emitter) content in a mixture of other plutonium isotopes from the Chalk River pile. Although their primary interest was in the β-emitter, they give an α-spectrum, and mention that the α-particles are counted with 100% efficiency in their system, which was a dibutyl phosphate solution of the plutonium in the scintillator.

In the present work, the three solvent-single phase system of aqueous solution-ethyl alcohol-toluene solution of the scintillator was used.

Instrument

A commercially available coincidence-type liquid scintillation spectrometer (Technical Measurements Corporation Liquid Phosphor Counter Model LP-1) was used.

Scintillator solution

The scintillator solution was made up as follows: 0·050 g of 1,4-di-2-(5-phenyloxazolyl)-benzene (POPOP) was dissolved in a small amount of toluene with gentle heating, and then 4·0 g of 2,5-diphenyloxazole (POP) were added together with sufficient toluene to make a total volume of 1 litre.

Sampling

The samples were contained in commercially available bottles (Owens-Illinois 10 dram Opticlear Snap Cap Vials). The solutions were made by placing 1 ml of the aqueous sample solution in the

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* This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

bottle, followed by 10 ml of absolute alcohol and 10 ml of the scintillator solution. A perfectly clear single-phase system resulted.

Operating conditions

The operating conditions to be fixed in the instrument consisted of the window adjustments (the lower and upper voltages of the analyser) and the voltage. Fig. 1 shows the effect of varying the high voltage at a fixed window. The blank reading was essentially constant from 950 to 1050 v (approx. 70 cpm) and rose slightly at 1100 v. Fig. 2 shows the effect of varying the window at a fixed voltage. The counting rates reached essentially the same plateau for the lower window edge settings of 3 and 4, and a slight decrease was noted as the lower window edge was increased to 5 and 6. The curves indicated a voltage between 975 and 1050 v, with the lower window edge between 3 and 4 and the upper window edge between 40 and 60, to be satisfactory.

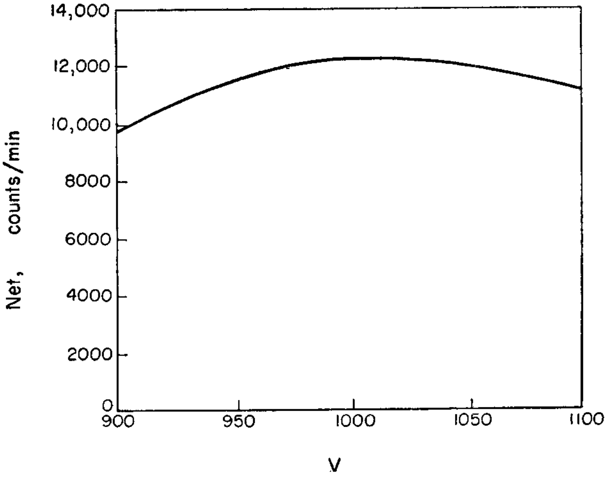

FIG. 1.—Variation of counting rate with voltage at a fixed window.

EXPERIMENTAL

In order to obtain accurate reproducible counts by the liquid scintillation method, it is essential that the final counting solution be colourless. In the separation scheme developed,[5] an anion-exchange column was utilised to absorb the plutonium from a strong hydrochloric acid solution. Iron was the only ion of any consequence to accompany the plutonium on and off the column, and posed a problem because of its colour in most solutions. Furthermore, small amounts of organic matter were also eluted from the column and caused interference unless removed. The organic matter was oxidised by evaporating with concentrated nitric acid. Instead of introducing an extra step to remove the iron, it was successfully complexed to form a colourless ion by using phosphoric acid.

Effect of type of acid

Preliminary work with the counting was done with perchloric acid because of its non-complexing nature. When standards were freshly prepared, there was no difference in measured activity from 1–4M acid solutions. Attempts to duplicate standards at several-day intervals yielded erratic results which were much lower upon standing. The results suggested adsorption of the plutonium on the counting bottle, because any plutonium thus adsorbed would contribute only half its disintegrations to the count. To check this possibility, a solution in which the count had decreased was discarded, the bottle was rinsed with alcohol, and was then made up for counting by adding perchloric acid and phosphor solutions. The last solution was again discarded, and the addition of acid and phosphor solutions were repeated. The results are shown in Table I.

Significant adsorption on the bottle was indicated, and a calculation from the counts obtained after the first treatment showed that the adsorption was approximately 23 % of the total activity in the bottle.

The plutonium in a perchloric acid solution is multi-positively charged and predominantly in the quadrivalent form.[2] Adsorption would be decreased by decreasing the positive charge, and the most obvious method would be to complex the plutonium with negative ions. Chloride, nitrate, sulphate, EDTA, and phosphate are all known complexers of plutonium.[4] The previous adsorption experiment was repeated using hydrochloric acid. Virtually no activity was left in the bottle after the original counting solution was discarded, indicating that no adsorption took place from a hydrochloric acid solution. A subsequent criterion for adsorption was a determination of the decrease in count after the solution made up for counting had stood overnight.

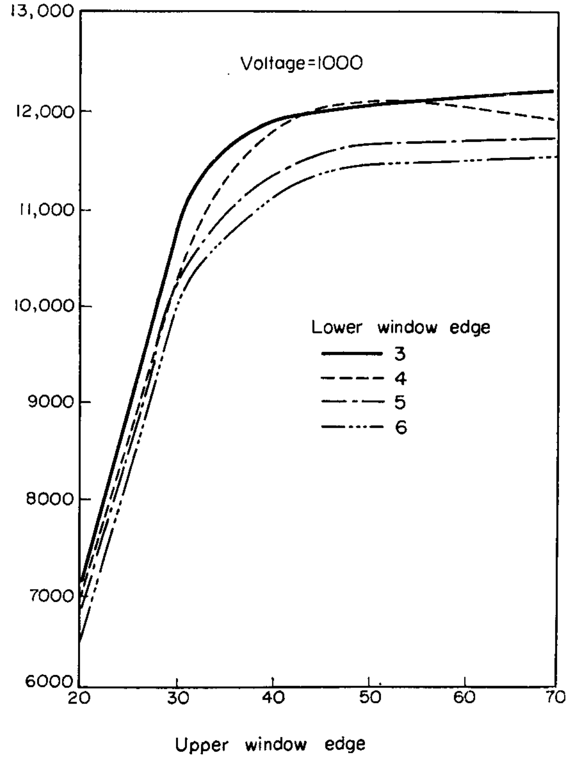

FIG. 2.—Variation of counting rate with window adjustment at fixed voltage.

TABLE I.—ADSORPTION OF PLUTONIUM FROM PHOSPHOR SOLUTIONS CONTAINING PERCHLORIC ACID

Sample No.	% of Original count after	
	1st Treatment	2nd Treatment
1	20·0	6·8
2	15·9	8·9

Because iron accompanied the plutonium in the separation scheme used,[5] its presence in the final counting solution produced complications because of its colour. Iron was added to various samples to note its effect on the counting rate. Hydrochloric acid and disodium EDTA solutions were satisfactory solvents in the absence of iron, but in the presence of 1 mg of iron, considerable quenching occurred in both cases because of the colour. Sulphuric acid and phosphoric acid both produced colourless solutions in the presence of iron. Sulphuric acid solutions gave approximately the same counts in the presence or absence of iron, but these counts, though steady, were several per cent lower than the standard. The most satisfactory acid for taking up the plutonium samples was phosphoric acid. Strengths of 1, 2 and 3*M* acid solutions gave identical, steady results in the absence or presence of 1 mg of iron.

Effect of temperature

As the sample chamber was placed in a freezer kept at −13°, the effect of temperature equilibration on the counting rate was determined. A blank sample showed no more than the usual variation in comparing the counting rate immediately upon placing in the chamber and after 90 min. A plutonium sample with an activity of approximately 12,000 cpm showed an increase of about 2% within the first 5 min and then maintained a steady rate for the balance of the 90-min test. The counting rates were exactly the same at window settings of 4 and 50 and at 3 and 60.

Procedure

Transfer a suitable volume of sample containing plutonium (entire elution from column may be utilised if suitably reduced in volume first) into the counting vial. Evaporate to dryness, and ash with concentrated nitric acid if any organic matter is indicated. To the dry bottle add exactly 1 ml of 3*M* H_3PO_4, heat gently, cool and add 10 ml of absolute alcohol and 10 ml of phosphor solution. Place the vial in the freezer containing the counter chamber for at least 5 min to permit temperature equilibration before counting.

DISCUSSION

The first advantage of a liquid scintillation method for counting plutonium is its high efficiency. Horrocks and Studier[1] have mentioned that they counted the α-activity of plutonium with 100% efficiency. Fig. 2 of the present paper shows that a plateau was reached and no further counts were obtained upon increasing the window. These results indicate that essentially 100% efficiency was obtained in the present work.

The fact that considerable amounts of iron may be tolerated because of the formation of a colourless complex with phosphoric acid permits the use of a simpler separation scheme for the plutonium, and thereby saves considerable time. The procedure utilised here permits great versatility in the size of sample counted, varying from a small aliquot to the entire sample as dictated by the amount of activity.

It was a distinct surprise to find adsorption of the plutonium on the counting bottle surface from a strong acid solution, and the reasons indicate that other multicharged ions should be similarly considered.

Zusammenfassung—Die Bedingungen für die Messung von Plutonium 239 in biologischem Material durch Zintillationszählung wurden studiert. Es wurde gefunden, dass beträchliche Mengen an Eisen in der Probelösung toleriert werden können, wenn Phosphorsäure zugesetzt und so das Eisen in einen farblosen Komplex übergeführt wird. Erheblich Mengen von Plutonium werden im Zählgefäss adsorbiert, wenn in perchlorsaurer Lösung gearbeitet wird. Auch in diesem Falle schafft Phosphorsäure Abhilfe durch Komplexieren des Plutoniums.

Résumé—Les auteurs ont précisé les conditions de la mesure de l'activité du plutonium 239 dans les milieux d'origine biologique au moyen des scintillateurs liquides. Des quantités considérables de fer peuvent être tolérées dans la solution si l'on ajoute de l'acide phosphorique pour former un complexe incolore. Des quantités appréciables de plutonium sont adsorbées sur les parois du récipient si l'on utilise de l'acide perchlorique; cette difficulté est eliminée par addition d'acide phosphorique qui complexe le plutonium.

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THE SEPARATION AND DETERMINATION OF PLUTONIUM IN DIVERSE BIOLOGICAL SAMPLES*

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Summary—A greatly simplified separation scheme for plutonium in biological samples has been devised. It is based on the absorption of an anionic form of quadrivalent plutonium in a strong hydrochloric acid solution by a strong base anion-exchange resin. The greatest difficulty in obtaining complete recovery from some samples was in getting the sample completely dissolved. For the acid-insoluble portion of samples such as faecal ash, it was necessary to resort to carbonate and bisulphate fusions. Elution from the ion-exchange column was accomplished with sulphurous acid, and the final determination was made by liquid scintillation counting.

INTRODUCTION

IN a study in which dogs were exposed to an aerosol containing plutonium, the entire animal and its excretory products were to be analysed for plutonium. Although this element is entirely radioactive, its determination through radioactivity measurements is difficult because the disintegrations yield primarily α-particles. The accurate measurement of α-particles, especially in low activities, necessitates the isolation of the element. Where plutonium analyses are done on a routine basis, an elaborate separation scheme is employed to isolate the element before counting.[1] In our laboratory such a separation scheme yielded an average recovery of 80% (with rather wide limits) from spiked bone and urine samples. Following the same procedure for ashed faecal samples resulted in extremely low recoveries (less than 5%).

The present work was undertaken to devise a separation scheme which would isolate the plutonium with uniform completeness from all types of samples, in as simple a manner as possible. The separation scheme turned out to be simplicity itself, but the recoveries were contingent upon solubilising the plutonium in the various samples, the difficulty of which varied considerably with the nature of the sample. The biological sample which contained by far the greatest portion of the administered plutonium was the faeces, which required drastic measures for complete solution.

EXPERIMENTAL

Solution and distribution in ashed samples

One of the usual procedures for plutonium analysis[1] stipulates solution of an ashed sample in 2*N* nitric acid, but such a procedure does not dissolve completely or solubilise all the plutonium in some samples. In the present work, 8*N* hydrochloric acid was used to take up ashed samples (either wet- or dry-ashed) as the first step in the separation scheme. Such a solution completely dissolved ashed soft tissues, urine and bone. However, for ashed faeces both 2*N* nitric and 8*N* hydrochloric acids left a considerable amount of insoluble material. Furthermore, the acid extract contained only a small

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* This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

fraction of the activity. In order to put the insoluble material into solution, it was necessary to fuse the material in a platinum dish with a sodium-potassium carbonate mixture and separate the fusion mixture into a water extract, an acid-soluble portion and a small insoluble portion. The last portion, together with a stain in the platinum dish, was dissolved in water after prior fusion with sodium bisulphate. Table I shows the distribution of plutonium in two typical samples of ashed faeces.

TABLE I.—DISTRIBUTION OF PLUTONIUM IN FAECAL ASH

Treatment	Activity, % Sample 1	 Sample 2
2*N* HNO_3 extract	3·32	3·96
Water extract of carbonate fusion	14·4	14·6
HCl extract of carbonate fusion	80·5	84·0
Bisulphate fusion of residue	1·79	0·57

The original ashed faecal samples contained appreciable quantities of silica from the diet, and it was thought that the acid-insoluble portion of the plutonium was contained in some insoluble calcium silicate. The silica was removed with hydrofluoric acid, and the samples were evaporated with sulphuric acid to remove the fluoride. The insoluble solid remaining after such treatment yielded the results in Table I. From such treatment, the insoluble ash would be expected to be largely calcium sulphate, and it was of interest to determine whether a calcium sulphate precipitated from an acid solution containing plutonium would behave similarly. Plutonium was added to a solution of calcium nitrate, and calcium sulphate was precipitated by addition of sulphuric acid. The water was evaporated and the remaining solid was placed in a muffle furnace at 500° overnight. The solid was treated similarly to a faecal ash, and the distribution of the activity is shown in Table II.

TABLE II.—DISTRIBUTION OF PLUTONIUM IN CALCIUM SULPHATE

Treatment	Activity, % Sample 1	 Sample 2
8*N* HCl extract	17·5	13·8
Water extract of carbonate fusion	5·6	13·4
HCl extract of carbonate fusion	75·5	71·2
Bisulphate fusion of residue	1·8	1·8

In order to prevent reprecipitation of calcium sulphate, it was necessary to separate the water-soluble portion of the carbonate fusion from the acid-soluble portion. Although the acid extract of the solid before the carbonate fusion contained more activity than the acid extract of the faecal ash sample (this may be through the use of a stronger acid), it is interesting to note that the bulk of the activity remained in the water-insoluble portion of the carbonate fusion. Both the acid treatment of the original ash and the water extraction of the carbonate fusion indicate that the bulk of the plutonium activity remains with the insoluble portion of the precipitate. Therefore, in order to obtain complete recoveries of plutonium in a separation scheme, it is necessary to devise some scheme whereby the sample is completely in solution in some step.

Separation scheme

The presence of large amounts of phosphate in biological samples makes extraction with tributylphosphate, thenoyltrifluoroacetone, and acetylacetone incomplete. Wish and Rowell[6] have shown that an anionic complex of plutonium is absorbed very strongly on Dowex 2 x 8 resin from a strong hydrochloric acid solution. Such a system would be ideal for biological samples because the strong acid would be a good solvent for ashed samples, and would repress the ionisation of phosphoric acid to such an extent that it would not complex plutonium. Furthermore, in samples such as faeces where the insoluble residue must be treated to give separate soluble fractions, these separate fractions may be passed through a single ion-exchange column separately for collection of all the plutonium which may be subsequently eluted. Of the other metals which form anionic chloride complexes,[2] iron is the only one of any consequence which accompanies the plutonium on and off the ion-exchange column.

If iron must be removed, an additional step involving the use of a mercury cathode[5] or an extraction of the plutonium with thenoyltrifluoroacetone[3] may be employed. In the present work it was found that considerable quantities of iron could be tolerated in the liquid scintillation counting method if phosphoric acid were used as the solvent.

The plutonium contained in any sample which is completely soluble in 8*N* hydrochloric acid may be absorbed on Amberlite XE-117 resin by passage through a column of appropriate size. For urine and soft tissue samples which do not contain much iron, 4 g of resin were sufficient to absorb all the plutonium; for faecal samples and food samples, 16 g of resin were sufficient; and for bone, liver and spleen, an 8-g column sufficed.

Solutions

Saturated sulphurous acid solution: Pass SO_2 gas into de-ionised water until saturated. The solution should be made freshly each day.

Concentrated HCl: Make up in the proportion of 80 ml of concentrated acid to 2 ml of concentrated nitric acid.

8*N HCl:* Make up in the proportion of 100 ml of 8*N* (2 volumes concentrated acid to 1 volume water) acid to 2 ml of concentrated nitric acid.

Column preparations

The resin used in the present work was Amberlite XE-117, 50-100 mesh, which Rohm and Haas has stated is the same as their commercial IRA-400 anion-exchange resin. For samples containing large amounts of absorbable ions such as iron, or large amounts of ions complexing plutonium such as phosphate, greater quantities of resin were used. The columns were of borosilicate glass with sintered discs to support the resin and with Teflon stopcocks. The sizes of the columns were as follows: for 4 g of resin a 10-mm i.d. column, for 8 g of resin a 15-mm column and for 16 g of resin a 19-mm column.

Pass through the column of appropriate size, successively, 50 ml of sulphurous acid, 50 ml of water, 80 ml of concentrated HCl, and 100 ml of 8*N* HCl solutions.

Preparation of plutonium samples

Faeces: The suitably ashed sample should be essentially dry for the following treatment:

(*a*) *Acid-soluble portion:* Add 100 ml of 8*N* HCl to the ashed sample and filter through a Whatman No. 40 filter paper. Label the filtrate solution No. 1, and retain.

(*b*) *Carbonate fusion:* Transfer the above filter paper and precipitate to a platinum dish, dry and burn off the filter paper. Add 1–2 ml of hydrofluoric acid and about 5 drops of concentrated sulphuric acid. Evaporate until the fumes of sulphuric acid disappear. Add about 4 g of sodium-potassium carbonate mixture (equal parts by weight), cover the dish, and heat over a Meker burner until the mixture is melted, rotating the dish to make certain that all the ash is in contact with the carbonate. After the mixture has cooled sufficiently, add water and warm until the cake has disintegrated. Filter through a Whatman No. 40 filter paper and wash several times with water. Neutralise the filtrate with hydrochloric acid and evaporate to near dryness. Add sufficient 8*N* HCl solution to dissolve all the solids, and label this solution No. 2.

The insoluble residue from the fusion is treated as follows: Add 8*N* HCl to the platinum dish and pass through the filter paper to dissolve the insoluble carbonates. Evaporate this solution to near dryness and add sufficient 8*N* HCl to dissolve all the solids. Label this acid-soluble filtrate No. 3.

(*c*) *Bisulphate fusion:* Place the previous filter paper in the platinum dish, dry and burn off the paper. Add a small amount of sodium bisulphate and heat over a burner until the fumes disappear. Cool and add a small amount of water to dissolve the cake. Add sufficient concentrated hydrochloric acid to make the final solution about 8*N*. Label this solution No. 4.

Urine: Because of the necessity of evaporating a large amount of liquid, the wet-ashing method is simplest in that borosilicate glass beakers may be used. The best method is to evaporate with concentrated nitric acid and a few drops of hydrogen peroxide repeatedly until the residue is white. Dissolve the ash in 100 ml of the 8*N* hydrochloric acid for addition to the ion-exchange column.

Bone: The simplest ashing procedure for bone is that of dry-ashing in a platinum dish at 500°. Dissolve the ash in the concentrated hydrochloric acid (100 ml of acid to 10 g of bone ash) for addition to the ion-exchange column.

Liver, spleen and other soft tissues: Dry-ashing in a platinum dish is the simplest procedure. Dissolve in the concentrated hydrochloric acid solution before addition to the column.

Absorption on column

Faeces: Add the various solutions from the complete treatment of the faecal ash to a 16-g pretreated column in the following order:

No. 1 Original hydrochloric acid soluble

No. 4 Solution from bisulphate fusion
No. 2 Water-soluble carbonate fusion
No. 3 Acid-soluble carbonate fusion

After each solution has been passed through the ion-exchange column, wash the column with several resin volumes of 8*N* hydrochloric acid before passing through the next solution.

Bone, liver and spleen: Add the solutions of the ashed samples to an 8-g pre-treated column and wash the column with 8*N* hydrochloric acid solution.

Urine and other soft tissues: Add the solutions of the ashed samples to a 4-g pre-treated column and wash the column with 8*N* hydrochloric acid solution.

Elution

Pass 100 ml of saturated sulphurous acid solution through the column and collect in a beaker. Evaporate the solution until the volume has been reduced sufficiently to transfer to a counting bottle, and continue evaporation until dry. If any organic matter is indicated, ash with concentrated nitric acid.

Counting

The details of the liquid scintillation technique have been described elsewhere.[4] To the dry bottle add exactly 1 ml of 3*M* H_3PO_4, heat gently, cool and add 10 ml of absolute alcohol and 10 ml of phosphor solution. Place the vial in the freezer containing the counter chamber for at least 5 min to permit temperature equilibration before counting.

Recovery results from various samples spiked with plutonium are shown in Table III.

TABLE III.—RECOVERY OF PLUTONIUM FROM VARIOUS SAMPLES

Type	Recovery, %
Faeces	101
	100·6
Dog diet	95·7
	99·9
Urine	101
	95
	101
	99·9
Bone	96
	94
	96
Liver	96·2
	98·4
Spleen	96·0
	97·6
	98·2

DISCUSSION

Wish and Rowell[6] studied the absorption of plutonium on an anion-exchange column, and they indicate the importance of keeping the plutonium in the quadrivalent state. In order to do this a small amount of nitric acid is added to the hydrochloric acid. The absorption of plutonium continues to increase as the hydrochloric acid concentration is increased, but the distribution is already heavily in favour of the resin at 8*N*. The use of 8*N* acid for biological samples is indicated because of two circumstances. In the initial acid treatment of the faecal ash, a large amount of the ash (but not a large fraction of the plutonium) is acid-soluble, and the insoluble residue must be removed by filtration. The concentrated acid caused disintegration of the filter paper whereas the 8*N* acid did not. In samples such as urine, which contain a large amount of sodium chloride, the solubility is greater in $8N$ acid than in $12N$ acid because of the lesser quantity of the common ion chloride.

The ion-exchange separation scheme is considerably shorter than the usual method[1] of bismuth phosphate and lanthanum fluoride co-precipitations with thenoyltrifluoroacetone extraction. For samples requiring fusion for complete solution, the separate fractions may be passed through the same ion-exchange column successively, thereby collecting all the plutonium on one column. The sulphurous acid elution probably works in the dual fashion of reducing the plutonium to some extent, as well as destroying the chloride complex through dilution. It has the further advantage of leaving essentially no residue when the solution is evaporated for counting. In a number of samples the sulphurous acid eluate was collected in successive portions of about 35 ml to determine the rate of elution. Even from a 16-g column almost all the activity was contained in the first two fractions.

The liquid scintillation[4] method for counting has several advantages. The counting efficiency is essentially 100%, and either the whole sample or an aliquot may be counted in the present procedure. The first step of the old method of counting plutonium consisted of evaporating a small aliquot on a planchet, drying and firing to remove any organic matter. In our experience this procedure often rendered some of the plutonium airborne and raised the background of the counting room.

The separation scheme described here is not entirely specific for plutonium,[6] but in the type of experiment for which it was devised the selectivity is adequate. If one were interested in extremely low-level quantities the amount of naturally occurring activity would be of interest. Therefore, samples of tissues and excreta from a dog which had not been exposed to plutonium were run through the separation scheme. A rough measurement was made of the activity which is not measured as plutonium (activity which is not retained on the ion-exchange column). Because of the large salt content of this portion, accurate liquid scintillation counting was not possible. The results are shown in Table IV.

TABLE IV.—ACTIVITY IN AN UNEXPOSED DOG

Sample	Weight, *g*	Activity in sample, *cpm* Through column	Activity in sample, *cpm* Retained on column
Lung lobe A	5·0	22	13
B	8·5	38	1
C	14·7	48	16
Bone: Rib	43·3	131	8
Thigh	141·5	115	48
Skin	155	0	13
Liver	106·6	107	12
Urine	(12 hr)	334	0
Faecal	(12 hr)	931	36

Although significant quantities of activity were found in the portion which ran through the column, these amounts are in line with those found by Hursh[7] for ^{40}K activity in man. The especially high count for the faecal sample is the result of the use of potassium carbonate for fusion of the insoluble residue. In view of the background count of 70–80 cpm, most of the activities retained on the column are hardly worthy of mention. The rather high level of the thigh bone was surprising. Not too many natural radioactive substances would be retained on an anion-exchange column, and the logical suspect would be uranium. By liquid scintillation counting, 1 μg of uranium gave a net count of approximately 1 cpm. This would give a figure of 0·34 μg per g of bone. Because of the unknown history of this one dog other than having no known exposure to plutonium, further speculation is unwarranted.

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Zusammenfassung—Eine wesentlich vereinfachte Methode zur Bestimmung von Plutonium in biologischem Material basiert auf der Adsorption von vierwertigem Plutonium in anionischer Form aus stark salzsaurem Medium an einem stark basischen Anionenaustauscher. Die grösste Schwierigkeit war die Probe komplet in Lösung zu bekommen. Für säureunlösliche Proben, wie z-B. Fäkalienasche, war Aufschluss durch Karbonat- oder Bisulfatschmelzen nötig. Eluierung von der Austauschersäule geschieht mit schwefeliger Säure. Die endgültige Bestimmung erfolgt durch Zählung in einem Flüssigkeits-Szintilationsrohr.

Résumé—Les auteurs ont mis au point une méthode de séparation très simplifiée du plutonium dans les milieux d'origine biologique. Elle est fondée sur la fixation d'un complexe anionque de plutonium(IV) en milieu acide chlorhydrique fort sur résine échangeur d'anions du type base forte. La plus grande difficulté rencontrée pour obtenir une récupération complète à partir de certains échantillons a résidé dans la dissolution complète de ceux-ci. Pour la partie insoluble dans les acides commes les cendres fécales, il a été nécessaire d'effecteur des fusions au carbonate et au bisulfate. L'élution sur colonne d'échangeur d'ions a été effectuée par de l'acide sulfureux et la mesure finale par comptage au moyen d'un scintillateur liquide.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF ZIRCONIUM IN IRON, COBALT AND NICKEL ALLOYS BY X-RAY FLUORESCENCE

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Summary—Microgram amounts of zirconium are separated from iron, cobalt and nickel alloys by precipitation with *p*-bromomandelic acid, following which the zirconium is determined by X-ray fluorescence. Replicate results are reported for metal samples containing 0·003-0·5% of zirconium. An evaluation of the accuracy of this procedure was made using National Bureau of Standards certified samples.

INTRODUCTION

TRACES of zirconium in iron, cobalt and nickel alloys have usually been determined by spectrophotometric methods; however, in highly alloyed samples an involved separation procedure must be undertaken before the zirconium is determined. The limit of detection for an emission spectrographic determination of zirconium in these materials is 0·01%, because interference by other elements prevents utilisation of the most sensitive lines.

The method herein proposed involves solution of the sample with nitric and hydrochloric acids, destruction of the nitric acid, and precipitation of the zirconium with *p*-bromomandelic acid. The precipitate is removed on a Millipore filter and measured by X-ray fluorescence. This procedure is rapid; only a partial separation of zirconium from alloyed elements is required; and the accuracy is equal to or better than that of spectrophotometric techniques, and is better than that of emission spectrographic methods. In addition, zirconium is differentiated from hafnium, which is not possible in most chemical procedures.

The gravimetric determination of zirconium using *p*-bromomandelic acid was first reported by Oesper and Klingenberg[1] and this technique has been widely used for macro amounts of zirconium and hafnium. More recently, Bricker and Waterbury[2] studied conditions for the precipitation of microgram quantities of zirconium with *p*-bromomandelic acid. In the laboratory of the present authors, laboratory conditions have been established for quantitative results with a single rather than a double precipitation, a shortened digestion time, filtration of the precipitate rather than centrifuging, and with a larger volume in beakers rather than in centrifuge tubes.

Salmon[3] and Gunn[4] reported the use of thin films for determining microgram amounts of elements by X-ray fluorescence. With the film thickness less than 0·005 inch, absorption and enhancement effects are negligible and a linear relationship exists between intensity and concentration. Salmon used thin sections of finely ground mineral materials between two sheets of Mylar film. Gunn was able to obtain good sensitivity for traces of several metals present in oils by evaporating an acid solution of the samples on filter paper and analyzing by X-ray fluorescence. It appeared to the present authors that filtration of precipitates would also provide suitable films.

Work in this laboratory has shown that proper precipitation of zirconium and filtration on a Millipore filter does yield thin films suitable for X-ray measurement. This not only increases the sensitivity of the X-ray method, but eliminates the need for separate sets of standards for each matrix of iron, cobalt or nickel.

APPLICABILITY

The procedure may be used to determine zirconium in any sample in which the major constituents are soluble in nitric and hydrochloric acids. Because of scattering and absorption of the X-rays, the highest accuracy is attained if acid-insoluble material accompanying the zirconium on the Millipore filter does not exceed 10 mg. In the presence of larger amounts of insoluble material a prior separation technique may be used, or a correction may be applied to the X-ray fluorescence analytical curve.

EXPERIMENTAL

Reagents and materials

The reagents used for this work were of reagent grade whenever available. Solid *p*-bromomandelic acid was obtained from A. D. MacKay, Inc., while Mylar film was purchased from DuPont. The Millipore filter pads were type HA with pore size of 0·45 μ and a diameter of 25 mm.

Apparatus

The X-ray fluorescence spectrometer was a Philips Electronics Bulk Spectrograph. Tungsten radiation with a lithium fluoride crystal was utilised. A Philips Electronics scintillation counter was used as the detector while the readout system was a Philips fixed-count scaler with an E.I.T. count register.

Separation of zirconium

A 0·1- to 1-g sample containing 30 to 700 μg of zirconium is placed in a 250-ml beaker, covered with a Speedyvap cover and dissolved by warming with 10 ml of hydrochloric acid and 5 ml of nitric acid. After the sample has evaporated to dryness it is cooled, treated with 6 ml of hydrochloric acid and carefully evaporated to moist dryness.

The salts are dissolved with 50 ml of water and 1 g of hydroxylamine hydrochloride is added plus 1 to 2 mg of paper pulp. The Speedyvap is replaced with a cover glass and the sample is heated to boiling. Three drops of 0·5% aerosol solution are added plus 10 ml of 0·1*M* *p*-bromomandelic acid, and the volume of solution is maintained at 50 ± 10 ml while the sample is boiled for 10 min. (If a red-brown precipitate forms during the digestion period this is dissolved by adding 1 or 2 g of hydroxylamine hydrochloride.) The sample is cooled to room temperature and the insoluble material is removed on a Millipore filter pad using vacuum filtration. The beaker and pad are washed with up to 50 ml of cool water containing a few drops of 0·5% aerosol solution.

The Millipore filter containing the zirconium precipitate is sandwiched between two sheets of 0·00025-inch Mylar film. A flat surface is obtained by stretching the Mylar film over a 30-mm plastic ring with a 25-mm aperture. An O-ring is placed over the outside surface of the plastic ring to maintain tautness.

Determination of zirconium

Excitation of the zirconium K-alpha spectrum is obtained by placing the precipitate side of the Millipore filter in the path of an X-ray beam emitted from a tungsten target X-ray tube operated at 50 KV and 45 MA. Samples and standards are diaphragmed to a 1-inch aperture. A small aluminum block is placed on the plastic ring opposite the precipitate side to prevent variation of the distance of the sample from the X-ray tube window caused by wrinkling of the Mylar around the edges of the plastic ring. Counts of 128,000—256,000 for the zirconium K-alpha peak position and 64,000 counts for background are used for fixed count operation. Each sample or standard is exposed twice. Exposure time is recorded at one sample position and then at 180° from the original position to decrease variation of X-ray intensity with surface roughness. Background counts/sec (taken at 23·80°, 2θ) are subtracted from peak counts/sec. The net counts/sec for both sample positions (0° and 180°) are averaged, and the amount of zirconium is determined by reference to an analytical curve. Synthetic standards, containing added quantities of zirconium, are used to plot the analytical curve which related Np (peak counts/sec) — N_B (background counts/sec) to μg of zirconium. The analytical curve is shown in Fig. 1. A high and a low standard are excited during each analysis to determine any shift of the analytical curve.

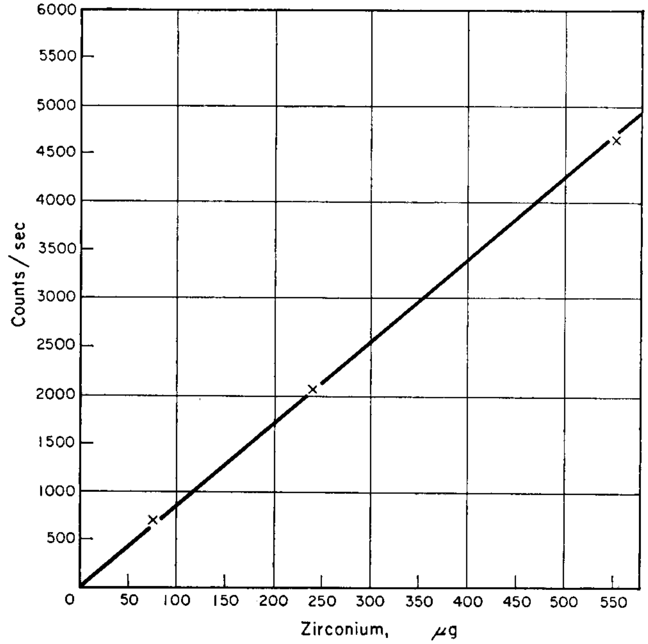

FIG. 1—Analytical curve for determination of zirconium.

DISCUSSION AND RESULTS

The precipitation of zirconium

Bricker and Waterbury[2] have studied factors in the precipitation of microgram quantities of zirconium with *p*-bromomandelic acid. They found that a hydrochloric acid concentration of 0·1 to 1·4*M* was satisfactory for the precipitation; however, the precipitate was slow to form and they recommend a 30-min digestion at 100° to ensure complete reaction. It was found in our laboratory that in the presence of paper pulp the digestion period can be shortened. Several portions of a solution prepared from an iron-base alloy were boiled for various periods, and gave zirconium recoveries as shown in Table 1. The results have an estimated standard deviation of 0·0005 %.

To reduce the solubility of the precipitate, the solution is cooled to room temperature before filtration. Precipitates from samples of another iron-base alloy were aged for periods ranging from 5 min to 24 hr before filtration. As is shown in Table II, this had no effect on the zirconium recoveries, and these results have a standard deviation of 0·0008 %.

Bricker and Waterbury[2] found it necessary to reprecipitate the zirconium in order

TABLE I.—THE EFFECT OF DIGESTION TIME ON THE PRECIPITATION OF ZIRCONIUM

Digestion time, *min*	Zirconium found, %
5	·016
10	·016
15	·016, ·015
30	·015, ·016

TABLE II.—THE EFFECT OF AGING OF THE PRECIPITATE ON THE RECOVERY OF ZIRCONIUM

Aging time	Zirconium found, %
5 min	·018, ·017
1 hr	·016, ·017
4 hr	·018, ·018
24 hr	·017, ·016

to remove contaminants which interfered in a spectrophotometric determination of the zirconium. Because moderate amounts of impurities have no effect on the X-ray fluorescence of zirconium a reprecipitation is unnecessary before using this procedure. It was found in our laboratory that zirconium recoveries were low after a reprecipitation of the zirconium, perhaps because of the slight solubility of zirconium *p*-bromomandelate.

Hydroxylamine hydrochloride is added to ensure complete destruction of nitrate before precipitation of zirconium. If a red-brown precipitate forms during the digestion period this can be dissolved by adding 1 or 2 g of hydroxylamine hydrochloride.

Interferences

If acid-insoluble materials are present in the samples to be analysed these will be removed with zirconium on the Millipore pad. Up to 10 mg of contaminants have little effect on the accuracy of the determinations; however, major amounts of titania, silica, niobium oxide, tantalum oxide or other acid-insolubles cause low results by absorbing and scattering the X-rays. The magnitude of this effect is shown by the results in Table III.

TABLE III.—THE EFFECT OF ACID-INSOLUBLE MATERIAL ON THE DETERMINATION OF ZIRCONIUM

	Zirconium content, %		
Sample No.	Certified value	Detnd. by X-ray	
Waspaloy 1192*	·027	·016	·016
Waspaloy 347*	·081	·060	·061
Nichrome 169*	·042	·038	·035

* National Bureau of Standards Waspaloy 1192 contains 2·72% titanium and 0·47% silicon; Waspaloy 347, 3·05% titanium and 0·29% silicon; and Nichrome 169, 1·42% silicon.

One method for eliminating the interference of coprecipitants is to add similar quantities of these elements to the standard samples used to establish the working curve. An alternative procedure is to remove the acid-insoluble elements before precipitation of the zirconium. The former approach will be less time consuming, especially if a large number of samples of approximately the same composition are to be analysed.

In order to determine if the zirconium had been incompletely separated from these samples, radiotracer studies were conducted with ^{95}Zr. A mixture of ^{95}Zr and ^{95}Nb isotopes was obtained from the Oak Ridge National Laboratory and the ^{95}Zr was removed from ^{95}Nb by the 2-thenoyltrifluoroacetone solvent-extraction technique described by Moore.[5] The tracer zirconium in chloride form was added to dissolved samples of Waspaloy and Nichrome which were then treated with *p*-bromomandelic acid in the usual manner. The tracer was satisfactorily recovered on the Millipore filter pad indicating that low results for these samples resulted from the zirconium measurement technique rather than from an incomplete separation procedure.

Accuracy and precision

An evaluation of the accuracy of this method for the separation and determination of zirconium was made by analysing standard samples from the National Bureau of Standards. Results obtained for the determination of zirconium in these materials are presented in Table IV.

TABLE IV.—THE ANALYSIS OF STANDARD SAMPLES FROM THE NATIONAL BUREAU OF STANDARDS

	Zirconium content, %		
Sample No.	Certified value	Detnd. by X-ray	
Low Alloy Steel 462	·063	·062	·061
Low Alloy Steel 464	·010	·0099	·0097
Synthetic Stainless Steel*	·029	·029	·029

* Composed of 42% N.B.S. Steel 464 and 58% N.B.S. Nichrome 169.

The results were fitted by standard procedures to the model $y = bx$, where y is the amount found, x is the certified N.B.S. value (assumed to be without error for this calculation) and b is the slope. The calculated estimate of b is 0·98 with a 95% confidence interval of 0·97–1·00. The estimated standard deviation for a single determination is 0·0006%.

The results appear to be slightly low, but when it is considered that the certified N.B.S. values also contain some error there is justification for considering the method to yield quantitative values over the comparison range. It is of interest to note that the results of Tables I and II yield estimated standard deviations of 0·0005% and 0·0008% respectively, which agree quite favorably with the 0·0006% calculated from the results of Table IV.

Several samples of iron-base and cobalt-base alloys were analysed in order to ascertain the precision of the X-ray fluorescence method for zirconium in concentration levels other than those reported in Tables I, II and IV. In most cases, replicate determinations were made on two or more days. Results are presented in Table V.

TABLE V.—THE DETERMINATION OF ZIRCONIUM IN IRON- AND COBALT-BASE ALLOYS

Material	Heat No.	Zirconium content, %
Kromarc.$^{(R)}$. 58 steel*	1	·0028, ·0031, ·0029, ·0029
Kromarc.$^{(R)}$. 58 steel*	2	·064, ·060
Nivco.$^{(R)}$. 10 alloy*	1	·21, ·21
Nivco.$^{(R)}$. 10 alloy*	2	·55, ·56

* Kromarc.$^{(R)}$. 58 steel contains 50% iron, 22% nickel, 15% chromium, 10% manganese and 2% molybdenum, while Nivco.$^{(R)}$. 10 alloy contains 75% cobalt, 22% nickel, and 2% titanium.

From these results it appears that a satisfactory precision is obtained for these other zirconium levels.

Zusammenfassung—Mikromengen Zirkonium werden von Eisen, Cobalt und Nickel in Legierungen durch Fällen mit p-Brommandelsäure abgetrennt. Das Zirkonium wird anschliessend durch Röntgenstrahlenfluoreszenz bestimmt. Mehrfachbestimmung werden für Proben mit 0,003–0,5% Zirkonium mitgeteilt. Eine Bewertung der Methode erfolgte auf Grund von Analysen von National Bureau of Standard Proben.

Résumé—Des quantités de zirconium de l'ordre du microgramme sont séparées d'alliages de fer, cobalt et nickel par précipitation par l'acide p.bromomandélique; le zirconium est ensuite dosé par fluorescence X. Des résultats sont donnés pour des échantillons métalliques contenant 0,003 à 0,5% de zirconium. Les auteurs ont évalué la précision de la méthode en utilisant des échantillons certifiés du "National Bureau of Standards".

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A NOMOGRAM FOR ACID-BASE TITRATIONS

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Summary—A mathematical treatment of acid-base titrations, based on the concept of conditional constants which is analogous to the treatment of complexometric titrations, is presented. Equations are derived for calculating the pH at the equivalence point, and the titration error when the end-point deviates from the equivalence point. The values of these quantities can be determined without complicated calculations from a nomogram included in the paper.

THE courses of acid-base titrations are illustrated by means of logarithmic diagrams in several textbooks.[1–3] Many problems associated with these titrations can be satisfactorily solved by reference to such diagrams. The courses of complexometric titrations of metals, on the other hand, are based on the use of so-called conditional constants[4,5] which are derived from stability (formation) constants with the aid of side-reaction coefficients (alpha coefficients).

In this paper a theoretical treatment of acid-base titrations is presented which is based on the use of conditional constants and side-reaction coefficients. Ringbom[6] has shown that every type of neutralisation reaction can be treated as a simple neutralisation of a monobasic acid (or a monoacid base) when the appropriate value of the conditional constant has been determined. This way of treating acid-base titrations offers a number of advantages when the titration system contains several acid-base systems. A complication associated with acid-base titrations that has to be taken into account is the ionisation of water.

In order to clarify the use of conditional constants in the treatment of acid-base titrations, we shall consider first the titration of a solution containing only one weak monobasic acid, HA_I, and then the titration of a solution containing two monobasic acids, HA_I and HA_{II}. Expressions will be derived that permit the calculation of the pH at the equivalence point of the titration and the error that results when the end-point of the titration differs from the equivalence point.

I. TITRATION OF A MONOBASIC ACID, HA_I

When a weak acid, HA_I, is titrated with an alkali metal hydroxide (a strong base), a hydroxo complex (a base) is produced in accordance with the equation

$$HA_I + OH^- \rightleftharpoons H_2OA_I^- \rightleftharpoons A_I^- + H_2O \tag{1}$$

The stability constant of the complex formed is defined by

$$K_{A_I}^{OH} = \frac{[A_I]}{[HA_I][OH]} = 1/k_{A_I} \tag{2}$$

where k_{A_I} is the basicity constant of the conjugate base of the acid ($pk_{A_I} + pk_{HA_I} = pk_w$; k_{HA_I} is the acidity (dissociation) constant of the acid, and k_w is the ionic product of water). The charges of the ions are omitted here and in the following discussion for the sake of clarity.

If we assume that no interfering side reactions take place in the solution, and denote by C_I the total concentration of the acid in the solution, the hydroxide ion concentration at the equivalence point where $[HA_I]_{eq} = [OH]_{eq}$ and $[A_I] \simeq C_I$ is given by

$$[OH]_{eq} = (C_I/K^{OH}_{A_I})^{\frac{1}{2}}, \tag{3}$$

and the hydrogen ion concentration by

$$[H_3O]_{eq} = (C_I/K^{OH}_{A_I})^{\frac{1}{2}}/K_W \tag{3a}$$

where $K_W = 1/([H_3O][OH]) = 10^{14}$.

The titration error can be read from the nomogram in Fig. 1. Because the solution contains no other acids ($C_{II} = 0$), scale B and the lines where C_{II} is zero are employed. A horizontal line is drawn from the value $\log (C_I K^{OH}_{A_I})$ ($= \log (C_I K_I)$) to its point of intersection with the line marked $C_{II} = 0$, and a vertical line is drawn from this point upwards until it intersects the line in the upper part of the nomogram corresponding to $\Delta pH = pH_{end} - pH_{eq}$. The ordinate of this point gives the percentage error. The abscissa of the point of intersection of the horizontal line and the line $\log K^{OH}_{A_I}$ ($= \log K_I$) in the lower left part of the nomogram gives pH_{eq}, the hydrogen ion concentration at the equivalence point.

Example 1: Determine pH_{eq} and the titration error in the titration of (*a*) a 0·1 molar and (*b*) a 0·01 molar acetic acid solution when the pH at the end-point differs from the pH at the equivalence point by ±0·5 pH unit. ($\log K^{OH}_{A_I} = 9{\cdot}3$.)

(*a*) The point of intersection of the horizontal line at the value $\log (C_I K^{OH}_{A_I}) = \log (C_I K_I) = \log (10^{-1} \times 10^{9\cdot3}) = 8{\cdot}3$ on scale B and the line $C_{II} = 0$ gives an error of about ±0·02% when $\Delta pH = \pm 0{\cdot}5$. The abscissa of the point where the horizontal line intersects the line $\log K^{OH}_{A_I} = \log K_I = 9{\cdot}3$ gives $pH_{eq} = 8{\cdot}8$.

(*b*) In the same way, the titration error is about ±0·6% and $pH_{eq} = 8{\cdot}4$ when the 0·01 molar acetic acid solution is titrated.

II. TITRATION OF AN ACID, HA_I, IN THE PRESENCE OF ANOTHER ACID, HA_{II}

When two acids, HA_I and HA_{II}, are present in the solution in concentrations C_I and C_{II}, respectively, and it is desired to titrate one of them, say HA_I, with a strong base, the reaction of the other acid HA_{II} with the titrant base (the complexing agent)

$$HA_{II} + OH^- \rightleftharpoons H_2OA_{II}{}^- \rightleftharpoons A_{II}{}^- + H_2O \tag{4}$$

represents an interfering side reaction whose influence is taken into account, as in complexometric metal titrations, by dividing the stability constant $K^{OH}_{A_I}$ by the alpha coefficient

$$\alpha_{OH(HA_{II})} = \frac{[OH] + [A_{II}]}{[OH]} = 1 + [HA_{II}]K^{OH}_{A_{II}} \simeq 1 + C_{II}K^{OH}_{A_{II}} \tag{5}$$

where

$$K^{OH}_{A_{II}} = \frac{[A_{II}]}{[HA_{II}][OH]}.$$

When several interfering acids are present, an alpha coefficient is evaluated for

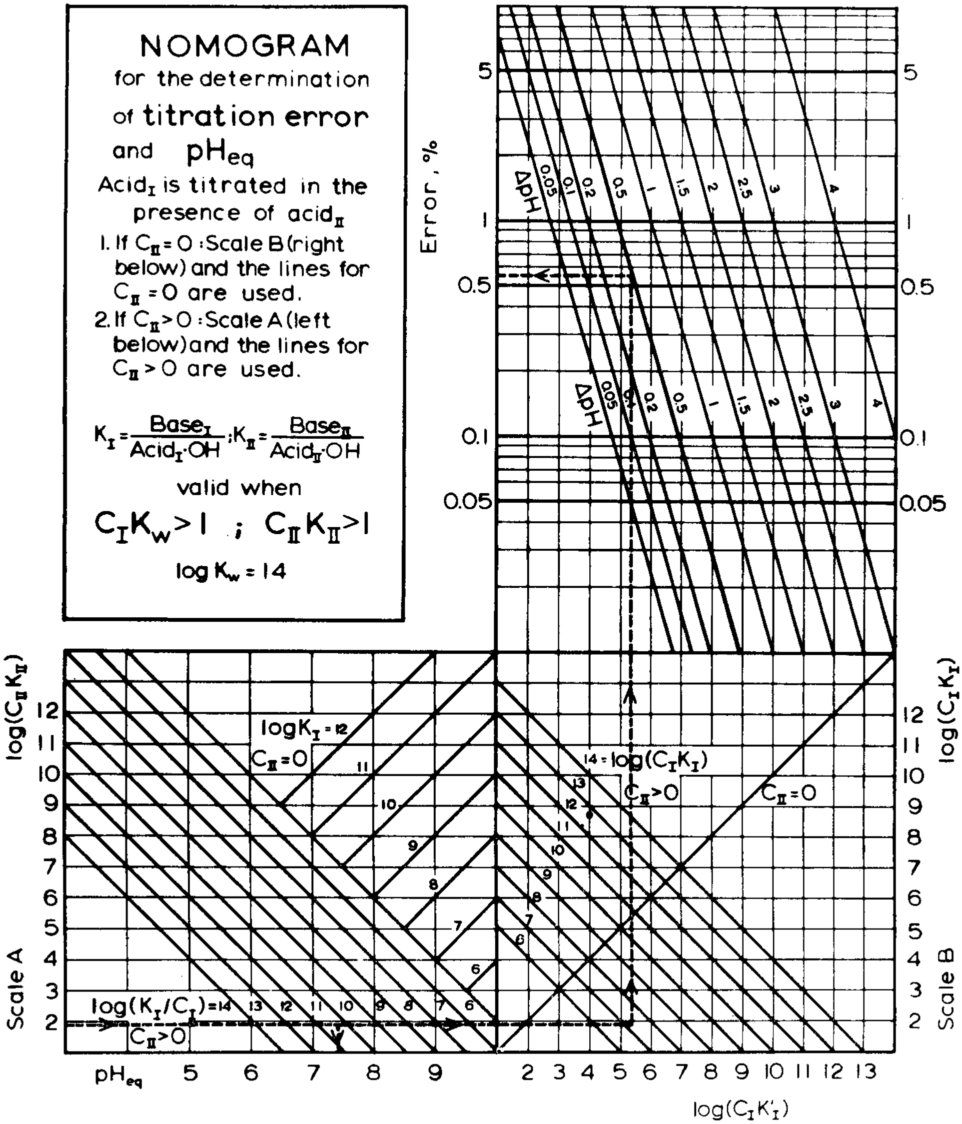

FIG. 1.—Nomogram for the determination of pH at the equivalence point, and of the titration error, in the titration of one weak acid in the presence of another weak acid.

each one, and the values are inserted in the following expression for the over-all alpha coefficient α_{OH}:

$$\alpha_{OH} = \alpha_{OH(HA_{II})} + \alpha_{OH(HA_{III})} + \ldots. + (1 - n) \tag{6}$$

where n is the number of interfering acids (4).

In addition, the acid HA_I to be titrated can interact with the solvent water according to

$$HA_I + H_2O \rightleftharpoons A_I^- + H_3O^+ \tag{7}$$

which represents the ionisation of the acid. The alpha coefficient corresponding to this interference is

$$\alpha_{HA_I(H_2O)} = \frac{[HA_I] + [H_3O]}{[HA_I]} = 1 + \frac{1}{[A_I]K^H_{HA_I}} \simeq 1 + \frac{K^{OH}_{A_I}}{C_I K_w} \tag{8}$$

where

$$K^H_{HA_I} = \frac{[HA_I]}{[H_3O][A_I]} = K_w/K^{OH}_{A_I}.$$

The mathematical treatment of the titration of one acid, HA_I, in the presence of another interfering acid can thus be based on the conditional constant defined by

$$K^{OH',HA_I'}_{A_I} = \frac{K^{OH}_{A_I}}{\alpha_{OH(HA_{II})}\,\alpha_{HA_I(H_2O)}} \tag{9}$$

The primed symbols introduced as superscripts to the constant are the components of the main reaction that participate in other concurrent reactions.

When the expressions given above for the apha coefficients are inserted in equation (9), we obtain

$$K^{OH',HA_I'}_{A_I} = \frac{K^{OH}_{A_I}}{(1 + C_{II}K^{OH}_{A_{II}})\left(1 + \dfrac{K^{OH}_{A_I}}{C_I K_w}\right)} \tag{10}$$

The resulting equation is a general one for the calculation of the conditional constant for the titration of one acid, HA_I, in the presence of another acid, HA_{II}. Provided that certain conditions are fulfilled, this equation can be simplified as shown in the following section.

II.I. *The side-reaction coefficient α_{OH} does not deviate from unity. One single acid species present*

When the solution contains only one acid, HA_I, or the other acid present is very weak, the product $C_{II}K^{OH}_{A_{II}}$ is zero or negligibly small compared with unity, and the coefficient α_{OH} is equal to unity. Equation (10) then takes the form

$$K^{OH',HA_I'}_{A_I} = \frac{K^{OH}_{A_I}}{1 + \dfrac{K^{OH}_{A_I}}{C_I K_w}}. \tag{11}$$

With the aid of this conditional constant the pH at the equivalence point and the error involved when the end-point of the titration of an acid with a strong base deviates from this equivalence point can be evaluated.

II.Ia. *Titration of a strong acid:* When the solution contains only a strong acid, $K_{A_I}^{OH}$ is greater than $C_I K_w$ and equation (11) then becomes

$$K_{A_I}^{OH',HA_I'} = C_I K_w. \tag{12}$$

At the equivalence point

$$[OH]_{eq} = (C_I K_{A_I}^{OH',HA_I'})^{\frac{1}{2}} = K_w^{-\frac{1}{2}} \tag{13}$$

$$[H_3O]_{eq} = K_w^{-\frac{1}{2}}, \tag{13a}$$

or the pH is equal to the square root of the ionic product of water ($K_w = 1/k_w$). The error in the titration is found by drawing a horizontal line from the value $\log (C_I^2 K_w)$ [$= \log (C_I K_I)$] on the scale B until it intersects the line $C_{II} = 0$, and drawing a line from the point of intersection upwards to the line giving the value of ΔpH. The percentage error can be read on the ordinate.

The lowest concentration, C_I, of a strong acid (at the equivalence point) that can be titrated with an error of $+0{\cdot}1\,\%$ when the end-point is determined with an accuracy of ± 1 pH unit (visual titration) is found to be 10^{-3} molar.

II.Ib. *Titration of a weak acid:* When the acid titrated is weak, $K_{A_I}^{OH} < C_I K_w$, the conditional constant will according to equation (11) be equal to the stability constant $K_{A_I}^{OH}$ of the hydroxo complex formed. The values of the pH at the equivalence point and the titration error are determined as described in section I.

II.2. *The side-reaction coefficient α_{OH} is greater than unity*

When the second acid in the solution is so strong that $C_{II} K_{A_{II}}^{OH}$ is greater than unity, equation (10) can be written in two forms depending on whether the constant $K_{A_I}^{OH}$ is greater or smaller than $C_I K_w$.

II.2a. *Titration of a strong acid in the presence of a weak one:* When a strong acid, HA_I (for which $K_{A_I}^{OH} > C_I K_w$), is titrated when a weak acid, HA_{II}, is present, the conditional constant is given by

$$K_{A_I}^{OH',HA_I'} = \frac{C_I K_w}{C_{II} K_{A_{II}}^{OH}}. \tag{14}$$

At the equivalence point

$$[OH']_{eq} = (C_I / K_{A_I}^{OH',HA_I'})^{\frac{1}{2}} = \left(\frac{C_{II} K_{A_{II}}^{OH}}{K_w}\right)^{\frac{1}{2}}. \tag{15}$$

The value of the primed quantity $[OH']_{eq}$ must, as in complexometric titrations, be divided by the corresponding alpha coefficient α_{OH} to obtain the true hydroxide ion concentration at the equivalence point.

$$[OH]_{eq} = [OH']_{eq}/\alpha_{OH}. \tag{16}$$

Because, according to equation (5),

$$\alpha_{OH} = 1 + C_{II} K_{A_{II}}^{OH} \simeq C_{II} K_{A_{II}}^{OH}, \tag{17}$$

we have at the equivalence point

$$[OH]_{eq} = \frac{1}{(C_{II} K_{A_{II}}^{OH} K_w)^{\frac{1}{2}}}, \tag{18}$$

and

$$[H_3O]_{eq} = \left(\frac{C_{II} K_{A_{II}}^{OH}}{K_w}\right)^{\frac{1}{2}}, \tag{18a}$$

which means that the titration should be continued to the pH of a solution containing the weak acid alone.

The titration error is found as above by entering on the scale B the value

$$\log(\mathrm{C_I}K_\mathrm{I}) = \log(\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH',HA_I'}}) = \log\left(\frac{\mathrm{C_I}^2K_\mathrm{w}}{\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}}\right). \tag{19}$$

Example 2: A solution 0·05 molar in hydrochloric acid and 0·01 molar in crotonic acid is titrated by a strong base. Determine the pH at the equivalence point and the titration error when $\Delta\mathrm{pH} = \pm 0{\cdot}4$ if (*a*) only hydrochloric acid, (*b*) the sum of the acids is to be determined. (Crotonic acid: $\log K_{\mathrm{HA}}^{\mathrm{H}} = 4{\cdot}7$; $\log K_{\mathrm{A}}^{\mathrm{OH}} = 9{\cdot}3$.)

(*a*) According to equation (14),

$$K_{\mathrm{Cl}}^{\mathrm{OH'}} = \frac{\mathrm{C_{HCl}}K_\mathrm{w}}{\mathrm{C_{HA}}K_{\mathrm{A}}^{\mathrm{OH}}} = \frac{10^{-1{\cdot}3}10^{14}}{10^{-2}10^{9{\cdot}3}} = 10^{-5{\cdot}4},$$

$$[\mathrm{OH'}]_{\mathrm{eq}} = (\mathrm{C_{HCl}}/K_{\mathrm{Cl}}^{\mathrm{OH'}})^{\frac{1}{2}} = 10^{-3{\cdot}35}.$$

Because $\alpha_{\mathrm{OH(HA)}} = 1 + \mathrm{C_{II}}\,K_{\mathrm{A_{II}}}^{\mathrm{OH'}} = 1 + 10^{-2}\,10^{9{\cdot}3} = 10^{7{\cdot}3}$,

$$[\mathrm{OH}]_{\mathrm{eq}} = 10^{-3{\cdot}35}/10^{7{\cdot}3} = 10^{-10{\cdot}65},$$

and

$$\mathrm{pH_{eq}} = 3{\cdot}35$$

Because $\log(\mathrm{C_{HCl}}\,K_{\mathrm{Cl}}^{\mathrm{OH'}}) = 4{\cdot}1$, the error (Fig. 1) is ±2%

(*b*) The magnitude of the titration error is determined by the strength of the weak acid present (compare the complexometric titration of a second metal $\mathrm{M_{II}}$ after the first metal $\mathrm{M_I}$ has been titrated).

By equation (3),

$$[\mathrm{OH}]_{\mathrm{eq}} = (10^{-2}/10^{9{\cdot}3})^{\frac{1}{2}} = 10^{-5{\cdot}6},$$

and

$$\mathrm{pH_{eq}} = 8{\cdot}4,$$

$\log(\mathrm{C_A}K_{\mathrm{A}}^{\mathrm{OH}}) = 7{\cdot}3$ and the titration error ±0·05%.

The total consumption of strong base is six times that corresponding to the crotonic acid present and hence the titration error is only one-sixth as great, or 0·008%.

II.2b. *Titration of a weak acid in the presence of another weak acid:* Since $\alpha_{\mathrm{HA(H_2O)}} = 1$ because the acid is only slightly dissociated, equation (10) becomes

$$K_{\mathrm{A_I}}^{\mathrm{OH',HA_I'}} = \frac{K_{\mathrm{A_I}}^{\mathrm{OH}}}{\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}}. \tag{20}$$

At the equivalence point

$$[\mathrm{OH'}]_{\mathrm{eq}} = \left(\frac{\mathrm{C_I C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}}{K_{\mathrm{A_I}}^{\mathrm{OH}}}\right)^{\frac{1}{2}}, \tag{21}$$

and the hydroxide ion concentration

$$[\mathrm{OH}]_{\mathrm{eq}} = [\mathrm{OH'}]_{\mathrm{eq}}/\alpha_{\mathrm{OH}} = \left(\frac{\mathrm{C_I C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}}{K_{\mathrm{A_I}}^{\mathrm{OH}}}\right)^{\frac{1}{2}} \Big/ (\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}) = \left(\frac{\mathrm{C_I}}{\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}K_{\mathrm{A_I}}^{\mathrm{OH}}}\right)^{\frac{1}{2}}, \tag{22}$$

and

$$[\mathrm{H_3O}]_{\mathrm{eq}} = \frac{(\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}K_{\mathrm{A_I}}^{\mathrm{OH}}/\mathrm{C_I})^{\frac{1}{2}}}{K_\mathrm{w}} = \left(\frac{\mathrm{C_{II}}/K_{\mathrm{HA_{II}}}^{\mathrm{H}}}{\mathrm{C_I}K_{\mathrm{HA_I}}^{\mathrm{H}}}\right)^{\frac{1}{2}}, \tag{22a}$$

where

$$K_{\mathrm{HA_I}}^{\mathrm{H}} = \frac{[\mathrm{HA_I}]}{[\mathrm{H_3O}][\mathrm{A_I}]} \quad \text{and} \quad K_{\mathrm{HA_{II}}}^{\mathrm{H}} = \frac{[\mathrm{HA_{II}}]}{[\mathrm{H_3O}][\mathrm{A_{II}}]}$$

The titration error is obtained from the nomogram by entering the diagram on scale B with

$$\log (\mathrm{C_I}K_\mathrm{I}) = \log (\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH',HA_I'}}) = \log \left(\frac{\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH}}}{\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}}\right) \tag{23}$$

The titration error and the pH at the equivalence point of the titration can conveniently be determined from the whole nomogram in Fig. 1 without laborious calculations. The concentration $\mathrm{C_{II}}$ is greater than zero and scale A and the lines for $\mathrm{C_{II}} > 0$ are used. A horizontal line is drawn from the point $\log (\mathrm{C_{II}}K_{\mathrm{A_{II}}}^{\mathrm{OH}}) = \log (\mathrm{C_{II}}K_{\mathrm{II}})$ on scale A to the right until it intersects the line $\log (K_{\mathrm{A_I}}^{\mathrm{OH}}/\mathrm{C_I}) = \log (K_\mathrm{I}/\mathrm{C_I})$ at a point in the lower left part of the nomogram whose abscissa is $\mathrm{pH_{eq}}$. When the horizontal line is continued to the right lower part of the nomogram until it intersects the line $\log (\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH}}) = \log (\mathrm{C_I}K_\mathrm{I})$, and a vertical line is drawn from the point of intersection to the line giving ΔpH in the right upper quadrant, the ordinate of the point of intersection gives the titration error.

Example 3: A 0·01 molar acetic acid solution 0·001 molar in boric acid is to be titrated. Determine the pH at the equivalence point and the titration error if $\Delta\mathrm{pH} = \pm 0{\cdot}5$. ($\log K_{\mathrm{Ac}}^{\mathrm{OH}} = 9{\cdot}3$; $\log K_{\mathrm{BO_2}}^{\mathrm{OH}} = 4{\cdot}9$.)

A horizontal line drawn from the point $\log (\mathrm{C_{HBO_2}}\, K_{\mathrm{BO_2}}^{\mathrm{OH}})$ [$= \log (\mathrm{C_{II}}\, K_{\mathrm{II}})$] $= 1{\cdot}9$ to intersect the line $\log (K_{\mathrm{Ac}}^{\mathrm{OH}}/\mathrm{C_{HAc}})$ [$= \log (K_\mathrm{I}/\mathrm{C_I})$] $= 11{\cdot}3$ at the point giving $\mathrm{pH_{eq}} = 7{\cdot}4$ and the line $\log (\mathrm{C_{HAc}}\, K_{\mathrm{Ac}}^{\mathrm{OH}})$ [$= \log (\mathrm{C_I}K_\mathrm{I})$] $= 7{\cdot}3$ at the point where $\log (\mathrm{C_I}K_\mathrm{I}') = 5{\cdot}3$. A vertical line from the latter point upwards intersects the line $\Delta\mathrm{pH} = \pm 0{\cdot}5$ at a point whose ordinate gives the titration error $\pm 0{\cdot}55\%$. The lines of this example are drawn in the nomogram.

If both acids, $\mathrm{HA_I}$ and $\mathrm{HA_{II}}$, are present at the same concentration, which is the case when the solution contains a dibasic acid, the conditional constant is computed from equation (20).

II.2c. *Titration of a dibasic acid to the first equivalence point:* If $\mathrm{C_I}$ denotes the total concentration of a dibasic acid, $\mathrm{H_2A_I}$, in solution, and the interaction of the acid with the solvent can be disregarded (*i.e.* when $\mathrm{C_I}$ exceeds the first dissociation constant, $k_{\mathrm{H_2A_I}}$, of the acid), equation (20) becomes (on the assumption that $\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH}} > 1$)

$$K_{\mathrm{HA_I}}^{\mathrm{OH'}} = \frac{K_{\mathrm{HA_I}}^{\mathrm{OH}}}{\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH}}} \tag{24}$$

where

$$K_{\mathrm{HA_I}}^{\mathrm{OH}} = \frac{[\mathrm{HA_I}]}{[\mathrm{H_2A_I}][\mathrm{OH}]}\,;\quad K_{\mathrm{A_I}}^{\mathrm{OH}} = \frac{[\mathrm{A_I}]}{[\mathrm{HA_I}][\mathrm{OH}]} = \frac{K_\mathrm{w}}{K_{\mathrm{HA_I}}^{\mathrm{H}}}. \tag{25}$$

As in the preceding section, at the equivalence point

$$[\mathrm{OH'}]_{\mathrm{eq}} = (\mathrm{C_I}/K_{\mathrm{HA_I}}^{\mathrm{OH'}})^{\frac{1}{2}}, \tag{26}$$

$$[\mathrm{OH}]_{\mathrm{eq}} = \frac{(\mathrm{C_I}^2 K_{\mathrm{A_I}}^{\mathrm{OH}}/K_{\mathrm{HA_I}}^{\mathrm{OH}})^{\frac{1}{2}}}{\mathrm{C_I}K_{\mathrm{A_I}}^{\mathrm{OH}}} = \frac{1}{(K_{\mathrm{HA_I}}^{\mathrm{OH}}K_{\mathrm{A_I}}^{\mathrm{OH}})^{\frac{1}{2}}}, \tag{27}$$

and

$$[\mathrm{H_3O}]_{\mathrm{eq}} = \frac{(K_{\mathrm{HA_I}}^{\mathrm{OH}}K_{\mathrm{A_I}}^{\mathrm{OH}})^{\frac{1}{2}}}{K_\mathrm{w}}. \tag{27a}$$

The last equation is the customary equation for the calculation of the pH of a solution of an acid salt of a dibasic acid. The same equation is obtained by putting $\mathrm{C_I} = \mathrm{C_{II}}$ in equation (22a).

By taking logarithms, equation (24) yields

$$\log K^{OH'}_{HA_I} = \Delta\log K - \log C_I \tag{28}$$

where $$\Delta\log K = \log K^{OH}_{HA_I} - \log K^{OH}_{A_I}.$$

The nomogram can be employed directly to obtain the titration error. It follows from equation (28) that the abscissa in the right lower quadrant is

$$\log (C_I K_I') = \log (C_I K^{OH'}_{HA_I}) = \Delta\log K \quad (= \Delta pk) \tag{29}$$

When carbonic acid is to be titrated to the first equivalence point, $\Delta\log K\,(= \Delta pk) = 10{\cdot}3 - 6{\cdot}4 = 3{\cdot}9$. If the pH at the equivalence point is determined with an accuracy of $\pm 0{\cdot}5$ pH unit, the error is seen from the nomogram to be about $\pm 3\,\%$ irrespective of the concentration (within reasonable limits). The jump at the equivalence point is as large with a 0·01 molar solution as when a 0·1 molar solution is titrated.

II.2d. *Titration of a dibasic acid to the second equivalence point:* The main reaction when a dibasic acid is titrated to the second equivalence point is

$$HA_I^- + OH^- \rightleftharpoons A_I^{2-} + H_2O. \tag{30}$$

The only reaction that can interfere is the dissociation

$$HA_I^- + H_2O \rightleftharpoons A_I^{2-} + H_3O^+. \tag{31}$$

The corresponding alpha coefficient is

$$\alpha_{HA_I(H_2O)} = 1 + \frac{K^{OH}_{A_I}}{C_I K_w}. \tag{32}$$

When this expression is introduced, the conditional constant is found to be

$$K^{OH,HA_I'}_{A_I} = \frac{K^{OH}_{A_I}}{[1 + K^{OH}_{A_I}/(C_I K_w)]}. \tag{33}$$

In most cases $\alpha_{HA_I(H_2O)}$ is unity, the conditional constant is equal to $K^{OH}_{A_I}$, and the hydroxide ion concentration at the equivalence point is given by equation (3). (Compare with the complexometric titration of a metal M_{II} when a metal M_I has been titrated.)

As two equivalents of strong base are consumed in the titration of the dibasic acid, the titration error read from the nomogram should be halved. The titration error can be directly obtained from the right upper quadrant of the nomogram by taking as the starting value on the scale of $\log (C_I K_I')$ the value

$$\log (4 C_I K^{OH}_{A_I}) = 0{\cdot}6 + \log (C_I K^{OH}_{A_I}). \tag{34}$$

In extreme cases, $\alpha_{HA_I(H_2O)}$ is greater than unity. This is the case with sulphuric acid ($\log K^{OH}_{A_I} = 12{\cdot}1$). Equation (33) then takes the form

$$K^{OH,HA_I'}_{A_I} = C_I K_w, \tag{35}$$

which represents the conditional constant when a solution of a strong acid is titrated [*cf.* equation (13)].

The above equations apply to the titration of bases by strong acids if the term [OH] in all equations is replaced by $[H_3O]$, and the base stability constants are replaced by the respective stability constants of the conjugate acids.

Acknowledgements—I wish to express my gratitude to Professor Anders Ringbom for stimulating discussions and comments relating to the manuscript.

Zusammenfassung—Eine mathematische Behandlung von Säure-Basen-Titrationen auf Grund des Konzeptes der konditionellen Konstanten in Analogie zu komplexometrischen Titrationen wurde durchgeführt. Gleichungen zur Berechnung des pH-Wertes im Äquivalenzpunkte und im Endpunkte, falls dieser vom Äquivalenzpunkt verschieden ist, werden abgeleitet. Die Werte dieser Parameter können ohne viel Rechnungen aus einem Nomogramm abgelesen werden.

Résumé—L'auteur présente un traitement mathématique des titrages acide-base, basé sur le concept des constantes conditionnelles et analogue au traitement des titrages complexométriques. Des équations sont dérivées pour le calcul du pH au point équivalent et de l'erreur de titrage quand le point final diffère du point équivalent. Les valeurs de ces quantités peuvent être déterminées sans calculs compliqués à partir d'un nomogramme.

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SHORT COMMUNICATIONS

The determination of thiomalic acid

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AN iodometric method has been recommended by Busev and Fan'[1] for the determination of thiomalic acid. According to them, 5·98 equivalents of iodine are taken up by 1 mole of thiomalic acid when the alkalinity of the solution during the reaction is kept in the range 0·3–3N by means of sodium hydroxide. However, we have found that the number of equivalents of iodine consumed depends on many factors, such as the order of addition of reagents, the temperature, the reaction time, and especially the alkalinity of the solutions, both within and outside the range suggested by Busev and Fan'. The nature of the results obtained by us seems to prevent the reaction from being of any analytical value. The use of potassium iodate, potassium bromate, potassium periodate or chloramine-T in place of iodine, under diverse conditions, as described below, also gave unsatisfactory results. We report here some of our observations, because they may be of value to those who would like to pursue the studies further.

EXPERIMENTAL

Thiomalic acid solutions of 0·01M concentration were prepared and standardised by the acrylonitrile method.[1] After treatment of known volumes of thiomalic acid solutions with a known excess of the oxidising agent (iodine, potassium iodate, potassium bromate, potassium periodate or chloramine-T) under various conditions as given below, the solutions were suitably acidified (potassium iodide was also added wherever necessary), and the iodine liberated (equivalent to the excess of the particular oxidant used) was determined with thiosulphate.

In Tables I and II are recorded the results of experiments carried out at 30° using iodine as the oxidant. The number of equivalents of iodine consumed increases with increasing alkali concentration and with the duration of the reaction, but does not attain a constant value. This is quite contrary to the findings of Busev and Fan'.

TABLE I.—DEPENDENCE OF I_2 CONSUMPTION OF THIOMALIC ACID ON ALKALINITY AT 30°

(Order of addition of reagents: Thiomalic acid—I_2—NaOH. Total volumes = 100 ml.)

Thiomalic acid taken, *mM*	I_2 taken, *meq*	Overall normality of NaOH	Reaction period, *min*	Iodine consumed, *meq*
0·1000	2·375	0·50	90	0·3761
0·1000	2·375	1·0	90	0·4453
0·1000	2·375	1·5	90	0·5054
0·1000	2·375	2·0	90	0·5627

The results of experiments carried out with alkaline iodine solutions at 90° are given in Table III. For the same reaction period, the amount of iodine consumed at 90° is more than that consumed at 30°. However, the values obtained are again variable and do not conform to any regular stoichiometry. The extent of oxidation of thiomalic acid depends on the order of mixing of the reagents; addition of alkali before iodine always leads to lower consumption of iodine. Reaction periods above 2 hr at 90° yielded only a slight increase in the oxidant consumed in every case.

TABLE II.—DEPENDENCE OF I_2 CONSUMPTION AT 30° ON REACTION PERIOD

(Order of addition of reagents: Thiomalic acid—I_2—NaOH.
Thiomalic acid taken = 0·1000 *mM*.
I_2 taken = 2·375 *meq*.
Overall normality of NaOH = 1·66.
Total volume = 100 ml.)

Time, hr	0·5	1·0	1·5	2·0	2·5	3·0	17
I_2 consumed, *meq*	0·4160	0·4802	0·5501	0·5771	0·5853	0·6091	0·6494

TABLE III.—DEPENDENCE OF I_2 CONSUMPTION ON ORDER OF MIXING OF REAGENTS.

(T = Thiomalic acid solution; B = NaOH solution; I = I_2 solution.
Overall normality of NaOH = 0·42.
Total volume = 100 ml.)

Thiomalic acid taken, *mM*	I_2 taken, *meq*	I_2 consumed in 2 hr at 90°, *meq*		
		T-B-I	T-I-B	I-B-T
0·1000	2·375	0·5091	0·6264	0·5310
0·2000	2·375	1·059	1·268	1·138

The trend of values obtained using alkaline potassium iodate and bromate solutions in place of iodine are indicated in Tables IV and V. The results clearly show that replacement of iodine by these reagents in no way provides a procedure for the determination of thiomalic acid. Chloramine-T and

TABLE IV.—OXIDATION OF THIOMALIC ACID WITH POTASSIUM IODATE

(Order of addition of reagents: Thiomalic acid—NaOH—KIO_3.
Total volume = 100 ml.)

Thiomalic acid taken, *mM*	Overall normality of NaOH	KIO_3 taken, *meq*	KIO_3 consumed, *meq*, after		
			2 hr at 30°	1 hr at 90°	3 hr at 90°
0·1000	0·41	0·2312	0·5230	0·5620	0·5943
0·1000	0·83	0·2312	0·5325	0·5923	0·5984
0·1000	1·25	0·2312	0·5413	0·6184	0·6534
0·1000	1·66	0·2312	0·5726	0·6357	0·6649
0·1000	2·08	0·2312	0·5874	0·6739	0·6862

TABLE V.—OXIDATION OF THIOMALIC ACID WITH POTASSIUM BROMATE FOR 2 HR AT 90°

(Thiomalic acid taken = 0·1000 *mM*.
Potassium bromate taken = 0·2319 *meq*.
Total volume = 100 ml.
Order of addition: Thiomalic acid—NaOH—$KBrO_3$.)

Overall normality of NaOH	0·25	0·50	0·75	1·00	1·25	1·50
$KBrO_3$ consumed, *meq*	0·3962	0·4289	0·4427	0·4638	0·5459	0·5669

potassium periodate gave similar results. The presence of many metallic ions, such as Co^{II}, Ni^{II} or Cr^{III}, did not materially affect the results. From our studies we conclude that none of the oxidants mentioned above would permit the development of a reliable method for the determination of thiomalic acid.

G. ARAVAMUDAN
C. RAMA RAO

Department of Chemistry
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Summary—The extent of oxidation of thiomalic acid by iodine, potassium iodate, potassium bromate, potassium periodate and chloramine-T depends on alkalinity, temperature and duration of reaction. Therefore these oxidants do not provide a satisfactory method for the determination of thiomalic acid.

Zussammenfassung—Das Ausmass der Oxydation von Thioapfelsäure durch Iod, Kaliumjodat, —bromat und —periodat, sowie Chloramin-T hängt von Temperatur und Alkalinität der Lösung, sowie Dauer der Reaktionseinwirkung ab. Daher ergibt die Anwendung dieser Oxydationsmittel keine zufriedenstellende Methode zur Bestimmung der Thiosäure.

Résumé—L'oxydation de l'acide thiomalique par l'iode, l'iodate de potassium, le bromate de potassium, le périodate de potassium et la chloramine-T, dépend de l'alcalinité, de la température et de la durée de la réaction. Par suite, ces oxydants ne permettent pas un dosage satisfaisant de l'acide thiomalique.

REFERENCE

[1] A. I. Busev and Chzhan Fan', *Talanta*, 1961, **8**, 470.

Separation of titanium from iron and aluminium

(*Received* 21 *August* 1962. *Accepted* 6 *September* 1962)

THE determination of titanium in iron alloys, titanium ores, and concentrates is always time consuming. The oxidative determination of tervalent titanium requires careful preliminary reduction in an inert atmosphere, and apparatus for performing the titration in the absence of aerial oxygen. For a gravimetric determination it is necessary to separate the titanium from iron and aluminium. By precipitation with cupferron in strongly acid medium, or by simple precipitation with excess of sodium hydroxide, it is possible to separate titanium from aluminium, but not from iron, which must first be precipitated as sulphide. An almost specific procedure for the precipitation of titanium with ammonia in the presence of EDTA was described some years ago by Přibil and Schneider.[1] Beryllium, uranium and quadrivalent tin are precipitated along with titanium, but these elements are rarely present in the materials under consideration. The main disadvantage of this method is the long time needed to complete precipitation of the titanium with ammonia, because of formation of the titanium-EDTA complex. In the original method it was proposed that the solution should stand for at least 5 hr, with thorough stirring from time to time. We have now found that EDTA can advantageously be replaced by triethanolamine. In the presence of triethanolamine and sodium hydroxide, the colourless iron-triethanolamine complex is formed, and aluminium remains in solution as either the triethanolamine or the hydroxo complex, but titanium is quantitatively precipitated, after a short period of boiling, as titanium hydroxide, free from adsorbed iron and aluminium and easily filtered off on paper. After it has been washed, the precipitate can be ignited and weighed as the oxide, but in this work we have used the complexometric method described by Bieber and Večeřa[2] based on the formation of a titanium-EDTA-peroxo complex and back titration of excess EDTA with bismuth nitrate, the indicator being Xylenol Orange.

EXPERIMENTAL

Reagents

Triethanolamine: 1 % and 20 % solutions.

Sodium hydroxide: 2*M*.

EDTA: 0·05*M*, standardised against lead nitrate.

Bismuth nitrate: 0·05*M*, acidified with nitric acid, and standardised against the EDTA, using Xylenol Orange as indicator.

Nitric acid: 1*M* and 5*M* solutions.

Ammonia solution: Concentrated solution diluted 1:1 with water.

Xylenol Orange: 0·2 % solution.

Metal nitrates or sulphates: 0·05*M* solutions

Procedure

To the acid solution containing titanium, iron and aluminium, add 20 ml of 20 % triethanolamine solution: the original solution must be acid enough to prevent any precipitation. Add 2*M* sodium hydroxide until the solution is decolorised, and boil for 1 min. Allow the precipitate to settle, and filter it off on a medium-porosity filter paper (e.g., Schleicher and Schüll No. 589).[1] Wash the precipitate five times with hot 1 % triethanolamine solution and twice with hot water. Dissolve the precipitate from the filter with 25–30 ml of hot 5*M* nitric acid, catching the solution in a 500-ml conical flask, and wash the filter thoroughly with hot water. Cool the solution somewhat, and add 10 ml of 30 % hydrogen peroxide, a measured volume of 0·05*M* EDTA (more than enough to complex the titanium) and a few drops of Xylenol Orange indicator. Add 1:1 ammonia solution until the red colour of the alkaline form of the indicator appears, and then adjust the pH of the solution to 1–2 with 1*M* nitric acid. Cool the solution thoroughly to below 20°, dilute if necessary, and titrate with 0·05*M* bismuth nitrate to the intense red colour of the end-point. The colour change is very sharp to 0·02 ml of titrant. The whole procedure takes only about 35 min, and some results obtained by it are shown in Table I.

TABLE I. DETERMINATION OF TITANIUM IN THE PRESENCE OF IRON AND ALUMINIUM

Taken, *mg*			0·05*M* EDTA added, *ml*	Back Titrn. 0·05*M* Bi, *ml*	Ti found, *mg*	Difference in Ti, *mg*
Ti	Fe	Al				
2·29	2·80	1·33	3·00	2·00	2·39	+0·10
2·29	27·99	1·33	5·00	4·03	2·32	+0·03
11·49	27·99	13·29	10·00	5·21	11·47	+0·02
27·97	27·99	13·29	12·00	2·53	27·70	−0·27
11·49	139·95	26·58	7·00	2·19	11·52	+0·03
34·46	2·80	1·33	20·00	5·50	34·72	+0·26
6·89	8·40	66·49	5·00	2·10	6·94	+0·05

Influence of other metals

Calcium and magnesium do not interfere, even if present in large amounts. Magnesium is co-precipitated, but is not titrated. Other bivalent elements are complexed with triethanolamine and may be slightly adsorbed on the titanium hydroxide. Those elements such as lead, zinc, cadmium and manganese, which form unstable complexes with EDTA in acid solution (pH 1–2) do not interfere. In the presence of a high concentration of copper, nickel or cobalt, it is advisable to add 0·5–1·0 g of EDTA and to boil the alkaline solution for 5 min instead of 1 to ensure quantitative precipitation of the titanium. The titanium hydroxide then appears as dense flakes which are less easily soluble in nitric acid. Some results are given in Table II.

TABLE II. DETERMINATION OF TITANIUM IN THE PRESENCE OF OTHER METALS

Metals taken, *mg*	0·05*M* EDTA added, *ml*	Back Titrn. 0·05*M* Bi, *ml*	Ti found, *mg*	Difference in Ti, *mg*
11·49 Ti, 139·95 Fe, 26·58 Al 6·08 Mg, 10·02 Ca, 15·89 Mn 14·67 Ni, 13·74 Cu, 16·35 Zn, 51·80 Pb	10·00	5·11	11·70	+0·21
11·49 Ti, 63·54 Cu, 14·67 Ni, 27·47 Mn, 14·75 Co	12·00	7·18	11·54	+0·05

The masking effect of triethanolamine in other separations is under study.

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RUDOLF PŘIBIL
VLADIMÍR VESELÝ

Summary—Titanium can be separated easily from iron and aluminium by precipitation with sodium hydroxide in the presence of triethanolamine. The precipitated titanium hydroxide is filtered off, dissolved in nitric acid, and determined complexometrically. Certain other elements are masked with EDTA. The proposed method is suitable for all types of material containing a considerable amount of titanium, such as Fe-Ti alloys, titanium ores or concentrates, or artificial titanates.

Zusammenfassung—Titan kann leicht von Eisen und Aluminium, durch Fällung mit Natronlauge in Gegenwart von Triäthanolamin getrennt werden. Der Niederschlag wird abfiltriert, in Salpetersäure gelöst und das Tilan komplexometrisch titriert. Eine Anzahl von Elementen wird mit ÄDTE maskiert. Die Methode ist für alle Arten von Material mit hohem Titangehalt, wie z.B. Fe–Ti–Legierungen, Titanerze und Konzentrate oder künstliche Titanate geeignet.

Résumé—Le titane peut être aisément séparé du fer et de l'aluminium par précipitation par la soude en présence de triéthanolamine. Le précipité d'hydroxyde de titane est filtré, dissout dans l'acide nitrique et dosé par complexométrie. On évite l'interférence d'un certain nombre d'autres éléments par addition d'EDTA. La méthode proposée convient pour tous les types de matériaux contenant de grandes quantités de titane comme les alliages fer-titane, les minerais de titane et les titanates artificiels.

REFERENCES

[1] R. Přibil and P. Schneider, *Chem. Listy*, 1951, **45**, 7; *Coll. Czech. Chem. Comm.*, 1950, **15**, 886.
[2] B. Bieber and Z. Večeřa, *Coll. Czech. Chem. Comm.*, 1961, **26**, 2081.

Talanta, 1963, Vol. 10, p. i. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

CZECHOSLOVAKIA

Monday–Saturday 4–9 *March* 1963: **Gas Chromatography Course:** *Czechoslovak Chemical Society, Brno Section.* Laboratory of Gas Analysis, Czechoslovak Academy of Science, Brno.

FRANCE

12 *mars* 1963: **Les methodes biochimiques de controle analytique dans les industries des cereales:** M. A. GUILBOT. Faculté de Pharmacie, Paris.

26 *mars* 1963: **Application de la chromatographie en phase gazeuse a l'etude de la chimie des corps gras:** M. J.-P. WOLFF. Faculté de Pharmacie, Paris.

UNITED KINGDOM

Wednesday 6 *March* 1963: **The Chemistry of Crime Detection:** Dr. H. J. WALLS: *Society for Analytical Chemistry, North of England Section* and *Royal Institute of Chemistry, North-East Section.* Chemistry Department, King's College, Newcastle-upon-Tyne. 6.30 p.m.

Friday 8 *March* 1963: **Annual General Meeting** followed by **Address of Retiring President, Dr.** A. J. AMOS: *Society for Analytical Chemistry.* Burlington House, London, W.1. 2.45 p.m.

Wednesday 13 *March* 1963: Symposium on **Pharmacological Screening of New Drugs:** *Society for Analytical Chemistry, Biological Methods Group.* Friends Meeting House, Euston Road, London, W.C.1. Whole day meeting.

Thursday 14 *March* 1963: **Refractory Analysis:** Mr. H. BENNETT: *Society for Analytical Chemistry, Midlands Section.* Technical College, Wolverhampton. 7.00 p.m.

Friday 15 *March* 1963: **Atmospheric Pollution:** Dr. B. T. COMMINS: *Society for Analytical Chemistry, Western Section* and *Royal Institute of Chemistry, South Wales Section.* University College, Singleton Park, Swansea.

Wednesday 20 *March* 1963: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Tuesday 26 *March* 1963: **Determination of Pesticide Residues:** *Society for Analytical Chemistry, Western Section* and *Physical Methods Group.* Bristol.

Thursday 28 *March* 1963: **Annual General Meeting** followed by **Steric Hindrance in Analytical Chemistry:** Professor H. M. N. H. IRVING: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham. 7.00 p.m.

Friday 29 *March* 1963: **The Forensic Chemist:** Dr. F. G. TRYHORN: *Society for Analytical Chemistry, Scottish Section* and *Royal Institute of Chemistry, Stirlingshire and District Section.* Lea Park Tearooms, Falkirk. 7.30 p.m.

Wednesday–Friday 3–5 *April* 1963: Symposium on **Soil Analysis and its Relation to Plant Composition and Growth:** Society of Chemical Industry, Agriculture Group. Bristol.

Application forms for registration and full details of the programme may be obtained from Dr. I. D. MORTON, Unilever Ltd., Colworth House, Sharnbrook, Bedford.

UNITED STATES OF AMERICA

Monday–Friday 4–8 *March* 1963: **Fourteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *American Chemical Society, Pittsburgh Section, Analytical Chemistry Group* and *Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel, Pittsburgh, Pa. (see *Talanta,* 1962, **9,** 629).

Sunday 31 *March–Friday* 5 *April*: **144 National Meeting:** *American Chemical Society.* Los Angeles, California.

Talanta, 1963, Vol. 10, pp. ii to iv. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Atlas of Analysis Lines: HALINA JAFFE. Hilger and Watts Ltd., London, 1962. £26.5.0.

THOSE of us who were trying to use the spectrograph in the twenties and thirties for analytical purposes will be reminded nostalgically by this work of Jacques Bardet's *Atlas de Spectres d'Arc*, dating from 1926 to which this is a direct successor. Although there are differences in detailed presentation of the material, the general purpose is the same.

The 50 segments of spectra here presented have been prepared at the Spectrochemical Laboratory of the Weizmann Institute of Science in Israel. They cover the rapid identification of the most suitable lines, for analytical purposes, of 69 elements.

The material is all presented on cards. First come seven cards describing briefly the method of using the Atlas, and then two Tables, listing the sensitive lines by elements and by wavelengths. The Atlas is presented on 50 cards, each carrying a photograph of a portion of the iron spectrum, enlarged to 12 inches × 1 inch, with, marked above and below, the sensitive lines of elements falling within the range of the segment.

There are three ranges covered. The first, from about 2475 A to about 3500 A, is given on 16 cards (*i.e.*, covering 16 feet in all), and is adequate for a great deal of routine analysis. The second range runs from about 3300 A to about 9000 A, on 17 cards, and is most useful for the alkali and alkaline earth metals. The third range is from about 3980 A to about 5500 A, on 17 cards, and is useful for complex (transition and inner transition metal) spectra or where increased resolution in the visible is required for some other reason.

These spectra are undoubtedly best used with a spectrograph similar to that on which the originals were prepared (a Hilger E478), since they are intended to be used by projection of the spectrum of the unknown on to the card, side by side with an iron arc standard, using a Hilger Spectrum Projector, in such a way that the iron arc of the standard and that on the card can be made to coincide. They can, however, be used with reasonable ease with instruments having not widely different dispersions.

The cards are beautifully printed, and the whole Atlas is contained in a very pleasant plastic-covered folder which gives every impression of being durable.

The price may at first sight seem high. But one should, however, compare this with the price of 200 Fr. (plus a surcharge of 20%!) for the 1926 Atlas; and one should compare the quality of the production (though my own copy of "Bardet" is in remarkably good condition after 35 years, for part of which, at least, it was used constantly); and particularly should one bear in mind that this is, in a sense, only an attachment to the spectrograph (and how many attachments, nowadays, cost so little!). With all these factors taken into account, one can recommend the Atlas to all spectrographic laboratories unreservedly.

CECIL L. WILSON

Gas-Liquid Chromatography. STEPHEN DAL NOGARE and RICHARD S. JUVET, JR. Interscience Publishers (John Wiley and Sons, New York and London), 1962. pp. xviii + 450. 105s.

THIS book relates the practical aspects of gas-liquid chromatographic separations to the principles on which such separations depend and also discusses the wide range of applications of this rapidly expanding branch of chemistry.

The authors state, in the preface, that they have attempted to enable the beginner in gas-liquid chromatography to have a working knowledge of the field after the first four chapters. These chapters give a general introduction, including earlier reviews of the subject, and an account of the practical methods and theoretical principles used in gas-liquid chromatography. The book then continues with a detailed account of the basic components of the apparatus, *i.e. The Liquid Phase, Detectors, etc.* This is followed by chapters on more specialised topics such as *Capillary Columns, Nonanalytical Applications, etc.* The final chapter on *Special Separations and Applications* indicates the wide range of applications of the method, and the large number of references (188) should be a particularly useful starting point for workers with a specific analytical problem. Every chapter includes many references to the original literature.

Throughout the book mathematical discussions of the theory are given where possible; inclusion of a table showing all the symbols used helps the reader to follow such arguments. Tables of relative retention data and of liquid phases recommended for particular analytical separations (together with literature references) are other most useful features. The standard of production of the book is high: the clarity of the diagrams deserves special mention.

In the reviewer's opinion, this volume will be most useful as an introduction to the field and as a guide to the extensive literature on the subject in laboratories where gas-liquid chromatography is being used or where there are problems which could be solved by this technique. This is a very good account of an important topic.

A. K. GALWEY

The analytical chemistry of polymers, Volume 12. Edited by G. M. Kline. **Part II—Analysis of molecular structure and chemical groups.** Pp. xiii + 619. 132s. **Part III—Identification procedures and chemical analysis.** Pp. vi + 566. 124s. Interscience Publishers, New York, 1962.

THE latest volume in the well-known "High Polymers" series has been issued in three parts, the second and third of which are being reviewed here. Part II deals with the examination of high polymers by physical methods, while Part III is concerned with identification procedures and the chemical analysis of high polymers.

In Part II a large number of techniques of physical chemistry are described, together with their application to the study of polymers. Chapters deal with molecular weight and size measurement; X-ray diffraction; optical measurements; differential thermal analysis; pyrolysis; mass spectrometry; ultraviolet and infrared spectrophotometry; fluorescence; chromatography; polarography and magnetic resonance spectroscopy. Each chapter is introduced by a brief, but informative, account of the appropriate technique and this is followed by a description of the way in which the technique can be applied in the study of high polymers. This book can be recommended not only for the high polymer content, but also for the readable accounts of the various experimental methods involved.

In Part III, attention is specifically directed towards the identification and chemical analysis of high polymers. One systematic approach is made in which physical tests, elementary analysis, chemical tests, *etc.*, are applied to polymer samples. A section on the microscopic study of polymers in conjunction with staining techniques is of interest. The now familiar techniques of radiochemical analysis are described and a large number of applications of this method are described. A short section on end-group analysis completes the book.

These volumes are well produced and provide a very readable account of the analysis and physical study of high polymers. The reviewer recommends these volumes not only to those concerned with high polymer chemistry, but also to those who would like to know more about the way in which modern techniques can be applied.

JAMES C. ROBB

Einführung in die qualitative anorganische Halbmikroanalyse, 3rd edition. GERHARD ACKERMANN VEB Deutscher Verlag für Grundstoffindustrie. Leipzig, 1962, pp. 175. DM14.–.

THIS little book is recommended for students, and for chemists in industrial and research laboratories who are not yet familiar with small-scale inorganic qualitative analysis. The fact that the third edition has been reached only about three years after the appearance of the first edition indicates that the earlier editions have enjoyed some popularity. And, one could add, a well-deserved popularity.

The changes from the second edition have not been extensive, though one point that deserves commendation is the introduction of IUPAC terminology. The present reviewer is also glad to note that the microscope is introduced in this course as a normal tool of the chemist; two pages of photomicrographs are included.

While English-speaking *students* are unlikely to use this book (except in a laudable attempt to improve their knowledge of the German language) all those concerned with the *teaching* of semimicro analysis can be recommended to acquire it, as a likely source of new ideas and new techniques.

CECIL L. WILSON

Mathematik für Chemiker: GEORG ALEXITS and STEFAN FENYÓ. Akadémiai Kiadó, Verlag der ungarischen Academie der Wissenschaften, Budapest, 1962. Pp. viii + 449. $10.80. In German.

THIS book is a straightforward and very clear exposition of some of the mathematics likely to be needed by present-day chemists. It begins at the beginning—with whole numbers, rational and irrational numbers, inequalities . . . the relationship of proportionality and its graphical and algebraic expression; and it proceeds at a seemingly unhurried pace to consider such topics as exponential functions and logarithms, differentiation and integration, differential equations, functions of several variables, line and surface integrals, probability theory, Fourier series, and finally, the solution of simultaneous equations and determinants. "Academic" matters such as the meaning of a differential coefficient are discussed carefully; but as well, many applications to chemical problems of the mathematical topics discussed are worked out in the text, and more than 200 short problems (with answers at the end of the book) are interspersed in the text. Also included are a short account of the use of slide rules, and a chapter on nomograms.

As a rough generalisation, it can be said that this book covers a largish proportion of the mathematics likely to be met by the chemist not working in one of the more mathematical fields such as valency theory or spectroscopy. For these latter there are likely to be many topics that are either omitted or are not taken nearly far enough. Thus, polar co-ordinates are considered only briefly, and spherical polar co-ordinates are not dealt with at all. Similarly, vectors are treated only briefly (the vector product of two vectors is not mentioned), general co-ordinate transformations and matrices are omitted, and the treatment of differential equations is not sufficient for most of the differential equations encountered in quantum theory.

The reviewer feels that because of its clarity and its well-chosen examples, this book can hardly fail to be useful to most chemists, besides providing, for the English-speaking reader, relatively painless practice with the German language. However, many physical chemists will need ultimately to use a more advanced text, which includes topics such as vectors and matrices, and which makes use of the compact notations that these provide.

The book is clearly printed on good paper, and looks well produced, although some pages came loose in the reviewer's copy in the course of two weeks' use.

A. D. E. PULLIN

Talanta, 1963, Vol. 10, p. v. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Determination of chromium, cobalt, iron and nickel in alloys: B. T. Kenna and F. J. Conrad. (19 *November* 1962).

Comparison of fifty-two spectrophotometric methods for the determination of nitrite: E. Sawicki, T. W. Stanley, J. Pfaff and A. D'Amico. (29 *November* 1962).

Radiochemical separation of strontium by amalgam exchange: Iqbal H. Qureshi and W. Wayne Meinke. (3 *December* 1962).

Über die Verwendung metallspezifischer Indikatoren bei Fällungstitrationen—VIII: Titration von Mikromengen Arsenat mit Bleimasslösung gegen PAR und SNAZOXS: Richard Püschel. (3 *December* 1962).

A thermogravimetric pyrolysis study of the interaction products of dihydrogen-di-(1,2,3-benzotriazolatium)-hexacyanoferrate-II with certain organic matters: R. F. Wilson and G. Henry Jr. (4 *December* 1962).

An analytical approach to chelating resins: G. Schmuckler. (6 *December* 1962).

Ammonium hexanitratocerate-IV as an oxidising agent-II: Potentiometric titration of oxalic and mandelic acids at room temperature: G. Gopala Rao, K. S. Murty and P. V. Krishna Rao. (10 *December* 1962).

Selective determination of trace quantities of silver using sorption of $Ag(NH_3)_2^+$ on silica: František Vydra. (12 *December* 1962).

Anion exchange of uranium, thorium, iron and aluminium in mineral acid-ether solutions: Separation of uranium from thorium, aluminium and iron: S. Urubay and J. Korkisch. (14 *December* 1962).

Eine Methode zur Konduktometrischen Bestimmung des Natriums: D. Ceausescu, I. Pîrvu and Filofteia Pîrvu. (21 *December* 1962).

The reactions of biacetyl, hydroxylamine and metal ions to form chelates: Orville E. Hileman, Jr., Paul R. Ellefsen, R. J. Magee and Louis Gordon. (22 *December* 1962).

Coulometric reduction of iridium^{IV} in perchloric acid media: G. A. Rechnitz and J. McClure. (24 *December* 1962).

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Use of masking agents in chelatometric titrations-II: β-aminoethylmercaptan as a masking agent: Koichi Yamaguchi and Keihei Ueno. (24 *December* 1962).

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Short Communications